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Effect of multiple distillation and head fraction removal on the volatile content of distillate from fermented coconut (*Cocos nucifera* L.) water

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Abstract: *Tuba* (fermented coconut sap) and *lambanog* (distilled *tuba*) production had long been a source of livelihood in the Philippines. However, the production of these alcoholic beverages is tedious and laborious starting with the collection of coconut sap. A potential substitute to coconut sap is coconut water. This study was conducted to determine the effect of multiple distillation and head fraction removal on the volatile components of distilled fermented coconut water. Multiple distillations were done thrice, diluting the distillate with tap water every distillation stage. The head fraction (established as first few drops amounting to 10% of the total volume of distillate) was also removed in Treatment 1 (T1) but retained in Treatment 2 (T2). The ethanol and methanol and ethyl acetate (EA) contents were measured using gas chromatography and titrimetric methods, respectively. The head fraction was found to be very volatile with 95-98% ethanol. There was a considerable decrease in ethanol between T1 (73-75%) and T2 (84-92%). Methanol content was found to be negligible in the head fraction removed at every distillation stage (8-16 ppm). On the other hand, there was a dramatic decrease in the levels of EA with head fraction removal from 27-138 ppm in T2 to 2-72 ppm in T1. EA also decreased with multiple distillations. Most importantly, the levels of methanol in all distillation stages of both treatments including the head fraction were within the legal limit. On the other hand, only the EA levels in the third distillation of T1 and its corresponding head fraction passed the legal limit.

Keywords: Alcoholic beverages, coconut, distillation, ethyl acetate, fermentation, methanol, ethanol

Introduction

The production of fermented coconut sap (toddy) or *tuba* is very common in many parts of the Philippines. When *tuba* is distilled, the result is a beverage locally called as *lambanog* or Philippine vodka containing 40-45% alcohol and used as base for many alcoholic premixes and flavored spirits. *Lambanog* plays an important role in the development and upliftment of the coconut industry because it serves as another form of coconut utilization, provides a means of employment, and generates additional income for farmers in the coconut-based areas. However, most of the *lambanog* makers do not control the temperature and length of distillation process which may account for the wide variation in quality of the product. The manufacture of *lambanog* involves a crude process, hence, low efficiency of fermentation and poor quality control. Sanchez (1986) further added that chemicals such as ethyl acetate (EA), methyl alcohol (methanol), n-propyl alcohol, isobutyl, and iso-amyl alcohol were detected using gas chromatography. Several techniques are now being employed to minimize the presence of these substances in distilled spirits since methanol metabolites are known to damage the central nervous system (Jackson, 1994) while EA imparts undesirable flavor and aroma (Dieguez *et al*., 2005). Even though methanol levels in alcoholic beverages are related to the pectic substances naturally present in the fruit material, careful monitoring during the distillation process must still be done to minimize methanol carry-over in the ethanol fractions (Dambergs *et al*., 2002). On the other hand, correct separation of the first fraction (head) containing toxic substances must be employed during distillation to ensure controlled level of EA (Madrera *et al*., 2006).

Tuba and *lambanog* production are tedious and laborious (Medina *et al*., 1997). A potential substitute to coconut sap in producing alcoholic beverages is coconut water. Coconut water contains several of the nutrients needed for growing yeasts. However, only 4% fermentable sugar is found in coconut water, hence, either sugar should be added or the water will have to be concentrated by some means (i.e. reverse osmosis) to increase its sugar content for alcohol production (Banzon *et al*., 1990). However, large quantities of this potential source of economically important drinks are being disposed off as by-product of desiccated coconut and copra manufacture resulting

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in lost or wasted food values and even aggravate environmental pollution as well. The objective of this study was to develop food uses from coconut water and improve the volatile composition of its distillate. It is hypothesized that multiple distillations and removal of head fraction during distillation will lessen the amount of unwanted volatile substances like methanol and ethyl acetate in the distillate of coconut water.

Materials and Methods

The study was conducted at the Food Microbiology Laboratory, Food Science Cluster, College of Agriculture, University of the Philippines Los Banos, Philippines from June to October 2008. Distillation of the fermented coconut water was done at the Agricultural Machinery Division (AMD) of the College of Engineering and Agro-Industrial Technology (CEAT), in the same University. The coconut water was collected from Los Banos public market.

Fermentation

The coconut water was filtered using cheesecloth after which, the sugar content was adjusted to 20^0Brix by adding refined sugar. Then, 10% of every 4 liters was separated in Erlenmeyer flasks, boiled, cooled and inoculated with *Saccharomyces ellipsoideus* to serve as yeast starter. On the other hand, 5 ml of sodium metabisulfite (SMS) was added to the rest of the remaining mixture. The jars were covered with aluminum foil and allowed to stand for 18-24 hours prior to addition of yeast starter. After adding the starter to the mixture, the jars were covered with fermentation lock and fermented at ordinary room temperature (30^0C) for 3 weeks. The clear liquid was siphoned off to clean jars then 5 ml of 10% SMS was added per 4 liters of the fermented coconut water to stop the fermentation.

Distillation

The distiller used in this study was composed of three major parts/sections: the boiler, the column and the condenser. The first section of the column was the rectifier where vapors pass through holes in a perforated plate separating the boiler to the rectifier. The second section of the column was the stripper. The stripper contained the condenser, a coil of soft copper pipe, surrounded with water as heat exchange medium, which condenses the vapors back to liquid state to "strip" its alcohol content further.

The fermented coconut water was divided into 2 treatments and distilled three times, reconstituting to original volume with tap water every distillation stage. For the first treatment (T1), the first few drops containing high levels of toxic compounds (head) were separated from each distillation stage, resulting in three samples coded T1 – I, T1 – II and T1 – III. The amount of the head fraction that was separated was established at 10% of the total distillate recovered from the 1st distillation stage. The head fractions removed were also coded as T1 – HI, T1 – HII and T1 – HIII. Ethanol and methanol contents and EA content was measured at every stage using gas chromatography and titration, respectively.

The second treatment (T2) was a control set-up wherein the head fraction is included in the distillate. The control also underwent multiple distillations as described above for T-1. The experimental set-up is shown in Figure 1.

Ethanol and methanol

The ethanol and methanol contents of the distillates from Treatments 1 and 2 were obtained by using gas chromatography (GC) at the National Institute of Molecular Chemistry and Biotechnology (BIOTECH), University of the Philippines Los Banos. The parameters for GC analysis, performed in three trials, are as follows:

Initial Temperature	: 190°C
Initial Column Time	: 0 minutes
Final Column Temperature	: 190°C
Injector Temperature	: 240°C
Detector Temperature	: 240°C
Detector	: FID
Column	: Porapak Q (100 – 120 mesh) 1.2m × 2.0mm glass
Carrier Gas (high purity N_2)	: 40mL/min
Volume of Sample Injected	: 1µL

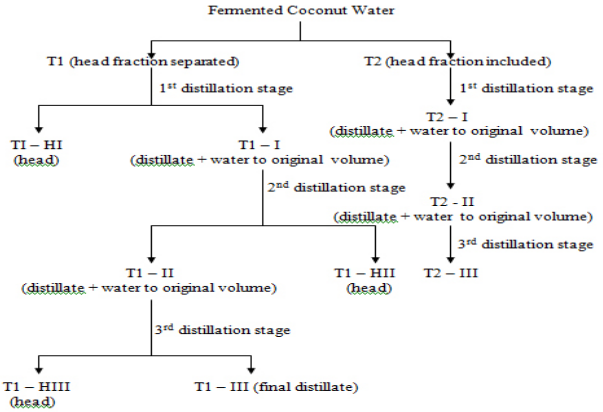

Figure 1. Experimental set-up for the distillation of fermented coconut water

Ethyl acetate

EA was analyzed in three trials as described in AOAC (2000). Briefly, 20 ml of the distillate was placed in a 250 ml Erlenmeyer flask. Then, 3 drops of phenolphthalein was added and the solution was

titrated using 0.1 M NaOH until a pink color persists for 1 minute. Then, 25 ml of 0.1 M NaOH was added before refluxing the solution for 1 hour. The excess alkali was titrated with 0.05 M H_2SO_4. The same procedure was done for blank solution containing 20 ml distilled water. The amount of 0.1M alkali used in saponification of esters was calculated as ethyl acetate (1 ml 0.1M NaOH = 8.8 mg ethyl acetate) using the formula:

$$\text{Amount EA} = H_2SO_4 \text{ used in titration of excess alkali}_{(\text{blank} - \text{sample})}$$

Results and Discussion

The distillation process consisted of two treatments. In the first treatment (T1) the head fraction, the first few drops at boiler temperature of 58-59^{0}C and stripper temperature of 48-50^{0}C, was separated. This fraction comprised 10% of the total amount of distillate and contained the most volatile compounds according to literature (Mangas *et al.,* 1996; Madrera *et al.,* 2006; Reche *et al.,* 2007). On the other hand, head fraction was not separated in the second treatment (T2).

Ethanol content

Table 1 establishes the volatility of the head fraction with nearly 100% ethanol (95-98%). There was also no considerable decrease in the ethanol content of the head fraction even with multiple distillations which could be accounted for by the uniformity of the distillation process; that is, the length of boiling and the time which dropping of distillate started were approximately the same in each of the three stages within treatments. Multiple distillations did not markedly affect the levels of ethanol in T1 with values ranging from 74-76% ethanol. Lower concentration of ethanol in T1 as compared to the values in T2 was apparently attributed to the separation of the ethanol-rich head fraction in T1. If the distillate will be used as fuel for agricultural machineries, separation of the head fraction is not recommended since it significantly lowered the amount of ethanol in the distillate. However, if the distillate is destined for human consumption, removal of the head fraction should be done because of the undesirable odor it imparted to distilled spirits. Also, most high-strength alcoholic beverages like gin and *lambanog* contained only 40% alcohol. Treatment 2 (T2) showed that the head fraction collected at 48-50^{0}C stripper temperature was diluted with the rest of the distillate fraction. Ethanol content at the end of every distillation stage in T2 ranged from 84-92%.

Table 1. Amount of ethanol, methanol and ethyl acetate present in the distillates from fermented coconut water

Sample code	Ethanol (%)	Methanol (ppm)	Ethyl acetate (ppm)
T1 – I	73.53 ± 0.98	47.64 ± 0.35	72.16 ± 0.49
T1 – II	73.40 ± 3.90	41.01 ± 1.27	41.36 ± 0.27
T1 – III	75.76 ± 0.25	49.27 ± 0.49	2.64 ± 1. 17
T1 – HI	97.99 ± 7.45	8.86 ± 2. 12	501.16 ± 0.93
T1 – HII	98.16 ± 3.30	2.74 ± 0. 79	175.56 ± 1.04
T1 – HIII	94.97 ± 3.47	16.61 ± 3.15	19.36 ± 1.12
T2 – I	92.35 ± 1.59	16.25 ± 3.69	124.96 ± 1.52
T2 – II	86.58 ± 1.11	18.87 ± 0.78	138.16 ± 0.71
T2 – III	84.09 ± 2.68	27.08 ± 5.89	27.08 ± 0.65

T1 – I : treatment 1, first distillation stage
T1 – II : treatment 1, second distillation stage
T1 – III : treatment 1, third distillation stage
T2 – I : treatment 2, first distillation stage
T2 – II : treatment 2, second distillation stage
T2 – III : treatment 2, third distillation stage
T1 – HI : head fraction of T1 – I
T1 – HII : head fraction of T1 – II
T1 – HII : head fraction of T1 – III

Methanol content

The methanol content in T1 which ranged from 47-49 ppm (Table 1) was much higher than the methanol content in T2 ranging from 16-27 ppm. Separation of the head fraction and multiple distillations did not considerably reduce the methanol content in the distillates of T1. This was contrary to what was expected since the head fraction should contain most of the volatile materials and removal of which should result in decreased levels of methanol. Deviation from the expected result may be due to any of the several factors like the pectin content of the fermentable substrate as well as to the presence of pectin methyl esterases (Madrera *et al.*, 2006). The raw material used in fermentation also has effects on methanol content. Madrera *et al.* (2003) noticed higher levels of methanol in manufacturing cider when apple juice concentrate was used rather than fresh must due to intense enzymatic activity in the former. Storage conditions like bacterial and fungal activity can also result in the production of methanol and negligence during the distillation process can increase methanol carry-over to the ethanol fraction (Dambergs *et al.,* 2002). Furthermore, delay in the distillation of the raw material after alcoholic fermentation contributed to increased methanol levels as observed by Dieguez *et al.* (2005) in Galician orujo spirit stored for prolonged period. However, Valverde *et al.* (1982) and Lund *et al.* (1983) had included coconut in their study for the amount of pectin in different fruits and vegetables. None of them used coconut water but used coconut meat instead. Furthermore, Banzon *et al.* (1990) and Woodroof (1970), two authors of books fully devoted to coconut, did not have a single mention of carbohydrates in coconut water rather accounting it as total sugars or reducing sugars solely. These literature reviews might mean that the amount of pectin in coconut water was negligible if not totally absent. Banzon *et al.* (1990) indicated

a total solids of 4.71% in coconut water, of which, 2.20-2.79% were reducing sugars and 0.104-0.512% were proteins. Minerals mainly potassium are also major components of the TSS. Only 0.5-1% could be assumed as the carbohydrate part of the coconut water which could not be attributed solely to pectin. Even the meat is not a significant source of pectin. Valverde *et al.* (1982) measured the pectin content of coconut meat as %AGA (anhydrogalacturonic acid) and obtained 0.51% (fresh basis) and 0.72% (dry basis). Of these values, the major part is of the insoluble pectin (Lund *et al.,* 1983) which meant that only a very small amount of coconut meat pectin could be soluble in the coconut water. These reviews suggested that the presence of higher methanol levels in T1 compared to T2 could not be attributed to the pectin content of coconut water. Even so, the deviation could still be attributed to the difference of the raw materials used in the fermentation. The coconut water used in this study was collected from different sources in Los Baños public market. Madrera *et al.* (2003), as cited earlier, have established how the raw material could increase methanol concentration. Furthermore, fungal and bacterial activities might have occurred during the collection of coconut water for T1 (Dambergs *et al.,* 2002). Although very minimal, these contaminations might have contributed to higher methanol concentration in T1 compared to T2. Further studies must be done to establish the effect of raw materials used in the fermentation to the methanol concentration after distillation.

Prolonged storage prior to distillation of the samples for T1 could also be one of the reasons underlying the deviation from the expected result. Samples for T1 and T2 were not distilled at the same day. T2 was distilled first on July 29, 2008 to establish the amount of the head fraction that will be separated in T1. The rest of T1 was distilled on July 30 and 31, 2008. The approximately 27- to 48-hour difference in distillation might have produced more methanol.

In conclusion, the removal of the head fraction did not significantly influence the methanol content of the distillate. The values of methanol in the head fraction ranged from 9-17 ppm (Table 1) which was irrelevant as compared to the legal limit of methanol. In fact, from the standpoint of ethanol and methanol contents, the head fraction should not be separated since separation did not considerably reduce the methanol levels but contributed to a significant loss in ethanol levels of the distillate based on the results established earlier.

Ethyl acetate content

To establish the importance of head fraction separation and multiple distillations to the aroma of the distillates obtained from T1 and T2, analysis for ethyl acetate (EA) was done. Several authors had distinguished EA to be the primary ester contributing to the aroma of distilled spirits. It exhibited low odor threshold and therefore were quite relevant for the beverage sensory properties (Nascimento *et al.,* 2008). It was considered as sensorial negative compound since it imparted undesirable aroma such as nuances of glue to distilled spirits (Ferrari *et al*., 2004).

The EA was present among the distillates of T2 ranging from 27-125 ppm (Table 1) which was apparently because this treatment did not employ head fraction separation. EA was also present among the distillates of T1, the highest being contained in the head fraction (19-501 ppm). This may be due to its low boiling point (77°C) and the high miscibility of EA in water which was expected to distill at the beginning of the distillation and be included in the head fraction.

It is also worthy to note the drastic decrease in the EA levels among T1 and T2 and in between the multiple distillation stages of each treatment. EA remarkably decreased in T1 as compared to T2 with the removal of the head fraction. The levels of this undesirable odor-causing ester also decreased from the first distillation at 72.16 ppm to the third distillation at an almost negligible amount of 2.64 ppm in T1. Deviation from the trend was observed in the first distillation of T2 at 124.96 ppm which increased to 138.16 ppm during the second distillation but nevertheless decreased in the third distillation at 27.08 ppm. The chemical test performed on the distillates obtained from the two treatments established that the head fraction separation and multiple distillations must really be employed to reduce the undesirable EA in distilled products thereby improving the aroma.

Legal limits of volatile compounds

The values obtained for the two undesirable volatile compounds present in the distilled coconut water (Table 2) were compared to the legal limits established by the European Union (EU) to answer the question on the legitimacy of coconut water for the production of distilled spirit for alcoholic beverages. The legal limit for methanol was 2800 ppm of 40% ethanol (Andraous *et al.,* 2004). Compared to the legal limits, the obtained methanol levels corresponding to ethanol concentrations in the samples were negligible. Methanol never accumulated to toxic levels under legitimate procedures (Andraous *et al.,* 2004) which strongly established that the methods employed in the fermentation and distillation of the distillates obtained

Table 2. Methanol and ethyl acetate content of distillates from fermented coconut water compared to legal limits according to literature

Sample code	Coconut water distillate		Legal limits	
	Methanol (ppm)	Ethyl acetate (EA) (ppm)	Methanol[a] (ppm)	EA (ppm)
T1 – I	47.64	72.16	5287.10	33
T1 – II	41.01	41.36	5138.00	33
T1 – III	49.27	2.64	5303.20	33
T1 – HI	8.86	501.16	6359.30	33
T1 – HII	2.74	175.56	6871.20	33
T1 – HIII	16.61	19.36	6647.90	33
T2 – I	16.25	124.96	6464.50	33
T2 – II	18.87	138.16	6060.60	33
T2 – III	27.08	27.08	5886.30	33

T1 – I : treatment 1, first distillation stage
T1 – II : treatment 1, second distillation stage
T1 – III : treatment 1, third distillation stage
T2 – I : treatment 2, first distillation stage
T2 – II : treatment 2, second distillation stage
T2 – III : treatment 2, third distillation stage
T1 – HI : head fraction of T1 – I
T1 – HII : head fraction of T1 – II
T1 – HII : head fraction of T1 – III
[a]Computed based on Andraous *et al.* (2004) that methanol legal limit for 40% ethanol is 2,800 ppm.

from fermented coconut water were safe for human consumption. On the other hand, the legal limit for EA was 33 ppm (Dambergs *et al.,* 2002). Based on the table, only the EA levels in the third distillation of Treatment 1 (T1-III) and its corresponding head fraction (T1-HIII) passed the limit. This meant that once smelled, the distillates from T1-I, T1-II and their corresponding head fractions (T1-HI and T1-HII, respectively) as well as the distillates from all the stages of T2, would convey nuances of glue thereby imparting undesirable aroma to the alcoholic beverages where these distillates will be added.

Conclusions

In conclusion, head fraction removal and multiple distillations were not important in methanol content reduction of distilled coconut water. In fact, the head fraction can be retained to prevent losses in ethanol. However, these two methods are strongly advised for significant reduction of EA in distilled spirit production. It could also be established that in terms of quality, coconut water could be utilized in producing distillate for alcoholic beverages. Moreover, production of alcoholic beverages out of coconut water could be a new source of livelihood in the coconut-producing regions of the Philippines and could also minimize environmental pollution caused by tons of coconut water being wasted as a by-product in the manufacture of other coconut products.

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