CODE OF PRACTICE FOR THE PREVENTION AND REDUCTION OF ETHYL CARBAMATE CONTAMINATION IN STONE FRUIT DISTILLATES

CAC/RCP 70-2011

I. INTRODUCTION

1. Ethyl carbamate is a compound that occurs naturally in fermented foods and alcoholic beverages such as bread, yoghurt, soy sauce, wine, beer, and particularly in stone fruit distillates, mainly those made from cherries, plums, mirabelles and apricots.

2. Ethyl carbamate can be formed from various substances inherent in food and beverages, including hydrogen cyanide (or hydrocyanic acid), urea, citrulline, and other N-carbamyl compounds. Cyanate is probably the ultimate precursor in most cases, reacting with ethanol to form ethyl carbamate. Therefore ethyl carbamate reduction measures should focus on hydrocyanic acid and other precursors of ethyl carbamate.

3. Ethyl carbamate is genotoxic and a multisite carcinogen in animals and is probably carcinogenic to humans.

4. Stone fruit distillates, in particular, contain ethyl carbamate in manyfold higher concentrations than other fermented foods and beverages. In stone fruit distillates ethyl carbamate can be formed from cyanogenic glycosides that are natural constituents of the stones. When mashing the fruit, the stones may be damaged and cyanogenic glycosides from the stones may come into contact with enzymes in the fruit mash. Cyanogenic glycosides are then degraded to hydrocyanic acid/cyanides. Hydrocyanic acid may also be released from intact stones during a prolonged storage of the fermented mash. During the distillation process hydrocyanic acid may be enriched in all fractions. Cyanide in the distillates may be oxidized to cyanate, which can react with ethanol to form ethyl carbamate. Certain environmental conditions such as exposure to light, high temperatures and the presence of copper ions promote the formation of ethyl carbamate in the distillate.

5. Although no strong correlation between the level of hydrocyanic acid and ethyl carbamate has been established so far, it is evident that under certain conditions high concentrations of hydrocyanic acid lead to higher levels of ethyl carbamate. A potential increase in ethyl carbamate formation has been associated with levels at or above 1 mg/l hydrocyanic acid in the final distillate. Based on practical

Adopted 2011.

experiences it can be assumed that from 1 mg of hydrocyanic acid up to 0.4 mg ethyl carbamate potentially can be formed in a non-equimolar relationship.

2. SCOPE AND DEFINITIONS

6. This Code of Practice intends to provide national and local authorities, manufacturers and other relevant bodies with guidance to prevent and/or reduce formation of ethyl carbamate in stone fruit distillates. Ethyl carbamate formation in other alcoholic beverages and foods is not covered in this Code.

7. The definitions below apply to this Code:
   a) **Stone Fruit** means for the purpose of this Code of Practice certain edible fruit of trees belonging to the genus Prunus of the rose family (Rosaceae), i.e. cherry, plum, peach and apricot.
   b) **Distillates** means, for the purpose of this Code of Practice, alcohol-rich products obtained after the distillation process and ready for consumption.
   c) **Stone Fruit distillates** means, for the purpose of this Code of Practice, the distillates for consumption, obtained after the distillation:
      – of the mash prepared by fermentation of crushed stone fruits,
      – of fermented stone fruit marc (pomace),
      – of mash obtained by fermentation and/or maceration of crushed and/or whole stone fruit in ethyl alcohol or alcoholic beverages.

3. GENERAL REMARKS

8. This Code covers all possible measures that have been proven to prevent and/or reduce high levels of ethyl carbamate in stone fruit distillates. When applying the Code for specific stone fruit distillates, measures should be carefully chosen from the viewpoint of benefit and feasibility. In addition, measures should be implemented in accordance with the relevant national and international legislation and standards.

9. It is recognised that reasonably applicable technological measures – Good Manufacturing Practices (GMP) – can be taken to prevent and reduce significantly high ethyl carbamate levels in stone fruit distillates. The reduction of ethyl carbamate could be achieved using two different approaches: first, by reducing the concentration of the main precursor substances (e.g. hydrocyanic acid and cyanides); second, by reducing the tendency of these substances to react to form cyanate.

4. TYPICAL PRODUCTION PROCESS

10. The production process for stone fruit distillates involves preparing mash by using whole stone fruits or their marc as ingredients, followed by fermentation and distillation. The process typically follows the steps listed below:
    a) preparing mash by crushing the whole ripe fruit for stone fruit spirit drinks or by using stone fruit marc for stone fruit marc spirit drinks;
    b) fermenting the mash in stainless steel tanks or other suitable fermentation vessels;
    c) in the case of using a maceration process, the mash is prepared by macerating crushed or whole fruit in ethyl alcohol or alcoholic beverages and stored for a period, without fermentation process;
    d) transferring the fermented mash into the distillation device, often a copper pot;
    e) heating the fermented mash by a suitable heating method in order to slowly boil off the alcohol;
    f) cooling the alcohol vapour in an appropriate (e. g. stainless steel) column where it condenses and is collected;
    g) separation of three different fractions of alcohol: ‘heads’, ‘hearts’ and ‘tails’;
    h) dilution to the final alcoholic grade.

11. During distillation, the heads boil off first. Components with low boiling point e.g. ethyl acetate and acetaldehyde are part of the heads. This fraction is generally unsuitable for consumption and should be discarded.

12. During the middle distillation run (the ‘hearts’), the principal alcohol in all spirits, ethyl alcohol (ethanol), is distilled. This part of the distilling run, where the content of volatiles other than ethanol is lowest and the purest fruit aromas are present, is always collected.

13. The ‘tails’ of the distillation include acetic acid and fusel oils, which are often identified by unpleasant vinegary and vegetal aromas. They are also discarded, but they may be re-distilled because some ethanol is invariably included with the tails.

5. RECOMMENDED PRACTICES BASED ON GMP’s

5.1 Raw materials and preparation of fruit mash

14. The raw materials and preparation of the fruit mash should be suitable to avoid the release of hydrocyanic acid, a precursor of ethyl carbamate.

15. The stone fruits should generally be of a high quality, not mechanically damaged and not microbiologically spoiled, as damaged and spoiled fruit may contain more free cyanide.

16. The fruit should preferably be de-stoned.

17. If the fruits are not de-stoned and/or the residues of fruits (marc) are used for preparing mash, they should be mashed gently avoiding the crushing of stones. If possible, stones should be removed from the mash.

5.2 Fermentation

18. Selected yeast preparations for the production of spirit drinks should be added to the mashed fruits, according to the manufacture's instructions for users, for a fast and "clean" fermentation.

19. Mashed fermented fruits should be handled with high standards of hygiene, and exposure to light should be minimised. Fermented fruit mashes containing stones should be stored as briefly as possible before distillation since hydrocyanic acid may also be released from intact stones during prolonged storage.

20. If the mash is prepared by macerating stone fruit into alcoholic beverages or ethyl alcohol, the stone fruit should be removed soon after the aroma of the stone fruit is adequately extracted.

5.3 Distillation equipment

21. Distillation equipment and the distillation process should be suitable, to ensure that hydrocyanic acid is not transferred into the distillate.
    a) Use of a copper still will limit carryover of ethyl carbamate–forming precursors into the distillate.
    b) The distillation equipment should preferably include automatic rinsing devices and copper catalytic converters. The automatic rinsing devices will keep the copper stills cleaned while the copper catalytic converters will bind hydrocyanic acid before it passes into the distillate.
    c) Automatic rinsing devices are not necessary in the case of discontinuous distillation. The distillation equipment should be cleaned by systematic and thorough cleaning procedures.
    d) When copper catalytic converters or other dedicated cyanide separators are not available, copper (I) chloride preparations can be added to the fermented fruit mash before distillation. The purpose of these preparations containing copper (I) ions is to bind hydrocyanic acid before it passes into the distillate. Copper (II) ions are without effect and should not be used.

22. While copper ions can inhibit formation of ethyl carbamate precursors in the mash and in the still, they can promote formation of ethyl carbamate in the distillate. Therefore, use of a stainless steel condenser at the end of the distillation device

rather than a copper condenser will limit presence of copper in the distillate and reduce the rate of ethyl carbamate formation.

5.4 Distillation process

23. Stones settled in the fermented mash should not be pumped into the distillation device.

24. Distillation should be carried out in such a way that alcohol is boiled off slowly and in a controlled manner (e.g. by using steam instead of a direct flame as the heating source).

25. The first fractions of the distillate, called 'heads', should be separated carefully.

26. The middle fraction, called 'hearts', should then be collected and should be stored in the dark. When the alcohol content of the actual distillate reaches 50% vol. at the receiver, collection should be switched to the 'tails', so that any ethyl carbamate that may have been formed is separated in the tail fraction.

27. Some manufacturers may redistill the separated tails, possibly containing ethyl carbamate. If the tails are used for re-distilling, they should be re-distilled separately, however for reduction of ethyl carbamate concentration it is preferable to discard the tail.

5.5 Checks on the distillate, re-distillation and storage

5.5.1 Hydrocyanic acid

28. Testing for hydrocyanic acid may be used as a simple test for ethyl carbamate in distillates. Therefore, the distillates should be regularly checked for their levels of hydrocyanic acid. The determination could be carried out by specific tests including kits for rapid testing of the hydrocyanic acid levels.

29. If the concentration of hydrocyanic acid in the distillate exceeds a level of 1 mg/l, re-distillation with catalytic converters or copper preparations is recommended.

30. Distillates should be stored in bottles that are lightproof (or filter ultraviolet light) or in covering boxes and not at higher temperatures.

5.5.2 Ethyl carbamate

31. Testing of ethyl carbamate is recommended for distillates in which the compound may already have been formed (e.g. distillates with unknown history of production,

distillates with higher levels of hydrocyanic acid, or storage at light or at high temperatures).

32. Additional distillation is effective in order to reduce ethyl carbamate in distillates.

6. GENERAL RECOMMENDATIONS

33. The national, state and local governments as well as the non-governmental organizations (NGOs, commercial associations and cooperatives) should provide their own basic training and update the information on mitigating ethyl carbamate in stone fruit distillates.

34. The non-industrial, small-scale preparation of these drinks should have available material with information on the specific recommendations based on good manufacturing practices and guidance on prevention and reduction of ethyl carbamate in the stone fruit distillates. Specifically, material should be made available to small-scale producers of stone fruit distillates.