

咖啡制作过程中丙烯酰胺减量措施的研究进展

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摘要: 咖啡因其独特风味和生物学功能成为世界 3 大饮品之首, 较高的人均日饮用量使其成为丙烯酰胺摄入较高的食品来源之一。因此, 采取有效措施减少咖啡饮品中丙烯酰胺的质量分数, 一直以来是全球关注的热点问题。咖啡饮品的所有制作加工阶段(包括生豆采集、焙炒加工、磨粉泡煮、罐装贮存等)都会影响最终产品中丙烯酰胺的质量分数。作者综述了咖啡饮品制作各个环节中丙烯酰胺的减量措施, 重点阐述了降低咖啡生豆中丙烯酰胺前体物质质量分数的方法、抑制丙烯酰胺生成的焙炒条件以及减少咖啡饮品中丙烯酰胺存留量的措施, 为生产安全健康的咖啡饮品提供依据。

关键词: 丙烯酰胺; 减量措施; 天冬酰胺; 咖啡生豆; 咖啡制作; 焙炒

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Reduction of Acrylamide during Processing of Coffee Products

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Abstract: The unique flavor and biological functions of coffee make it one of the top three beverages in the world. The high daily consumption per capita makes it one of the food sources with high acrylamide intake. Therefore, taking effective measures to reduce the content of acrylamide in coffee drinks has always been a hot issue of global concern. The acrylamide content in the final product could be affected by all the processing stages of coffee beverage production (including raw material selection, roasting, milling, brewing, conditions of storage, and etc.). This review summarized the reduction measures of acrylamide in all aspects of coffee beverage production, focusing on the methods to reduce the content of acrylamide precursor in raw coffee beans, the roasting conditions to inhibit the formation of acrylamide, and the measures to reduce the retention of acrylamide in coffee drinks, with an aim to provide beneficial enlightenment for the production of safe and healthy coffee drinks.

Keywords: acrylamide; reduction measures; asparagine; raw coffee beans; coffee making; roasting

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咖啡是世界3大饮品之首,具有降血糖血脂、神经保护等生物学功能^[1-2]。一款咖啡饮品的制作需要经过咖啡生豆的采集、焙炒加工、磨粉泡煮、罐装贮存等过程^[3]。其中,咖啡生豆在高温焙炒阶段发生了美拉德、焦糖化等系列反应,产生的大量新化合物使咖啡具有了独特的风味^[4-5]。然而,美拉德反应也是食品污染物——丙烯酰胺形成的主要途径^[6-9]。咖啡因在全球范围内的人均日摄入量过高,成为丙烯酰胺的高贡献食品之一^[10-13]。因此,如何有效采取措施降低咖啡饮品中丙烯酰胺的质量分数成为全球关注的重点问题^[14-17]。

作者综述了咖啡饮品制作各环节中降低丙烯酰胺质量分数的措施,主要包括降低咖啡生豆中丙烯酰胺前体物质的质量分数、改变焙炒条件抑制丙烯酰胺的生成以及减少咖啡饮品中丙烯酰胺的存留量,可为咖啡研究人员或生产经营企业减少咖啡饮料中丙烯酰胺的质量分数提供参考,为生产健康安全的咖啡饮品提供有益启示。

1 降低咖啡生豆中丙烯酰胺前体物质的质量分数

由于基因组成、生长环境等的差异,不同品种咖啡生豆化学组成种类和比例也有所不同,包括丙烯酰胺的前体物质(如天冬酰胺、葡萄糖等)^[18-20],因此咖啡生豆的筛选和加工处理影响最终咖啡饮品中的丙烯酰胺质量分数。

阿拉比卡和罗布斯塔是咖啡饮品制作中最常用的生豆品种,可单独或混合使用。不论焙炒条件如何改变,罗布斯塔总是比经同样处理的阿拉比卡产生的丙烯酰胺更多^[21-23],如Lantz等人将2种咖啡生豆同时进行中等程度焙炒,最终罗布斯塔生成的丙烯酰胺平均质量分数为378 $\mu\text{g}/\text{kg}$,而在阿拉比卡中仅为251 $\mu\text{g}/\text{kg}$ ^[21]。另外,Esposito发现在阿拉比卡和罗布斯塔的混合咖啡生豆中,在轻度、中度、深度焙炒后检测到罗布斯塔的丙烯酰胺质量分数均最高^[24]。这是由于罗布斯塔中天冬酰胺质量分数更高^[25-26],而天冬酰胺是丙烯酰胺的限制性前体物质^[17,27]。尽管也有研究表明丙烯酰胺生成量与蔗糖质量分数呈正相关^[28],但其与天冬酰胺质量分数的相关性仍然更加显著。

因此在咖啡饮料生产过程中,可通过筛选咖啡生豆的品种或改变不同品种咖啡生豆的比例来降

低丙烯酰胺前体物质的质量分数。另外,未成熟的咖啡生豆中游离天冬氨酸的质量分数比成熟咖啡豆更高^[29],还应尽量避免混入未成熟的咖啡生豆。

刚收获的咖啡生豆需要进行干法或湿法的加工处理^[30],以保证其品质稳定。相较于干法加工处理,未成熟的咖啡生豆经湿法处理后,天冬氨酸质量分数明显降低^[31],同时主要还原糖(如葡萄糖和果糖)的质量分数也降低80%^[32]。因此,对咖啡生豆进行湿法加工处理可有效降低丙烯酰胺前体物质的质量分数。

在咖啡豆焙炒前,可以通过添加天冬酰胺酶以水解天冬酰胺,将其催化成天冬氨酸和氨^[33-34],从而降低咖啡豆中游离天冬酰胺的质量分数,控制丙烯酰胺生成^[35]。天冬酰胺酶水解的最适温度为60 $^{\circ}\text{C}$ ^[36],其酶活力表示为ASNU,是指在标准条件下(pH 7.0、30 $^{\circ}\text{C}$)每分钟能产生1 mol氨的天冬酰胺酶量。常采用固定化^[37-38]、定点突变^[39-40]等方式来提高天冬酰胺酶的活力及稳定性。

Correa等将咖啡生豆浸泡在含有5 000 ASNU/kg天冬酰胺酶溶液的锥形瓶中,在60 $^{\circ}\text{C}$ 、200 r/min条件下轻轻摇晃2 h,然后在80 $^{\circ}\text{C}$ 烤箱里放置约2 h使咖啡豆完全干燥,焙炒研磨后丙烯酰胺质量分数为65 $\mu\text{g}/\text{kg}$,比未经酶处理的空白咖啡样品低77%~85%^[41]。此外罗布斯塔的天冬酰胺质量分数比阿拉比卡更高,因此需要更高的酶活力或更久的水解时间才能达到与阿拉比卡一样的抑制效果^[42-43]。

然而,由于天冬酰胺酶的水解不完全和咖啡生豆表面的渗透率较低,导致酶与咖啡豆内部天冬酰胺的接触效率并不高。研究人员通过流动蒸汽预处理、在水里浸泡蒸煮、适量增压或减压等方式^[34,40,44-46],让天冬酰胺酶更多地进入咖啡豆内部,而不是停留在其表面。

2 改变焙炒条件抑制丙烯酰胺的生成

咖啡豆焙炒过程中发生的美拉德反应,是丙烯酰胺生成的关键阶段^[47-48]。影响美拉德反应速率的因素包括反应的时间、温度、原料水分活度、环境压力、使用的添加剂等。但咖啡生豆中的水分质量分数较低,水分活度也比较低,对焙炒加工过程中丙烯酰胺的生成量影响相对较小^[16]。因此可以通过改变咖啡豆焙炒条件来控制美拉德反应程度,如焙炒的时间、温度、工艺、空气、压力和是否加入抗氧化

剂,甚至是对焙炒咖啡豆进行后处理及改变贮存温度,最终降低咖啡饮品中丙烯酰胺质量分数。

咖啡生豆的焙炒通常采用两种模式:高温短时间、低温长时间^[4,49]。温度和时间是咖啡焙炒的关键参数,它们共同决定了咖啡的焙炒程度,不同的焙炒程度不仅影响了咖啡风味,也显著影响着丙烯酰胺的生成量^[50-52]。

Schouten 将阿拉比卡和罗布斯塔 2 种咖啡生豆进行由轻到深 5 种程度的焙炒^[53],结果发现 2 种样品在轻中度焙炒时丙烯酰胺生成量最高;阿拉比卡为 (730 ± 30) $\mu\text{g}/\text{kg}$,罗布斯塔为 $(1\ 130\pm10)$ $\mu\text{g}/\text{kg}$ 。随着焙炒程度的增加,2 种咖啡豆样品中的丙烯酰胺质量分数从最高值开始迅速下降,分别为 85%和 88%,最终接近。Rattanasat 等将咖啡生豆在 210、230、250 $^{\circ}\text{C}$ 进行焙炒^[54],结果发现在 250 $^{\circ}\text{C}$ 焙炒几分钟的轻烤咖啡豆中丙烯酰胺质量分数最高,且随着焙炒温度的降低和焙炒程度的提高,烘炒咖啡豆中丙烯酰胺的质量分数显著降低。

丙烯酰胺在咖啡生豆焙炒过程开始时迅速形成,并在达到最大后又很快减少^[22,24]。如 Alshaw 将咖啡豆在 125 $^{\circ}\text{C}$ 下烘焙 30~60 min,前半小时丙烯酰胺逐渐增多,当延长至 40 min 时,丙烯酰胺质量分数增加到最大值 (330.03 ± 8.71) $\mu\text{g}/\text{kg}$;再继续焙炒至 50、60 min,丙烯酰胺质量分数慢慢减少,但都略大于 30 min 时的质量分数^[55]。Bertuzzi 等^[28]在咖啡烘焙的变化温度(90~215 $^{\circ}\text{C}$)下研究了丙烯酰胺的形成过程,发现丙烯酰胺质量分数在 10 min 时(175~177 $^{\circ}\text{C}$)达到最大值 $(1\ 045\pm28)$ $\mu\text{g}/\text{kg}$,随后迅速降低,最终降至 300 $\mu\text{g}/\text{kg}$ 左右。

丙烯酰胺质量分数先增加后减少的现象可能是由于随着咖啡焙炒的进行,美拉德反应前体物质不断被消耗,导致丙烯酰胺生成量减少^[56],或是丙烯酰胺在焙炒过程中被降解^[57]或者直接挥发^[58]。另外,美拉德反应产物之一的类黑素,可以控制咖啡焙炒过程中丙烯酰胺的形成和降解途径,因此也可能会使丙烯酰胺质量分数随焙炒的进行而越来越低^[59-61]。

可以通过改变焙炒工艺来降低咖啡中丙烯酰胺质量分数。研究发现,在流化床烘焙机中进行轻度焙炒、在鼓式烘焙机中进行中度焙炒和在传统烤箱中进行深度焙炒时,咖啡样品中丙烯酰胺的质量分数最低^[62]。

焙炒过程中的空气流速、湿度等参数对烘炒咖

啡豆中丙烯酰胺的质量分数有显著影响^[63]。无论温度如何,增大风速都会加剧丙烯酰胺的生成;在较高的焙炒温度下,增加焙炒空气的湿度会降低丙烯酰胺的生成。

过热蒸气具有较高的加热能力和无氧性等优点,被认为是一种可替代热空气的焙烧介质。在过热蒸气中进行焙炒的咖啡豆比在热空气中的品质更高^[64],且丙烯酰胺生成量更低^[54]。也有实验表明,在饱和蒸气中焙炒可将丙烯酰胺质量分数降低 10%^[21]。

在咖啡生豆的焙炒过程中,可以通过降低压力以使焙炒温度达到丙烯酰胺的沸点(如真空条件下,丙烯酰胺的沸点为 125 $^{\circ}\text{C}$),从而促进丙烯酰胺的挥发来降低其质量分数。真空下焙炒的咖啡豆的丙烯酰胺质量分数比常压下减少了 50%,且咖啡豆颜色和口感与传统工艺相似^[65]。

抗氧化剂如白藜芦醇、葛根素、花青素等常被用于抑制或减少食品中丙烯酰胺的生成^[66-68]。硒作为一种抗氧化剂,可参与美拉德反应生成有机硒化合物^[69],有效降低咖啡焙炒过程中生成的丙烯酰胺质量分数,如添加 108.9~165.3 $\mu\text{g}/\text{kg}$ 硒的咖啡生豆,焙炒后丙烯酰胺的抑制率达 52.8%;此外,加硒后在过热蒸气中焙炒,抑制率可达到 73.9%^[70]。

对焙炒后的咖啡豆进行适当处理,可以降低丙烯酰胺质量分数。Lee 等^[71]对经过焙炒后丙烯酰胺质量分数为 35.4 $\mu\text{g}/\text{kg}$ 的咖啡豆进行电晕放电等离子体射流处理(常压下 1.5 A 输入电流、58 kHz 工作频率),60 min 后丙烯酰胺质量分数降低 32%,且对焙炒咖啡豆的感官特性没有影响。

研究表明,咖啡中的丙烯酰胺质量分数在贮存过程会有所降低,其损失程度受贮存的时间、温度、压力等环境条件的影响^[72]。Hoenicke 等^[73]发现焙炒咖啡豆在室温下贮存 6 个月后,丙烯酰胺质量分数降低了 40%~65%,但在 -40 $^{\circ}\text{C}$ 下贮存的冷冻咖啡豆没有丙烯酰胺降解,说明可通过适当增加咖啡豆的贮存温度来减少丙烯酰胺质量分数。实验中还发现即使是在真空包装下的咖啡豆,其中的丙烯酰胺也会随着贮存时间的推移而逐渐减少。

3 减少咖啡饮品中丙烯酰胺的存留量

咖啡饮品中丙烯酰胺质量分数取决于咖啡豆或咖啡粉末中游离的丙烯酰胺的转移,以及与丙烯

酰胺共存的物质,可以通过降低丙烯酰胺的提取效率,加入丙烯酰胺酶或改变丙烯酰胺存在状态,最终降低咖啡饮品中丙烯酰胺质量分数。

Badoud 等人^[58]通过稳定同位素标记法证实咖啡生豆经焙炒生成的丙烯酰胺有 50% 是游离可溶形式,很容易从咖啡粉末转移到咖啡饮品中^[74]。然而由于饮食习惯和煮制技术的差异,不同地区在咖啡饮品制作时采用了不同的研磨度、粉水比、萃取时间和萃取温度等,这些参数都将显著影响最终咖啡饮品的丙烯酰胺质量分数^[75]。

Michalak 等人^[76]比较了 4 种不同方式制备的咖啡饮品中丙烯酰胺质量分数的大小,结果为:煮咖啡(土耳其咖啡)>浸泡法(法式压榨咖啡)>萃取法(过滤咖啡)>意大利压榨法(浓缩咖啡),丙烯酰胺提取率从土耳其咖啡的 95% 降到浓缩咖啡的 52%。虽然浓缩咖啡浓度最高,但由于在制作过程中,咖啡与水的接触时间较短,丙烯酰胺提取不完全^[21-22,77],因此提取率最低。

冷萃咖啡是指在室温或更低温度下制作的咖啡饮品^[78-79]。常见的冷萃咖啡包括冷泡咖啡和冰滴咖啡^[80-81],都比热煮法的粉水接触时间更长。因此,冷萃咖啡的丙烯酰胺质量分数通常高于热煮咖啡,且随着提取时间的延长,丙烯酰胺的提取率也增高^[82-83]。

Mauro 等研究了使用超临界 CO₂ 萃取技术来降低咖啡饮品中的丙烯酰胺质量分数^[23]:当萃取时间在 525 min 以下时,丙烯酰胺的去除率为 8%~45%;当萃取时间提高到 1 305 min 时,萃取效率最高可达 79%。同时,适当增加萃取的温度及添加乙醇改变萃取液极性,都可提升丙烯酰胺的萃取效率。最佳的工作条件是 100 ℃、200 Pa、体积分数 9.5% 的乙醇溶液。

咖啡饮品制作完成后,可添加丙烯酰胺酶来降低其中的丙烯酰胺质量分数。从雷氏菌^[84]和土杆菌^[85]中提取出的丙烯酰胺酶可将丙烯酰胺水解成羧酸和氨气。Cha 的研究表明^[86],在咖啡煮制后,当温度降至 70~75 ℃ 时,向每 100 mg 咖啡饮品加入 10 mL 丙烯酰胺酶,可消除咖啡饮品中 50% 的丙烯酰胺,且该酶在此温度范围时仍很活跃。Bedade 等人研究了丙烯酰胺酶对烘焙咖啡中丙烯酰胺的去除效果^[87],以柠檬酸为交联剂,碳二亚胺盐酸盐/N-羟基琥珀酰亚胺为活化剂,并用壳聚糖包被海藻酸钙微珠来固定部分纯化的丙烯酰胺酶。该固定化丙烯酰胺

酶对速溶咖啡饮品中的丙烯酰胺消除效果非常显著,且具有较好的热稳定性和贮存稳定性,可重复使用 4 次。

Narita 等将 20 种氨基酸添加到罐装咖啡中,并在 121 ℃ 热处理 6 min,结果发现加入半胱氨酸后,丙烯酰胺质量分数降至极低^[88]。这可能是由于半胱氨酸的巯基和赖氨酸的氨基对丙烯酰胺的 C=C 键的亲核攻击作用^[89-90]。Yoshioka 等^[91]研究发现,罐装咖啡牛奶在贮存过程中,丙烯酰胺质量分数随时间增加而减少,且贮存温度越高,减少越快。在牛奶咖啡中发现了 75.3% 的丙烯酰胺-蛋白质复合物,表明了丙烯酰胺减少的主要去向,其中赖氨酸和半胱氨酸对丙烯酰胺的减少作用尤为显著。这种丙烯酰胺与蛋白质的反应现象以前也有报道^[92-94]。但这些加合物形成的反应速度较慢,或是反应受到限制。此外,项雷文等的实验发现,丙烯酰胺对美拉德反应产物的光谱性质有显著影响,证实丙烯酰胺可能会与美拉德反应产物产生加合作用,从而降低其质量分数和毒性^[95-96]。

4 展 望

生产出更加健康安全的咖啡饮品是研究人员和咖啡企业的共同目标,作者综述了在咖啡饮品制作的各个环节中可用于降低丙烯酰胺质量分数的措施。首先,可选择丙烯酰胺前体物质质量分数更少的咖啡生豆品种作为饮品制作的原料,并通过湿法加工处理、添加天冬酰胺酶等方式将其质量分数进一步降低。在咖啡生豆的焙炒阶段,可以通过控制焙炒的温度和时间来适当增加咖啡豆的焙炒程度,使生成的丙烯酰胺质量分数更低。同时,可通过使用不同的焙炒工艺、改变空气湿度、降低压力、添加抗氧化剂等措施来抑制焙炒所产生的丙烯酰胺质量分数。焙炒后的咖啡豆可通过电晕放电等离子体射流方式来减少丙烯酰胺质量分数,也可在咖啡豆贮存时适当提高贮存温度以促进丙烯酰胺的降解。在咖啡泡煮阶段,可采取减少粉水接触时间的方式进行咖啡饮品的制作,以降低丙烯酰胺的提取率。此外,超临界萃取技术也可用来降低咖啡饮品中丙烯酰胺的质量分数。最后,可向咖啡饮品中添加丙烯酰胺酶或氨基酸等丙烯酰胺加合物,从而降低最终咖啡饮品中丙烯酰胺的存留量。

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