

Studies on freeze-withering in black tea manufacturing

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Abstract

In order to reduce the withering time during black tea manufacture, freeze-withering was attempted, which resulted in flaccid leaves with increased cell membrane permeability in a shorter period of time. The freeze-withered leaves had similar amounts of quality precursors as that of the conventionally withered leaves. The resultant black tea was better in quality than those manufactured without withering and after normal withering. Manufacturing of fresh leaves resulted in comparable levels of theaflavins, but the tea was not acceptable due to its harshness. Increased cell membrane permeability during freeze-withering showed that the leaf attained a sufficient degree of physical wither. The decreases in the levels of chlorophyll showed that chemical withering had also been achieved during freeze-withering, which is supported by the increased levels of caffeine.

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1. Introduction

Tea is the second largest drink consumed in the world after water. Black tea is manufactured from the tender leaves and buds of the evergreen shrub *Camellia sinensis* (L.) O. Kuntze. Tea manufacturing consists of four stages, namely withering, rolling, fermentation and drying. Of these, withering is the first and most important step in tea manufacture. Withering is the most expensive process in terms of time, money and energy. Withering is done to make the leaf ready, physically and biochemically, for effective rolling, fermentation and drying processes. The chemistry of withering has been studied by many scientists. Withering results in (a) an increase in the levels of amino acids (Roberts & Wood, 1951), caffeine content (Sanderson, 1964), sugars (Owuor & Orchard, 1989) and polyphenol oxidase activity (Ullah &

Roy, 1982), (b) changes in chlorophyll content (Wickramasinghe, 1975), (c) formation of precursors of volatile flavour compounds (Mahanta & Baruah, 1989) and (d) an increase in cell membrane permeability (Sanderson, 1968). All these changes, except for cell membrane permeability, are independent of moisture loss during withering. As the polyphenols and polyphenol oxidase are spatially separated in tea leaf, an increase in cell membrane permeability is important in facilitating the mixing of substrates and enzymes involved in tea fermentation.

Even though cell membrane permeability is not a chemical phenomenon, it is a prerequisite for the occurrence of the chemical reactions, which contribute to the final tea quality. If cell membrane permeability were to be achieved in a shorter period, tea factories would be able to handle greater amounts of leaf per day. Earlier work along these lines (Ramaswamy, 1989) aimed at the process parameters alone and freeze-withering was tested for its suitability for reconditioning (RC) type of manufacture only. Importance was not given to the biochemical changes taking place in the leaf. A comparison of freeze-withering with normal withering was carried out by Ranganath, Marimuthu,

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Raju, and Ramaswamy (1991, 1994) but those studies were done without removal of surface moisture. The importance of thawing is to remove the surface moisture effectively and to fine tune the physical wither, so that the leaves will not clog in the rotorvane during manufacturing. Hence, the present study has been undertaken to study the physical and biochemical changes taking place during freeze-withering.

2. Materials and methods

Clonal tea leaves (UPASI-9) used in this study were collected from UPASI Experimental Farm, Valparai, situated at 1050 m above MSL. Two kilograms of leaves were processed immediately, as soon as they are plucked, without giving any withering. Freeze-wither was done by keeping the leaves in a deep freezer at $-20\text{ }^{\circ}\text{C}$. Following this, thawing was carried out in a stream of warm air ($35\text{ }^{\circ}\text{C}$) for 30 min with the leaves spread at the rate of 9 kg per square metre in a withering trough. Freeze-withered leaves were drawn at regular intervals (2, 4, 6 and 8 h) and were processed by following standard manufacturing practices of CTC rolling, fermentation and drying.

Green leaf samples were drawn at regular time intervals and analysed for chlorophyll (Chl.), carotenoids (Harborne, 1973), polyphenols (Dev choudhury & Goswami, 1983) and catechins (Swain & Hillis, 1959).

To assess the extent of the increase in cell membrane permeability in frozen leaf, tests were carried out for polyphenols and catechins which leached out into cold water by keeping a definite quantity of green leaf samples in 100 ml of distilled water at room temperature for 2 h. Electrical conductivity and pH of the cold water extract were also determined.

Leaf samples were cut in a miniature CTC machine, five times, and allowed to ferment at $25\text{ }^{\circ}\text{C}$ and 95% RH. Fermented *dhool* was dried in a mini fluid-bed drier to a final moisture content of three per cent. Tea samples, thus manufactured, were sorted using an 'Endecott' sieve shaker and the pekoe fannings grade fraction was taken for analysis. During fermentation, known quantities of *dhool* were withdrawn and analysed for formation of theaflavin, as prescribed by Ullah (1977).

Theaflavins (TF), thearubigins (TR), highly polymerized substances (HPS) and total liquor colour (TLC) were determined by the procedures given by Thanaraj and Seshadri (1990) and Lakshminarayanan and Ramaswamy (1978). Water extract was estimated as per Indian Standard (1999). Caffeine content was determined by the method of Newton (1979). The briskness index [$\text{BI} = \text{TF} \times 100 / (\text{TF} + \text{caffeine})$] and colour index [$\text{CI} = \text{TF} \times 100 / (\text{TR} + \text{HPS})$] were also worked out. A portion of sample was sent to professional tea tasters for organoleptic evaluation. The teas were tasted and the order of preference was assigned to each of the attributes, such as leaf colour, infused leaf outturn, liquor and briskness among the different treatments. Impressions on the flavour and an overall

comment were also recorded. The experiment was repeated thrice and the results were analysed statistically using SPSS software, version 7.5.

3. Results and discussion

3.1. Green leaf biochemical constituents

The visual observations made on the physical characters of frozen, normally withered and fresh leaf samples are presented in Table 1. When clonal tea leaves were frozen, the leaf colour did not change, but the leaf became flaccid and the permeability increased. The leaf appeared to have attained enough physical and chemical wither. Polyphenols and catechins of the freeze-withered leaves were found to decrease as the freezing time increased (Table 2). However, the values for polyphenols and catechins were equivalent to those obtained on normal withering for 16 h. There were not as many changes in the levels of chlorophyll and carotenoids due to freeze-withering up to 6 h, as there were on normal withering. That there was a mild reduction in the level of chlorophyll, indicated that chemical withering did take place during freeze-withering.

3.2. Cell-membrane permeability studies

Cell-membrane permeability studies revealed that the degree of permeability resulting after 16 h of normal withering was achieved within 2 h of freeze-withering. The pH of the cold-water extract decreased due to the leaching of polyphenols, catechins and organic acids (Table 3). The electrical conductivity was found to increase, due to the presence of greater amounts of electrolytes and organic acids. The levels of polyphenols and

Table 1
Withered leaf characters after freeze-withering and normal withering (From three replicate observations of physical assessment)

| Characters | Fresh | Freeze | Normal |
|-----------------|--------|---------|---------|
| Colour | Green | Green | Green |
| Texture | Turgid | Flaccid | Flaccid |
| Physical wither | – | ++ | ++ |
| Chemical wither | – | ++ | ++ |

Table 2
Green leaf biochemical constituents as affected by freeze-withering

| Treatment | Polyphenols (%) | Catechins (%) | Total Chl ^a | Carotenoids ^a | Caffeine (%) |
|--------------|-----------------|---------------|------------------------|--------------------------|--------------|
| Fresh leaves | 25.2 | 15.6 | 1541 | 139 | 2.12 |
| F.W.2 h | 22.2 | 13.6 | 906 | 146 | 2.37 |
| F.W.4 h | 22.1 | 13.0 | 899 | 154 | 2.43 |
| F.W.6 h | 21.1 | 12.6 | 901 | 158 | 2.41 |
| F.W.8 h | 20.2 | 11.5 | 812 | 144 | 2.35 |
| Normal 16 h | 21.9 | 13.9 | 845 | 136 | 2.70 |
| CD at 5% | 2.74 | 1.34 | 217 | 15.1 | 0.54 |

CD – critical difference; F.W. – freeze-withering.

^a mg/g fresh weight.

Table 3
Electrolyte leaching during freeze-withering

| Treatment | pH | EC (dS m ⁻¹) | Polyphenols (%) | Catechins (%) |
|--------------|------|--------------------------|-----------------|---------------|
| Fresh leaves | 6.29 | 0.01 | 0.15 | 0.04 |
| F.W.2 h | 6.04 | 0.10 | 1.59 | 0.81 |
| F.W.4 h | 5.99 | 0.18 | 2.13 | 1.08 |
| F.W.6 h | 5.78 | 0.23 | 2.52 | 1.24 |
| F.W.8 h | 5.57 | 0.28 | 3.64 | 2.76 |
| Normal 16 h | 5.78 | 0.15 | 0.90 | 0.45 |
| CD at 5% | 0.14 | 0.05 | 0.57 | 0.43 |

CD – critical difference; F.W. – freeze-withering; EC – electrical conductivity.

catechins in the cold-water extract (obtained by leaching), increased with freezing time. This could be due to extensive damage to the cell walls by freezing. As the freezing time increased, cell distortion also increased and resulted in more electrolyte leakage. This shows that adequate chemical withering was achieved due to freeze wither. Thus, freeze-withering makes the leaf ready within 2 h of freeze treatment as against 16 h of conventional withering.

3.3. Fermentability studies

The fermentability of normally withered and freeze-withered samples was assessed by the formation of TF during fermentation (Fig. 1). From the graph, it is obvious that the freeze-withered leaves resulted in more

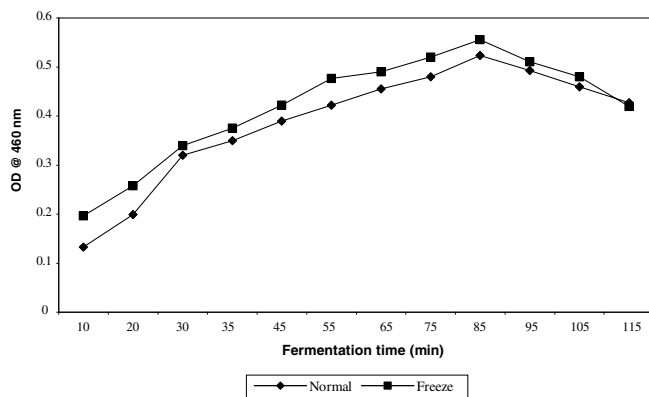


Fig. 1. Effect of freeze-withering on fermentability of withered leaves.

Table 4
Effect of freeze-withering on made tea quality

| Treatment | TF (%) | TR (%) | HPS (%) | TLC | TSS (%) | Caffeine (%) | BI | CI |
|--------------|--------|--------|---------|------|---------|--------------|------|------|
| Fresh leaves | 1.33 | 7.76 | 9.00 | 4.19 | 40.0 | 2.82 | 32.1 | 7.94 |
| F.W.2 h | 1.36 | 8.61 | 9.38 | 4.36 | 38.0 | 2.90 | 31.9 | 7.56 |
| F.W.4 h | 1.43 | 8.76 | 8.96 | 4.66 | 38.5 | 3.07 | 31.8 | 8.07 |
| F.W.6 h | 1.27 | 8.45 | 9.61 | 3.99 | 38.3 | 3.08 | 29.2 | 7.03 |
| F.W.8 h | 1.28 | 8.26 | 9.36 | 4.13 | 38.3 | 3.08 | 29.4 | 7.26 |
| Normal 16 h | 0.90 | 8.14 | 13.05 | 5.00 | 36.6 | 3.05 | 22.8 | 4.25 |
| CD at 5% | 0.11 | 0.80 | 0.74 | 0.68 | 2.88 | 0.77 | 3.14 | 1.62 |

CD – critical difference; F.W. – freeze-withering; BI – briskness index; CI – colour index.

theaflavins than the normally withered ones. Since no change in fermentation time was observed, cell-membrane permeability must have increased sufficiently in freeze-withering.

3.4. Made tea analysis

Theaflavin levels were higher in leaves freeze-withered for 4 h (Table 4) and the liquor was brighter than that of other teas. This may be due to adequate cell rupture, achieved through freeze-withering. Due to freeze-withering, the substrates (polyphenols) and enzyme (polyphenol oxidase) were brought into contact and effective reaction was possible. This result is in agreement with the findings of Ramaswamy (1989). Thearubigins and HPS failed to show any distinct trend. Normally withered leaves resulted in teas with higher levels of HPS, which in turn increased the colour of the liquor. Total soluble solids (TSS), which have a direct impact on the cuppage of tea, were found to increase with freezing time.

The level of caffeine was found to be stable, regardless of withering treatment (Table 4). Increase in caffeine is one of the measures of the degree of chemical wither achieved by the leaf. This result is in line with that reported by Ramaswamy (1989). However, it contradicts result reported by Ranganath et al. (1991, 1994). This could be due to the thawing temperature employed after freeze treatment. In the earlier report, thawing was carried out at room temperature, which would probably have been inadequate to remove the surface moisture. It has already been established that withering temperature influences the biosynthesis of caffeine and that there is a significant increase in the level of caffeine due to withering at 35 °C (Muthumani, Senthil Kumar, Rajappan, Senthil Kumar, & Kalidass, 2002). Thus, thawing at 35 °C resulted in an increase in caffeine level in made tea.

The briskness and colour indices were worked out as suggested by Ramaswamy (1986). For better teas, the colour index should be between 5 and 11 in order to have the liquor balanced between colour and briskness. When the colour index value exceeded 11, then teas lacked colour, while, when it fell below five, the liquor was coloury and flat with low briskness. The normal range of briskness index proposed for south Indian teas ranged from 12.5 to 22.5. Brighter liquors will have a briskness index

Table 5
Organoleptic evaluation of black tea samples^a

| Treatment | Leaf colour | Infused leaf out turn | Liquor | Briskness | Flavour | Comment |
|--------------|-------------|-----------------------|--------|-----------|-----------|---------|
| Fresh leaves | 6 | 5 | 6 | 6 | Greenish | Harsh |
| F.W.2 h | 2 | 2 | 1 | 1 | Very good | Brisker |
| F.W.4 h | 3 | 3 | 3 | 3 | Good | Good |
| F.W.6 h | 4 | 4 | 4 | 4 | Good | Good |
| F.W.8 h | 5 | 6 | 5 | 5 | Average | Average |
| Normal 16 h | 1 | 1 | 2 | 2 | Very good | Brisker |

^a Based on order of preference ($n = 2$).

above 22.5, but, when it drops below 17.5, the liquor tends to be harsh and, when it exceeds 17.5, the liquor becomes more brisk. The briskness and colour index values observed in our study are presented in Table 4. Both briskness and colour indices of freeze-withered samples were much higher than those of the normally withered samples.

3.5. Organoleptic evaluation

Organoleptic evaluation can indicate the degree of acceptance of the product by the consumer. The results of organoleptic evaluation are presented in Table 5. These results are based on the order of preference among the samples tasted. In leaf characters, the teas produced from normally withered leaves were rated highest, but, on the basis of liquor characters, the teas produced from freeze-withered leaves stood first. Tea from fresh leaves was rated poor due to greenish and harsh taste. Thus the tea from leaves freeze-withered for 2 h was rated equivalent to the one from normally withered leaves.

Thus overall freeze-withering for 2–4 h resulted in teas with better quality and cup characteristics. While, the initial investment will be high to install a freezing facility, it should reduce the cost of production in the long run.

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References

- Dev choudhury, M. N., & Goswami, M. R. (1983). A rapid method for the estimation of total polyphenolic matters in tea (*Camellia sinensis* L.). *Two and a Bud*, 30, 59–61.
- Harborne, J. B. (1973). In *Phytochemical methods* (pp. 205–207). London: Chapman and Hall Ltd.
- Indian Standard (1999). Tea – Determination of water extract (First revision). IS 13862:1999.
- Lakshminarayanan, K., & Ramaswamy, S. (1978). Towards optimising fermentation during manufacture. In *Proceedings of the twenty third UPASI conference* (pp. 34–47). Bulletin No. 35.
- Mahanta, P. K., & Baruah, S. (1989). Relationship between process of withering and aroma characteristics of black tea. *Journal of the Science of Food and Agriculture*, 46, 461–468.
- Muthumani, T., Senthil Kumar, R. S., Rajappan, S. T., Senthil Kumar, C. M., & Kalidass, S. (2002). Effect of withering temperatures on clonal black tea quality. *UPASI Tea Research Foundation News Letter*, 12(1), 5.
- Newton, J. M. (1979). Spectrophotometric determination of caffeine in coffee products – collaborative study. *Journal of Association of Official Analytical Chemists*, 62, 705–708.
- Owuor, P. O., & Orchard, J. E. (1989). Changes in the biochemical constituents of green leaf and black tea to withering: a Review. *Tea*, 10, 53–59.
- Ramaswamy, S. (1986). Improving tea quality in south India. *UPASI Tea Scientific Department Bulletin*, 41, 12–24.
- Ramaswamy, S. (1989). Freeze withering for CTC tea manufacture. *Proceedings of 29th UPASI Scientific Department Bulletin*, 43, 44–52.
- Ranganath, S. R., Marimuthu, S., & Raju, K. (1994). Effect of withering process on biochemical composition and green leaf quality aspects of black tea (*Camellia sinensis* (L) O.Kuntze). *Journal of Plantation Crops*, 22(1), 36–43.
- Ranganath, S. R., Marimuthu, S., Raju, K., & Ramaswamy, V. (1991). Freeze withering. *UPASI Tea Research Institute News Letter*, 1(1), 8.
- Roberts, E. A. H., & Wood, D. J. (1951). The amino acids and amides of fresh and withered tea leaf. *Current Science*, 20, 151–153.
- Sanderson, G. W. (1968). Changes in cell membrane permeability in tea flush on storage after plucking and its effect on fermentation during manufacture. *Journal of the Science of Food and Agriculture*, 19, 637–639.
- Sanderson, G. W. (1964). The theory of withering in tea manufacture. *Tea Quarterly*, 35, 146–163.
- Swain, T., & Hillis, W. E. (1959). The phenolic constituents of *Prunus domestica*. I. The quantitative analysis of phenolic constituents. *Journal of the Science of Food and Agriculture*, 10, 63–68.
- Thanaraj, S. N. S., & Seshadri, R. (1990). Influence of polyphenol oxidase activity and polyphenol content of tea shoot on quality of black tea. *Journal of the Science of Food and Agriculture*, 51, 57–69.
- Ullah, M. R. (1977). Alternative test for assessment of fermentation. *Proceedings of Tocklai Conference*, 29, 75–77.
- Ullah, M. R., & Roy, P. C. (1982). Effect of withering on polyphenol oxidase level in tea leaf. *Journal of the Science of Food and Agriculture*, 33, 492–495.
- Wickremasinghe, R. L. (1975). Tea. *Advances in Food Research*, 24, 229–286.