Technical Report No. 126

CARIBBEAN RUM - ITS MANUFACTURE AND QUALITY

BY

David D.H. WEST - Sugar Tech. Research Unit, Barbados.

RHETT HARRIS - West India Rum Refinery, Barbados

September 1987.

SUGAR TECHNOLOGY RESEARCH UNIT

Research Centre, Edghill, St. Thomas, Barbados, W.I.

CONTENTS

CARIBBEAN RUM - ITS MANUFACTURE AND QUALITY

BY

RHETT HARRIS - WEST INDIA RUM REFINERY, BARBADOS
DAVID H. WEST - SUGAR TECHNOLOGY RESEARCH UNIT, BARBADOS

---

1. SUMMARY

The historical development of the sugar cane and rum industries of the Caribbean are outlined showing the early importance of these industries to the development of the area.

All aspects of the technical production of rum are discussed including feedstock options, fermentation techniques, distillation practices and the ageing and blending of rum as is practiced in each of the Caribbean countries. The characteristic quality of light, heavy, blended and aged rum is shown by GLC analysis of typical sample from each area.

The relationship between amino nitrogen and the production of n-propyl alcohol is discussed and the results of an investigation that monitored the levels of amino nitrogen in final molasses and sugar cane are given.

2. HISTORY

Sugar cane has been cultivated for approximately 2000 years. It originated in Asia and spread to Spain and in the early 15th century via North Africa and Siscily. It was introduced to the Caribbean in the late 15th century by Christopher Colombus. By the 16th century the Spanish and the Portugese were producing sugar in the New World on a large scale. In Hispaniola (Dominican Republic), Cuba and Puerto Rico the Spanish were producing sugar and molasses and it is very likely that a distilled spirit was being produced from fermented cane juice and molasses. The Portugese were producing sugar, molasses and a distilled spirit from fermented molasses in the regions of Pernambuco and Bahai in Brazil.

In the 17th century the English, French and Dutch began to colonise the smaller Caribbean Islands, with Barbados becoming the second British Caribbean Colony in 1627. Experimentation with sugar cane in Barbados began in the mid 1630's with Dutch assistance brought in by the British from Pernambuco which they then held. Soon after 1640 Barbados was producing acceptable quality sugar and was distilling spirit from skimmings of the copper taiches and from fermented molasses.

The origins of the word 'Rum' are subject to much speculation. Some claim that it may have been derived from the latin for sugar saccharum. Others claim origins from the Spanish word 'Ron' (= Rum) arguing that the Spanish probably had distilleries in the Caribbean before the arrival of the English.[1] The strongest claim comes from Barbados[2] where an anonymous 1650 description of the island states that

> *"the chief fuddling they make in the Island is Rumbullion alias Kill Devill, and this is made of sugar cane distilled - a hot hellish and terrible liquor:"*

soon after Rumbullion was abbreviated to Rum as confirmed by a General Court of Connecticut Order in 1654 to confiscate

> *"whatsoever Barbados liquors, commonly called rum, Kill Devill or the like."*

In these early times Caribbean molasses, sugar and rum were traded in Connecticut, New England and Virginia in exchange for salted fish, pork and beef, dairy products, flour, lumber and livestock. Caribbean rum was introduced into England in the late 17th century and had become well known by the 18th century. Today Caribbean rum is sold in the USA, Canada, UK, Europe, Australia and New Zealand, and is a major foreign exchange earner for each of the producing countries. A list of the major producers and their annual production capacity is given below.[3]

RUM PRODUCTION

Figure 1

Country	Proof Imperial Gallons	Litres of Pure Alcohol
Antigua	250,000	650,000
Bahamas	4,000,000	10,400,000
Barbados	3,500,000	9,100,000
Guyana	6,500,000	16,900,000
Jamaica	11,424,300	29,703,180
St. Lucia	200,000	520,000
St. Vincent	150,000	390,000
Trinidad & Tobago	6,600,000	17,160,000
TOTAL:	32,624,300	84,823,180

3. DEFINITION

The definition agreed to and accepted by the major producers is as follows.

> *"Rum shall be the spirit obtained only by alcoholic fermentation and distillation of molasses, syrups or cane sugar obtained during the extraction of cane sugar or of sugar cane juice. Production must be carried out in such a way that the product has the aroma and flavour derived from the natural volatile elements contained in the above materials or formed during the fermentation or distillation process of the named raw materials."* 4

4. RAW MATERIALS

Molasses is the raw material used by the major producers. Small producers in Dominica and Grenada use cane juice or mixtures of cane juice and molasses. Molasses is the preferred raw material because it contains more sugar per unit volume, lower bacterial loading, has a much longer shelf life than cane juice and is available year round.

Molasses quality varies depending on the variety of sugar cane, climatic conditions, fertilising practices, processing conditions at the sugar factory and handling and

storage conditions. All of these variables have a significant effect on both the quality of the rum produced and the alcohol yield or fermentation efficiency. The analysis of an average quality Caribbean Molasses may be taken as follows.[5]

Figure 2

AVERAGE CARIBBEAN MOLASSES

Brix (Hydrometer)	85.00°Bx
Total Sugars (as Invert)	52.00% w.w.
Ash (Sulphate)	8.00% w.w.
Nitrogen	0.75% w.w.
Gums	2.50% w.w.
pH	5.5

This analysis may be compared with the criteria and ratios for grading molasses for rum production developed by Arroyo and given below.[6]

Figure 3

TYPICAL MOLASSES GRADES

Criteria	Good	Fair	Poor
Brix	87.6	85.4	84.2
Sucrose % w.w.	36.4	31.3	34.6
Reducing Sugars % w.w.	19.6	20.0	13.5
Total Sugars % w.w.	58.0	52.9	49.9
Ash % w.w.	7.3	9.4	11.6
Nitrogen % w.w.	1.1	0.5	0.5
P_2O_5 % w.w.	0.2	0.1	0.2
Gums % w.w.	2.0	2.6	3.8
pH	5.5	5.7	5.3
Ratios			
Total Sugars/Ash	7.95	5.63	4.30
P_2O_5/Nitrogen	0.18	0.17	0.40
Gums/Total Sugars	0.03	0.05	0.08
Alcohol/Total Sugars % w.w.	46.5	44.0	39.0

Three criteria not shown above are Unfermentable Sugars expressed as a percentage by weight, colour expressed as international units and organoleptic appraisal.

Good quality molasses should have low unfermentable sugar, a colour between 100,000 - 200,000 international units

and a sweet fruity smell and taste. Normally molasses that has been subjected to high processing and storage temperatures will not meet these criteria.

For example, the GLC analyses of an 8 month old Barbados Molasses that entered storage at 120°F was as follows.

Figure 4 Analyses of 8 month old Molasses

% Sucrose	29.3%
% Fructose	10.3%
% Glucose	3.9%
F/G Ratio	2.6:1

Since the F/G Ratio would have been approximately unity prior to thermal decomposition, the loss of glucose is 6.4% or 12.8% of the Total Sugar (as R.S.) originally present in the molasses.

Further the table below shows sugar losses by thermal decomposition under controlled conditions at 40 and 60°C as reported by United Molasses for samples of Trinidad and Jamaica molasses. The data is given for a 15 day period at 3 day intervals. This study indicated that whereas thermal decomposition is negligible at 40°C a 3% loss is incurred in 15 days at 60°C.

Figure 5 % Change In Sugar Content At High Temperature

Time elapsed	Trinidad Molasses		Jamaican Molasses	
	40°C	60°C	40°C	60°C
3 days	nil	-0.83	-0.07	-1.13
6 days	+0.04	-1.12	-0.10	-1.84
9 days	+0.16	-1.66	-0.09	-2.46
12 days	+0.12	-1.97	-0.09	-2.98
15 days	+0.16	-2.56	-0.08	-3.46

5. FEEDSTOCK COST COMPARISON

The cost and analysis of other raw materials available to Caribbean Rum Producers are compared with blackstrap molasses in the Table below.

Comparison of Raw Material Values

Figure 6

Feedstock	% Solids (Brix)	% Available Total Sugars (as Invert)	Relative US $ Value/ tonne
Blackstrap Molasses	88	55	50.00*
High Test Molasses	80	65	59.00
Raw Sugar	99.5	103	93.50
Sugar Cane	17	14	12.50

*Assumed value of US $50.00/tonne Blackstrap Molasses

Using typical analyses for each feedstock and an assumed value of US $50.00/tonne for blackstrap molasses, the relative value of each feedstock is calculated in terms of fermentable sugars.

The table shows that at US $50.00/tonne for blackstrap molasses the relative values of raw sugar is 4.25¢/# which is only a fraction of the current cost of sugar production in the Caribbean.

Similarly, the relative value of sugar cane is approximately US $9.00/tonne after deducting processing cost. The current cost of production of sugar cane, although highly dependent on the relative value of local currency to the US dollar, is in the range of US $35.00 to US $85.00. Consequently sugar cane is only used as a feedstock under special circumstances.

The cost of High Test Molasses is similar to that given for raw sugar and consequently is not considered to be a viable option as a fermentation feedstock.

Figure 7 attached is a ready reference graph showing the relative values of molasses, cane and raw sugar.

6. MOLASSES TREATMENT

Calcium salts present in the molasses precipitate out as scale in the distillation units reducing performance and efficiency. To solve this problem, chemical clarification can be carried out with alumina and calcium phosphate or by adding sulphuric acid with subsequent heating followed by cooling and settling or centrifuging. Unfortunately these methods have very high capital and operating costs and do incur a significant loss of sugar.[5]

Bacteria present in the molasses can be destroyed by pasteurisation of diluted molasses in continuous high temperature short time pasteurisers, however temperature control must be precise to avoid the destruction of naturally occurring nutrients or cause molasses degradation via the Milliard and Carmelisation reactions. Here again capital and operating costs are considerable.[7]

In general it has been found that molasses pre-treatment promises a lot more than it actually delivers and by and large the major producers have avoided this procedure.

In the Caribbean scaling problems are controlled by injecting an approved food grade complexing agent into the feed to the analyser column. Although the precise reaction of these scale inhibitors is not fully understood it is clear that non-crystallisable complexes are formed and these are deposited as a sludge which can be washed away with high pressure water.

Similarly the bacterial problem is controlled by the use of a combination of sterilisation and antiseptics, such as amonium bifloride in the yeast propagation stage. This control is necessary to ensure that a high yeast concentration is developed during the fermentation stage, so that its predominance will inhibit the growth of other micro-organism which could be detrimental to the quality and yield of the rum producers. It is also important to ensure that a sufficiently high concentration of alcohol is produced in the fermenters to act as a natural antiseptic to bacterial action on sitting.

All of the major rum producers in the Caribbean mix molasses and water in some type of mechanical, automatic or

semi automatic mixing/blending unit to produce a molasses wash of approximately 17-24°Brix corresponding to a 10-15% total sugar. At this point the pH of the wash is adjusted between 4.8 and 5.0 with sulphuric acid and liquid nutrients e.g. ammonium sulphate, ammonium phosphate are added via independent metering pumps. To illustrate the importance of mixing I'Anson[5] reports a 15% increase in yield after installing mechanical mixing in a plant where mixing was previously done by hand.

7. FERMENTATION

The choice of yeast specie and strain has a most important influence on the quality and the amount of rum produced during fermentation. The yeast selected should

1) maximise conversion of sugar to alcohol
2) be temperature and alcohol tolerant
3) produce desirable organic by-products known collectively as congeners or congenerics, such as acids, aldehydes, esters and higher alcohols in the desired amounts and proportions
4) ferment at a suitable rate to reduce the risk of infection by undesirable bacteria.

In the production of light rums, the main aims are for a low congeneric level and high alcohol yield. These criteria are best met using the quick fermenting budding type saccharomyces yeasts. On the other hand the fission type schizosaccharomyces strains are more suitable for the production of the heavier types of rum where the primary objective is congener formation rather than alcohol yield.[8]

As a result of the international consumer demand for lighter rum, the budding type yeasts predominate fermentation flora in Caribbean distilleries, but fission type yeasts are still used in the production of the highly flavoured heavy rums of Jamaica, Guyana and the French islands.

Once the yeast strain has been selected, propagation from pure yeast is achieved either in a tropically adapted yeast culture plant or by the use of semi aerobic "bub" stages commencing with sterilised wash in the laboratory and finishing in stainless steel "bub tanks" or propagators in the

distillery.

The contents of these tanks are used to inoculate the main fermenters. For a rapid rate of fermentation the "bub" or inoculant is first pumped to the fermentation tank which is then filled with molasses wash. Using this technique, fermentation will have reached optimum activity by the time the fermenter is filled. For a slower fermentation the incculant is added after the fermenter has been filled with wash. Slow fermentations are used for heavy rums.

A caribbean rum distillery utilising a rapid fermentation usually requires three bub stages in the laboratory and two in the distillery before the final fermentation. Each 'bub' stage takes 18 to 24 hours and the final fermentation takes 20 to 26 hours. The quantity of inoculant used is about 12% of the final wash and contain 2-3% yeast mass.

Advantageous or spontaneous fermentation is still practiced in a few Caribbean rum distilleries. The fermenters or mixing tanks are simply filled and left to ferment relying on airborne yeasts, naturally occurring yeasts in the molasses or yeasts from previous fermentations attached to the fermenter walls. These fermentations can take from two to four days.

Most literature on fermentation insists that for maximum alcohol yields, fermentation temperatures must be held at 31 to 32^{o}C. Unfortunately these temperatures are impossible to achieve without expensive refrigeration, in most tropical distilleries. However, most yeast strains used in the Caribbean are temperature tolerant giving their best results at 34 to 36^{o}C with some capable producing alcohol at 40^{o}C. In fact these tropical yeasts are very sluggish alcohol producers at lower temperatures.

Plate type heat exchanges are used extensively for cooling because their high coefficient of heat transfer allows adequate heat removal with modest equipment at temperature differentials of only 5 ^{o}C. The low temperature differential is important since the temperatures of the cooling water is unlikely to be less than 28^{o}C and is frequently considerably higher.

At the end of fermentation the alcoholic concentration in the fermenters will be between 5 to 10% ethyl alcohol by volume depending on the type of yeast, the original sugar concentration in the fermenter and the fermentation temperature.

Once fermentation is complete the vessels are allowed to rest for 6 to 12 hours, allowing suspended solids and dead yeast cells to settle out on the fermenter bottoms prior to distillation.

Batch fermentations are preferred by the Caribbean Rum Producers because this offers some flexibility and opportunity for the tailor making of specific types of rum. There are however a few semi-continuous systems in operation but no full scale continuous fermentation systems are used in the Caribbean.

A peculiarity to Jamaica and the French Islands is the practice of using 'dunder' in the production of their high ester heavy rums.[5,7] 'Dunder' is the lees of previous distillations which have been allowed to age and ripen by bacterial action. The matured dunder is added to the molasses wash prior to fermentation. Symbiotic fermentation by the yeast and bacteria produce the precursors for the formation of high ester concentrations in subsequent distillation in pot stills. This symbiotic fermentation has been shown by Arroyo to reduce the time required to complete the fermentation for heavy rums.

8. DISTILLATION

Caribbean Rum Distillers utilise both batch and continuous distillation processes. Batch distillation is carried out in pot stills of varying sizes, design, materials of construction and design. Continuous distillation is carried out in two, three or four columns. Continuous stills are constructed of stainless steel and copper.

Barbados, Guyana and Jamaica produce rum in both pot stills and continuous stills, while the Bahamas, Trinidad and Tobago, Antigua, St. Lucia and St. Vincent utilise continuous stills only.

8.1 Pot Stills

Pot stills in use in Jamaica and Guyana consist essentially of a wash still, a low wines retort, a high wines retort, a condensor and spirit receiver Figure # 8 The fermented wash is pumped to the wash still and heated by either direct firing or a steam coil. The first distillate, called low wines, is distilled in the low wines retort to produce a second distillate, called high wines, which is distilled in the high wines retort to produce the finished product rum. Heads and tails are collected as fractions at the start and finish of the distillation respectively, while strong rum is collected during the middle period of distillation known as the the 'middle run'. The heads and tails are re-used for the next distillation in the high wines and low wines retorts respectively. The desired strength of the rum is about 80% v.v. alcohol and to achieve this it is sometimes necessary to install a small rectifier on top of the high wines retort.

Pot stills in Jamaica are made entirely of copper while in Guyana the pots are made of local hard woods, greenheart and wallaba, with swan necks, pipework and condensors made of copper. [5]

Pot still rum produced in Guyana and Jamaica are heavy highly flavoured rums. In addition the Jamaica rums have a very rich fruity aroma as a result of the use of 'dunder' in the fermentation.

A lighter pot still rum is produced in Barbados. This rum is distilled from a mixture of fermented wash and a medium type continuous still rum. The distillation is carried out in a copper pot still, fitted with a rectifier, to produce a product at a strength of about 60% v.v. alcohol. This product is redistilled in another copper pot still fitted with a rectifier to produce double distilled pot still rum at a strength of about 80% v.v. alcohol.

8.2 Continuous Stills

Two column continuous stills were introduced to the Caribbean in the late 19th Century. Today the bulk of the rum produced in the Caribbean is of the continuous still type augmented with small amounts of pot still rum to produce individual brands of international repute. Two column stills have for the most part been replaced by three and four column stills with the capability of producing a large spectra of spirit from heavy continuous right through to neutral spirits. A two column still consists essentially of an analyser column and a rectifier column Figure # 9 . An aldehyde column introduced between the analyser and rectifier effectively constitutes a three column still Figure #10, while a hydroselector column added between the aldehyde column and the rectifier produces a four column still Figure #11 The analyser column is made of stainless steel and contains approximately 20 widely spaced distilling plates specifically designed to cope with high concentrations of suspended and dissolved solids.

The aldehyde and hydroselector columns are made of either stainless steel or copper and contain approximately 20 plates and 40 plates respectively. The rectifier is made of copper and contains approximately 68 plates. The plates in these columns are closely spaced and are highly efficient units for refining clean alcohol water mixtures. These columns are heated by steam, the choice of direct or indirect methods being dictated by the quality of spirit required, the quality of the steam available and the cost of fuel and water used to generate steam. Some highly energy efficient arrangements exist where vapour may be taken from one column to drive another. Reflux is supplied to the top of these columns from stainless steel or copper condensers. It is inadvisable to supply high strength reflux to the top of the analyser column because this encourages the deposit of calcium sulphate scale which reduces performance and increases down-time for manual cleaning.

Pre-heated fresh wash is passed through a degaser to remove carbon dioxide and undesirable odours, and then to the analyser solumn, where stripping of the wash takes place producing an overhead product at a strength of 50 to 60% volume alcohol. A portion of this is passed to the aldehyde column for further concentration and removal of a small overhead "heads" fraction. In the case of a three column still, the bottom from the aldehyde column is passed to the rectifier when it joins the remaining vapour from the top of the analyser to be rectified to a strength of 94 to 96% v.v. alcohol. Rum at this strength is withdrawn from plate #52-62. A small heads fraction is also removed from the rectifier condenser. Higher alcohols accumulate in a band in the region above the rectifier feed plate, the exact plate being determined by the reflux ratio at which the column is operated. The band of accumulation is narrowest at high reflux ratios and widest at lower reflux ratios, hence more higher alcohols will find their way into the products at low reflux ratios. A side cut in higher alcohols is therefore drawn off from the correct plate and passed to a decanter, where it is washed continuously with water to remove the insoluble amyl alcohols and recover alcohol. The recovered alcohol and water is recirculated through the still. On occasions there may be an accumulation of water soluble n-propyl alcohol and this may necessitate another side cut higher up the column.

In the case of a four column still, the analyser and aldehyde column work as one unit to produce a pre-concentrated spirit free of organic acids, at approximately 80% v.v. alcohol, allowing for the removal of a small heads fraction. The pre-concentrated spirit is transferred to the hydroselector column where hot soft water is added at the top and extractive distillation at low alcoholic concentration of 8 to 12% v.v. alcohol takes place. Under these conditions the majority of aldehydes, esters and higher alcohols are more volatile than alcohol

and hence distil up the column and are removed in a moderate heads fraction. Clean spirit at 8 to 12% v.v. alcohol is transferred to the rectifier to be concentrated to 95.5% to 96.5% v.v. alcohol. In the rectifier column a heads fraction is removed and recirculated through the still and a side cut is provided for small amounts of higher alcohols that may have escaped removal in the hydroselector. Most four column still installations are equipped with suitable valves, blanks and piping, to allow the unit to operate as either a two or three or four column still. This flexibility in the configuration of the still allows the distiller an opportunity to manufacture from heavy continuous still rums right through to neutral spirits. The Bahamas, Barbados, Guyana, Jamaica and Trinidad and Tobago all have this capability.

9. MATURATION

Despite much research and experimental work the only reliable method for maturing is by ageing in white oak barrels. In the Caribbean once-used American whiskey barrels are common for maturing rum.

Barbados is peculiar in using both charred and decharred barrels while all of the other major producers use charred barrels exclusively.

Pot still rum is stored in barrels directly from the still at 80% v.v. alcohol. Continuous still rum is reduced in strength from 95% v.v. alcohol to 80% v.v. alcohol and in some cases as low as 63% v.v. alcohol and then put into barrels.

Heavy pot still rums require several years maturation while light continuous still rums may only need 12 to 18 months. Jamaica and Guyana pot still rums require 5 to 6 years maturation in most cases and may be as much as 10 to 12 years for the more highly flavoured types.[5]

Barbados pot still rum is quite acceptable after 3 years maturation. The average maturation period for light and medium continuous still rums in the Caribbean is approximately 2 years.

The changes that take place to the rum during ageing are as a result of chemical reactions between the organic components in the distillate and as a result of reactions between the distillate and extracts from the barrel wood. A wooden barrel is a porous container and therefore allows the passage of vapours out of the barrel and air into the barrel by diffusion. The chemical reactions that take place between the organic components in the distillate are mainly oxidations and condensations that produce acetaldehyde from ethanol, acetic acid from acetaldehyde, and ethyl acetate from ethanol and acetic acid. The distillate and barrel wood components react to produce ethanol lignin and aromatic aldehydes and sugars are extracted from the hemicellulose of the wood. Tannins and colour are also extracted.

It appears that a charred barrel is more active than an uncharred barrel and produces more congeners and a darker rum.

Higher alcohols take little part in any of these reactions and their levels remain essentially the same as is the original distillate.

Aldehydes and acids increase rapidly during the first year but further storage produces little change. Esters increase at a constant rate throughout the period of maturation, and this may be used to indicate the period of maturation if the analysis of the raw rum and the conditions of storage are known.

The quality of the aged rum is directly influenced by the maturation time, temperature, the strength of the rum, the ratio of contact area to volume of the barrel, the age of the barrel and whether the barrel is charred or decharred.

The rate of ageing is dependent on the contact area and the temperature, and it is reported that the rate of ageing at 35^{o}C is approximately twice that at 25^{o}C, unfortunately the price paid for this is an increase in the annual loss rate from 5% to 10%. [7]

After maturation the various types of rum are blended, married, reduced in strength with high quality demineralised water, colour adjusted with caramel, filtered and finally bottled for delivery world wide.

10. QUALITY

Throughout this paper many references have been made to the various types of rum produced by each of the major Caribbean Rum Distillers. Figure #12 shows the major chemical differences of pot still and continuous still rums from Barbados, Guyana and Jamaica.

Typical Analyses of Pot and Continuous Still Rums

Figure 12

Country	Congeners	Pot Still Rums	Continuous Still Rums	
			Medium	Very Light
Barbados	Aldehydes	45.0	4.0	2.0
	Esters	13.0	4.0	2.0
	Higher Alcohols	93.0	15.0	5.0
Guyana	Aldehydes	18.1	4.0	0.4
	Esters	24.3	9.5	1.1
	Higher Alcohols	363.0	84.5	3.7
Jamaica	Aldehydes (calc as acetaldehyde)	16.0	32.1	0.4
	Esters (calc'd as ethyl acetate)	120.0	49.0	4.1
	Higher Alcohols (calc'd as cumyl alcohol)	290.0	117.0	1.1

These samples are current distillation ex still and results are quoted in mg/100 ml absolute alcohol from gas chromatography analysis.

Figure 13 shows the chemical differences between popular aged blended rums from Barbados, Guyana, Jamaica and Trinidad and Tobago. Results are quoted in mg/100 ml absolute alcohol from gas chromatography analysis.

The Analysis of Popular Rum Brands in the Caribbean

Figure 13

Country	Congeners	Type of Rum		
		White Rum	#1 Dark Rum	#2 Dark Rum
Barbados	Aldehydes	8.0	12.0	15.0
	Esters	18.0	20.0	14.0
	Higher Alcohols	18.5	24.0	33.0
Guyana	Aldehydes	-	13.0	-
	Esters	-	12.0	-
	Higher Alcohols	-	141.0	-
Jamaica	Aldehydes	12.0	29.0	-
	Esters	21.0	38.0	-
	Higher Alcohols	26.0	93.0	-
Trinidad & Tobago	Aldehydes	14.0	15.0	22.0
	Esters	12.0	15.0	15.0
	Higher Alcohols	61.0	59.0	33.0

Results are quoted in mg/100 ml alcohol from gas chromatography analysis.

Figure 13 reveals the current trends towards lighter rums in the Caribbean. Among the more popular brands, the Barbados rums are the lightest in character and the Guyana rums are the heaviest.

The data also shows that the Jamaica rums have the highest ester content and the Guyana rums the highest higher alcohols.

With respect to quality the importance of organoleptic assessment must never be overlooked since some of the components which are analytically grouped may contribute good or bad characteristics to the rum.

11. AMINO NITROGEN AND N-PROPYL ALCOHOL

In Barbados, molasses is delivered to the distilleries from the sugar factories during the crop season which lasts from February to June. From early March 1985 it was noticed that during fermentation there was excessive foaming, shorter fermentation times, higher fermentation temperatures, and that the level of N-propyl alcohol in the light rum produced had increased.

Samples of the 1985 molasses along with samples of 1984 molasses and a mixture of 1983 and 1984 molasses were analysed for total amino nitrogen, and this data is reported below.

Figure 15

Year	Amino Nitrogen in Molasses ($\mu g/ml^{-1}$)
1985	3158
1984	2369
1983 + 1984	1119

These results indicate that the concentration of amino nitrogen in final molasses had increased steadily over the period under review.

Further, two analyses of the fermented wash prepared from the 1985 molasses, indicated excessively high levels of n-propyl alcohol as is shown below.

Alcohol Content of Fermented Wash

Barbados Molasses 1984 - 1985

Figure 16

Higher Alcohols	Molasses Ex 1984 Crop	Molasses Ex 1985 Crop	
		A	B
n-propyl alcohol	54	111	85
iso-butyl alcohol	16	25	18
iso-amyl alcohol	106	198	219

Results quoted in mg/100 ml absolute alcohol.

N-propyl alcohol levels of 40 to 50 mg/100 ml absolute alcohol in the fermented wash can be reduced to 6 to 8 mg/100 ml absolute alcohol by distillation to 95 - 96% v.v. alcohol in a three column still and that level is quite acceptable. However, when the levels in the fermented wash are approximately doubled, then unacceptably high levels occur in the light rum product.

The levels of iso-butyl and iso-amyl alcohol encountered here can be easily reduced to acceptable levels by distillation to 95 - 96% v.v. alcohol and counter current washing with water, separation and decantation of the properly selected side cut from the rectifying column. Iso-butyl and isc-amyl alcohol can be completely removed by low strength extractive distillation in the hydroselector column of a four column still. Unfortunately n-propyl alcohol is more difficult to remove because it is soluble in water and hence does not separate out in a decanter. Further, even at the lowest alcohol concentration encountered in the hydroselector column, the volatility of n-propyl alcohol is only slightly

higher than that of ethyl alcohol (Unger & Coffey 1975) and consequently separation is very tedious.

Since n-propyl alcohol is so difficult to remove during distillation, it is therefore very important that its concentration in the fermented wash be kept within a tolerable range.

During the first 3 months of the 1986 sugar crop analysis of the molasses for amino nitrogen and analyses of the fermented wash for n-propyl alcohol were again performed and these results are presented in figure # 17.

1986 Crop Molasses

Amino Nitrogen and N-Propyl Alcohol

Figure 17

Factory	Average Total Nitrogen - 1st 3 Months 1986 Crop Molasses	Average N-Propyl Alcohol in Wash from 1st 3 Months 1986 Crop Molasses
Andrews	2933 $\mu g/ml^{-1}$ at 90°Bx	52.3 mg/100 ml absolute alcohol
Bulkeley	3623 " " "	65.3 " " "
Carrington	3399 " " "	57.0 " " "
Foursquare	2841 " " "	58.3 " " "
Haymans	3753 " " "	63.0 " " "
Portvale	3410 " " "	68.7 " " "

This data has also been plotted on figure # 18 which gives the Linear Regression Equation for the 6 pairs of analyses. The correlation coefficient for the regression equation is 0.65 which indicates a weak relationship and a larger number of samples would be necessary before any definite conclusions could be stated. Nevertheless, the data does suggest that if the amino nitrogen level in molasses was reduced to the low 2000's, as in the early 1980's, then it is highly probable that n-propyl alcohol in the fermented wash would not exceed 40-50 mg/100 ml of absolute alcohol. As stated previously a 3 column still can reduce this level of amino nitrogen to 6 to 8 mg/100 ml of absolute alcohol. In addition to the above, experiments were also conducted to

determine if the use of inorganic nitrogen, in the form of ammonium sulphate, would reduce the level of n-propyl alcohol in the fermented wash. The results of this study were very similar to those of Parfait and Jouret who found a reduction in the level of iso-amyl alcohol, but an increase in the level of n-propyl alcohol.

According to Äyräpää,[10] the formation of n-propyl alcohol seems to obey no clear rules, but with limited concentrations of nitrogenous compounds, it increases with the content of nitrogen.

Äpräpää[10] also found that at higher nitrogen concentrations large amounts of n-propyl alcohol were produced although the actual quantity was largely independent of the concentration of nitrogen present.

12. AMINO NITROGEN IN BARBADOS MOLASSES

Over the past 7 years Barbados Sugar Industry Limited (BSIL) has monitored the level of amino nitrogen in the molasses produced at each factory on a weekly basis. This data has been normalised at 90^{o} Brix and is reported in Figure # 19 appended. The amino nitrogen was determined by the Ninhydrin colourmetric method and the data is reported as $\mu g\ ml^{-1}$.

These analyses were carried out on the composite sample representative of the factories' total annual production and consequently does not necessarily represent the molasses used by the distillery.

The data in Figure # 19 shows that there was an increase in the amino nitrogen content of Barbados molasses from about $2200 \mu g\ ml^{-1}$ in the early 1980's to over $3300 \mu g\ ml^{-1}$ in the past 3 years. This represents a 50% increase and to date we are unable to give any satisfactory explanation for the increase.

The weekly value for amino nitrogen levels for each factory is shown in Figure #20. The plot shows a weekly variation that evidently reflects cane quality, and indicates that as the cane matures there is a reduction in the level of amino nitrogen. The actual reduction in amino nitrogen content was from about $3600 \mu g\ ml^{-1}$ to about $3200 \mu g\ ml^{-1}$

which is hardly significant in terms of the 2200 $\mu g\ ml^{-1}$ that existed between 1980 and 1982.

13. THE PRESENCE OF AMINO NITROGEN IN SUGAR CANE

To provide further information an amino nitrogen in sugar cane, two major commercial varieties were monitored over a 45-day period during the 1986 harvest season.

13.1 Sampling

Two varieties of sugar cane, B-62163 which represents about 80% of the cane harvested annually in Barbados and B-73382 a new promising variety were sampled at approximately monthly intervals during the first half of the harvest period.

Each sample of cane was subsampled to represent 5 specific areas of the cane stalk.

The leafy portion of the cane was severed at the natural break-point of the cane. This weak point which coincides with the growing point or apex of the cane as shown in Figure #21. The portions sampled were as follows.

The uppermost subsample T1, represents the leafy sheath material in the area beyond the growing point.

Subsample T2 represents the immature cane in the area of the growing point together with the associated leaf sheaths.

Subsample T3 represents the uppermost fully developed portion of the cane and is taken as the intermode immediately below the attachment of the lowest green sheath.

Subsample M represents the cane at the mid point of the stalk and the section taken

is the intermode half way along the length of the mature stalk.

Subsample B represents the most mature portion of the cane and the section taken is lowest fully developed intermode.

On each occasion the cane portions represented by the subsamples above were peeled to remove the rind and leafy material and analysed as follows.

TR - The rind from subsamples T1, T2 & T3
MR - The rind from subsample M
BR - The rind from subsample B

13.2 Juice Extraction

The subsamples of cane and rind were prepared by chopping and dry disintegration and the juice extracted in a hydraulic press at 5000 psig.

13.3 Juice Analysis

The extracted juice was analysed for total soluble solids by Refractometric Brix, % Reducing Sugars by Lane & Eynon method of copper reduction and amino nitrogen by the ninhydrin reaction. In this reaction, the free amino group is oxidised according to the equation:

$$\text{Ninhydrin} + RCH(NH_2)COOH \rightarrow \underset{\text{Hydrindantin}}{RCHO} + NH_3 + CO_2 +$$

The liberated ammonia reacts with the hydrindantin and ninhydrin to form a blue complex, the intensity of which is directly proportional to the concentration of amino nitrogen present and is measured on a Uv-vis spectrophotometer.

13.4 Results

The results of these analyses are summarised in Figures 22-24 which gives the average of the analyses for each set of determinations.

These analyses show the expected increase in % Brix and decrease in % Reducing Sugars over the period of maturity together with the profile of the components along the length of the cane stalk and in the rind.

The data on amino nitrogen clearly indicates a higher level of amino nitrogen in both the T1 samples and the rind samples. The T1 samples are of the order of 3-5 times higher in amino nitrogen than is the middle portion of the cane. Also the rind samples are 3-7 times higher in amino nitrogen than is the whole stalk.

Quantitatively the contribution of amino nitrogen by the T1 sample and the rind samples is considerably less than that implied by the analyses, since the total quantity of T1 and rind material is unlikely to exceed 20% of the total cane stalk except in cases of inadequate removal of tops during harvesting.

However, since rum manufacturers are primarily concerned with maintaining the content below a critical value, then it is possibel that current amino nitrogen methods of harvesting and juice extraction in Barbados' factories could possibly have contributed to a higher than acceptably level of amino nitrogen in the molasses. In particular the recent introduction of cane shredders has intensified cane preparation increasing juice extraction by up to 2%. This additional juice has, in the main part, been obtained from the rind portion of the cane as a result of the disintegration of the hard fibrous rind by the shredders. The hypothesis that increased extraction increases the level of non sugars in juice, is supported by Fort and McKaeg[11] who showed that about one third more nitrogen is in the whole mill juice than in crusher juice. The same effect has been demonstrated by Geerlings,[12] who showed that the percentage of nitrogenous non sugar increases in second and third mill juices indicating the considerable influence of extraction on the level of non sugars in the juice to be processed.

Similarly the recent introduction of mechanical harvesters and the inevitable decline in the control of manual cutting operations have also lead to an increase in the percentage of green leafy material processed.

Although the effects of increased juice extraction and the processing of increased quantities of leafy material are difficult to measure, it would be safe to assume that the trend of leaf material has been towards the extraction of additional quantities of amino nitrogen during recent years.

However since comparable data on the amino nitrogen content of Barbados' Molasses is not available for the years prior to the introduction of mechanical harvesting and cane shredders, it is impossible to make a definitive statement.

Further, it must be pointed out that no attempt has been made to identify nor quantify the individual amino nitrogen compounds present as this is known to have a considerable effect on the formation of n-propyl alcohol during fermentation.

Conclusion

The levels of amino nitrogen in various portions of the cane stalk indicate that an increase in the extraneous matter content of the harvested cane or increased juice extraction will increase the amino nitrogen content of the molasses. Further work should be carried out to monitor the effect of fertiliser applications on amino nitrogen as Hance[13] has found this to be important.

Literature Cited

1. Clutam, D.W. (1974) Flavour Industry 5, 286
2. Campbell, P.F. (1985) The Story of Barbados Rum. Barbados Rum Book.
3. Private Communication West India Rum and Spirit Producers Association
4. Draft Barbadian and Jamaican Standards on Rum
5. I'Anson, J.A.P. Rum Manufacture, Process Biochemistry July 1971.
6. Arroyo Rafael, Manufacture of Rum, Sugar, December 1941
7. Kampen, W.H., Sugar y Azucar, July 1975
8. Arroyo Rafael, Manufacture of Rum, Sugar, January 1942
9. Parfait, A. & Jouret, C., Formation of higher alcohols in rum
10. Unger, E.D. & Coffey, T.R., Production of light-bodied rum by an extraction distillation process
11. International Sugar Journal, July 1934, page 272
12. Geerlings, Cane Sugar 2nd Edition page 131
13. Hance, F.E., Proceedings Hawaiian Sugar Planters Association Report 37 (1932) page 27.

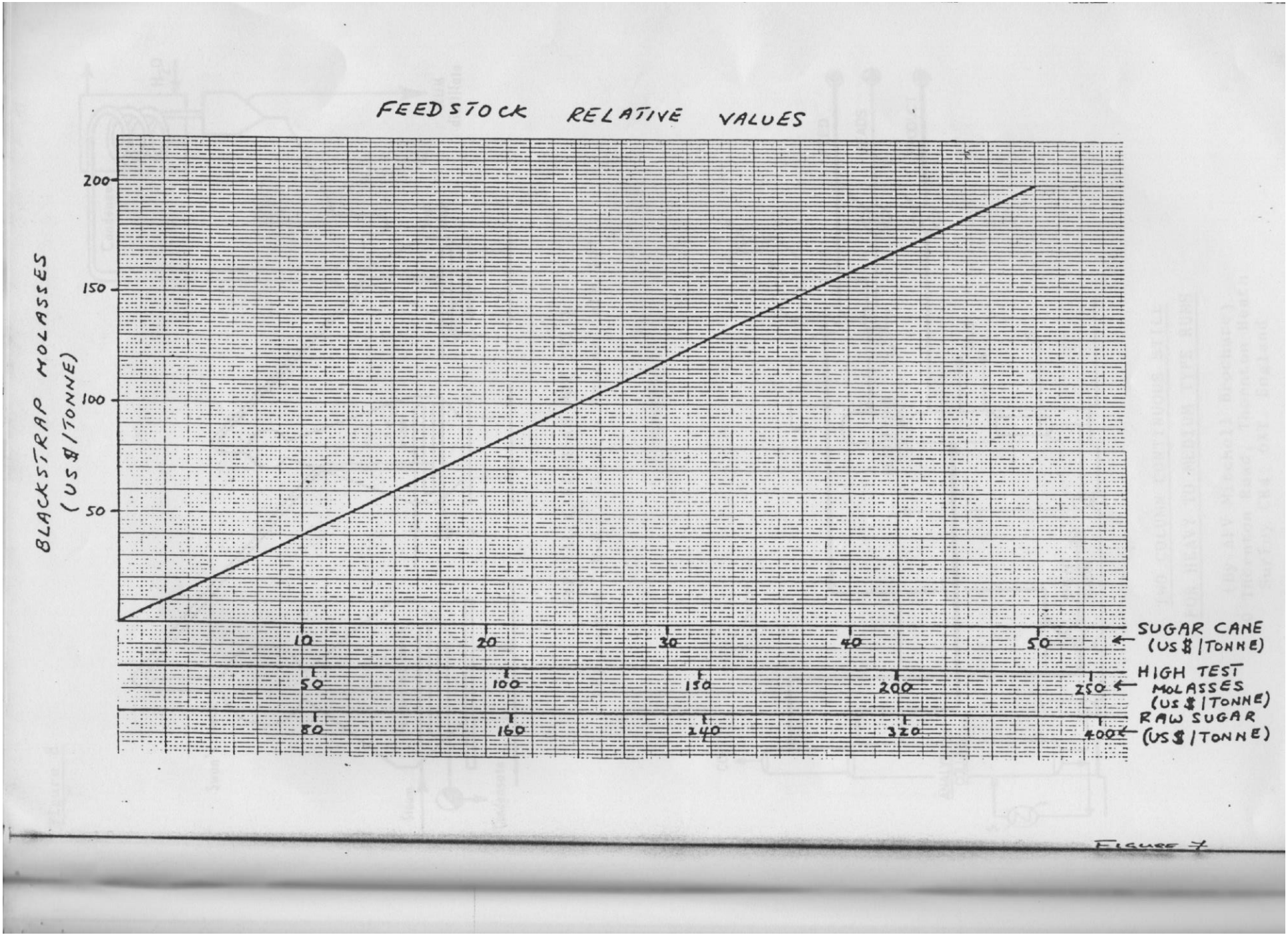
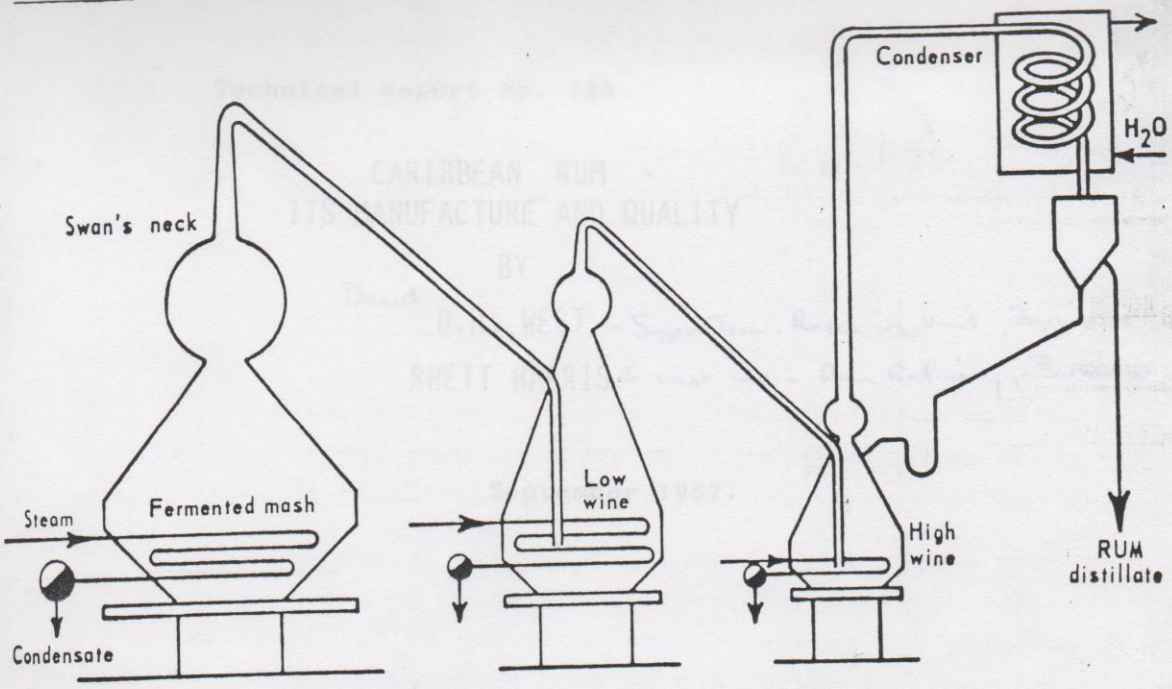

FEEDSTOCK RELATIVE VALUES
BLACKSTRAP MOLASSES (US$/TONNE)
200
150
100
50
10
20
30
40
50
SUGAR CANE (US$/TONNE)
50
100
150
200
250
HIGH TEST MOLASSES (US$/TONNE)
80
160
240
320
400
RAW SUGAR (US$/TONNE)

FIGURE 7

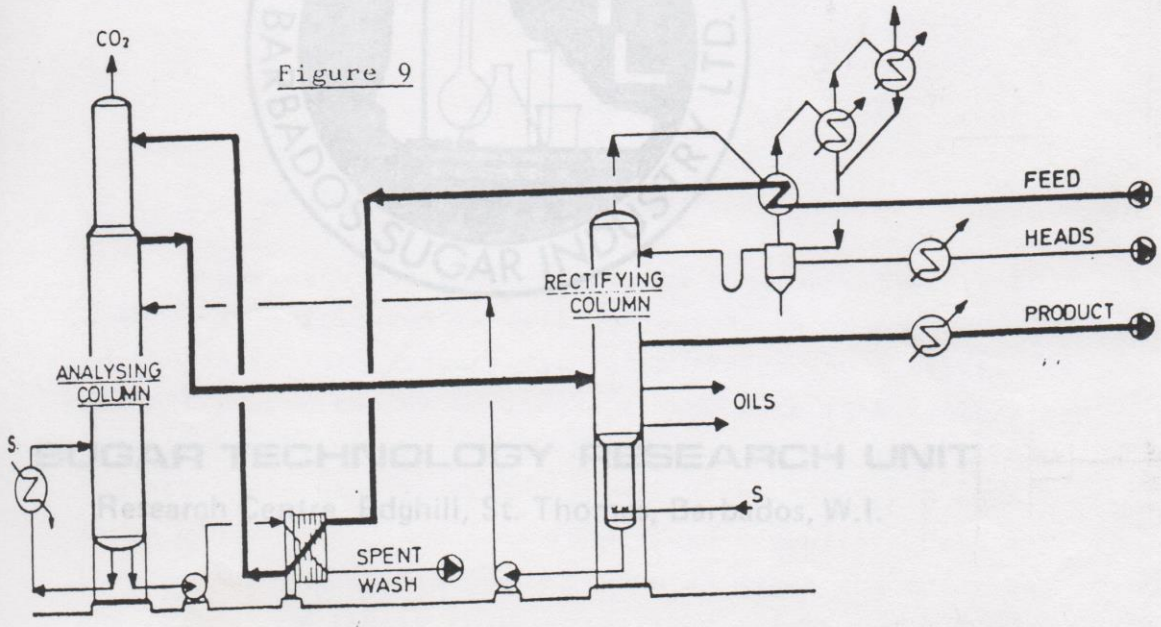
Figure 8



TYPICAL CARIBBEAN POT STILL

(By Kampen, W.H. Sugar y Azucar July 1975)

Figure 9

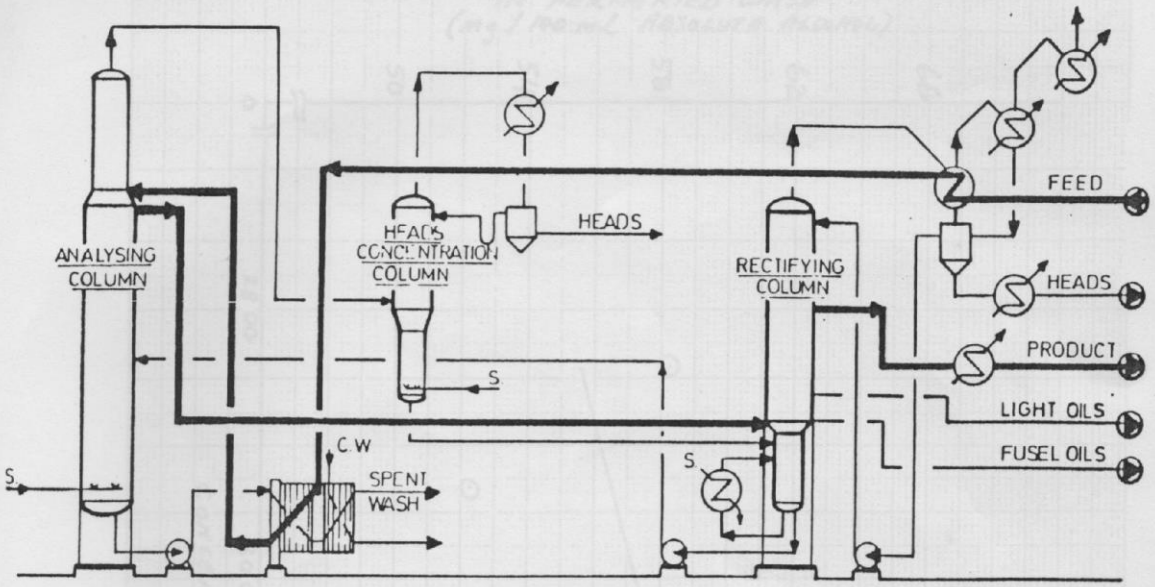


TWO COLUMN CONTINUOUS STILL

FOR HEAVY TO MEDIUM TYPE RUMS

(By AFV Mitchell Brochure)
30 Thornton Road, Thornton Heath
Surrey CR4 6XT England

Figure 10

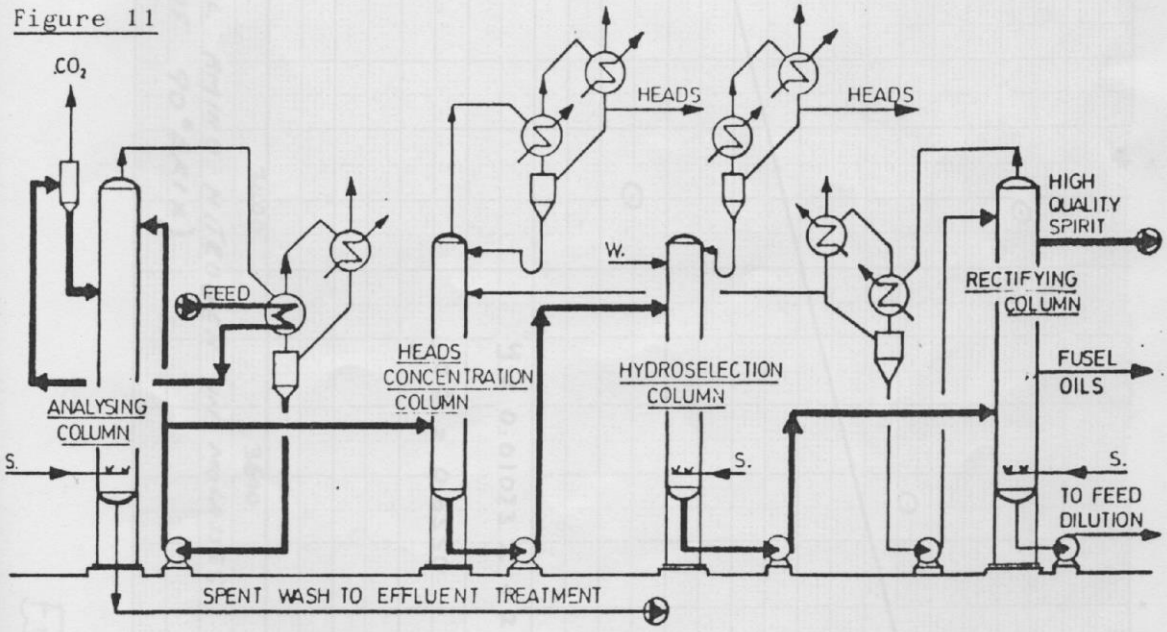


THREE COLUMN CONTINUOUS STILL

FOR MEDIUM/LIGHT TYPE RUM

(By APV Mitchell Brochure)
30 Thornton Road, Thornton Heath
Surrey CR4 6XT England.

Figure 11



FOUR COLUMN CONTINUOUS STILL

FOR EXTRA LIGHT RUM AND NEUTRAL SPIRITS

(By APV Mitchell Brochure)
30 Thornton Road, Thornton Heath
Surrey CR 4 6XT England.

AMINO NITROGEN AND n-PROPYL ALCOHOL IN MOLASSES WASH

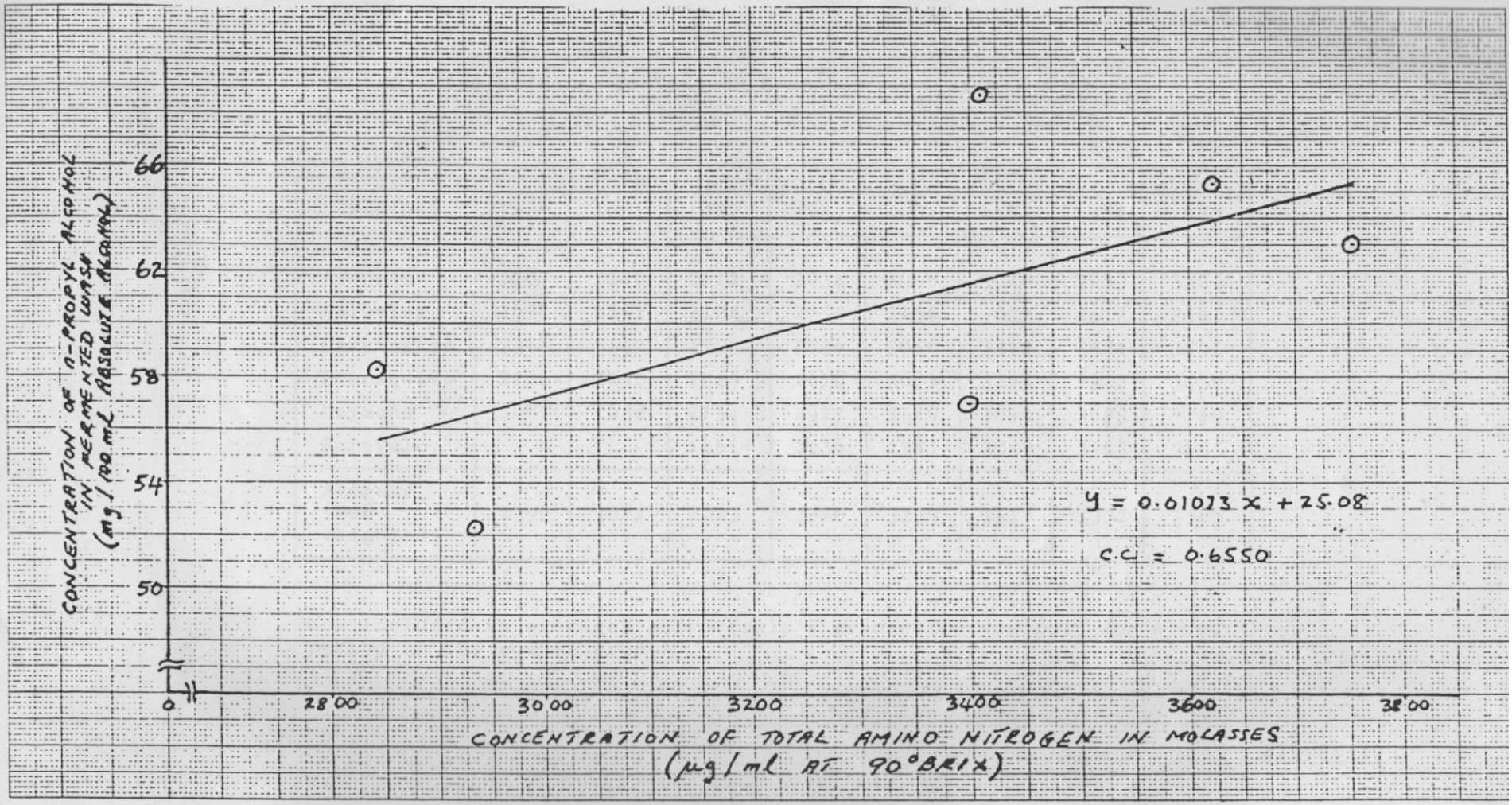


FIGURE 18

TOTAL AMINO NITROGEN CONTENT OF BARBADOS' BLACKSTRAP MOLASSES

FACTORY	1980	1981	1982	1983	1984	1985	1986	1987
Andrews	2707	2246	2112	2934	2968	3640	3063	3325
Bulkeley	2677	2257	2124	2755	3159	3637	3517	3567
Carrington	2398	2152	1798	2736	3056	3313	3434	3567
Foursquare	2121	2058	1949	2670	3681	3265	2922	3439
Haymans	2081	1658	2134	2927	3589	3992	3693	3140
Portvale	-	-	1261*	2236	2981	3257	3363	3155
Average (Not weighted)	2397	2074	2023	2710	3239	3517	3332	3366

*Not included in averages as Portvale's production was only for a test period at the end of crop.

FIGURE 19

AMINO NITROGEN CONTENT OF FINAL MOLASSES (90 °BRIX)
WEEKLY COMPOSITES 1986 CROP

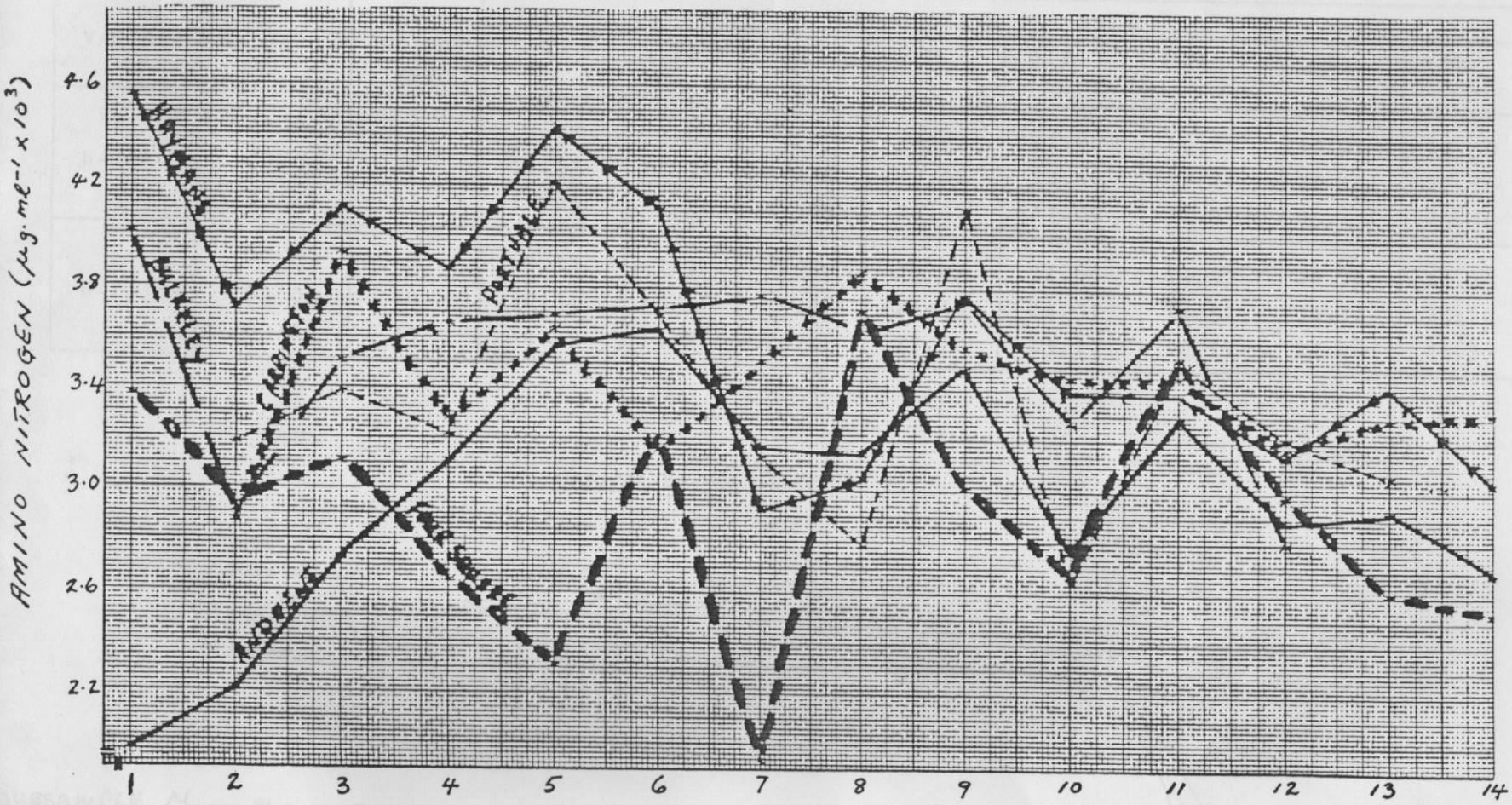
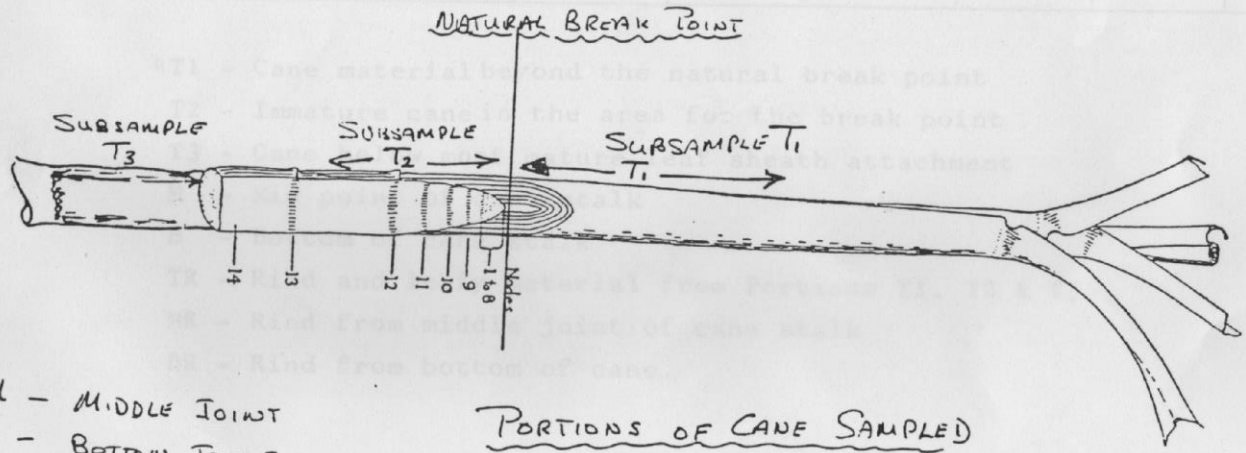


FIGURE 20

ANALYSIS OF JUICE EXTRACTED FROM PORTIONS OF CANE STALK

VARIETY	DATE	DAYS ELAPSED	PERCENTAGE (%) BRIX							
			*T1	T2	T3	M	B	TR	MR	BR
B-62163	02/07	0	9.47	7.19	13.86	21.01	21.93	10.73	19.41	24.50
	03/05	26	11.67	11.35	18.46	22.66	22.60	13.47	20.19	22.56
	03/24	45	11.99	8.53	17.69	23.32	23.09	18.08	25.47	25.50
B-73382	02/07	0	9.38	7.57	16.80	20.27	21.65	13.57	20.27	24.43
	03/05	26	10.34	12.21	19.48	21.56	24.37	14.52	20.72	25.20
	03/24	45	14.69	14.65	23.27	23.70	25.13	16.72	22.96	26.27

FIGURE 22



SUBSAMPLE M – MIDDLE JOINT
" " B – BOTTOM JOINT.

PORTIONS OF CANE SAMPLED

ANALYSIS OF JUICE EXTRACTED FROM PORTIONS OF CANE STALK

VARIETY	DATE	DAYS ELAPSED	PERCENTAGE (%) R. S.							
			*T1	T2	T3	M	B	TR	MR	BR
B-62163	02/07	0	1.39	2.31	2.68	1.88	0.21	1.86	1.70	1.00
	03/05	26	0.63	2.91	1.68	0.36	<0.10	1.12	0.49	0.14
	03/24	45	0.96	2.21	1.47	0.21	<0.10	0.77	0.10	0.10
B-73382	02/07	0	0.50	1.44	1.21	0.14	<0.10	-	0.59	0.20
	03/05	26	0.42	0.72	0.24	0.29	<0.10	0.55	0.32	0.13
	03/24	45	0.90	0.53	<0.10	0.11	<0.10	0.74	0.68	0.25

*T1 - Cane material beyond the natural break point
T2 - Immature cane in the area for the break point
T3 - Cane below most mature leaf sheath attachment
M - Mid point of cane stalk
B - Bottom of cane stalk
TR - Rind and leafy material from Portions T1, T2 & T3
MR - Rind from middle joint of cane stalk
BR - Rind from bottom of cane.

Figure 23

ANALYSIS OF JUICE EXTRACTED FROM PORTIONS OF CANE STALK

VARIETY	DATE	DAYS ELAP-SED	PERCENTAGE (%) AMINO NITROGEN							
			*T1	T2	T3	M	B	TR	MR	BR
B-62163	02/07	0	0.32	0.07	0.08	0.12	0.16	0.34	0.45	0.98
	03/05	26	0.30	0.06	0.08	0.06	0.06	0.39	0.65	0.80
	03/24	45	0.30	0.12	0.08	0.06	0.08	0.47	0.54	0.79
B-73382	02/07	0	0.32	0.07	0.05	0.18	0.67	0.50	0.75	1.16
	03/05	26	0.27	0.16	0.18	0.09	0.31	0.48	0.40	0.79
	03/24	45	0.44	0.65	0.19	0.10	0.37	0.57	0.58	1.30

*T1 - Cane material beyond the natural break point
T2 - Immature cane in the area for the break point
T3 - Cane below most mature leaf sheath attachment
M - Mid point of cane stalk
B - Bottom of cane stalk
TR - Rind and leafy material from Portions T1, T2 & T3
MR - Rind from middle joint of cane stalk
BR - Rind from bottom of cane.

Figure 24