THE MOLASSES

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1. Introduction

The history of the Word 'molasses' ('Melasse' in German and Dutch) is not mentioned in Etymological dictionaries since it is quite definitely and clearly derived from the Romanic languages. It occurs in the same word from and with the same meaning in French, la mélasse, *i.e.* syrup or sugar honey and it has its counterparts in other Romanic languages, melassa (Italian), melaza (Spanish)*, melaço (Portuguese), going back to the feminine form of the Latin adjective mellaceus, -a, -um, *i.e.* honey-like, and ultimately, to mel (Latin), honey. Accordingly, it originally was used in the context (substantia) mellacea, *i.e.* honey-like substance. The change in meaning appears in the Spanish suffix -aza, which expresses a coarsening, whereby attention is directed to the character of the substance as a coarse, thick crude honey. Any attempt, therefore, to derive the word from the Greek μελασ (melas), black, is misdirected.
The term 'molasses' is applied to the final effluent obtained in the preparation of sugar by repeated crystallization. The amount of molasses obtained and its quality (composition) provide information about the nature of the beets (local conditions of growth and effects of the weather) and the processing in the sugar factory, such as the efficiency of the juice clarification, the method of crystallization during boiling, and the separation of the sugar crystals from the low-grade massecuite.
In white sugar factories the yield of molasses is in the neighbourhood of 4% on beets, corresponding to up to 25% on sugar. With an average sugar content in the beets of 16-18% only 13 to 14% of the sugar will be recovered as a commercial product. As an average, 2.2-2.6% sugar on beets will go into the molasses when raw sugar is produced. The yield of molasses is affected by various factors and differs from batch to batch. The daily storage loss in Western Europe is estimated at 0.062% sugar on stored beets or 0.1% sugar decrease in the white sugar yield, resulting in the differences shown in Table 1 for each 1% sugar decrease in stored beets.

TABLE 1

INCREASE IN MOLASSES PRODUCTION FOR STORAGE LOSSES OF 1% OF SUGAR IN BEETS[1]

Beet press juice			Syrup (*Q*)	Sugar yield (%)	Molasses on beet (%)
Dry substance (%)	Sugar (%)	Purity (*Q*)			
19.1	16.5	86.4	93.5	13.7	3.5
18.6	15.5	83.3	90.4	12.0	4.9
	1.0			− 1.7	+ 1.4

If the concept molasses is to be strictly defined it is necessary to distinguish between theoretical and practical molasses. The *theoretically final molasses is* a mixture of sugar, nonsugars and water, from which no saccharose crystallizes under any conceivable physical and technically optimum conditions, with no regard to time. If relatively more favourable conditions for crystallization are maintained (low water content, low temperature, long crystallization time, thin layers of the syrup film) the crystallization might be so extended that with intensive centrifugation of the molasses a quotient (*Q*) of 49 would be attainable. *Q* represents the percentage of sugar in the total solid content of the molasses.
The lower the purity or purity coefficient, the more closely a syrup approaches theoretical molasses. Unusual specimens of molasses, produced in experimental studies, have quotients from 45 to 50. The *practically obtainable molasses* is the end syrup from which, with maintenance of the technical conditions promoting crystallization, no significant additional amounts of saccharose can be recovered by further concentration. In this sense molasses with purity quotients above 64 are no longer true molasses they are crystallisable syrups.

* Miel residuaria, or final molasses, is usually described in Spanish publications in the Western Hemisphere as 'mieles finales'. High test molasses is referred to as mieles ricas.

The objective of the sugar industry is to produce molasses whose purity is as low as possible. Commercial molasses ordinarily have a quotient around 60, *i.e.* approximately 48 % sugar is present in molasses whose solids content is 80%.

$$Q = \frac{100 \times S}{T} = \frac{100 \times 48}{80} = 60$$

(Q denotes purity quotient of molasses; S is sugar content; T represents dry substance.)

Efforts to understand and master the conditions leading to exhausted molasses are as old as the sugar industry itself. Since the formation of molasses and the problems of crystallization of sugar are closely related, a clear understanding of the influences of the nonsugar substances on the crystallization of the saccharose from aqueous solutions simplifies the study of the formation of molasses. The many studies along these lines can be divided fundamentally into two categories.

(i) *Mechanical theory of molasses formation*

This old theory is based on the decrease in the rate of crystallization which depends on the speed with which the dissolved sugar molecules are transported out of the liquid on to the crystal surface as well as on the rate at which they are built into the crystal lattice.

(ii) *Chemical theory of molasses formation*

This theory is based on the mutual solubility influences in the system: water sugar, salts or nonsugar components. In many studies of the influence of the nonsugar components on the solubility of sucrose, pure substances or mixtures of pure substances have been employed, but they did not always correspond to the complicated relationships prevailing in molasses. The use of ion exchangers made it possible to start these investigations directly on molasses. It has been found that nitrogenous materials have practically no effect with respect to the sucrose solubility; potassium and sodium have considerably stronger molasses-producing properties than calcium and lithium. Because of the economic significance of the composition of final molasses there is great permanent interest in the sugar industry in being able to calculate beforehand the amount of molasses that may be expected, *i.e.* at the time of delivery and processing of the beets. Such preliminary methods of estimation are based on values derived from experience such as:

a) the ‘ash factor’, *i.e.* the molasses usually has a weight ratio ash : sugar of 1**:**5;
b) the ‘harmful’ beet nitrogen; it is assumed that in the molasses there is a constant ratio 1 **:** 25 between nitrogen and sugar;
c) diagrams or formulae which, with the inclusion of a few supplementary analytical data, give the amount of the molasses of the beet from the polarization of the beets and the purity of the thick juice (evaporator syrup);
d) numerical relationships between the sugar content of the beet and the alkalis in the diffusion juice;
e) The ‘exhaustibility quotient’, which is a numerical value of the molasses and which can be used in the control of the crystallization operation.

The literature dealing with molasses is scattered among numerous publications and reports on parts of this topic in general and special problems, and is frequently not easily accessible. The author's book *Die Melasse,* Institut für Gärungsgewerbe, Berlin, 1956, contains a comprehensive review of the European literature complete to 1955/56.

2. Final Molasses

(a) General Remarks

With respect to the raw material a distinction has to be made into:
(i) beet molasses (beet sugar molasses);
(ii) cane molasses (cane sugar molasses), whose average compositions are presented in Table 2.

TABLE 2

AVERAGE COMPOSITION OF BEET AND CANE MOLASSES[3]

Constituent	Beet molasses (%)		Cane molasses %	
Water		16.5		20.0
Organic constituents				
Sugars: Saccharose	51.0		32.0	
Glucose	—		14.0	62.0
Fructose	—	53.0	16.0	
or Invert sugar	1.0		—	
Raffinose	1.0		—	
Nonsugars: Nitrogenous materials, free and bound acids, soluble gummy substances		19.0		10.0
Inorganic constituents (ash)				
SiO_2	0.1		0.5	
K_2O	3.9		3.5	
CaO	0.26		1.5	
MgO	0.16		0.1	
P_2O_5	0.06		0.2	
Na_2O	1.3	~ 11.5		8.0
Fe_2O_3	0.02		0.2	
Al_2O_3	0.07			
Soda and carbonate residue (as CO_2)	3.5			
Sulfate residue (as SO_3)	0.55		1.6	
Chlorides	1.6		0.4	
		100.0		100.0

Four kinds of beet molasses have to be distinguished; three of them of special interest:

(a) *raw sugar molasses or green molasses:* this is formed during the production of raw sugar;
(b) *white sugar molasses:* this is obtained in factories which wash the yellow raw sugar crystals with steam in the centrifuges and which produce affinades or white sugar;
(c) *refinery molasses*: this results from the raw sugar after redissolving and crystallizing during the production of refined sugar; an accumulation of raffinose in this molasses is observed;
(d) *discard Steffen molasses or desugared molasses*: this is formed from desugarizing of molasses and is of minor commercial importance.

With respect to chemical composition the three main kinds of beet molasses do not show characteristic differences, taking into account the normal variations in composition. It is difficult to determine the origin of an unknown molasses by analysis and as a rule it is impossible to do so even by means of an intensive examination in the laboratory. The chemical compositions of the four kinds of molasses are given in Tables 3 and 4.

TABLE 3

CHEMICAL COMPOSITION OF DIFFERENT TYPES OF BEET MOLASSES[4]

(g in 100 g, referred to equal water content)

Constituent	Beet molasses				
	Raw sugar molasses	White sugar molasses	Refinery molasses	Final molasses	Cane molasses
Water	20.0		20.0	20.0	20.0
Organic materials	72.6	About the	72.7	75.8	76.5
Total sugar (as saccharose)	51.4	same as	49.3	50.5	58.9*
Total nitrogen	1.7	raw sugar	1.6	0.5	0.5
Crude protein	0.09	molasses	0.06	0.04	
Ash (carbonate free)	7.4		7.3	4.2	3.5

* 38.4 saccharose; 21.6 invert sugar.

Refinery molasses contain less nitrogenous nonsugars; likewise they are usually darker than the other two kinds of beet molasses. The different kinds of molasses are alleged to be variously suited to biological (fermentation) processes, but there are some open questions about this point.
Beet molasses has a characteristic odor; it reacts alkaline (pH about 8.0). Cane molasses are acid and have a more acidulous or fruity-aromatic odor; only rarely do they show an alkaline reaction (pH > 7).
The highly viscous molasses is not a homogeneous liquid or true solution of sugar in a nonsugar solution; molasses always contains suspended components of varying composition and in varying amounts. These materials include

(a) Constituents in the raw material (beet or cane) which have gone through the stages of the sugar factory unchanged and which cannot be removed economically; for example, the so-called harmful nonsugar components or colloidal finely suspended nonsugars.
(b) Constituents that originate during the manufacturing operations or are changed in such a manner that they finally reach the molasses; for instance, the degradation products of the sugars and proteins in insoluble form.
(c) Nonsugars which become insoluble during the concentration and crystallization process as a result of their low solubilities in highly concentrated solutions.

The complicated composition of the molasses (compare Table 2) and the individual components will be discussed with special emphasis on beet molasses.
The components of molasses include:
Major components (water, sugar, nonsugars) and *minor components* (trace elements, vitamins and growth substances).

TABLE 4
AVERAGE COMPOSITION OF GERMAN MOLASSES
(According to values from the Institut für Zuckerindustrie, Berlin[4])

Season	Number of molasses studied			Dry substance in undiluted molasses by refractometer (brix)			Purity quotient (*Q*) from brix and saccharose by the raffinose formula			Polarization		
	1	2	3	1	2	3	1	2	3	1	2	3
1924/25	36	20	11	76.9	77.4	76.3	61.9	61.6	60.8	47.0–53.4	47.7–53.3	46.9–52.1
1925/26	104	33	21	78.9	78.9	78.1	61.3	62.0	60.3	45.5–55.1	47.6–53.8	47.3–52.5
1926/27	40	17	9	78.4	78.3	78.0	61.8	62.1	59.9	46.9–55.2	47.9–51.1	48.0–54.9
1928/29	35	16	10	78.6	78.9	78.6	60.8	61.4	58.8	46.7–52.2	48.2–52.9	46.6–50.1
1930/31	33	16	9	77.8	78.3	78.7	62.3	60.9	59.8	47.2–55.8	48.3–53.7	47.4–54.5
1934/35	31	16	9	78.1	79.1	80.0	61.3	60.7	59.0	44.7–53.0	47.8–53.1	47.2–51.7
1939/40	26	10	—	77.4	78.2	—	62.1	61.2	—	46.4–56.6	47.4–53.0	—

1 refers to raw sugar molasses, 2 to white sugar molasses and 3 to refinery molasses.

Ash content (sulphate ash — $^1/_{10}$)			Total N referred to organic nonsugar (%)			Percentage of molasses with more than 1% raffinose content			Color (extinction coefficient at 480 mμ)			Ratio of the extinction coefficient of the different molasses		
1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
9.89	10.20	10.58	9.33	8.64	8.65	100.0	95.0	100.0	45.1	39.9	50.2	1	0.89	1.11
10.00	10.15	10.45	9.75	9.56	9.33	62.5	57.6	71.4	21.6	24.7	37.7	1	1.14	1.71
10.47	10.14	10.99	9.03	8.55	8.64	70.0	82.4	88.9	18.5	19.7	35.6	1	1.07	1.93
9.79	10.22	10.40	9.65	9.07	9.18	22.9	56.3	40.0	20.4	21.6	40.2	1	1.06	1.97
9.74	10.34	10.80	10.00	9.81	9.56	78.8	93.8	100.0	17.3	21.4	33.7	1	1.25	1.96
9.70	10.20	10.88	9.52	9.36	9.29	22.6	56.3	44.4	20.0	24.2	38.7	1	1.21	1.93
9.78	9.78	—	9.44	9.20	—	100.0	100.0	—	17.2	23.4	—	mean value 1 : 1.10 : 1.77		

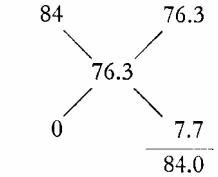
(b) Major Components

(i) Water

The water in molasses is mostly unbound but a part is held as hydration water or hydrate water. Commercial molasses have an average water content of 20%. The original end-products in the factory contain 12-17% water.

The dilution to the usual commercial water content is practiced not primarily for economic reasons, but partly to dissolve microscopic sugar crystals passed into the molasses, and mainly in order to make it easier to move the molasses by means of pumps, especially in winter, when the molasses usually has to be warmed to reduce its viscosity.

The dilution of molasses is usually calculated by the familiar mixing rule. For example, if it is desired to arrive at a molasses of 76.3 brix, the volume of water to be added to 76.3 parts of original molasses of 84 brix will be 7.7:



or 100 parts of the original molasses must in this case be diluted with $10.1 = \frac{7.7 \times 100}{76.3}$ parts of water.

The parts of water required to bring molasses to the usual commercial concentration of beet molasses of 76.3 brix are given in the publication of the Verein der Zuckerindustrien and are reproduced in Table 5.
In general, the water used in the manufacturing process in the sugar factory has no effect on the formation of the molasses, provided the water is not too high in soluble salts.

TABLE 5

WATER TO BE ADDED FOR ADJUSTING THE CONCENTRATION OF MOLASSES[4, 6]

Original molasses (brix)	Water to be added (%)	Original molasses (brix)	Water to be added (%)
77	0.9	84	10.1
78	2.2	85	11.4
79	3.5	86	12.7
80	4.8	87	14.0
81	6.2	88	15.3
82	7.5	89	16.6
83	8.8	90	17.9

(ii) Carbohydrates in the molasses:

(α) *The molasses carbohydrates.* The sugar in beet molasses consists predominantly of saccharose, but some invert sugar and raffinose are present (*cf.* Tables 2-4). It should be pointed out that from the standpoint of the sugar manufacturer the term ‘sugar’ devotes saccharose exclusively and consequently all substances, with the exception of saccharose, are included in the ‘nonsugar components’ (brix *minus saccharose;* in this case, however, not brix *minus pol).* Raffinose and invert sugar fall in the category of nonsugar components. If cane molasses were judged on sugar content by this standard (which obviously is used only in the beet sugar industry), it would not fare well. The term "nonsugar components" is limited in another manner in grading cane molasses. Invert sugar is included with sucrose as total sugars. This includes certain nonfermentable reducing substances, which are however reported in the determination of the total sugar by copper reduction methods. One of the reasons for the presence of these substances is the conversion of a slight portion of the ‘sugars’ on boiling. These materials have a reducing action; they show no tendency to crystallize and therefore enter the molasses.
The raffinose (also known as melitriose or gossypose* is present in the beets. When beets are harvestecl, around 0.3-0.5% of the sugar present, *i.e.* 0.05-0.1% or more of the beet weight, consists of raffinose, whose quantity may double during prolonged storage and which in general undergoes considerable variations showing their effects in the molasses (Table 6).The raffinose withstands the temperatures and the alkalinity to which it is exposed during the manufacturing process, and practically all of it eventually enters the molasses. There is no raffinose in cane molasses. Under normal conditions (*cf.* Tables 3 and 4) beet molasses contain 0.5-2% raffinose, and under abnormal circumstances this figure may rise to as high as 10%. Around 15% raffinose is normal for blackstrap refinery molasses. As is known, rising raffinose contents lead to increased inaccuracies in the single polarization; the optical rotation of raffinose (plus-sugar) is 1.8 times as great as that of saccharose. The enzymatic decomposition of raffinose is discussed later.

* Gossypose was isolated from cotton seed in 1884 by RITTHAUSEN. In 1843 raffinose had been identified by BFRTHELOT from *Eucalyptus manna* and given the name melitose.

TABLE 6

AVERAGE RAFFINOSE CONTENT OF GERMAN MOLASSES[5]

(According to values from the Institut für Zuckerindustrie, Berlin[4])

Season	Raw sugar molasses	White sugar molasses	Refinery molasses
1924/25	1.69	1.13	1.21
1925/26	1.72	1.07	1.40
1926/27	1.74	1.24	1.63
1928/29	0.68	0.98	0.94
1930/31	1.32	1.54	1.52
1934/35	0.74	1.06	0.95
1939/40	1.54	1.50	—

Generally speaking the raffinose content of molasses is approximately of the same magnitude as the invert sugar content. As mentioned above, the raffinose originally present in the beets passes through the entire manufacturing process. The invert sugar coming from the beet has a different fate. Whereas 1% of invert sugar is offen present in raw juice, only 0.2% is found in clarified juice because a considerable destruction of the invert sugar occurs during the purification of the juice. Taking into account the effect of the concentration of nonsugars from syrup to molasses, this corresponds with 0.8% of invert sugar in the molasses. According to American data molasses almost always contains much more than 1% invert sugar, which could indicate that new invert sugar is formed after the juice has been purified.

Invert sugar in molasses originates partly from the beets, which normally contain 0.1%, though beets which have been frozen or that have spoiled contain considerably more than this amount. Invert sugar is also produced during the manufacture of sugar as a result of the hydrolysis of saccharose. The rate of the hydrolysis increases with rising temperature and with falling pH. The inversion products, *i.e.* glucose and fructose, represent a loss of saccharose and cause a lowering of quality of the raw sugar because under the conditions of sugar manufacture and refining these hexoses are partly converted into acids and coloring matters. The lowest saccharose losses have been observed at higher temperatures in the pH range from 8 to 9. At pH 12 (liming) these losses amount to around 0.5%/h, whereas at pH 9 (evaporation and boiling) only about 0.05% of the sugar present is destroyed per hour. In an alkaline medium one of the decomposition products of fructose is lactic acid, but the invert sugar mixture also yields furfurol, oxymethylfurfurol, trioxyglutaric acid, trioxybutyric acid, formic acid, acetic acid, and carbon dioxide. The corresponding oxidation products are known to be formed when air has access to the system.

However, the inversion products are interesting from other viewpoints. Invert sugar reacts also with amino acids and the lower peptides of the sugar juices to give coloring materials. This reaction is dependent an the pH; at pH 4.9 there is a rather slight formation of melanoidins, which are produced in considerable amounts[6] at pH 9. It may be stated in regard to the invert sugar content that it should not be permitted to reach any considerable concentration in the molasses; high amounts of invert sugar point to acidic action during the manufacturing process in the sugar factory and result in a lowering of the quality (purity) of the molasses with respect to the degradation or decomposition of saccharose in the sugar juices and the related consequences in the composition of the molasses, it must be pointed out that the molasses may be exposed to similar conditions, namely acid or basic milieu, during the sterilizing and clarifying steps in the fermentation plant or in the yeast factory. The degrading or decomposing influence of elevated temperatures are exceedingly dependent on the prevailing pH (Tables 7 and 8). Model experiments show that increasing amounts of sugar are inverted in saccharose solutions at a raised temperature acting over 10 minute periods (*e.g.,* 0.1, 0.5, 1.0%) at various steps in the acid region[7].

TABLE 7

INVERSION OF MOLASSES SUGAR IN RELATION TO pH AND TEMPERATURE

(According to data from the Institut für Zuckerindustrie, Berlin[4])

pH	2	3	4	5	6	7	Amount inverted sugar
	45	65	85	108	127	—	1.0%
°C	38	48	78	102	120	—	0.5%
	28	45	65	85	107	112	0.1%

In a similar way losses result from boiling of alkaline sugar solutions because of the decomposition of the saccharose molecule. The magnitude of losses is as shown in Table 8. The alkaline degradation of saccharose leads not only to glucose and fructose, but also to psicose and other carbohydrates. Consequently, psicose is also detected in beet molasses. Experience has shown that these changes also occur in molasses under conditions corresponding to those existing in the manufacture of beet or cane sugar. The divergent composition of cane molasses is due to the peculiarity of the sugar cane and the manufacturing conditions. A striking feature is the considerable content of reducing sugars (Table 2). The analytical values of cane molasses vary over wide ranges depending on the various origins of the products. The saccharose content lies between 25 and 40%, the content of reducing sugars between 12 and 30% and the total sugar content is more than 50%.

TABLE 8

DESTRUCTION OF SACCHAROSE IN RELATION TO pH[4]

pH	Saccharose destroyed (%)
9	0.03
10	0.1
11	0.25
12	0.45
12.5	1.2

Galactinol and *myoinositol* also accumulate in beet molasses. Myoinositol is a stereoisomer of the inositol found in grains, and galactinol is a compound of myoinositol with a sugar, namely *o*-α-D-galacto-pyranosylmyoinositol. Galactinol, which is precipitable in varying degrees by basic lead acetate, can have a considerable effect on the determination of raffinose. When molasses is desugared by the baryta process, both of these compounds make up a considerable proportion of the carbohydrates other than saccharose and raffinose.

Finally, molasses sometimes contain another non-reducing sugar namely the trisaccharide *kestose,* which does not occur in the beets and is only formed through the action of micro-organisms during the manufacturing process. It consists of 2 molecules of fructose and 1 molecule of glucose.

(β) *Influence of micro flora on the molasses carbohydrates.* Kestose is one of a series of products which owe their formation to the influence of microbial activity during the manufacturing process. The formation of *oligosaccharides* in the molasses can be ascribed exclusively to such activity. Oligosaccharides can also be found especially in raw and thin juices obtained from beets that have been damaged and infected. For example, it was found that a mixture of chemically different oligosaccharides was present to a considerable extent in the juice prepared from beets that had been attacked by molds. One of the materials isolated and recovered in a pure state from such juice was identical with the trisaccharide obtained from invertase preparations of *Penicillium spinulosum,* namely *o*-α-D-glucopyranosido (1→2)-*o*-β-*d*-fructofuranosido-(1→2)-β-*d*-fructofuranoside. This sugar, which also was established as a metabolic product of several other micro-organisms, is closely related chemically to kestose.

The formation of oligosaccharides can already occur in infected beets (for instance botrytis infection) through the transfructosidase effect on the proportion of glucose to fructose and can

affect this ratio in the raw juice. Acid-forming organisms also intervene, they too exert an effect on the glucose-fructose equilibrium. The activity of the microflora thus brings about the formation of a non-equimolar invert sugar mixture in the juice stations, but this activity plays only a minor role in this part of the manufacturing operation in affecting the glucosefructose ratio because the predominant part of the invert sugar is destroyed when the juice is purified.

The growth of the micro-organisms involved here is due primarily to their carbohydrate metabolism and consequently entails a loss of sugar. Accordingly, it is quite proper to discuss here the microflora in molasses even though they apparently do not really belong in a review of the composition and properties of the final discharge liquor or in a presentation of the molasses carbohydrates and the degradation of sugar.

The micro-organisms present in molasses are brought in with the beets and are necessarily carried along with the soil that clings to the slices. Since it is well known that each gram of soil carries several billion micro-organisms or their spores, high germ counts will be found in the crude juice of even well-cleaned beets. A count of 1 million/ml is accepted as normal, and this figure may rise to 20 million/ ml or higher when the beets are dirty.

The micro-organisms in molasses have in part withstood the manufacturing operations or have entered the juice during the processes conducted in the beet- or sugar-house, or they have entered the molasses in storage. Most of these belong to especially resistant strains (spores) which develop into bacteria. Some of the typical inhabitants of soil pass into the sugar factory along with the beets and are not significantly damaged even by heating to 100°C for several hours in the course of the manufacturing operations. Other spore-formers, such as *Bacillus subtilis*, come from the air.

The method by which the juice is prepared is of influence on the composition of the microflora in the crude juice and hence, to a certain extent, it is also the determining factor for the species of organisms appearing in the molasses (Table 9). When battery diffusion is employed, aerobic spore-formers predominate in the raw juice, but other cocci, yeasts and fungi are also present. The cocci predominate when tower diffusion is used[9].

TABLE 9

INFLUENCE OF THE EXTRACTION PROCESS ON THE MICROFLORA IN THE RAW JUICE OF SUGAR MANUFACTURE[4, 9]

Organisms identified by WINDISCH, Berlin	Number of isolated strains in the starting cultures		Remarks
	Battery diffusion	Tower diffusion	
Bacillus subtilis	13	4	
Bacillus pumilus	5	3	Protein and saccharose decomposers
Bacillus megatherium	1	1	
Leuconostoc	—	9	Powerful saccharose-decomposing and mucus-forming
Sreptococcus faecalis	—	2	
Candida krusei	—	2	
Saccharomyces fragilis	—	1	
Endomyces lactis	—	1	
Alcaligenes marshalli (powerful acid-consuming bacteria)	—	1	Probably introduced accidentally
Erysipelothrix rhusiopathiae (cause of swine erysipelas)	1	—	

The ratio of *Bacillus subtilis, Bacillus pumilus,* and *Bacillus megatherium* in the raw juices from battery and tower extractors is 13 : 4, 5 : 3, and 1 : 1. Probably other non-identified micro-organisms, which have not proliferated, are also present in the crude juices. This is true, for instance, of the *Lactobacilli.* Among these organisms the vegetative cells are resistant up to 90°C. The cocci that are well protected against thermal and chemical influences by a mucous film withstand, as do the spores, the manufacturing operations and are still present in the molasses.

The primary function of the diffusion system is to achieve a good and efficient extraction of the beet slices. Since certain operating temperatures are prescribed, it is inevitable that conditions will

be created in the diffusion equipment which may be favorable for the growth of bacteria. Divergent relations in the microflora with respect to the amounts of lactic acid formed were found in eight factories of the British Sugar Corporation, depending on the extraction equipment used (for instance, diffusion battery, R.T. drums, *i.e.* Tirlemont drums, as well as rapid tanks). Of course, it must not be forgotten that the lactic acid present in the crude juice is only one of the sources of the lactic acid found in the molasses, but it seems rather certain that characteristic differences are shown in the molasses depending on the type of diffusion employed. The molasses coming from factories with R.T. drums contained 2.5 g lactic acid/100 kg sugar as an average, those with diffusion batteries showed 3.4 g, and factories with rapid tanks had a mean content of 3.6 g lactic acid/100 kg sugar. However, absolute regularity may not be deduced from these findings, since one of the factories with battery diffusion had almost the lowest lactic acid content in the molasses.

The typical microflora in molasses includes primarily hay bacilli and fungus moulds, but an organism found in one molasses need not be present in another. For the most part the micro-organisms in molasses can be regarded as accidental infections. By appropriate trials with diluted molasses solutions it was shown that molasses, despite its low contentof phosphate, is nevertheless a good nutrient medium for a good number of organisms, including yeasts, moulds and bacteria[11]. Coli bacteria, isolated from human urine, showed no growth for instance in about 7% molasses solution, but they did grow in a 1% solution. Hence the microflora of molasses can consist of yeasts *(Torula, Mycotorula Mycoderma, Candida, Schizosaccharomycetes)* and fungus molds *(Penicillium, Aspergillus, Mucor)* as well as many kinds of bacteria[4].

Various reports have been issued concerning the kind and extent of the infection of molasses. Samples of cane molasses taken from molasses tanks contained 3000 to 310,000 mesophilic bacteria/g (15-40°C) and 1200 to 16,500 thermophilic bacteria (40-60° C). The mesophilic organisms thrive during the dilution of the molasses. Others have reported 29-500 million/g molasses; yeast-like organisms and bacilli predominated while micro- and diplococci were present in lesser numbers. Organisms producing ammonia, hydrogen sulfide, and mercaptans were isolated as well as those giving rise to butyric, acetic and lactic acid; also denitrifying bacteria and, in some molasses, also *Bacteria coli anindolicum.* If temperatures above 70°C are maintained and rapid working is practiced, the incipient bacterial metabolism is impeded during the operational processes and the saccharose losses are kept low. Slight amounts of metabolic products that are formed are carried through the manufacturing stages into the molasses. These infection products also include the higher molecular polysaccharides known as dextran (see Page 91) and levulosan which result from the action of leuconostoc.

When the conditions are favorable, the formation of dextran can spread and cause many difficulties. Molasses and molasses residues should not be diluted in molasses containers since the dextran fermentation can set in at even relatively high osmotic pressure and even at pH values below 8. The fouling of piping and filters which may eventually result in complete clogging, is especially annoying.

It is not customary to make a microscopic examination of molasses for appraisal purposes. It is not easy to recognize at a glance a molasses, strongly infected with leuconostoc, which appears faultless from an analytical point of view. From among the large number of strains of micro-organisms isolated from molasses, four species were cultured in 20% sugar solution and characterized in detail[14]. After two days incubation the quantity ratio of the four species of bacteria was 2.3 **:** 2.3 **:** 1.0 **:** 1.2. The two main micro-organisms were *Bacillus cereus* and *Bacillus cereus var. mycoides,* which produce levulosans through polymerization of the fructose fraction of the saccharose and cause shifting of the fructose-glucose equilibrium sharply toward the glucose side. The situation is the reverse in the case of the dextranformer *Streptococcus mesenteroides* mentioned above, which forms dextran solely from saccharose and consumes only the glucose component in the formation of mucus.

(iii) Nonsugar components

Viewed from the standpoint of sugar technology, the nonsugar components include all constituents of beet molasses except saccharose. For practical reasons raffinose and invert sugar were treated above with saccharose. A knowledge of the sugar contents and quotients is not sufficient to characterize a molasses sample and thus to define 'normal molasses.' Special significance has to be attached to the nonsugar constituents, not only as to their total amounts, but especially as to the components.
Disregarding the water content, the nonsugar constituents of molasses can be classified as organic and inorganic nonsugars.

(α) *Organic nonsugars*

Nitrogenous nonsugars. Of special interest in the nonsugar components containing nitrogen found in molasses are the plant bases betaine and amino acids present as such in the cell content, and formed in slight amounts from proteins and protein degradation products by alkaline hydrolysis during the production and purification of the raw beet juice. When the sugar is extracted from the beet slices, the nitrogenous nonsugar components are carried into solution; about half of the nitrogen of the diffusion juice is found in the molasses. The nitrogenous portion of the beet substance makes up around 1% or more, corresponding with 0.15-0.2% beet nitrogen, consisting of about 20% amino acid nitrogen (0.04% beet), and of this about half consists of glutamic acid (0.02% beet). The nitrogen content of beet molasses ranges from around 1.2 to about 2.2% The distribution of the nitrogen content of the nitrogenous nonsugars (Table 10) shows, for average N-values of beet and molasses, the approximate proportions of the nitrogen in the individual beet N-components occurring in the molasses (column 6). This distribution is based on a molasses yield of 4 kg/100 kg beets.

TABLE 10

DISTRIBUTION OF THE N-CONTENT OF NITROGENOUS NONSUGARS IN BEETS AND MOLASSES[4]

N-component	Beets		Molasses		Approximate percentage of beet-N to N of corresponding molasses
	(g/100 g)	(%)	(g/100 g)	(%)	
1	2	3	4	5	6
Protein-N (soluble and insoluble)	0.1	50	0.07	~4	2–4
Amino-N	0.04	20	0.58	32	50–60
(glutamic acid-N)	(0.02)	(10)			
Plant base-N (chiefly betaine)	0.04	20	1.12	63	~100
Amide-N, Ammonia-N, Nitrate-N	0.02	10	0.02	~1	3–5
	0.20	100	1.80	100	

2.5 ton beets gave ~ 100 kg molasses.

There is a quantitative and qualitative shift of the nitrogen content during the manufacturing process from the beets to the last run off. Of the two main N-nonsugars of the beet, protein and betaine, a trace of the protein is found in the molasses, all the betaine being concentrated in this by-product. The earliest investigation on molasses relative to their N-composition showed the approximate distribution of the total nitrogen content as listed in Table 11.

Recent studies yielded the following values:

A) with 1.61% molasses nitrogen, around 0.6% or 37.3% of total nitrogen is betaine-nitrogen and 0.67% or 41.6% of the total nitrogen is amino nitrogen (after hydrolysis)[6];
B) with 2.1% total nitrogen, about 0.95% is monoamino acid-nitrogen, 0.57% is base-nitrogen, 0.45% is amino-nitrogen, 0.10% is nitrate nitrogen, 0.02% is ammonia-nitrogen and 0.11% is protein-nitrogen.

TABLE 11

DISTRIBUTION OF THE TOTAL NITROGEN CONTENT OF MOLASSES[4]

	Average of 16 molasses (%)	% in original molasses	% in molasses dry substance
Ammonium salts	2.61	0.0383	0.0485
Amides	1.62	0.0246	0.0313
Amino acids	30.91	0.4583	0.5768
Betaine (and protein)	64.84	0.9839	1.2520
N content	~ 100	1.5051	1.9086

Almost all amino acids are readily soluble in water; only tyrosine and cystine have a low solubility.
The amino acids of the beet (in large amounts: glutamic acid, leucine, isoleucine, alanine, aspartic acid, glycocoll, valine, γ-aminobutyric acid; in lesser amounts or traces: tyrosine, proline, phenylalanine, cystine, serine, lysine, arginine, histidine, methionine, threonine, and tryptophan) are partly present in the raw material as protein building units and partly dissolved in the cell juice. Only the γ-aminobutyric acid occurs in the free form in the cell juice; its origin is biologically explained as the result of decarboxylation of glutamic acid.

$$\underset{\text{glutamic acid}}{HOOC\text{-}CH_2\text{-}CH_2\text{-}CHNH_2\text{-}COOH} \xrightarrow{-CO_2} \underset{\gamma\text{-aminobutyric acid}}{HOOC\text{-}CH_2\text{-}CH_2\text{-}CH_2NH_2}$$

Under the prevailing alkaline reaction during purification, the amino acids readily dissolve; they are not precipitated by lime. Accordingly all the amino acids in raw juice pass through the manufacturing processes almost unaltered and enter the molasses. Glutamic acid is an exception; for the most part it is present in the cell juice as such and for a small part in the form of the semi-amide glutamine.
The 5-membered ring compound pyrrolidone carboxylic acid, whose properties differ from those of the starting material, is formed in the raw juice and it increases progressively during the manufacturing process, both from glutamine (with loss of ammonia) and from glutamic acid (with loss of water). The glutamic acid, which contains about 9% nitrogen, is present in the molasses mainly as pyrrolidone carboxylic acid. Glutamic acid can be reformed easily through hydrolytic rupture of the ring by acids or bases. The largo-scale production of glutamic acid employs preferably molasses slops (fermentation and desugared vinasses).

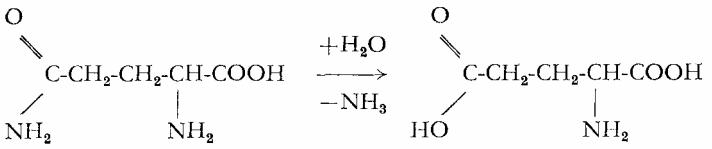
TABLE 12

COMPOSITION OF NITROGENOUS NONSUGARS IN FRENCH BEET MOLASSES

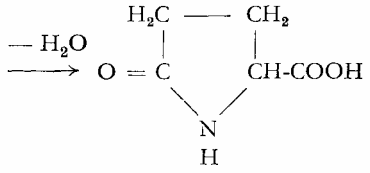
(According to data from DUBOURG and coworkers[4, 18])

Substance	56 Molasses of 1951/52 season (% of nonsugar content) Min.	Average	Max.	46 Molasses of 1952/53 season (% of nonsugar content) Min.	Average	Max.
Nitrogenous materials in the molasses	7.9	24.32	39.8	15.7	21.72	29.6
Amino acids	3.9	6.80	13.2	4.4	8.04	15.3
Glutamic acid	0.6	1.20	2.0	0.6	1.51	3.0
Aspartic acid	0.4	0.93	2.1	0.3	0.87	1.6
Serine	0.05	0.47	1.1	0	0.63	1.8
Glycocoll	0	0.25	0.8	0.1	0.56	1.4
Alanine	0.1	0.77	2.0	0.3	1.03	2.2
Tyrosine	0	0.16	0.5	0	0.20	0.7
γ-Aminobutyric acid	0.3	0.83	2.0	0.4	1.28	2.5
Valine	0.1	0.45	0.9	0.1	0.31	0.9
Leucine	0.9	1.60	3.1	0.3	1.57	4.4
Pyrrolidone-carboxylic acid				4.0	12.98	36.0
Sum of the amino acids				8.1	20.96	40.8

The glutamic acid content of molasses is given as 2.7%[15]; together with the part present in the form of pyrrolidone carboxylic acid, it is more than 50% of the entire amino acid content.



glutamine glutamic acid



pyrrolidone-carboxylic acid

Table 12 shows the distribution of the amino acid components of beet molasses, determined by chromatographic methods[18] and referred to the total organic and inorganic nonsugar content. The computation to 100 nonsugar (brix minus pol) denotes that the approximately 30% nonsugar materials of the molasses (sum of the nitrogenous and nitrogen-free nonsugars) were taken as the reference unit. Accordingly, in the French molasses there is present, as an average, 3.5 to 4% of pyrrolidone carboxylic acid or 0.5% free glutamic acid.

The nitrogen content and the proportion of amino acid nitrogen were determined before and after hydrolysis, especially the concentration of glutamic acid including the pyrrolidone carboxylic acid, in 41 molasses of the year 1953/54 and in 21 molasses from 1954/55. The results are given in Table 13.

TABLE 13

THE MOLASSES NITROGEN AND THE AMINO ACID NITROGEN CONTENT OF MOLASSES BEFORE AND AFTER HYDROLYSIS[4, 17]

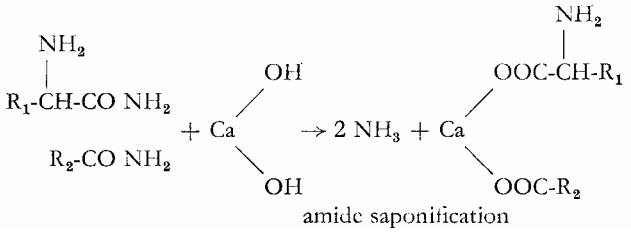
Component	Average value 1953/54 (%)	1954/55 (%)	Max. (%)	Min. (%)
Total nitrogen	1.61	1.61	2.06	1.24
Amino nitrogen:				
(a) before hydrolysis	0.29	0.27	0.40	0.15
(b) after hydrolysis	0.67	0.75	1.01	0.45
Glutamic acid including pyrrolidone-carboxylic acid	3.40	4.00	5.50	2.20

TABLE 14

DISTRIBUTION OF THE AMINO ACID CONTENT OF HYDROLYZED MOLASSES[4, 6]

Amino acid	% present
Glutamic acid	4.17
Leucine–isoleucine	0.55
Aspartic acid	0.37
Glycocoll	0.30
Valine	0.30
γ-Aminobutyric acid	0.30
Alanine	0.28
Tyrosine	0.21
Proline	0.11
Phenylalanine	0.09
Cystine	0.05
Serine	0.05
Lysine	0.03
Arginine	0.03
Histidine	0.03
Total	6.87

As an average, the amino acid content of molasses is 6 to 7% *i.e.*, around 1/3rd of the 20% of the nitrogenous nonsugars of the molasses is present as amino acids.
The quantitative distribution of the amino acids of a hydrolyzed German molasses with a total nitrogen content of 1.93% is presented in Table 14[6]. The amide content of beets is small and is given as 0.02%. There can be an enormous increase of the amide nitrogen content in dry years. Because of the action of the alkali at the high temperatures prevailing during the purification of the juice and evaporation, the amide nitrogen is split from the glutamine and asparagine, with the formation of the corresponding acidic amino acids (glutamic acid or pyrrolidone-carboxylic acid and aspartic acid). As a result, the original amide nitrogen of the beets appears in the molasses partly as amino nitrogen. This process, known as amide saponification, occurs predominantly during the first carbonation (pH 12.5).



amide saponification

Beets and molasses contain a trace of ammonium salts. The ammonia nitrogen content of molasses is accordingly always very low and is suitably determined together with the amide nitrogen. Also the nitrate nitrogen in the molasses is low. The amounts of ammonia and nitrate nitrogen in the

various molasses vary slightly from case to case. The range of variation is given in Table 15, and Table 16 shows the average content of nitrate nitrogen and ammonia nitrogen in German beet molasses. Finally, slight amounts of lower amines, methylamine and trimethylamine, appear in beet molasses as cleavage products from decomposition of the betaine.

TABLE 15

NITRATE AND AMMONIA NITROGEN CONTENT OF GERMAN BEET MOLASSES OF THE 1925/26 SEASON

(From data from the Institut für Zuckerindustrie, Berlin[4])

Type of molasses	Number of molasses studied	Nitrate nitrogen (%)	Ammonia nitrogen (%)
Raw sugar	104	0.03–0.13	0.01–0.03
White sugar	33	0.03–0.13	0.01–0.03
Refinery	21	0.04–0.08	0.01–0.02

Molasses contain a small amount of albuminous (protein) materials. The average quantities are:

raw sugar molasses	0.09% (1.7% of total nitrogen)
refinery molasses	0.06% (1.6% of total nitrogen)
blackstrap	0.04% (0.5% of total nitrogen)

The dissolved beet protein materials (acid isoelectric point at pH 5.2; alkaline isoelectric point at pH 10.9) flocculate with the pectin in the processing of the juices. Alkaline hydrolysis results in a partial degradation of the protein products, causing incomplete precipitation.

TABLE 16

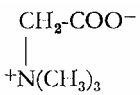
AVERAGE NITRATE AND AMMONIA NITROGEN CONTENT OF GERMAN BEET MOLASSES

(From data furnished by the Institut für Zuckerindustrie, Berlin[4])

Type of molasses	1925/26		1926/27		1928/29	
	Nitrate-N (%)	NH_3-N (%)	Nitrate-N (%)	NH_3-N (%)	Nitrate-N (%)	NH_3-N (%)
Raw sugar	0.064	0.017	0.049	0.015	0.046	0.023
White sugar	0.058	0.012	0.044	0.011	0.049	0.016
Refinery	0.060	0.011	0.050	0.012	0.040	0.019

The purines and pyrimidines, which are formed as secondary products when lime acts on the beet pulp, especially from components formed from nucleic acids, are not precipitated in the purification of the juice and accumulate in the molasses. Their absolute quantity is small. For example, 100 g of a molasses sample contained 4.63 mg adenine, 1.02 mg guanine, 0.45 mg xanthine, and 0.22 mg hypoxanthine[6].

From the standpoint of quantity, *betaine is* the most important of the plant bases found in beets, where it is present to the extent of 0.3%. Beet molasses can contain up to 6.7% of betaine, the structure of which is:



The absolute quantity of betaine nitrogen in molasses is reported to vary from 0.077-0.252%. Since it is easily soluble in water and very resistant to chemical and enzymatic influences, betaine passes practically quantitatively into the molasses. The formation of trimethylamine, $(CH_3)_3N$,

when betaine is subjected to dry distillation, is of importance in the processing of molasses slops. As mentioned above, traces of its cleavage product, trimethylamine, are found in molasses. Determination of nitrogen in samples of molasses from 18 sugar factories during six seasons showed that the mean total nitrogen content varies considerably over the years and that there are substantial differences between the individual factory analyses. With the average total nitrogenous nonsugars between 29 and 36%, the betaine nitrogen values remained fairly constant, even though these values were between 33 and 43% of the total nitrogen[19]. In general, the betaine values of today are lower than those shown in earlier analyses (Table 17).

TABLE 17

NITROGEN CONSTITUENTS IN MOLASSES*

(According to CLAASSEN[4, 96])

Constituent	1925/26		1926/27		1927/28	
	% in molasses	% of total N	% in molasses	% of total N	% in molasses	% of total N
Total nitrogen	1.81	100.0	1.71	100.0	1.69	100.0
Ammonium salts and amides	0.082	4.5	0.084	4.9	0.110	6.5
Amino acids	0.858	47.4	0.686	40.4	0.740	43.6
Betaine, etc.	0.870	48.1	0.940	54.7	0.840	49.9

* The values given are average values.

Data furnished by the Dormagen Sugar Factory[60] for the years from 1932 to 1954 (Table 18) show the effect on the average nitrogen content of the deliming of clarified juices by ion exchangers. The nitrogen content was determined by the unmodified Kjeldahl process. For comparison the data have been recalculated in terms of the dry substance content of a molasses of 78 brix. The yearly figures were computed from the averages of the weekly analyses.

The rainfall during the growing season of 1947 was very scanty and consequently the molasses nitrogen from that year was exceptionally high; this figure was not included in the calculated average. Ion exchangers were used from 1950. The average nitrogen content for the operating periods from 1932 to 1954 was 1.72%; during the period when the ion exchangers were not used (1932-1949) the nitrogen content was 1.75% compared to 1.65% in the period 1950-1954 when ion exchangers were used. According to these results, the decrease in the total nitrogen content during the time the ion exchangers were in use was 0.1 %, or 5.7 %, if recalculated to 100 parts of total nitrogen[60]. This decrease in the molasses nitrogen must, however not be ascribed unconditionally to the action of the ion exchangers.

It is an accepted practice to use the factor 6.25 when computing the N-content into terms of protein. As pointed out above, the nitrogenous nonsugars of molasses do not consist of crude protein, but chiefly of mono- and dibasic amino acids, acid amides, betaines together with small amounts of peptones and nitrates. Since about the half nitrogenous constituents of molasses consist of betaines (averaging 12% N) and one half of amino acids, including the amides (averaging 10.5-11% N), the factor 8.5 is more correct for calculating the content of nitrogenous nonsugars in the molasses from the N-content.

TABLE 18

NITROGEN CONTENT OF MOLASSES FROM THE DORMAGEN SUGAR FACTORY, GERMANY[60]

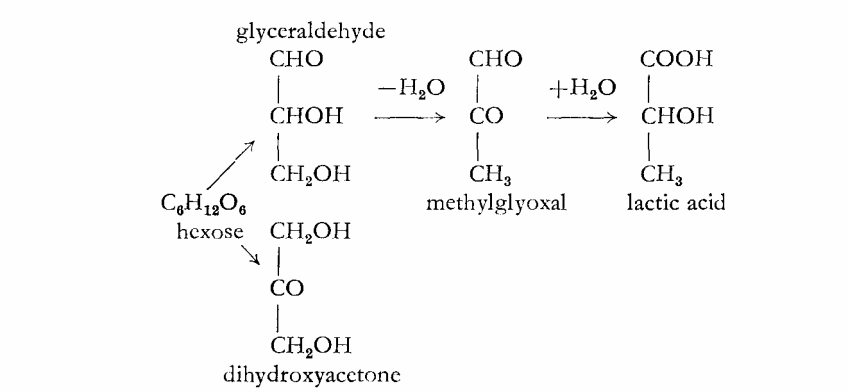
Without ion exchanger action		With ion exchanger action	
Season	% N on basis of 78 brix	Season	% N on basis of 78 brix
1932	1.57	1950	1.57
1933	1.82	1951	1.66
1934	1.91	1952	1.64
1935	1.81	1953	1.69
1936	1.63	1954	1.69
1937	1.90		
1938	1.84	Average	1.65
1939	1.86		
1940	1.67		
1941	1.63		
1942	1.72		
1943	1.74		
1944	1.58		
1945	1.76		
1946	1.63		
1947	(2.32)		
1948	1.86		
1949	1.83		
Average	1.75		

The average figure from all seasons of 1932–1954 (except 1947) is 1.72%.

Nitrogen free organic nonsugars. Among the N-free organic nonsugar substances present together with the beet pectins, are hemicelluloses, better known as *arabans* and *galactans* and their cleavage products arabinose and galactose. In contrast to pectin, these materials are not precipitated during the carbonation, but withstand the purification almost unaltered and are found in the molasses (1.22-1.56 %)[20].

The dicarboxylic acids present in the beet (oxalic, malonic, succinic, glutaric and adipic) and hydroxycarboxylic acids (glycolic and lactic, malic and tartaric as well as citric acid) are largely removed during the purification of the juice (predefecation). The following *organic acids* are found in molasses[16]: oxalic (0.01%), hydroxyglutaric, lactic (0.5%), saccharinic acids, humic acids and arabic acids. The volatile acids (formic, acetic, butyric, propionic as well as valeric) are normally present to a slight extent in molasses. Table 61 in the section dealing with the manufacture of yeast gives analytical data regarding these acids. The main cause for the occurrence of butyric acid is the reuse for diffusion of waters taken from the settling basin. Because of bacterial activity it is only after the extraction has been in progress for several weeks that the butyric acid along with the reused water from the settling basin reaches the diffusion operation and starts accumulating in the molasses. The undesirable formation of butyric acid can be avoided if, as in continuous diffusion methods, the press water is reused directly in the sugar factory.

Calcium lactate is soluble in water and constitutes a certain part of the undesirable soluble calcium salts. Lactic acid is invariably formed during the course of the manufacture of sugar; it is a secondary product of the decomposition of saccharose. The carbon chain of the hexoses of invert sugar is ruptured in an alkaline medium, and at elevated temperatures a conversion to lactic acid via methylglyoxal occurs.



Each gram of invert sugar destroyed yields 0.3 g of lactic acid. The glucose fructose ratio of the slight amount of invert sugar, which is not destroyed under the strong alkaline conditions prevailing during the purification of the juice, indicates that the destruction of fructose is greater than that of glucose.
The change in the pH, when molasses solutions were sterilized under pressure, indicates that acid is produced during this operation by decomposition of a part of the molasses sugars. Molasses solutions sterilized, firstly, for two hours and, secondly, for one hour, with an interval of 24 hours, under a pressure of 2 atmospheres showed the decrease in pH indicated in Table 19.

The organic N-free nonsugars increase slightly during the course of sugar manufacture or refining, because sugar is decomposed and converted into nonsugars. However, these changes are too small quantitatively to serve as a basis for distinguishing between the various molasses.
Among the organic nonsugars in cane molasses, aconitic acid has to be mentioned as a typical constituent of sugar cane accumulating in the molasses. Sugar cane with a high content of aconitic acid contains usually less recoverable sugar. Varieties of cane exceptionally high in aconitic acid have to be considered with suspicion as they are usually giving low yields. Due to the short growing season in subtropical regions, cane grown in Louisiana and Florida is rather high in aconitic acid (0.1-0.2%); the resulting molasses can contain 3-7% of aconitic acid on dry substance. Colouring matters must be included among the organic nonsugar components of molasses. Sugar beets contain no colouring materials, but they do contain colour-forming substances. Sugar and nonsugars participate in the production of colour (caramel substances, melanoidines) or nonsugars as such (phenol-iron complexes, melanins) are responsible. The degree of discoloration is related primarily to pH and temperature. The discoloration in sugar juices increases threefold for each 10°C rise in temperature of processing. Colouring matter is formed not only when bases or acids react, but also, to some extent, from decomposition of saccharose. These mixtures of colour-conferring materials are referred to in the literature under various names, such as caramelan, caramelene, carameline, saccharan and fuscazinic acid. In addition, furfural derivatives are formed simultaneously together with volatile compounds (aldehydes, such as acrolein) and also carbon dioxide.
The colouring matters that appear in the course of sugar manufacture can be divided into the following groups[6]:

A) *Caramel materials*. These substances are the results of thermal decomposition (including loss of water) of saccharose; they contain no nitrogen. At constant pH the formation of caramel is directly proportional to the effective temperature.
B) *Polyphenol-iron complexes.* Pyrocatechol, which occurs in the epidermis and the head of beets (in amounts around 0.02%) leads to a yellow-greenish discoloration of the sugar juices resulting from the formation of a pyrocatechol-iron complex. This is not entirely removed during the defecation of the juice and can be found in molasses.
C) *Melanoidines.* An opinion regarding these condensation products of reducing sugars and amino acids was advanced in the discussion of invert sugar as an ingredient of molasses (see page 11). Above all others, aspartic acid is involved in the production of colour. The best known of these condensation products is fuscazinic acid (fuscus = dark; azin from azote -nitrogen) which plays a large part in the discoloration.

D) *Melanins.* Beet tyrosinase*, which belongs to the polyphenol-oxidases, contains copper in its active group. On access of air it introduces the oxidation of various aromatic compounds (pyrocatechol, tyrosine) and products blackish-grey discolorations. This reaction, known as melanin-formation, requires only the enzymatically catalyzed oxidation for its initiation and then proceeds as a chain reaction passing through red and red-brown intermediate stages to orthoquinone-like compounds. Since this discoloration can be removed almost completely in the predefecation, melanins seldom appear in molasses.

The most important groups of colouring materials found in beet molasses are caramel substances, melanoidines, and iron-polyphenol compounds. Table 20 shows their formation in the course of the individual manufacturing stages.
The properties and reactions of the two chief groups of colouring materials of beet molasses are shown in Table 21.

TABLE 20

FORMATION OF COLORING MATTERS IN THE SUGAR FACTORY

(According to TULLIN[4, 6])

Stage in factory	Caramel substances	Mela-noidines	Iron polyphenol compounds	Melanins
Beet slices press juice	0	0	0	+
Raw juice	0	0	+	+ + +
Juice purification	0	+	+ +	0 (removed)
Syrup	(+)	+ +	+ + +	0
Sugar house	(+ +)	+ + +	+ + + +	0

0 = no color formation; + = color formation.

TABLE 21

REACTIONS OF COLORING MATTERS OF BEET MOLASSES

(According to ANDRES[1, 4])

Reagents and properties	Caramel materials	Invert sugar degradation products (melanoidines) formed in alkaline solution
Neutral lead acetate	no precipitate	yellow-brown precipitate
Basic lead acetate, concentrated	precipitate	
Lime water	solution darkens on warming	
Carbonic acid	solution pales	lime precipitates
Fehling's solution	reduced	reduced
Coloration	clear red–brown to dark brown	yellow–brown
Solubility	soluble in water and 84% alcohol, almost insoluble in 95% alcohol, insoluble in amyl alcohol and ether	soluble in alcohol
Color according to STAMMER* (°St.)	900	1800

* The coloring power of a 1% molasses solution is approximately 980–1000 °St.

* Since BERTRAND (1895), tyrosinases have been understood to be enzymes which oxidize the amino acid tyrosine to produce eventually the dark colored mclanin. Crude enzyme solutions oxidize tyrosine to 3,4-dihydroxyphenylalanine (`Dopa') and in a corresponding manner also certain other monophenols (monophenolase or true tyrosinase). However, orthodiphenols are also oxidized by such enzyme solutions to the respective orthoquinones (diphenolase).
This viewpoint is probably subject to revision in so far as the oxidation of tyrosine to Dopa represents a non-enzymatic reaction between tyrosine and an orthoquinone catalyzed by free, not protein-bound, metal ions (Cu, Co, V, Ni). Consequently, the name tyrosinase in this connection should be removed from the literature, since monophenolase probably does not exist[21].

Sugar factories are not concerned with the production of light-colored molasses. Their interest resides in rendering harmless the coloring matters present or formed in processing, and in conventing them as far as possible into the molasses. Molasses from factories using milk of lime defecation are darker than those from plants applying dry lime defecation. The mean colour of the German beet molasses during the years 1924 to 1940 was in the ratio of the extinction coefficients of raw sugar **:** White sugar **:** refinery molasses as 1 **:** 1.10 **:** 1.77 (*cf.* Table 4). The individual groups of colored nonsugars in molasses (*cf.* Tables 20 and 21) behave very differently physically; the molasses color is extremely inconstant generally speaking. In order to gain some insight into relations in the color character, the extinction was measured in three regions (see Table 53). In decolorization experiments the curves of the decolorized molasses did not run parallel; dark molasses lost considerably more color than light molasses on treatment with equal amounts of carbon[20]. The question of the color of beet molasses is closely related to the molasses colloids; about 85% of the molasses color is carried by irreversible colloids[22]. The problem of the colloids and suspended materials is particularly important to the yeast-making properties of the molasses. If a blue complementary color (optical brightener) is used in the centrifugals, or the blueing agents are introduced early in the boiling process in the vacuum pans, a part of the dyes gets into the molasses as impurities. Inorganic ultramarine and indanthrene, a harmless coal tar dye of the anthraquinone series, are used mainly. For use in the sugar industry, indanthrene is furnished as a colloidal paste. Only a small fraction adheres to the sugar crystals. When the blueing is conducted in the centrifugals this amounts occasionally to only 0.01% of the quantity added; the amount of dye used is only 50 g/ton and is only a fraction of a percent of the weight of sugar. Almost all of the dye passes into the molasses. Under certain conditions the indanthrene can be converted into the alkali- and temperature sensitive leuco dye. When ultramarine is used as the blueing agent, the quantity applied is 20-60 g per boiling of a ton of massecuite[23]. Even weak acids destroy ultramarine with evolution of small amounts of hydrogen sulfide. The blueing of sugar was practically abandoned in Germany prior to World War II and since then has been practiced to only a slight extent in other countries. The ban on the blueing of sugar issued during the war years has not yet been lifted officially. A recent inquiry among the sugar factories in West Germany showed that none of them employ this procedure and that the factories have no interest in restoring this practice in the future. In contrast to various non-German molasses, the molasses of German sugar factories are free of ultramarine and indanthrene. The discussion of the blueing materials that may have entered the molasses is by no means the closing section of the account of the color of molasses. It is necessary to consider primarily the questions of the colloidal and suspended nonsugars. This will be discussed in connection with the inorganic nonsugar substances.

(β) *Inorganic nonsugars*

Molasses contain a large variety of salts. These inorganic nonsugar materials increase the solubility of saccharose and they are important for their molasses-producing characteristics. This applies particularly to sodium and potassium, which in the fresh juice are mostly bound to acids (for instance, oxalic acid). During defecation with lime, insoluble calcium salts result along with the so-called ‘natural’ alkalinity:

$$Ca(OH)_2 + (COOK)_2 \rightarrow (COO)_2Ca + 2\ KOH$$

In the juices from altered beets (long storing, frost) the sodium and potassium are also partly bound to other acids with the result that soluble nonprecipitable calcium salts are formed in the defecation. The juice then Lacks the corresponding amount of natural alkalinity; this is hell to be detrimental. Whereas juices with sufficient natural alkalinity can be processed without danger of inversion, this is not true for Juices with a low natural alkalinity. The lime alkalinity has to be removed with the lowest possible lime content (0.008-0.015% CaO) because of the danger of incrustation during evaporation as well as difficulties during crystallization. The natural lime alkalinity in the clarified juices is replaced by sodium alkalinity by the addition of Soda. The addition leads to a varying soda content in the molasses and explains the fact that frequently there is more Na_2O in the molasses than in the corresponding quantity of beets (*cf.* Table 24).
The inorganic nonsugars are included in the determination of the ash. The amounts and composition are influenced by the soil and weather conditions as well as by the beet varieties.

Depending on the soil conditions, an increasing quantity of ash was found in the following order: clay soil, sandy soil, marshy soil. A comparison of earlier analyses with recent values shows in general that the ash content of beets has decreased with progress in the selection of newer beet varieties. Only general statements can be made about the ash content of beets, and the same is true of molasses. The mean ash content of beets is ± 0.75 % that of beet molasses is ± 10 %. The content of ash or salt has practical significance, since the solid content of the vinasses and also the yield of thick slops (35°Bé) depend on the salt content. The composition of carbonate-free ash of sugar beet molasses is given in Table 22.
The sulfate method (carbonated ash = sulfated ash minus 1/10) is simple and rapid for determining the ash content of molasses. It is used in many cases to determine the carbonated ash[5], although this procedure is also not free of sources of loss. The conductometric method of determining the ash has not found general acceptance in the fermentation industry.

TABLE 22
COMPOSITION OF CARBONATE-FREE BEET MOLASSES ASH[4]

Constituent	Max. (%)	Min. (%)	Average (%)
Potash (K_2O)	72.74	66.15	69.85
Soda (Na_2O)	15.86	9.42	12.17
Lime (CaO)	7.09	4.37	5.70
Magnesia (MgO)	0.78	0.00	0.37
Ferric oxide (Fe_2O_3)	0.45	0.01	0.24
Phosphoric acid (P_2O_5)	0.80	0.23	0.60
Sulfuric acid (SO_3)	2.56	0.59	2.04
Silica (SiO_2)	1.45	0.00	0.41
Chlorine (Cl_2)	11.32	8.51	10.26

About 80%, of the crude ash is made up of potassium and sodium carbonate, the other 20% represents chlorides, sulfates, phosphates, and silicates. The so-called soluble ash, *i.e.* the water-soluble part of the total ash, consisting of the carbonates, chlorides, and sulfates of the alkali metals, can be separated from the insoluble carbonated ash, consisting mainly of calcium carbonate (lime ash).
The range of the magnesia content in molasses ash as shown in Table 22 is of interest. If the beet finds little lime in the soil it takes up magnesia instead; if lime fertilizer is applied the beet leaves the magnesium in the soil. Beets grown on lime-rich soil may produce an MgO content in the molasses of zero if pure and magnesium-free water is used for processing.
The low phosphoric acid content of molasses indicates that the greatest part of this nonsugar is precipitated as insoluble calcium phosphate in the purification.

TABLE 23
AVERAGE COMPOSITION OF THE ASH OF BEET MOLASSES
(From data obtained from the Institut für Zuckerindustrie, Berlin[4])

Constituent	1 %	2 %	3 %	100 parts ash contain 1	2	3
Silica (SiO_2) and insolubles	0.0325	0.027	0.052	0.34	0.26	0.52
Ferric oxide and alumina (Fe_2O_3 + Al_2O_3)	0.045	0.025	0.077	0.47	0.24	0.78
Lime (CaO)	0.265	0.3475	0.118	2.80	3.43	1.19
Magnesia (Mg)	0.009	0.0117	0.002	0.09	0.11	0.02
Sulfuric acid (SO_3)	0.398	0.378	0.280	4.20	3.63	2.83
Chlorine (Cl)	0.429	0.415	0.406	4.53	3.98	4.10
Alkalis as chlorides	8.41	8.69	8.85	88.71	83.40	89.30
Potash (K_2O)	4.49	4.81	4.69	47.36	46.16	47.33

1 refers to raw sugar molasses, 2 to white sugar molasses and 3 to refinery molasses.

Comparison of the composition of the ash of raw sugar molasses, white sugar molasses, and refinery molasses (Table 23) reveals a striking similarity between these products. Raw sugar molasses and refinery molasses show but slight differences in their alkali content and they are almost alike in their potassium salt content. Likewise, the proportions of other constituents (SiO_2, Al_2O_3, CaO, MgO, SO_3) do not warrant any conclusions about the nature of the molasses. These values are affected by the process employed in the sugar factory and by the purity of the applied materials such as water and limestone. If individual components of the ash of beets and molasses are studied, and if it is assumed that the quantity of molasses amounts to 4% of the beets processed, it is possible to draw certain conclusions (see Table 24).

TABLE 24

RELATION BETWEEN THE ASH CONTENTS OF BEETS AND MOLASSES

(According to OLBRICH[4])

Constituent	Average values of the ash constituents		Recovered % of ash components of processed beets in molasses ash
	Beets (%)	Molasses (%)	
K_2O	0.25	4.0	~ 60–65
Na_2O	0.04	1.2	~ >100
CaO	0.06	0.30	~ 20
MgO	0.06	0.15	~ 10
P_2O_5	0.08	0.06	~ 3
SO_3	0.03	0.55	~ 70–75

Besides the loss during the extraction in the pulp, there are also losses in the inorganic nonsugars during defecation and evaporation, specifically in P_2O_5 and MgO and also the CaO, whereas relatively small or no loss of the alkali oxides or Cl and SO_3, occurs. The composition of the ash of the molasses is influenced by various steps in the manufacturing process. The increase in the Na_2O content resulting from the addition of soda ash has already been mentioned. The sulfurous acid, introduced for purification and for color improvement, is partly oxidized to sulfates, but some of it passes on to the molasses in the form of alkali sulfites. If considerable amounts of these get into the molasses the odor of hydrogen sulfide can often be detected during fermentation and the quality of the baker's yeast prepared from such molasses may suffer. If the sulfite content is too high, the sulfur dioxide liberated during the process may be reduced to sulfide and may react with iron and cause the yeast to blacken. The sulfur dioxide employed in the sulfuring of juices was accounted for as follows: 9% as sulfite, 7% as sulfite, 30.6% as sulfur-bearing nonionizable compounds[1]. The normal amount of sulfurous acid (as SO_2,) in most samples of raw sugar and white sugar beet molasses reaches values that are only in the third or fourth decimal place; higher values were found in exceptional instances, such as in a strikingly light-colored molasses which contained 0.08% SO_2[24]. This fact can be explained as due to the refining operation. The slight amount of SO_2 adhering to the raw sugar is easily oxidized during storage. The highest observed values during the season of 1934/35 were 0.0205 or 0.0282% SO_2, *i.e.* lower than the value 0.125% of SO_2 stated by CLAASSEN to be harmless in the manufacture of yeast from beet molasses.

(γ) *Molasses properties dependent on nonsugar materials*

The colloidal properties, the nature of the suspended materials, and the buffering power of molasses are dependent on the organic and inorganic nonsugar substances in the molasses.

TABLE 25

CLASSIFICATION OF COLLOIDS IN DISPERSE SYSTEMS[4]

ORDER OF MAGNITUDE OF MOLASSES COLLOIDS

Classification	Suspensions (coarse disperse solutions)	Colloids (colloidally dispersed solutions)	True solutions (molecularly dispersed solutions)
Separation (for instance)	Filtration	Ultrafilter	Diffusion, dialysis
Method of making visible	Eye Magnifying glass Optical microscope (limit of visibility at 270 mμ)	To 5 mμ in TYNDALL cone (ultramicroscopy)	By ultramicroscopy with electron beams
Order of magnitude	> colloids	In typical cases: 10^{-4}–10^{-6} mm 0.1–0.001 μ 100–1 mμ	< colloids

mm	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}
mμ	10^{6}	10^{5}	10^{4}	10^{3}	10^{2}	10^{1}	1	0.1 (= 1Å)
	← Suspensions				Colloids		True solutions →	

Molasses colloids. For the sake of convenience the colloids can be arranged in a continuous system. Colloids are disperse systems, the degree of dispersion of which ranges from 0.1 to 0.001 μ (Table 25). The molasses colloids are situated between filterable solid materials, dirt and suspended materials (suspensions) and molecular dispersions. It is probable that the molasses colloids, for the most part, are adsorption compounds formed between pectin-like materials and sugar, gummy substances, and mucina.

It is very difficult to measure and define the colloid content of molasses. Since molasses contains particles differing widely in size and in charge, as well as in relative amount, it is not possible to characterize these dispersed materials precisely. All that can be reported is a one-sided statement regarding the colloid 'content' such as the amount by weight, or the nature of the charge, or the degree of turbidity, or the particle number.

Colloids in molasses are sometimes positive and sometimes negative. The electronegative colloidal particles coagulate when the negative charge is neutralized by hydrogen ions. Conversely, the electropositive colloids are coagulated by negative hydroxyl ions. Salts may have an agglomerating or dissolving effect on the colloidal particles.

The 'particle number' was measured by counting the diffraction images exhibited by 36 German molasses after they had been diluted to 12 brix using a micrometer eyepiece to examine the Tyndal cone against a dark background[25]. No relationship was found between the 'particle number' and the color of the molasses. Due to the protein content, most colloidal particles are found in the raw juice. Every step in the defecation process removes colloidal particles but their number increases during the boiling process when they finally accumulate in the molasses.

An average of 1,000,000 particles per cubic millilitre was found by ultramicroscopic counting (Table 26).

TABLE 26

PARTICLE NUMBERS OF JUICES AND MOLASSES IN MILLIONS

(According to HIRSCHMÜLLER[4, 25])

In solutions of 12 brix	Per mm³ of original substance	Particles/mm³ referred to 1 mg dry substance/mm³	Mobile particles (%)
Raw juice	14	10	10
Thin juice	0.5	4	1
Molasses	1	8	—

Statements regarding the amount by weight of the molasses colloids reveal the difficulties of this determination. PAINE, BADOLLET and KEANE[26] state that the weight of the colloids in cane molasses amounts to 0.20-0.44%, of which 20-90% are soluble in water. The molasses colloids are 96% organic; the small remainder is inorganic in nature. VAVRUCH[27] reported that the precipitate formed by alcohol addition, which amounted to 4% on molasses, consisted of about 2/3 of its weight of organic material of predominantly colloidal nature; the latter contained 20% ash, 10% saccharose, 12% CaO, 2.5% total nitrogen, 3.0% MgO and 1.0% P_2O_5. According to BRODOWSKI[22] the molasses colloids amount to 1.07% by weight. In addition to a slight amount of higher fatty acids, two colloidal fractions were found, namely:

A) *irreversible colloids* (insoluble in water) characterized by acid or amphoteric nature, having an intense dark brown color (representing up to 85% of the molasses color) and with a high nitrogen content (around 7.5-8.7%);
B) *reversible colloids* (soluble in water) recognizable by their neutral chemical character, light brown color, and low nitrogen content (around 4%); they contain about 25% araban; hexoses may be detected in the hydrolyzed products. The weight of the reversible colloids exceeds that of the irreversible portion.

Beet molasses contains a number of negatively charged colloids, which can be flocculated by various acids. The coagulation optimum for hydrochloric acid is at pH 3.2. The concentration of a solution most favorable for coagulation is 30-40 brix (Table 27); at higher concentrations of molasses there is a decrease in the coagulation rate. The coagulation and sedimentation proceed three to four times faster in solutions that have not been filtered, *i.e.* the rate and extent of the formation of the flocks are promoted by the suspended nonsugars. Heat increases the flocculation. Complete coagulation was obtained in a 20% molasses solution at pH 3.2, kept at 80° for 2 minutes, and then 5 minutes at pH 5.7. The negatively charged molasses colloids include the caramel substances and the melanoidines, which are both closely related to the humus substances and which coagulate only in the acid region, namely below pH 6.9[28]. The brown residues obtained by drying the precipitates are more strongly colored as the pH decreases; the flocks obtained in the pH range from 6.9 to 8.0 have a dirty grey color.

TABLE 27

FLOCCULATION TIME OF THE MOLASSES COLLOIDS

(PREFILTERED SOLUTIONS) AT ROOM TEMPERATURE IN MINUTES[4, 28]

Concentration of the molasses solution (brix)	pH				
	2.8	3.2	4.2	4.7	6.2
10	300–500	40–45	65	135	210
20	300–500	30–35	60	130	200
30	300–500	20–25	45	120	190
40	300–500	25			

Suspended materials in molasses. There is a smooth transition from the colloidal state to coarsely dispersed solutions. For practical reasons the filterable materials are included among the suspended substances. The composition of the materials suspended in molasses shows a number of significant variations. The more effective the filtration of the juice in the sugar factory, the lower the suspended matter content of the molasses. The solid content in beet molasses averages from 0.3-0.5% as a rule. Table 28 gives examples of the divergent nature and the varying composition of the suspended materials. The latter correspond to the solids obtained by filtering molasses and washing the residues with water before drying.

TABLE 28

SLUDGE SAMPLES FROM MOLASSES FILTRATION

(According to WOHRYZEK[4, 20])

Constituent	Molasses A (%)	Molasses B (%)	Molasses C (%)
In the dry substance:			
Ash	59.09	32.17	60.98
Fat	12.95	25.96	10.03
Oxalic acid	10.96	10.20	7.92
In the ash:			
Silica	18.92	33.64	49.38
Ferric and aluminium oxides	9.83	13.06	26.52
Copper oxide	2.49	3.02	—
Lime	36.21	27.07	16.67
Magnesia	2.71	2.79	1.08
Sulfuric acid	8.31	6.04	trace
Phosphoric acid	2.44	2.78	trace
Carbonic acid	19.28	11.40	—

If it is desired to remove completely the suspended materials the molasses is diluted to three times its original volume and filtered. The deposits obtained contained, for instance, 9.5% oxalic acid, 16.5% lipids and 51% ash; the latter contained 33% SiO_2, 27% CaO, 2 % P_2O_5 along with CO_2, SO_3, MgO, Al_2O_3 and Fe_2O_3. The composition of the suspended matter as represented by the moist unwashed filter residue is given in Table 29. The suspended matter in molasses should he removed as a mechanical long with the colloids. Examples of the composition of the sediments are[30]: 0.05% protein, 0.03% nucleides, 0.12% fiber substance, 0.10% fatty substances and wax, 0.01% Chlorophyll together with 0.06%, foreign materials.

TABLE 29

COMPOSITION OF SUSPENDED MATTER IN BEET MOLASSES

(According to WOHRYZEK[4, 20])

Constituent	Percentage
Water	51.32
In the dry substance	
Inorganic substances insoluble in HCl	56.57
Silica and sand	1.19
Ferric and aluminium oxides	1.04
Sodium carbonate	4.39
Potassium carbonate	1.22
Magnesium carbonate	1.07
Calcium carbonate	15.46
Calcium sulfate	0.33
Lime (CaO)	3.23
Calcium phosphate	0.41
Lime bound to organic acids	0.76
Lipids	4.11
Sugars	5.00
Total organic substances	3.90
Nitrogen (organic)	0.57

Reference has already been made to the fact that the coarsely dispersed particles have a positive action in molasses clarification since they serve as coagulation centers during the flocculation of the colloids. The buffer action of molasses depends on the content of nonsugars, and the buffering characteristics of molasses are a consequence of the chemical composition. Buffering is the ability of a molasses to withstand the addition of acid or alkali without change of its acid-base character. For instance, if a strong acid, as *e.g.* HCl, is added to a mixture of sodium acetate and acetic acid, the acidity will change slightly; the hydrochloric acid will react with the sodium acetate giving sodium chloride and acetic acid, but the latter being a weak acid does not change the acidity (pH) substantially. This same effect is observed if HCl is added to molasses. The acid undergoes a double decomposition with the organic potassium and sodium salts, yielding the corresponding chlorides; the organic acids liberated change the pH of the molasses but slightly. The nonsugar composition of the molasses functions as a pH regulator. The addition of 1 ml of N acid to a litre of water (pH 7) shifts the pH to 3; a molasses solution adjusted to neutrality (pH 7), diluted 25-fold, Shows a shift to pH 6.6 with the same volume of 1 N acid added; at 50-fold dilution the resulting pH is 6.0[31, 32].

TABLE 30

DETERMINATION OF THE BUFFERING CHARACTER OF MOLASSES OF VARIOUS ORIGINS: ELECTROMETRIC AND CONDUCTOMETRIC TITRATION OF A MOLASSES SOLUTION OF ABOUT 12 BRIX

(According to data from the Institut für Zuckerindustrie, Berlin[4, 33])

Additions to 100 ml solution (ml)		Characteristic	Raw sugar molasses			White sugar molasses			Refinery molasses		
			West Germany	Central Germany		North Germany	West Germany	North Germany	Without Designation of Origin		
N-H_2SO_4	N-NaOH										
7.0			3.81	4.38	4.02	3.93	3.92	4.04	3.86	3.82	3.78
5.0			4.09	5.00	4.46	4.26	4.25	4.31	4.19	4.14	4.15
4.0			4.51	5.79	4.67	4.48	4.62	4.61	4.42	4.34	4.32
3.0			4.84	7.24	5.00	4.71	4.72	4.86	4.68	4.59	4.67
2.0			5.90	8.86	5.50	5.17	5.09	5.25	5.03	4.91	5.00
1.5			7.00	9.27	6.11	5.62	5.34	5.59	5.25	5.12	5.26
1.0			7.92	9.52	6.97	6.52	5.81	6.18	5.76	5.46	5.88
0.5			8.70	9.74	7.92	7.53	6.73	7.05	6.80	6.04	6.81
—	—	**pH**	**9.13**	**10.02**	**8.66**	**8.31**	**7.71**	**7.95**	**8.26**	**7.01**	**8.41**
	0.5		9.39	10.03	8.82	8.67	8.32	8.53	8.61	7.83	8.59
	1.0		9.63	10.38	9.19	8.97	8.70	9.01	8.98	8.52	8.90
	1.5		9.87	10.69	9.45	9.26	8.99	9.24	9.29	8.82	9.23
	2.0		10.11	10.97	9.75	9.38	9.53	9.46	9.53	9.06	9.47
	3.0		10.32	11.38	10.24	9.91	9.95	9.98	10.16	9.63	10.14
	4.0			11.60	10.56	10.24	10.37	10.18	10.75	10.20	10.56
	5.5			11.78	10.96	10.74	10.79	10.65	11.15	10.69	10.90
7.0			1.942	2.002	1.986	1.915	2.108	2.047	1.856	1.988	2.112
5.0			1.875	1.940	1.911	1.806	2.032	1.953	1.761	1.898	2.030
4.0			1.835	1.928	1.893	1.765	1.980	1.926	1.723	1.862	1.995
3.0			1.776	1.898	1.857	1.727	1.943	1.883	1.700	1.841	1.972
2.0			1.760	1.876	1.820	1.703	1.920	1.864	1.656	1.804	1.942
1.0			1.742	1.862	1.813	1.663	1.896	1.826	1.625	1.770	1.914
0.5			1.729	1.854	1.795	1.653	1.875	1.813	1.609	1.759	1.897
—	—	**% Ash**	**1.709**	**1.837**	**1.774**	**1.629**	**1.850**	**1.796**	**1.603**	**1.751**	**1.893**
	0.5		1.740	1.874	1.799	1.683	1.881	1.826	1.622	1.775	1.924
	1.0		1.788	1.904	1.834	1.697	1.931	1.877	1.658	1.787	1.947
	1.5		1.817	2.036	1.856	1.739	1.940	1.906	1.692	1.817	1.967
	2.0		1.864	2.101	1.909	1.765	1.990	1.935	1.711	1.837	2.020
	3.0		1.917	2.240	1.984	1.865	2.075	2.012	1.798	1.889	2.099
	4.0			2.376	2.081	1.930	2.153	2.100	1.876	1.966	2.212
	5.0			2.519	2.118	2.022	2.263	2.210	2.038	2.056	2.351

The strength of the buffer action depends on the concentration and the character of the buffering materials.

The nonsugar substances of molasses contain the buffer materials. The lower the purity quotient (*Q*), the greater the proportion of nonsugars and the higher the content of buffer materials. Weak organic acids and bases, and their salts, are involved in this reaction.

The buffering action does not extend itself in the same degree over the entire pH range; it is restricted in a typical manner to a specific pH range. The buffer materials of molasses are weak carboxylic and amino acids, which buffer in the acid region mainly between pH 3 and 5. When molasses contains notable amounts of phosphates, the buffering is emphasized between pH 6 and > 7.

The electrometric or conductometric titration yields information concerning the fundamental character of the buffering characteristics of beet molasses from various sources. The buffering action given in Table 30 was measured by the changes in pH observed on the gradual addition of acids and alkalis. These titration curves are rather flat at pH 4 to 6 and pH 9 to 11, corresponding to the buffering action[33, 34]. The buffering action falls off toward the neutral point. The electrometric and conductometric values agree in their general trend. Analogous to the findings on the chemical composition of raw sugar, white sugar and refinery molasses, there is no fundamental difference in the buffering characteristics.

(c) Minor Components

The treatment of the composition of molasses would be incomplete without some discussion of the minor components, *i.e.* those which are present in relatively slight amounts.

(i) *Trace elements*

In addition to the constituents of the ash noted above, molasses also contains many elements in very low concentrations, the so-called trace elements. Barium, lead, boron, iron, cobalt, copper, silver, silicon, strontium, thallium and zinc have been detected in molasses. Iodine, manganese and molybdenum have also been reported[35]. The data given in Table 31 were obtained from analyses of molasses processed in the German sugar factory Waghäusel. The reported mean values are approximations.

The problems as to which of there elements have special vital significance with respect to the growth of the beets, and which of them are present because of the locality in which the beets were grown cannot be answered completely.

TABLE 31

AMOUNTS OF COBALT, BORON, IRON, COPPER, MANGANESE, MOLYBDENUM AND ZINC IN BEET MOLASSES

(According to values by RIEHM and BARON[4, 35])

Running No.	Co (p.p.m.)	B (p.p.m.)	Fe (p.p.m.)	Cu (p.p.m.)	Mn (p.p.m.)	Mo (p.p.m.)	Zn (p.p.m.)
1	0.57	2.9	76	3.2	15	0.20	33
2	0.32	2.8	146	2.8	12	0.09	31
3	0.62	2.6	102	3.9	12	0.19	34
4	0.52	2.0	81	1.2	10	0.15	26
5	0.74	3.7	167	9.8	27	0.26	40
6	0.76	4.2	221	8.4	29	0.18	39
Average	0.59	3.0	115	4.9	18	0.20	34

p.p.m. = γ/g; mg/kg; g/t.

For instance, it has been established that lack of boron results in dry rot and decay of the heart of the beets. Accordingly, molasses from healthy beets always contains a trace of boron. The quantity of the trace elements in a molasses can have a distinct effect on its utilization. It is known that cobalt, iron, copper and manganese are essential to life. A special role is played by cobalt; it may be present in amounts up to 0.5 mg/kg (0.5 p.p.m.) in molasses. In certain diseases of dairy cattle there is an indication of a cobalt deficiency. Since beet molasses contains a relatively large amount of cobalt it has been permanently accepted as a palliative or remedy in cases of lack of cobalt.

TABLE 32

THE COBALT CONTENT DURING BEET SUGAR MANUFACTURING

(According to values by RIEHM and BARON [4,35])

γ Co/100 g Dry substance		Material	Relative quantity (kg) (beet = 100)	γ Co in corresponding amounts of fabrication products (column 4)	
Sample a	Sample b			Sample a	Sample b
1	2	3	4	5	6
0.8	1.8	Beets (fresh)	100	0.8	1.8
0.9	1.2	Raw juice	118	1.0	1.5
1.7	2.0	Thin juice	125	2.0	2.2
6.3	5.8	Syrup	28	1.6	1.8
54.5	51.0	Molasses	4	1.9	2.2

Certain variations are found in the cobalt content of molasses (Table 31), but this content may result from incomplete cleaning of the beets. If small amounts of the soil are left on the beets after washing, especially those that are wrinkled or have been nicked by the plow the cobalt content of the juice will increase because the soil contains more cobalt than the beets. Up to 100 mg cobalt/kg soil has been reported[35]. The behavior of the cobalt throughout the manufacturing process is given in Table 32. The cobalt in the beets will be found almost entirely in the molasses. The defecation process has no effect on the cobalt content of the clarified juice. The cobalt ions are probably kept in solution through the formation of complex salts with organic compounds from the beets.

An example of the qualitative and quantitative content of the trace elements in molasses is provided by Swedish studies (Table 33).

TABLE 33

MOLASSES TRACE MATERIALS

(According to MENZINSKY[4, 36])

Trace elements in Swedish beet molasses	Raw sugar molasses (%)	Refinery molasses (%)
Sr	0.004	0.004
Cu	0.001	0.0015
Mn	0.0015	0.0015
Zn	+	0.005
B	+	(+)
Be	(+)	(+)
Cr	(+)	+
La	(+)	0
Li	+	+
Ni	(+)	(+)
Pb	(+)	+
Rb	+	+

The measured concentrations of chromium and nickel are less than 0.3 p.p.m. and that of lithium below 5 p.p.m., while other trace elements, not included in the quantitative data, are present in amounts of less than 10 p.p.m.[36].

(ii) Vitamins and growth substances

It is sometimes assumed that the vitamin content of cane molasses is of no significance but the results of various studies are not in agreement with this statement (see Tables 34 and 35). Pantothenic acid seems to be remarkably sensitive to the various operations such as the clarification. In cane molasses the content of biotin is especially noteworthy; as a rule it is higher than the average in beet molasses (about 4 γ/100 g) (Table 35). In those instances in which the biotin content of beet molasses is insufficient for producing a high yield of yeast, it is feasible to add some cane molasses, in fact up to 20%, and with excellent success[37].

TABLE 34

VITAMIN AND GROWTH MATERIAL CONTENT OF CANE MOLASSES[4]

Constituent (γ/100 g)	Cane molasses from Mexico original molasses	Cane molasses from Cuba original molasses	Molasses dry substance
Vitamin B_1	140	—	—
Vitamin B_6	700	—	—
Pantothenic acid	12,000	—	—
Biotin	65	10.8	12.9

On the other hand, the amount of pantothenic acid in cane molasses may be so low that it may be advantageous to add some beet molasses. Beet molasses provide a good source of growth substances for yeast, with the exception of nicotinic acid and folic acid; cane molasses are superior to beet molasses with regard to all growth factors.

TABLE 35

BIOTIN CONTENT OF VARIOUS MOLASSES[4]

Type of beet molasses		γ Biotin per 100 g molasses	γ Biotin per 100 g molasses dry substance
Swedish raw sugar	1.	4.3	5.5
	2.	3.2	4.2
	3.	4.5	5.4
	4.	3.2	5.2
	5.	3.6	4.7
	6.	4.0	5.1
English		4.6	6.1

Mostly of German origin	γ Biotin per 100 g molasses			
	1.	7.5	8.	3.0
	2.	10.5	9.	3.3
	3.	7.5	10.	2.5
	4.	2.8	11.	2.0
	5.	1.5	12.	4.4
	6.	8.5	13.	3.2
	7.	3.1		

Average values: Swedish molasses, 3.91 γ biotin/100 g; German molasses, 3.83 γ biotin/100 g.

Table 36 shows the requirements for maximum yields of yeast in relation to the growth substance demands compared with the average growth substances which can be supplied by different kinds of molasses[37].

TABLE 36

QUANTITIES OF GROWTH SUBSTANCES NEEDED FOR THE HIGHEST YIELDS OF YEAST AS COMPARED TO THE GROWTH SUBSTANCES OF THE RAW MATERIALS

(According to WHITE[4, 37])

Constituent	Amounts of growth materials required for max. yeast yields (γ/100 g molasses)	γ/100 g Molasses				γ/100 g Malt wort (calculated on the basis of 50% fermentable sugar)
		Beet	Cane refinery	Normal cane	Cane*	
Biotin (Bios II)	29	4–13	100–180	270–320	30–40	10
Pantothenic acid (Bios III)	5,000	5,000–11,000	1,600	5,400	250	2,500
Inositol (Bios I)	120,000	577,000–800,000	250,000	600,000	85,000	480,000

* Not molasses in the usual sense but high test cane molasses; see Section 'High Test Molasses' (page 576).

As shown in Table 37, molasses contains not only pantothenic acid, inositol, and above all biotin, but also other growth substances. The answers to the questions as to whether and to what extent these materials exert a stimulative effect on the growth of the yeast and what conditions are determinative require more study.

The broad variation range in the vitamin and growth substance contents of molasses is quite understandable because many factors influence these amounts, extending from the growth of the beets through the manufacturing processes until the end-product is produced, and even the latter can undergo changes during the time of storage. The validity of comparisons of the data assembled from different sources can not be guaranteed because agreement between the methods of study is seldom assured.

The vitamin content of the sugar beet is not high in itself. The amounts of vitamins found in sugar beets or beet products are given in Table 38. Vitamin C (Z-ascorbic acid) is not present in molasses.

TABLE 37

CONTENT IN γ PER 100 GRAMS OF VITAMINS AND GROWTH SUBSTANCES[4]

Constituent	From processing of beets		Average of 8 beet molasses		From processing of sugar cane			
	Molasses	Effluent I	Original molasses	After defecation	Molasses	High test molasses (cane invert syrup)	Cane syrup	For comparison (corn steep liquor)
	1	2	3	4	5	6	7	8
Vitamin B_1 (aneurin, thiamin)	130	80	400	390	830	160	130	640
Vitamin B_2 (lactoflavin, riboflavin)	41	20	—	—	250	62	60	510
Vitamin B_6 (adermin, pyridoxin)	540	280	556	599	650	160	100	910
Pellagra protective material, pp-factor or nicotinic acid(niacin) and nicotinic acid amide (niacin amide, nicotylamide)	5,100	3,600	4,287	4,271	2,100	240	120	8,900
Pantothenic acid (anti-grey hair factor)	130	75	—	—	2,140	270	600	510
Folic acid (pteroylglutamic acid)	21	15	—	—	3.8	1.5	1	12
Biotin (vitamin H)	5.3	2.2	2.80	2.54	120	32	17	49

The vitamin C content from the beet, up to 70% of which is destroyed in the extraction process, is finally completely destroyed in the juice in the course of the manufacturing process.

TABLE 38

VITAMIN AND GROWTH SUBSTANCES CONTENT OF BEETS AND BEET PRODUCTS
(According to ROGERS and MICKELSON[4, 38])

Vitamin and growth substance content (γ/100 g)	Beets	Beet leaves	Dry cosettes
Vitamin B_1	100	240	55
Vitamin B_2	100	550	20
Vitamin B_6	130	440	18
Nicotin acid amide	240	1090	trace
Pantothenic acid (as Ca salt)	190	570	21
Folic acid	2.6	31	—
Biotin	0.75	2.3	0.1

Bibliography p. [illegible]

On the basis of the fact that around 4 kg of molasses result from 100 kg of beets, it is striking that almost the entire amount of nicotinic acid contained in the beets arrives in the molasses (Table 39). The reason is the stability of niacin against physical and chemical forces. The other B-vitamins suffer more or less loss during the manufacturing process in the sugar factory in three ways:

1) through incomplete extraction of the beets and through the pressing water of the beets;
2) through the operations of juice purification and concentration, *i.e.* the effect of temperature and chemicals;
3) through the conditions prevailing during boiling and crystallization.

TABLE 39

INFLUENCE OF PROCESSING ON THE B-VITAMINS OF SUGAR BEET

(According to ROGERS and MICKELSON[4, 38])

Substance	% on weight of beets	% of Vitamin Content						
		B_1	B_2	B_6	Niacin	Panto-thenic acid	Folic acid	Biotin
Sugar beet	100	100	100	100	100	100	100	100
Diffusion juice	140–160	75	65	23	94	65	40	72
Molasses I	6.5–7.5	5.6	1.4	15	105	2.8	40	21
Molasses (final)	4.0–4.5	5.5	1.7	18	90	2.9	34	30

Up to 25% of the vitamin B_1 is not extracted. The portion which enters the juice is destroyed almost completely by heat, alkalinity and treatment with sulfur dioxide. Vitamin B_2 suffers a similar fate. Only approx. 25% of the vitamin B_6 gets into the extracted juice, but almost all of this arrives in the molasses. Losses of pantothenic acid occur in the extraction but it is destroyed to a greater degree in the purification. Folic acid is not unstable, but it is lost mainly because of insufficient extraction. In the case of biotin the extraction loss is exceeded by the loss due to physico-chemical instability. About one-third of the initial biotin and folic acid content of the beets is present in the molasses.

(d) Other Properties of Molasses

Several physical characteristics of molasses should be included in the discussion of the composition of this material. These properties are of more or less importance to any industry that processes molasses.

(i) Viscosity of molasses

Viscosity (viscidity, internal friction) designates the resistance offered by a liquid in motion or when a solid object is moved within the liquid. The unit of viscosity is the poise or the centipoises (1 poise = 100 centipoises (cp) = 1,000,000 micropoises). The poise is defined as the viscosity which requires a force of 1 dyne to bring about a relative displacement at the rate

TABLE 40

VISCOSITY COEFFICIENT OF BEET MOLASSES AND OTHER MATERIALS[4]

Viscosity coefficient (poise)	Absolute (at 18 °C)	Relative (at 20 °C)
Ethyl ether	0.00238	~ 0.1
Water	0.015	1
Glycerin	10.7	~ 1000
Beet molasses (75 to 82 brix)	~ 40–600	~ 4000–60,000

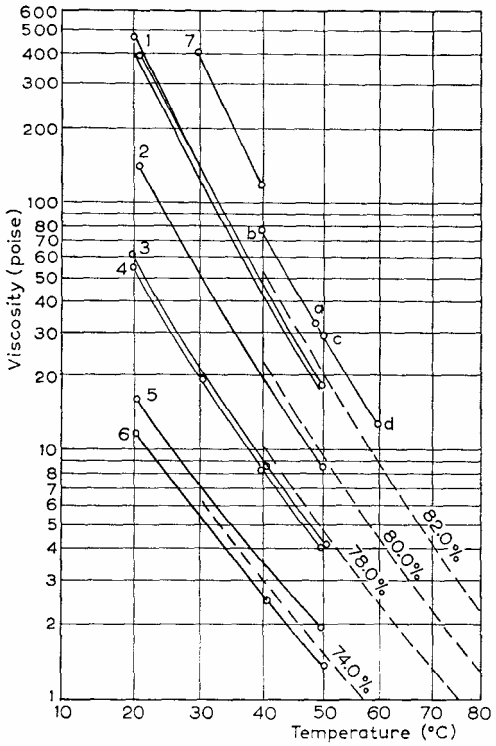


Fig. 11 1. The temperature dependence of the viscosity of Russian beet molasses (solid lines) and of pure saccharose solutions (broken lines) of corresponding concentration.

of 1 cm, second of two liquid surfaces, each 1cm^2, and separated from each other by 1cm of liquid. In addition to this absolute viscosity there is also used the relative viscosity, which employs a reference value. For example water has unit viscosity. Molasses show great differences in viscosity (Table 40), which are due principally to the varying solid contents and, to a lesser degree, to the quality of the raw material (frozen beets) and the purification of the juices. At a temperature of 10°C, the viscosity of factory molasses may be so great that it can no longer be determined by means of outflow viscosimeters or other similar measuring instruments[39].
The viscosity of individual molasses depends on the temperature and the water content. Figs.11/1-11/6 shows the great dependence on temperature and concentration. At a constant temperature of about 20°C, the initial molasses viscosity decreased from 471 to 56 poises when the molasses concentration was lowered from 82.3 to 78.5 brix. When the molasses adjusted to 78.5 brix was heated to 50°C, the viscosity fell from 56 poise at 20°C to 4 poise (see Fig. 11/1).
Table 41 shows the great change in viscosity with slight variations in temperature.

TABLE 41

VISCOSITY OF BEET MOLASSES IN RELATION TO THE TEMPERATURE[4, 40]

Molasses I has the following characteristics: 78.4 brix; 48.1 pol; 1.78% raffinose; 0.06% invert sugar; 10.66% ash. Molasses II: 84.2 brix; 50.3 pol; 1.79% raffinose; 0.49% invert sugar; 11.9% ash.

Molasses I				Molasses II			
		Viscosity (cp)				Viscosity (cp)	
°C	Specific gravity	Absolute	Change per °C	°C	Specific gravity	Absolute	Change per °C
50.3	1.3744	364.2	20	55.5	1.3747	1,100.2	70
50.1	1.3745	372.9	20	54.2	1.3760	1,193.5	80
48.9	1.3753	407.5	25	53.0	1.3768	1,332.3	100
48.8	1.3755	408.5	25	52.9	1.3770	1,354.8	110
47.6	1.3761	436.8	35	51.9	1.3778	1,448.7	120
47.0	1.3765	474.2	35	51.7	1.3780	1,484.6	130
46.1	1.3770	488.3	37	50.4	1.3792	1,632.3	160
45.9	1.3772	495.4	38	49.9	1.3795	1,739.6	160
44.4	1.3782	564.6	47	47.1	1.3820	2,174.6	200
43.9	1.3785	591.3	48	45.5	1.3835	2,689.0	225
42.9	1.3792	629.4	50	45.2	1.3837	2,658.4	240
42.4	1.3795	671.0	55	43.7	1.3850	3,074.8	280
41.0	1.3805	714.6	60	42.4	1.3860	3,428.9	320
40.7	1.3807	759.8	65	40.7	1.3876	4,046.3	430
39.4	1.3815	836.1	73	39.0	1.3890	4,947.0	560
38.7	1.3820	880.5	78	37.9	1.3900	5,511.6	700
37.1	1.3832	1,014.4	87				
36.6	1.3835	1,041.8	100				

Viscosity studies of twelve molasses from the Philippine Islands showed that each specimen had a different 'critical' viscosity. By critical viscosity is meant a sudden and marked increase in viscosity as soon as a specific dry substance content is exceeded, *e.g.*, by several tenths. The critical viscosity region of cane molasses is above 79 brix, usually between 81 and 85 brix[41]. FRENKEL[42] gives the following expression for the relation of viscosity to temperature in the case of liquids:

$$\eta = A \times 10^{B/T}$$

where

η = dynamic viscosity
T = absolute temperature
A and B are constants

If the expression is put into the logarithmic form, it becomes:

$$\log \eta = \log A + \frac{B}{T}$$

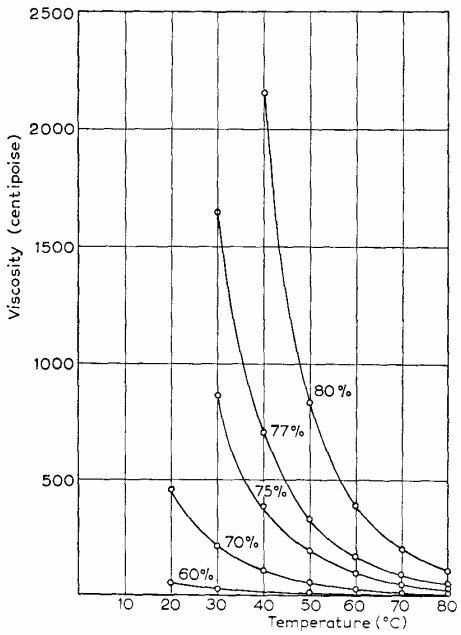


Fig. 11 2. Dependence of viscosity on temperature for various molasses concentrations.

Straight lines must be obtained for liquids if their viscosity is inserted on the logarithmic scale and the temperature is given as 1/ T. The FRENKEL equation does not apply exactly for sugar solutions (the lines are curved slightly). The formula is nevertheless useful for practical purposes. As shown in Fig. 11/1, the lines for molasses (solid lines) are practically parallel to those for sugar solutions, but it should be noted that the sugar solutions (broken lines) have been adjusted to the corresponding sugar concentrations (brix).
Consequently, it is possible to construct the temperature-viscosity relation of a molasses if no more than one viscosity measurement at any known temperature is available. Even the molasses 7 in Fig. 11/1 obtained from altered beets follows this parallelism.

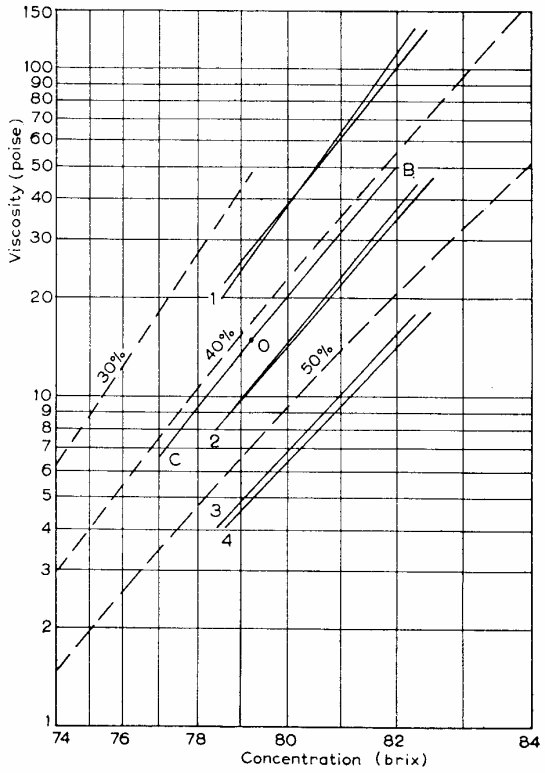


Fig. 11/3. Concentration dependence of the viscosity of Russian beet molasses (solid lines) and of pure sugar solutions (broken lines).

Accordingly, the viscosity values of sugar solutions can be applied with sufficient accuracy to molasses of corresponding concentrations, as is done in Fig. 11/2 for molasses of various concentrations.
The relations for pure sugar solutions are likewise valid for the concentration-viscosity relation of molasses. The lines of molasses run parallel to those of pure sugar solutions. It is possible to establish the concentration-viscosity curve of a molasses if only a single viscosity is known at any known concentration (Fig. 11/3).
The following expression was proposed by KAGANOFF for the concentration-viscosity relation of sugar solutions:

$$\eta = A \times 10^{Bb\,(100\,-\,b)}$$

η = dynamic viscosity
b = brix of the solution
A and B are constants

When put into the logarithmic form, the formula is:

$$\log \eta = \log A + B \frac{b}{100 - b}$$

The logarithm of the viscosity is proportional to the ratio of the dry substance content and water content. In order to obtain straight lines in a coordinate system it is necessary to plot the viscosity on the logarithmic scale against the fraction $\frac{b}{100 - b'}$ as was done in Fig. 11/3 for molasses (solid lines) as well as for pure sugar solutions (broken lines).
A nomogram constructed on the basis of the KAGANOFF expression is usable for approximate calculations but it is not suited for precise comparisons. BREITUNG[43] in the Institut für Zuckerindustrie, Berlin, made accurate determinations of the viscosity of molasses, in which use was made in sugar technological investigations of the free flow viscosimeter of UMSTÄTTER which used a long capillary. The accuracy of the measurements was adjusted to the particular requirements and varied between ± 0.2 and 0.5%. A coefficient (V_M) was developed to define the viscosity behavior. In this an average molasses functioned as the reference liquid; all viscosities were compared at 40°C:

$$V_M = 100\,\frac{\tau_M - T}{T} \text{ or } V_M = 100\left(\frac{\tau_M}{T} - 1\right)$$

T = dry content of molasses at 40° C
τ_M = dry content of average molasses at 40° C and same viscosity

TABLE 42
EUROPEAN MOLASSES ARRANGED ACCORDING TO VISCOSITY VALUES
(According to BREITUNG[43])

No.	Country*	ρ_{40}	brix	°St	P	V_M	On 100 g dry substance ash Pol	Sacch.	Raff.
				Group A					
1	Sw	1.3708	75.41	4.040	5.538	+ **2.51**	62.3	59.7	1.36
2	Ir	1.3847	77.56	8.599	11.91	+ **2.50**	61.7	61.1	0.31
3	Sw	1.3739	75.89	4.528	6.221	+ **2.36**	61.1	59.1	1.09
4	Ir	1.4024	80.25	23.37	32.77	+ **2.19**	61.2	60.3	0.47
5	Fr	1.4183	82.64	61.46	87.16	+ **1.78**	60.5	58.2	1.23
6	Fr	1.4169	82.45	52.45	74.32	+ **1.60**	59.5	57.0	1.36
7	Sw	1.3837	77.40	5.890	8.150	+ **1.41**	61.4	59.7	0.89
8	Tu	1.3955	79.21	11.18	15.60	+ **1.24**	63.6	55.8	4.20
9	Ir	1.4000	79.89	14.31	20.04	+ **1.14**	60.7	58.9	0.96
10	Tu	1.3894	78.27	7.386	10.26	+ **1.09**	66.3	62.0	2.36
11	Fr	1.4102	81.44	26.21	37.53	+ **1.09**	60.4	58.6	0.99
12	Sw	1.3776	76.45	3.965	5.462	+ **1.05**	60.5	58.5	1.08
13	Sw	1.3719	75.58	3.082	4.228	+ **0.99**	61.7	58.4	1.74
14	Ge	1.4095	81.33	23.26	32.79	+ **0.85**	64.3	61.5	1.51
15	Tu	1.4095	81.33	22.66	31.95	+ **0.76**	61.5	57.9	1.95
16	Ge	1.4129	81.84	26.91	38.02	+ **0.63**	64.9	60.1	2.59
17	Sw	1.3689	75.11	2.397	3.282	+ **0.36**	63.3	58.7	2.45
18	Sw	1.3903	78.41	6.279	8.730	+ **0.36**	62.7	58.8	2.09
19	De	1.3775	76.45	3.367	4.639	+ **0.29**	63.5	58.9	2.44
20	De	1.3825	77.22	4.147	5.733	+ **0.26**	61.3	57.1	2.28
Average		1.3923	78.71	15.77	22.22	+ **1.22**	62.1	59.0	1.67
				Group B					
21	De	1.3829	77.28	4.219	5.835	+ **0.25**	61.1	56.9	2.31
22	Sw	1.3821	77.14	3.929	5.431	+ **0.12**	59.1	57.0	1.14
23	Be	1.3905	78.46	5.726	7.962	− **0.04**	61.8	58.8	1.66
24	Be	1.3988	79.71	9.026	12.63	− **0.08**	61.1	57.9	1.76
25	Be	1.3955	79.21	7.306	10.20	− **0.13**	59.8	55.5	2.34
26	Be	1.3921	78.70	5.757	8.014	− **0.32**	60.4	56.3	2.19
27	Sw	1.3977	79.55	7.370	10.30	− **0.53**	62.8	60.0	1.51
28	Be	1.4029	80.33	9.903	13.89	− **0.55**	62.0	59.4	1.42
29	Ge	1.4038	80.48	9.392	13.19	− **0.89**	63.7	62.2	0.85
30	Ne	1.3994	79.80	6.283	8.793	− **1.37**	62.7	61.4	0.75
31	Ge	1.4147	82.12	14.95	21.15	− **1.45**	63.1	61.2	1.02
32	De	1.3959	79.27	5.097	7.115	− **1.48**	61.6	58.2	1.84
33	Ne	1.4029	80.33	6.909	9.692	− **1.69**	63.5	61.2	1.21
34	Ge	1.4140	82.02	12.78	18.08	− **1.79**	63.7	61.6	1.18
35	Ne	1.4048	80.63	6.989	9.818	− **2.01**	63.2	62.1	0.60
36	Ge	1.4172	82.47	12.94	18.34	− **2.29**	61.9	60.6	0.67
37	Ne	1.3933	78.87	3.583	4.992	− **2.45**	67.5	65.4	1.16
38	Ne	1.3929	78.80	3.461	4.821	− **2.53**	65.9	63.6	1.26
39	Ne	1.4083	81.15	6.134	8.639	− **3.07**	67.8	66.4	0.78
40	Ne	1.4043	80.54	4.940	6.938	− **3.13**	65.4	63.7	0.92
Average		1.3997	79.84	7.335	10.29	− **1.27**	62.9	60.5	1.33

* Be = Belgium; De = Denmark; Ge = Germany; Fr = France; Ir = Ireland; Ne = Netherlands; Sw = Sweden; Tu = Turkey.

On 100 g dry substance ash								
Inv.	Cond.	Sulfate	Total N	CaO	Alkali	pH	ε_{546}	Surface tension
				Group A				
0.36	10.70	11.13	2.447	0.461	− 0.132	6.34	15.02	57.32
1.76	10.45	10.57	2.497	0.480	− 0.211	6.00	6.34	58.40
0.34	11.14	11.23	2.640	0.253	− 0.130	6.73	11.00	56.98
1.68	10.73	10.99	2.298	1.268	− 0.450	5.57	46.53	57.98
0.69	11.31	11.39	2.714	0.871	− 0.113	6.12	7.81	57.48
0.44	11.92	12.14	2.649	0.699	− 0.118	6.42	9.29	57.15
0.12	12.24	12.37	2.489	0.180	+ 0.064	8.22	7.46	56.14
0.08	11.72	11.91	1.966	0.630	+ 0.128	8.70	12.69	61.49
0.87	12.16	12.48	2.515	1.492	− 0.211	5.93	13.74	57.15
0.43	10.85	11.00	2.163	0.132	− 0.038	7.60	10.34	60.82
0.42	11.57	11.97	2.633	0.045	− 0.131	6.70	8.86	59.07
0.39	12.63	12.61	2.549	0.322	− 0.079	7.22	3.15	56.06
0.36	12.42	12.28	2.627	0.345	− 0.093	7.42	3.38	58.23
0.19	12.69	12.65	2.077	0.580	− 0.036	7.33	12.01	57.73
0.02	12.74	12.42	1.170	1.839	+ 0.138	9.08	8.96	61.83
0.25	12.24	12.30	2.262	0.229	+ 0.048	7.55	15.26	58.65
0.04	12.56	12.55	2.303	0.206	+ 0.067	8.44	7.69	54.98
0.03	12.85	12.95	2.256	0.171	+ 0.215	9.31	7.77	55.56
0.20	14.38	14.06	2.045	0.122	− 0.013	7.72	5.78	55.56
0.32	13.79	13.79	2.279	0.197	− 0.039	7.84	8.24	57.57
0.45	12.05	12.14	2.329	0.526	− 0.057	7.31	11.07	57.81
				Group B				
0.25	13.73	13.73	2.303	0.175	+ 0.052	8.37	8.00	56.81
0.24	12.86	12.90	2.464	0.148	− 0.051	8.12	2.45	55.14
0.15	13.31	13.27	2.267	0.234	+ 0.038	8.03	5.30	58.07
0.21	13.91	13.54	2.357	0.240	− 0.051	7.87	5.59	58.15
0.38	13.65	13.57	2.464	0.270	− 0.050	7.35	9.31	58.15
0.55	13.83	13.57	2.480	0.275	− 0.090	6.75	12.05	59.24
0.00	13.04	13.14	2.004	0.075	+ 0.522	10.12	6.06	56.81
0.10	13.50	13.61	2.265	0.129	+ 0.075	8.59	3.79	59.24
0.57	13.30	13.07	2.044	0.231	− 0.109	6.70	13.94	59.24
0.67	14.15	14.05	1.993	0.409	− 0.116	6.99	9.02	58.23
0.25	13.91	13.78	2.108	0.192	− 0.048	7.74	15.34	57.98
0.22	15.51	14.73	2.070	0.055	+ 0.032	8.23	4.02	57.14
0.58	14.12	14.05	1.893	0.187	− 0.090	6.93	11.67	59.24
0.17	14.30	13.47	2.129	0.123	+ 0.072	8.20	13.86	57.98
0.51	14.46	14.12	1.927	0.212	− 0.101	6.72	7.29	56.48
0.08	14.56	14.40	2.107	0.136	+ 0.200	9.12	10.49	57.69
0.25	14.63	13.60	1.656	0.037	− 0.066	6.88	5.01	58.07
0.10	15.31	14.36	1.702	0.079	+ 0.013	8.12	3.54	59.15
0.66	15.46	13.97	1.517	0.274	+ 0.076	7.32	10.01	65.59
0.09	15.62	14.47	1.730	0.055	+ 0.118	8.87	3.65	59.49
0.30	14.16	13.77	2.074	0.177	+ 0.021	7.85	8.02	58.40

The following general relationship was established: if we have two molasses of the same viscosity at a given temperature, but of different densities, these two molasses will have approximately the same viscosity at all temperatures. In the diagram (Fig. 11/4) the starting point for comparison is the viscosity of the molasses at 40°C (abscissae). The related ordinate value of the corresponding temperature-viscosity curve gives the viscosity at the selected temperature.

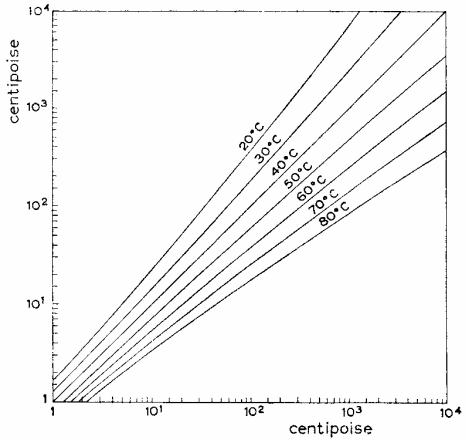


Fig. 11/4. Diagram for converting molasses viscosities at temperature T to the corresponding viscosities at other temperatures (according to BREITUNG, 'Institut für Zuckerindustrie', Berlin).

Forty molasses and forty syrups from the most varied regions of Europe were classified according to their viscosity behavior; it was found that most of the juices were less viscous than pure sugar solutions of the same density. The juices with the lowest viscosity came from the Lower Rhine region. Their viscosity was exceeded by others by more than 500% at 82 brix and 40°C (Table 42).

The purity quotient of a technical sugar solution is of minor significance with respect to its viscosity behavior. The kind and ratio of the nonsugars are decisive. High conductivity and low lime content point to low viscosity. Invert sugars etc. normally occur in such slight amounts in beet molasses that their influence on viscosity is hardly measurable.

Molasses behave in every respect similarly to the syrups from which they originated. The viscosity of syrups tends to increase during the course of the season, and is independent of the purity quotients.

Technical sugar solutions show a smaller decrease of viscosity with rising temperature than pure sugar solutions. A diagram has been worked out which makes it possible to read the viscosity of the molasses at various temperatures.

The viscosity is not notably affected by the pH below 7.0. In the alkaline region the viscosity increases in an approximately logarithmic fashion. This rise becomes noticeable only at pH values above 11, which occur only in thin juices.

Calcium-, sodium- and potassium-molasses are obtained by cation exchange. Normal molasses lie between the corresponding sodium- and potassium-molasses with respect to viscosity behavior. An enrichment with Ca^{2+} ions raises the viscosity, while a K^+ exchange lowers it. In an exchange of Ca^{2+} for Na^+ the viscosity is lowered. However, if the K^+ content of the syrup is displaced by Na^+ the viscosity rises. The conductivity falls when the viscosity is raised by ion exchange and *vice versa.*

All studies along these lines prove that the quantity and composition of the electrolytes are of the highest importance with regard to the viscosity behavior of technical sugar solutions. A less significant role is played by the non-electrolytes. The viscosity is one of the reasons why the theoretically possible desugaring of molasses is not achieved technologically in sugar factories. On the other hand, the viscosity is not responsible for the formation of molasses.

The effect of concentration and temperature on the molasses viscosity is of significance in the practical manufacture with respect to the amount of molasses flowing through pipes or pumps, as well as to the discharge under natural differences of gravity and centrifugal forces. Since the viscosity of the molasses falls at a given temperature with decreasing concentration and at constant concentration with rising temperature, the question arises, taking into consideration the pumps available, whether in a given case the throughput should be improved by warming and/or by dilution of the commercial molasses. The kind of pumps used will affect the decision as to what viscosity will provide the upper limit of the throughput, *i.e.* at which viscosity the full output of the pumps will be reached.

Using a small geared pump (conveying capacity 8 litres/min at 360 rev/min) the volume moved was measured in the case of a molasses having 77 brix in relation to the molasses concentration (Fig. 11/ 5) and also the volume put through in relation to the temperature of the molasses (Fig. 11/6)[39].
In Fig. 11 /5 the amount of molasses displaced is shown in relation to the dry substance of the molasses and also in relation to the mixture ratio water: molasses.

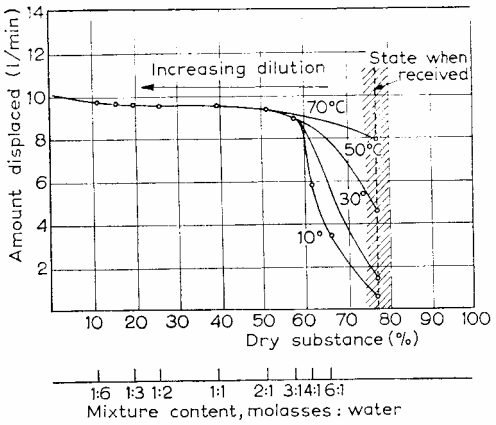


Fig. 11/5. Quantity of beet molasses displaced in relation to the molasses concentration.

The mixture ratio refers to the volume of water and molasses, *i.e.* in a mixture ratio of 3 **:** 1 there is 1 litre of water to each 3 litres of molasses. The course of the curve shows that the volume of original molasses transported at 10°C is only 0.65 litre/min and that with decreasing solid content to 58 brix it rises sharply to 9 litres/min. The volume pumped per unit time is only slightly affected by any further dilution.

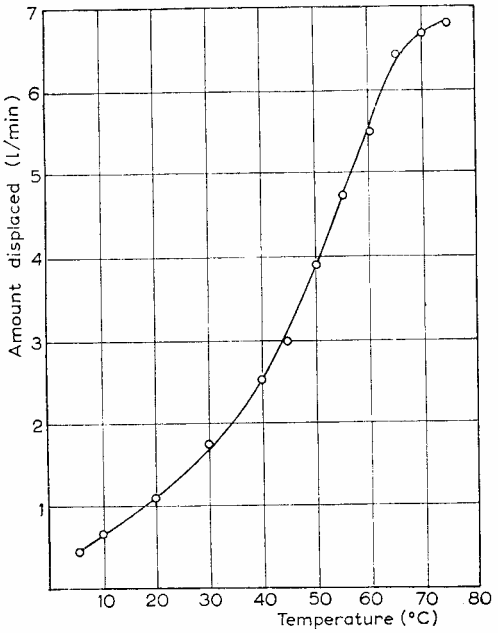


Fig. 11/6. Quantity of beet molasses of 77 brix concentration displaced in relation to the temperature.

Warming the molasses can also increase the volume pumped; it is remarkable that if the original molasses is heated to 70°C it has the same fluidity as molasses diluted to 60 brix. The amounts transported under the above conditions in relation to the dependence on the temperature of the molasses are shown in Fig. 11/6.

The volume moved increases parabolically from 6 to 63°C; the curve gradually flattens at higher temperatures. It has been found that the viscosity of molasses can be lowered by dilution at constant temperature or by heating at the concentration at which it is delivered, and by a proper combination of these two procedures. With molasses of which the concentrations are below 58 brix, the temperature has little effect which regard to practical pumping accomplishments.
It is recommended to use warm water for diluting purposes because molasses mixes more readily with warm water. This is particularly to be recommended in all cases in which subsequent clarification or sterilizing steps are planned. Infra-red sources, which can be brought up easily have been proposed for unloading molasses from tank cars; they may have distinct advantages over other methods of heating, especially if inexpensive night current is available for use in winter[45].

(ii) Specific heat of molasses

A knowledge of the specific heat of molasses is needed for calculating the heat transfer in heating and cooling. The specific heat (*c*) or the heat capacity of a substance gives the number of heat units or calories required to raise the temperature of 1kg from 14.5 to 15.5°C at atmospheric pressure. Under these conditions the heat capacity of water is taken as unity ($c = 1$). The specific heat of a substance is not a constant value, but is dependent on the absolute temperature. Consequently, the specific heat of almost all solid and liquid substances differs according to the prevailing temperature.

TABLE 43

SPECIFIC HEAT OF MOLASSES AND OTHER SUBSTANCES[4]

Substance	Specific heat In (cal/kg/°C)
Ethyl alcohol at 0°; 25°; 50°; 100°; 150°C	0.535; 0.580; 0.652; 0.824; 1.053
Raw sugar, crystal sugar at 20–40, 60 and 80°C	0.3; 0.33; 0.35
Sugar, dry and molasses cosettes	0.35
Massecuites	0.45–0.5
Molasses	0.5
Fresh cosettes and press cosettes	0.85–0.9
Sugar juices (thin juice)	0.93
Diffusion slices (not pressed), wet slices	1.00

In technical computations which extend over a certain temperature range, the mean value of the specific heats at the initial and the final temperatures, the so-called mean specific heat (c_m) is used. As may be seen from Table 43, the specific heat of molasses is usually given as 0.5[4].
In sugar solutions the specific heat is dependent on the temperature, the concentration and the composition (purity). At the turn of the centum it was found that the specific heat decreases with increasing concentration in impure sugar solutions[46]. This is apparent from Table 44.

TABLE 44

DECREASE OF SPECIFIC HEAT WITH RISING CONCENTRATION IN SYRUPS AND MOLASSES[44]

Syrup		Molasses	
Brix	Spec. heat *(c)*	Brix	Spec. heat *(c)*
0	1.00	0	1.00
16.8	0.88	10.0	0.94
38.8	0.74	22.1	0.85
52.8	0.65	30.6	0.80
56.8	0.63	39.7	0.73
64.0	0.58	50.2	0.67
68.0	0.55	60.8	0.60
77.0	0.49	60.4	0.54

TABLE 45

EXPERIMENTAL VALUES FOR THE SPECIFIC HEATS OF IMPURE SUGAR SOLUTIONS[4, 47]

No.	Brix	Q	Specific heat at °C		
			20.6	51.1	81.1
a	b	c	d	e	f
1	15.0	94.3	0.9115	0.9241	0.9390
2	15.0	79.6	0.9081	0.9172	0.9304
3	15.0	62.8	0.9027	—	0.9278
4	15.0	59.6	0.9025	—	0.9274
5	15.0	51.8	0.9071	—	0.9311
6	40.0	94.3	0.7699	0.7992	0.8225
7	40.0	79.6	0.7635	0.7879	0.8112
8	40.0	62.8	0.7562	0.7808	0.8009
9	40.0	59.6	—	—	0.7984
10	40.0	51.8	0.7610	0.7901	0.8122
11	65.0	94.3	0.6258	0.6658	0.6967
12	65.0	79.6	0.6222	0.6557	0.6842
13	75.5	83.2	—	0.6054	0.6391
14	76.7	59.6	—	—	0.6118
15	76.8	51.8	—	—	0.6270
16	81.8	62.8	—	—	0.5894

The specific heat increases with rising temperature, and at the same concentration and purity is linear with respect to the temperature. An important fact is that at the same temperature the heat capacity of molasses is lower than that of pure sugar solutions. The lower the purity quotient the lower the specific heat of the molasses, *i.e.* at constant concentration and temperature the specific heat falls with decreasing purity.

The data in Table 45 were selected from extensive experimental investigations[47]; they show the changes in the specific heat in relation to temperature, concentration and purity.

The following equation gives for practical purposes the relation between the heat capacities, concentration, temperature and purity[47]:

$$c = 1 - (0.6 - 0.0018\,t + 0.0011\,[100 - R]) \times \frac{Bx}{100}$$

where

c = specific heat (heat capacity) in cal/kg
t = temperature in °C (*cf.* columns d, e, f)
Bx = % dry substance of the solution (column b)
R = purity (purity quotient O) of the solution (column c).

According to this empirical formula the specific heat of a molasses with a purity of 62.8% diluted to 40 brix and heated to 51.1°C (*cf.* Table 45, No. 8, column e) is:

$$c = 1 - (0.6 - 0.0018 \times 51.1 - 0.0011\,[100 - 62.8]) \times \frac{40}{100}$$
$$c = 1 - 0.54894 \times 0.4 = 0.7804$$

The practical importance of an exact knowledge of the specific heat of the molasses is demonstrated in the manufacture of yeast (see Table 67).

(iii) ***Contraction of molasses***

Viscosity and specific heat of molasses do not exhaust the practical interest in the degree of dilution. The dilution of molasses is accompanied by a decrease in volume. The property of solid or liquid substances (for instance, sugar, alcohol, etc.) to decrease in volume when dissolved in, or diluted with, water is well known; it is called contraction. The specific gravity of a concentrated solution does not change linearly with the degree of dilution; the specific gravities deviate more or less from a straight line according to the degree of increasing or decreasing contraction (solids per unit of volume). The contraction of impure sugar solutions is greater than of pure sucrose solutions. This is one of the reasons why the actual content of dry solids cannot be learned precisely by determining the specific gravity.

The contraction can be measured from the volumes of the molasses and water which are the two components in the dilution process (Table 46); it is the difference between the weights per litre which can be obtained from conversion tables (see Table 96) and from the given brix related to the specific gravity.

TABLE 46

CONTRACTION IN DILUTION OF MOLASSES[4]

Property	80 brix	40 brix	20 brix
(a) Weight of 1 liter in kg (from spec. grav. from Table 96)	1.416	1.179	1.083
(b) Hence 1 kg in liters	0.7062	0.8481	0.9233
(c) 1 kg molasses of 80 brix		0.7062 l	0.7062 l
(d) x kg water		1.0000 l	3.0000 l
(e) x kg solution (c + d)		1.7062 l	3.7062 l
(f) 1 kg solution (without contraction)		0.8530 l	0.9266 l
(g) 1 kg solution (as in b, *cf.* Table 96)		0.8481 l	0.9233 l
(h) Contraction (f — g)		4.9 ml	3.3 ml

A molasses with 80 brix at 20°C has by definition the same specific gravity or the same density as a pure 80% sugar solution at 20°C. The contraction which occurs on diluting the molasses in a ratio of 1 : 1 deviates considerably from the contraction observed with a pure sugar solution of the same specific gravity because the nonsugars of the molasses affect the decrease in volume in a different way. The ordinary brix tables and brix hydrometers refer to pure sugar solutions.

TABLE 47

CONTRACTION ON DILUTION OF BEET MOLASSES* AT 20°C REFERRED TO 1 KG OF THE MOLASSES DILUTED 1 : 1 (column c) DETERMINED BY PYKNOMETER MEASUREMENTS AT 20° C OF THE UNDILUTED MOLASSES (column a) AND OF THE MOLASSES DILUTED 1 : 1 (column b) COMPARED WITH THE CONTRACTION OF PURE SACCHAROSE SOLUTIONS OF THE SAME DENSITY ON DILUTION 1 : 1 (column d)

Brix of the molasses		Contraction (ml)		
		Molasses	Pure sugar solutions	Difference (c — d)
a	b	c	d	e
80.7	82.4	8.2	5.2	3.0
74.9	76.2	6.6	4.2	2.4
79.3	80.4	7.0	5.0	2.0
79.15	80.2	6.9	5.0	1.9
78.55	80.1	7.7	4.8	2.9
77.2	78.4	6.8	4.6	2.2
76.3	77.5	6.7	4.8	1.9

* According to PAAR[50].

Since the contraction of molasses is greater than that of a sugar solution of the corresponding density, no accurate values are obtained in the determination of the dry substance content of the molasses by the dilution method. No strict rules can be given regarding the difference between the contraction of molasses and that of pure sugar solutions. The observed contraction differences (Table 47, column e) are irregular and vary with the density, specific gravity, the purity of the molasses and the composition of the nonsugars[49, 50].

The temperature correction for the specific gravity behaves in a similar fashion. If the density is not determined at the calibration temperature, (for instance at 20°C) the temperature correction applies, strictly speaking, only to pure sugar solutions and not to molasses, whose coefficient of expansion likewise will differ from that of a pure sugar solution.

(iv) *Coefficient of expansion of molasses*

The coefficient of expansion is a specific property of all materials. Liquids have a cubical coefficient of expansion, which gives the relative change in volume per degree of temperature rise (Table 48).

The *apparent* thermal expansion of a liquid is observed in practice since the container is also subjected to a volume change. The *real* coefficient of expansion is obtained by subtracting the increase in volume of the container; the calculation of this correction is hardly of significance in practical work dealing with molasses. The change of volume related to the heating or cooling differs for most liquids at various temperature intervals. Some coefficients of expansion *(a)* at 18°C are given in Table 48. Exact data for molasses are still unavailable.

TABLE 48

COEFFICIENTS OF EXPANSION OF SEVERAL SUBSTANCES[4, 137]

Substance	α	$10^5\ \alpha$
Ethyl alcohol	0.00110	110
Methyl alcohol	0.00119	119
Propyl alcohol	0.00098	98
Iso-propyl alcohol	0.00106	106
Amyl alcohol	0.00088	88
Iso-amyl alcohol	0.00093	93
Glycerine	0.00050	50
Water	0.00018	18
43.2% saccharose solution	0.0002247	22.47
Molasses	0.00043	43

Table 49 shows the thermal volume change of pure saccharose solutions in comparison with the accepted standard values for water.

TABLE 49

THE TEMPERATURE-DEPENDENT CHANGE IN VOLUME OF PURE AQUEOUS SOLUTIONS OF SACCHAROSE OF VARIOUS CONCENTRATIONS

(Compare HIRSCHMÜLLER, *Principles of Sugar Technology*, Vol. I, p. 30)

Volume at 20°C = 1.0000

	Change in volume (%) at concentrations of (brix)								
°C	0	10	20	30	40	50	60	70	75
20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.26	0.27	0.30	0.33	0.36	0.38	0.40	0.40	0.38
40	0.60	0.63	0.68	0.72	0.76	0.79	0.81	0.82	0.78
50	1.02	1.06	1.12	1.17	1.20	1.23	1.25	1.25	1.21
60	1.52	1.58	1.63	1.67	1.69	1.71	1.71	1.71	1.66
70	2.09	2.15	2.18	2.23	2.27	2.25	2.15	2.15	2.14
80	2.74	2.75	2.79	2.81	2.83	2.80	2.68	2.68	2.63
90	3.42	3.44	3.47	3.45	3.43	3.40	3.22	3.22	3.16
100	4.11	4.18	4.17	4.13	4.09	4.03	3.80	3.80	3.70

No useful data are given in the literature concerning the temperaturevolume relations for impure sugar solutions and molasses. It is appropriate to apply to molasses the values obtained for solutions of saccharose[51]. If 1000 hectolitres are cooled from 70 to 20°C the decrease in volume, on the basis of the thermal coefficients, is 2090 litres für water and 2270 litres for 40% sugar or molasses solutions. When hot molasses are handled, it is worthwhile to take account of the coefficients of expansion to calculate the amount of solids.

(v) Elevation of the boiling point of molasses

It was pointed out that the behavior of molasses often differs substantially from that of pure sugar solutions of corresponding concentrations. This is due to the composition of molasses and especially to its content of nonsugars. Compared with pure sugar solutions, molasses not only shows a greater contraction on dilution and a lower specific heat, but also a greater elevation of boiling point. This subject will be discussed here briefly since this characteristic is of little practical interest with respect to molasses.

The changes in the boiling point observed when molasses is heated to the boiling point for purposes of sterilization or inversion are given in Table 50, in dependence on dry substance content and purity, compared with the boiling point of pure water.
The boiling points of cane- and beet-molasses of varying concentration are practically the same; they are always higher than those of corresponding pure saccharose solutions. The difference amounts to 3-5°C at concentrations between 75 and 85 brix, and 1-2°C in the region of the clarification concentrations (40-60 brix[52, 53]).

TABLE 50

BOILING POINT ELEVATION OF SUGAR SOLUTIONS OF VARIOUS PURITIES (*Q*)

Elevation in °C

Brix	Pure saccharose solution ($Q = 100$)	Beet molasses ($Q = 62$)	Cane molasses ($Q = 60$)
5	0.05	0.05	0.05
10	0.1	0.2	0.15
15	0.2	0.35	0.25
20	0.3	0.5	0.45
25	0.45	0.75	0.70
30	0.6	1.1	0.95
35	0.8	1.5	1.30
40	1.05	1.95	1.70
45	1.4	2.5	2.20
50	1.8	3.15	2.80
55	2.3	4.0	3.50
60	3.0	5.0	4.45
65	3.8	6.2	5.50
70	5.1	8.0	7.10
75	7.0	10.3	9.40
80	9.4	13.6	12.30
85	13.0	18.2	16.40
90	19.6	26.9	23.70

(vi) ***Shifts in pH in molasses with temperature changes***

The pH of molasses changes substantially with temperature. In the case of water it is known that the change in pH (see Table 51) is due to the change of the dissociation constant with the temperature. The ion product (H^+) x (OH^-) has different values at different temperatures. The neutral point which is characterized by pH = pOH depends on the temperature. Pure water is neutral at 22°C where the pH (= pOH) is 7, but as the temperature rises the neutral point falls so that at 100°C the neutral pH
6.16 and at 200°C the neutral pH = 5.7 (Table 51).
With increase in temperature the ion concentration increases by a multiple but the relative ionic activity, which may depend on a shifting of the initial equilibrium, *i.e.* a change in the original ratio of the (H^+) and (OH^-) ions, does not necessarily change. With respect to the temperature-dependent change of pH it is necessary to distinguish two processes:

A) a quantitative similar change of the (H+) and the (OH^-) concentration ions as in pure water, which results in no titratable change;
B) a pH shift due to a unilateral excess of (H^-) ions as compared with (OH^-) ions, or *vice versa.* This shows itself in a change which can be measured by titration.

TABLE 51

CHANGE OF pH IN RELATION TO THE TEMPERATURE[4, 54]

Temp. (°C)	Water			pH of refinery molasses	pH of raw molasses
	K_{H_2O}	P_{H_2O} = $-\log K_{H_2O}$	pH = pOH		
18	$0.73 \cdot 10^{-14}$	14.14	7.07	—	—
20	$0.85 \cdot 10^{-14}$	14.07	7.035	8.65	8.60
22	$1.00 \cdot 10^{-14}$	14.00	7.00	—	—
30	$1.90 \cdot 10^{-14}$	13.72	6.68	8.43	8.38
40	$3.80 \cdot 10^{-14}$	13.42	6.71	8.24	8.17
50	$5.66 \cdot 10^{-14}$	13.25	6.625	8.05	7.96
60	$12.60 \cdot 10^{-14}$	12.92	6.46	7.86	7.77
70	$21.25 \cdot 10^{-14}$	12.68	6.34	7.72	7.60
80		~ 12.5	~ 6.25	7.56	7.43
100	$48.00 \cdot 10^{-14}$	12.32	6.16	—	—
200		~ 11.4	~ 5.7	—	—
	pH change from 20–80 °C			— 1.09	— 1.17
	Temp. coefficient per 10 °C (mean)			— 0.181	— 0.195
	After cooling to 20 °C			8.69	—

The first case applies to the change of pH with temperature as observed with water. Processes a and b hold simultaneously for impure sugar solutions such as molasses.
The effect of the temperature on the pH is affected by the nature and amount of the buffering material; without knowledge of it and if it is not given due consideration, it is impossible to make any predictions in an individual case as to the extent to which the pH of a molasses will change with rising temperature. It is shown in Table 51 that the initial pH value is not reached precisely by re-cooling a molasses that had been heated previously to 80°C; the resulting pH at 20°C is often 0.1 pH unit lower than the original value. It may be due to the elimination of CO_2 on heating.

3. High Test Molasses

High test molasses, which is also called cane high test molasses, invert molasses and cane invert syrup, has been manufactured in Cuba and Puerto Rico since 1931 by evaporation of the partly inverted cane juice. Strictly speaking, high test molasses is not a molasses but an inverted syrup. When the demand für molasses sugar exceeds the normal molasses supply, considerable amounts of inverted syrup, *i.e.* high test molasses, are produced, for instance, 1.75 million tons (331 million gallons) in 1941 in Cuba, with a production of 0.9 million tons (175 million gallons) of blackstrap molasses, *i.e.*, final molasses. As a result of the import restrictions of 1954, the production of high test molasses was resumed in Cuba in 1954 and 1955. In 1954 about 679,400 tons and in 1955 1.2 million tons of high test molasses were produced, of which in 1954 414,000 tons were exported to the U.S.A., and in 1955 777,000 tons to the U.S.A. and 380,000 tons to Great-Britain. The production of molasses in Cuba in 1954 was about 1.1 million tons, and in 1955, 1.03 million tons.
The composition of high test molasses, as can be seen from Table 52, differs markedly from that of the traditional molasses; these differences must be taken into account. Because of their high sugar content, high test molasses are used in the U.S.A. mainly for the production of alcohol. In Europe high test molasses has been used only in England (Distillers Company Ltd.) for the manufacture of industrial alcohol.

TABLE 52

COMPOSITION OF HIGH TEST MOLASSES

Major constituents (%)			Minor constituents (γ/100 g)		
Constituents	Acc. to UNDERKOFLER and HICKEY[55]	Acc. to WHITE[37]	Constituents	Acc. to ROGERS and MICKELSON[38]	Acc. to WHITE[37]
Water	14–19	8–14	Vitamin B_1	160	—
Dry substance	81–86	86–92	Vitamin B_2	62	—
Total sugar as invert sugar	72–79	70–86	Vitamin B_6	160	—
Total N	0.07–0.20	0.05–0.25	pp-Factor	240	—
Carbon	—	28–36	Pantothenic acid	270	250
Total ash	2–3	1.8–3.6	Folic acid	1.5	—
P_2O_5	0.2–0.6	0.03–0.22	Biotin	32	30–40
CaO	0.03–0.30	0.15–0.35	Inositol	—	85–100
MgO	0.01–0.03	0.12–0.25			
K_2O	0.7–1.4	0.2–0.7			
SiO_2	—	0.07–0.25			
Al_2O_3	—	0.002–0.01			
Fe_2O_3	—	0.001–0.005			

The low ash content of high test molasses is of particular interest; it resembles beet molasses in its low P_2O_5 content; the K_2O, MgO, CaO and nitrogen contents are only a fraction of these in beet and cane molasses. The specific gravity of high test molasses is given as 1.43; the pH value is around 6.0. With regard to its content of growth materials, a notable feature is the low inositol content of high test molasses, which is below the amount required for a maximum yield of yeast. When high test molasses is manufactured, not only the total sugar production from cane is disregarded, but, in fact, inversion is purposely initiated by addition of inorganic acids (sulfuric or hydro-chloric) and since 1941 by addition of invertase-rich yeasts to avoid corrosion. Partial inversion is necessary to prevent crystallization of saccharose while the concentrated molasses is stored and shipped[55].

The biological partial inversion of high test molasses is connected which the formation of notable amounts of invertase-synthesized oligosaccharides (five components). These include chiefly kestone (component III in the nomenclature of BACON and EDELMAN) which consists of fructose (2 molecules) and glucose (1 molecule), and is fermentable. The component II of the oligosaccharide is a trisaccharide also derived from fructose and glucose. The compositions of components IV and V, present in very small quantities, are not yet known. The total sugars, calculated as glucose after acid hydrolysis, show approximately the following composition[57]:

ketose, components I, II, IV, 15-19%
saccharose and component V, 28-31%
glucose and fructose, 53-54%

The production of high test molasses in Puerto Rico[103] does not differ from the ordinary manufacture of sugar up to the evaporation. As soon as the concentration of the clarified juices reaches 64 brix, about half of the saccharose present is inverted by heating to 83-96°C for around 90 minutes with hydrochloric acid. Then the pH is brought to 7.0-7.1 with technical sodium hydroxide, the boiling continued to the desired concentration of about 76 brix, and the vacuum apparatus discharged at about 71°C. Without special cooling arrangements the high test molasses leaves the factory and reaches the storage tanks at a temperature of 63-65°C. The stored high test molasses offered no problems during 6 months in storage before the last portions were shipped and did not suffer appreciable change in composition. In contrast, cane molasses are extremely sensitive when stored under similar conditions, especially at high concentrations and there is danger of a spontaneous decomposition, resulting in total destruction of the molasses (compare Tables 112 and 114). However according to LOPEZFERRER[113], the total sugar content of a high test molasses, when stored at 60°C, fell from 78.2% to 74.34% in 23 days (3.78%, loss of total sugar) and suffered an additional loss of 0.52%, *i.e.* the content fell to 73.82% in the next 6 weeks.

4. Composition of Molasses from Various Countries

Except for refinery cane molasses derived from imported raw cane sugar, Spain is the only European country that has interest in the regular use of cane molasses from its own production; the cane sugar region in Southern Spain is the only remaining European source of cane molasses. Countries producing both cane and beet molasses include the United States, China and Japan. The world areas in which sugar cane and sugar beets are grown reflect the climatic conditions involved in this branch of agriculture.
The raising of sugar cane presupposes a tropical climate with high temperatures and good rainfall or sufficient irrigation.
Sugar beets grow best on humus-rich and sandy soils which are deep and fertile; light, sandy and marshy soils are unsuitable. During the summer the beet crop needs much rain, but dry sunny weather is necessary while the beets are maturing and forming sugar.
The two-year statistical studies made at the Institut für Zuckerindustrie in Berlin provide much information about the Composition and the physical and chemical properties of European beet molasses[58]. Table 53 gives average values taken from these representative investigations.
The special importance of these extensive studies resides in the possibility of using them in the comparison of European molasses since, as a result of the uniform analytical methods used; the data are not vitiated by the methodical deviations present in so many data given in the literature.
The following methods are employed:

- ***Dry residue:*** actual dry substance in 100g of sample; determined by drying at 70°C *in vacuo* after mixing with sand.
- ***Refractometer* solids:** dry substance determined with Zeiss Refractometer.
- ***Refractometer* 1:1:** dry substance determined refractometrically after dilution with an equal weight of water and multiplication by 2.
- ***Pyknometer:*** dry substance by means of DOMKE tables applied to the immersion ratio 20/20°C in air.
- ***Pyknometer* 1:1:** dry substance after dilution with an equal weight of water and multiplication by 2 (DOMKE table).
- ***Polarization:*** per 100 g true dry substance; international sugar scale (sugar degrees = °S); clarification with liquid basic lead acetate.
- ***Saccharose:*** by the CLERGET formula per 100g true dry substance; polarization as above and polarization after inversion at 20°C.
- ***Raffinose:*** by the raffinose formula per 100 g true dry substance; raffinose = 0.5405° (polarization minus saccharose).
- ***Invert sugar:*** per 100 g true dry substance; determined with MÜLLER solution; titration according to SPENGLER, TÖDT and SCHEUER.
- ***Ash, conductometric:*** per 100 g true dry substance; conductivity measurement after dilution of 5 g syrup to 100 ml, or 0.5 g molasses + 4.5 g raffinade to 100 ml; conductometer according to TÖDT-GOLLNOW.
- ***Ash, sulfated:*** sulfated ash – 1/10 per 100g true dry substance; ashing at 750°C.
- ***Total nitrogen:*** per 100 g true dry substance by KJELDAHL method; digestion with phosphoric-sulfuric acid in the presence of mercury and copper sulfate.
- ***Lime (CaO) :*** titration with soap solution by PELLET method; lime content per 100 g true dry substance.
- ***Alkalinity (% CaO):*** titration alkalinity in g CaO per 100 g dry substance; titration with *N*/280 H_2SO_2 or with *N*/280 NaOH; if acidic, the values in the table are designated by - (minus).
- ***pH :*** determined with glass electrode after dilution 1 : 1.
- ***Extinction coefficient :*** at 436 mμ, 546 mμ and 579 mμ, using HIRSCHMÜLLER-BECHSTEIN spectrophotometer and mercury light; measurement of 1 g molasses diluted to 100 ml and adjusted to pH 7 after filtration (ε is calculated per 1cm layer thickness and 1 g dry substance per 1ml).
- ***Surface tension:*** in dynes/cm^2; measurement with stalagmometer in solution of 30 brix.
- ***Viscosity:*** in centipoises at 20°C at a dilution of 50 brix.

TABLE 53
COMPOSITION AND CHARACTERISTICS OF EUROPEAN BEET MOLASSES
(Average values from studies of the Institut für Zuckerindustrie, Berlin[4,58])

Composition and characteristics	Sweden		Denmark		Ireland		Netherlands		Belgium	
	a	b	a	b	a	b	a	b	a	b
Per 100 *substance*:										
Dry solids	75.91	77.00	76.57	77.18	84.61	80.31	81.94	77.99	83.03	81.78
Refractometer	76.2	—	77.0	—	83.2	—	80.9	—	81.7	—
Refractometer 1 : 1	—	78.7	—	78.1	—	82.6	—	79.8	—	83.3
Pyknometer	—	76.4	—	77.6	—	77.0	—	78.8	—	80.5
Pyknometer 1 : 1	76.7	77.8	78.5	79.0	85.6	81.8	85.1	81.9	84.7	83.8
pH	7.01	7.93	7.09	8.41	6.21	5.97	7.87	7.34	7.20	8.06
Per 100 *g dry substance*:										
Polarization	63.5	61.9	62.8	61.9	61.0	61.8	65.8	65.5	63.7	61.7
Saccharose	58.9	59.3	57.9	58.0	59.5	60.9	62.6	63.9	59.2	58.9
Raffinose	2.48	1.38	2.69	2.11	0.80	0.59	1.76	0.86	2.43	1.44
Invert sugar	0.23	0.19	0.43	0.20	0.86	1.23	0.27	0.54	0.20	0.25
Ash, conductometric	11.36	12.16	12.97	14.41	10.82	11.25	13.58	14.98	13.30	13.89
Ash, sulfated	12.24	12.20	13.07	14.16	11.21	11.36	13.55	14.08	13.42	13.65
Total nitrogen	2.424	2.442	2.415	2.171	2.585	2.384	1.983	1.682	2.340	2.309
Lime (CaO)	0.335	0.310	0.155	0.116	1.029	0.753	0.135	0.223	0.138	0.155
Alkalinity (% CaO)	0.007	0.017	–0.005	0.024	–0.024	–0.013	0.006	0.011	0.011	0.018
Extinction coefficient:										
436 mμ	37.86	29.81	42.28	26.47	61.33	44.68	24.53	36.21	40.43	32.02
546 mμ	10.00	7.66	10.22	5.94	14.56	12.41	5.93	7.62	11.23	8.12
579 mμ	6.88	4.99	7.59	4.13	9.92	6.47	4.42	5.20	8.11	5.45
Surface tension	—	57.52	—	56.77	—	58.78	—	60.22	—	58.22
Viscosity	—	14.05	—	14.30	—	14.00	—	13.85	—	13.38

a refers to 1952/53 and b refers to 1953/54.

Germany		France		Switzerland	Azores	Spain		Turkey	Values from all samples		
a	b	a	b	a	a	a	b	b	Min.	Average	Max.
84.11	83.13	83.25	85.44	84.90	79.14	81.09	80.65	78.65	72.15	80.9	88.34
82.8	—	82.4	—	82.3	78.4	80.8	—	—	72.4	80.8	86.0
—	84.9	—	88.5	—	—	—	82.6	79.3	76.4	81.9	90.8
—	82.9	—	—	—	—	—	79.7	78.4	74.3	78.6	83.6
86.4	85.1	84.5	86.1	88.1	84.5	82.8	83.0	79.9	73.2	82.8	91.9
7.29	7.51	6.18	6.26	7.02	7.16	7.24	7.42	8.35	5.51	7.28	10.12
64.3	63.5	62.8	60.0	65.3	65.4	61.0	60.5	63.6	55.7	62.9	69.0
61.1	61.2	60.3	58.5	62.4	64.1	59.0	58.9	58.7	55.2	60.0	67.1
1.73	1.25	1.31	0.83	1.55	0.72	1.12	0.88	2.65	0.00	1.55	4.20
0.42	0.37	0.89	0.62	0.36	0.15	0.25	0.23	0.19	0.00	0.41	3.41
12.36	13.04	11.36	11.57	13.45	19.46	13.63	14.67	12.04	9.83	12.86	19.46
12.52	12.85	11.28	11.69	13.24	17.06	13.55	14.13	12.13	9.75	12.86	17.06
2.354	2.173	2.666	2.708	2.185	1.631	2.392	2.404	2.020	1.170	2.308	2.946
0.401	0.271	0.382	0.568	0.033	0.253	0.524	0.891	0.776	0.027	0.398	1.839
0.011	0.029	–0.025	0.004	0.004	0.009	0.003	0.035	0.040	–0.487	–0.033	0.522
51.85	48.47	61.23	38.12	23.24	48.81	43.81	28.45	37.43	7.98	39.86	92.40
15.08	13.26	14.42	9.31	5.13	14.74	12.17	8.06	10.95	1.54	10.33	46.53
10.43	9.03	10.20	5.79	3.73	9.21	8.07	5.59	7.37	1.00	6.98	12.19
—	58.09	—	57.22	—	—	—	60.82	60.34	54.98	58.81	65.59
—	14.23	—	13.75	—	—	—	13.52	14.84	12.75	13.91	18.12

When the molasses of the different factories were compared with the corresponding thick juices (syrups), it was found that on calculation to 100 nonsugars, the nitrogen content in syrups and molasses agree very closely. As the result of addition of solo ash or other chemicals in processing, there was a slight increase of ash % nonsugars; this was also caused by the loss of organic nonsugars. The color % nonsugars of the molasses is more than 5 times the color of the corresponding thick juices.
For comparison, total sugar is given as glucose in the analyses of the various types of American molasses (Table 54). American beet molasses show no significant differences from European beet molasses (compare Tables 2-4 and 54).

TABLE 54

ANALYSES OF AMERICAN MOLASSES AND MOLASSES LIKE RAW MATERIALS[4, 55]

Analysis (%)	Cane Molasses						Hydrol		
	Normal cane molasses, cane blackstrap molasses (sugarhouse, blackstrap m., refiners blackstrap m.)			High-test molasses, cane high-test molasses, invert molasses, cane invert syrup			Maize molasses, corn-hydrol, corn molasses		
	Min.	Mean	Max.	Min.	Mean	Max.	Min.	Mean	Max.
Specific gravity	1.39	1.42	1.44	1.42	1.43	1.45	—	—	—
pH (dilution 2 : 1)	4.5	5.5	6.0	—	6.0	—	4.0	4.3	4.5
Water	16	19	23	14	17	19	26.4	26.9	27.4
Dry substance	77	81	84	81	83	86	72.6	73.1	73.6
Inverted total sugar as glucose	52	56	65	72	75	79	52	54.1	55
Total N	0.4	0.7	1.5	0.07	0.10	0.20	0.05	0.06	0.07
Ash	7	9	11	2	2.25	3	6.2	6.6	7.2
P_2O_5	0.6	0.9	2.0	0.2	0.3	0.6			
CaO	0.1	0.5	1.1	0.03	0.10	0.30			
MgO	0.03	0.07	0.10	0.01	0.02	0.03			
K_2O	2.6	3.6	5.0	0.7	0.9	1.4			

A molasses-like material, entirely foreign to Europe, is produced in the U.S.A. under the name 'Hydrol'; it is also called corn molasses or corn hydrol. It is the residue resulting from the manufacture of dextrose from corn starch. In addition to glucose, it contains salts and reversion products of hydrosates of corn starch. It is of little value for yeast production; it is entirely lacking in growth substances and has a high NaCl content (around 5-6%).
Cane molasses differ considerably in composition from beet molasses; the quality of the cane and the manufacturing processes applied are significant for the composition. The composition of Brazilian cane molasses given in Table 55 were reported by JAYME ROCHA DE ALMEIDA[4, 59].

TABLE 55

COMPOSITION OF BRAZILIAN CANE MOLASSES[4, 59]

Constituent (%)	Max.	Min.	Mean
Brix	91.60	79.35	83.20
°Bé	48.70	44.70	42.80
Specific gravity	1.49628	1.41165	1.43750
Polarization	41.85	10.68	28.12
Saccharose	46.90	15.70	32.25
Reducing sugar	39.90	9.66	20.98
Total sugar	58.70	47.70	52.20
Apparent purity	53.90	30.00	42.45
Glucose coefficient	41.80	33.60	37.70
Sulfuric acid	1.20	0.175	0.3
Acetic acid	0.081	0.015	0.05
Nitrogen substance	12.00	2.80	8.20
Ash	9.40	4.58	8.20
Water	26.70	16.40	19.05
Dry substance	87.48	73.50	80.55
The following are the main constituents of the ash of Brazilian cane molasses:			
Potash (K_2O)	7.00	3.00	5.00
Silica (SiO_2)	1.55	0.60	0.80
Calcium (CaO)	1.50	0.30	0.90
Magnesium (MgO)	0.70	0.10	0.40
Phosphorus (P_2O_5)	0.50	0.10	0.30
Sodium (Na_2O)	0.50	0.15	0.25

With reference to Table 54, attention is directed to a communication from Brazil reporting that cane molasses in that country can have a total sugar content as low as 46 to 49% molasses with 57%, total sugar are occasionally 'sugared up' with raw sugar before being shipped.
A yeast factory in North Africa once received a shipment of a commercial variety of molasses known as 'dry molasses'. This material was a highly concentrated cane molasses which solidified on cooling. Its water content was 8.2% and its composition was that of ordinary cane molasses. With respect to its use in the manufacture of yeast, it was found that its assimilation value was very low, although the total nitrogen content was 0.32% The dissolved dry material revealed a high degree of infection.

5. Utilization of Molasses

(a) General Survey

The utilization of molasses has always been a pressing desire of the sugar factories. The following discussion will present a survey of the known fundamental possibilities for making use of this product. The emphasis will be primarily on matters relating to molasses as raw material rather than on the technical details of individual processes.
This introductory survey section has to start with a discussion of a specific property exhibited by molasses in a high degree, namely its viscosity, which affects the whole molasses-processing industry. The high viscosity (see page 36) is responsible for the difficulty of handling molasses. Whereas viscosity has technological significance in the sugar factory during crystallization and centrifugation, in the processing industries it causes mechanical problems in emptying barrels, removing molasses from tank cars, and in transport through pipe lines with or without pumps. The high viscosity may also play a practical role when efforts are made, on one hand, to secure the most favorable flow and pumping characteristics and good distribution ability while, on the other hand, keeping the concentration as high as possible (*cf.* Fig. 11/5 and 11/6 on page 43).
The relationships involved in the qualitative and quantitative variations of molasses characteristics are of direct interest to consumers in different degrees. The manufacturer of stock feeds has a subordinate interest in the detailed composition of molasses. On the other hand, those who ferment are concerned with the fermentable sugar content, while the yeast manufacturer pays special attention to the over-all composition, namely the content of nitrogenous compounds as well as the total amount of sugars present.

(i) Recovery of the molasses sugar

A number of procedures were developed for recovering the sugar contained in molasses but those processes have now lost most of the importance they once enjoyed (from around 1880 on). The strontium process, once used particularly in many German sugar factories, was in use up to 1945 only in the 'Dessauer Zuckerraffinerie'. This plant is now shut down. New suggestions for recovering sugar from molasses have come recently from Frellstedt.
The principal objectives of the desugaring processes are given here in rough outline to give a complete picture of the utilization of molasses.

Saccbarate process. In the historic osmosis process (DUBRUNFAUT 1863) use was made of the difference in the migration rate of saccharose compared with that of dissolved salts; the objective was to obtain a solution of higher purity that was capable of delivering sugar crystals on concentration. Proposals to remove sugar from molasses with the aid of electrolysis have not met with any commercial success.
The desugaring processes put into actual practice are based, almost without exception, on the formation of saccharates. The latter are slightly soluble complex compounds of saccharose with oxides of the alkaline earths: lime, strontium and barium. The saccharates are decomposed when treated with CO_2.
The STEFFEN lime process is used in several countries, including the Soviet Union; it is employed more often than the barium process; the latter process has the advantage of also desugaring molasses containing much raffinose[116]. Among the residual products from the desugaring factories, the desugared vinasses or desugared molasses as the end-product have some practical interest. The formation of three waste products will be briefly outlined, using the strontium process as an illustrative example. Molasses is diluted three or four times and filtered to remove suspended material. Strontium hydroxide ($Sr(OH)_2.8H_2O$) is added to the hot molasses solution and distrontium saccharate ($C_{12}H_{22}O_{11}.2SrO$) precipitates. The desugared mother liquor, which contains most of the nonsugars, is removed by filtration (see Table 28). The saccharate, separated from the desugared vinasse, is cooled by suspension in water and decomposes into insoluble crystalline strontium hydroxide and soluble monostrontium saccharate ($C_{12}H_{22}O_{11}.SrO.5H_2O$). On saturation with carbon dioxide the saccharate decomposes into sugar and strontium carbonate. The carbonate is removed by filtration to be reconverted into strontium hydroxide, and the sugar solution is processed in the usual way. The end-product obtained after sugar crystallization is blackstrap or desugared vinasse (*cf.* Table 3). The yield of saccharose is approximately 90%, of the sugar in molasses, *i.e.* as an average 42kg of sugar are recovered from 100kg of molasses. The blackstrap averages 15% raffinose, but it has less ash and a low nitrogen content. Ordinarily it is not used for fermentation.
The recovery of sugar from molasses by the STEFFEN process is growing in importance in the Soviet Union, where it is known as 'lime separation'[90]. By the end of the 6th Five-Year Plan (1960) about half of the Russian sugar factories are expected to be equipped with modern molasses desugaring equipment. The Time desugaring method is based on the formation of tricalcium saccharate in the cold through the use of an excess of lime.
The most important condition for the production of this saccharate is the use of very finely ground lime and the maintenance of a temperature of not higher than 20°C. The tricalcium saccharate precipitates on heating; the mono- and dicalcium saccharates are transformed into the insoluble tri-calcium saccharate:

$$3\ C_{12}H_{22}O_{11}.CaO \rightarrow C_{12}H_{22}O_{11}.3CaO + 2\ C_{12}H_{22}O_{11}$$
$$3\ C_{12}H_{22}O_{11}.2CaO \rightarrow 2\ C_{12}H_{22}O_{11}.3CaO + C_{12}H_{22}O_{11}$$

The lime desugaring process can be outlined as follows. Lime (from limestone of superior quality containing not less than 96% $CaCO_3$) from the kiln is disintegrated into fragments smaller than 6cm length and ground in ball mills. The powdered lime is separated by means of blowers and collected in cyclones; the collected powder is transported to a distributing conveyor. The excess air from the cyclone is discharged through an air filter retaining the fine lime dust. The powdered lime goes from the distributor over a proportioning device into the 'precipitator', *i.e.* a reaction vessel provided with a system of cooling elements.

The molasses is prepared in a separate tank in such a manner that the temperature of the solution does not exceed 20°C, with a sugar content of about 5% and a brix value around 9.0. This solution is charged to the precipitator and the powdered lime is added continuously. Since the reaction between lime and sugar is exothermic, the solution has to be cooled continuously (with water at 9-10°C). The amount of cooling water and the flow rate of the molasses solutions are adjusted to keep the solution temperature below 20°C. The reaction requires about 12minutes. The procedure is in most factories batchwise; the solution is pumped to the vacuum filters. The density of the suspension of trisaccharate and liquor is about 23 brix. The saccharate is washed with cold water.
The composition of the tricalcium saccharate remaining in the filters is approximately as follows:

Sugar	14.2%
CaO	15.6%
Water	64.05%
Apparent purity	95.5%
Raffinose	6.55%
Actual purity	84.5%
Apparent standard-purity	96.22%

The CaO content is 110% of the sugar content.
The cold wash liquor contains 0.41% sugar with an alkalinity of 0.70%. The amount of lime is 127% of the weight of sugar in molasses. This cold saccharate filtrate from the vacuum filters, together with the cold wash liquor (163% of the weight of the cold saccharate) is led to a heating tank (open vessel) in which it is heated to 90°C by the injection of steam. This heated liquor is filtered over vacuum filters. The resulting alkaline filtered solution (3.6 brix, 0.17% CaO, alkalinity 0.78) is a waste product which is used for irrigation or for the recovery of potash.
The calcium disaccharate precipitated by heating has the following composition: 76.8% water; 9.6% dissolved lime; 95.4% apparent purity; 11.0% sugar; 85% CaO bound to saccharate (per 100 parts saccharate); 96.23% apparent standard purity. The hot saccharate is mixed with the cold trisaccharate (in total 350% with respect to the processed molasses). This saccharate milk passes through the measuring device for milk of lime and goes directly to the first carbonation of the beet sugar factory.
Certain nonsugars are precipitatecl along with the trisaccharate. These coprecipitated substances include raffinose, which yields a tricalcium raffino-sate in the first carbonation unit. It decomposes with production of calcium carbonate and raffinose. The processing of molasses by this desugaring process is always accompanied by an enrichment of raffinose, whose content may reach 5% or higher. It does not pay to process molasses containing 3.5% raffinose or more; this has to be eliminated The economy of a lime desugaring is determined not only by the yield of sugar but by the quantity of molasses to be processed. By processing molasses from other factories and by maintaining a minimum output of waste molasses, the profitability can be increased. With favorable precipitation conditions it is possible to produce a saccharate cake which, after careful washing followed by carbonation, yields a syrup with a purity of 93.0% for cold saccharate and 95.0% for hot saccharate. These excellent results are seldom attained in factory practice. In 1954 the desugaring of molasses in the Ertiljski sugar factory yielded saccharates with an average purity of 91.0%, molasses with a purity of 59.4%, and a loss of sugar of 3.31% in the waste vinasse, based an the weight of processed molasses. If it is assumed that the actual purity of the saccharate and the molasses is 0.5% less than the apparent purity, and if the undetermined losses in the desugaring of the molasses and in the factory are estimated at 0.5% and 2.25%, on the basis of the weight of the molasses processed, the yield (Z) of refined sugar is:

$$Z = 100 - (3.31 + 0.5 + 2.25) - \frac{1.43(100 - 90.5)(100 - 3.81)}{90.5} = 79.5\%$$

This excellent result was obtained as a result of the high quality of the limestone (97.1-97.9% $CaCO_3$). The yield was only 75.5% when limestone containing 90-92% calcium carbonate was used. The Ertiljski sugar factory processed 40-50tons of molasses per day obtained from around 1560 metric tons of beets. The white sugar recovered was of standard quality.

Process employing ion exchangers. All of the nonsugars (salts, amino acids, betaine) which are present in the ionic state can be removed from clarified juice by ion exchangers. The yield of sugar is increased and the amount of molasses is reduced. In this procedure the action of anion and cation exchange resins on clarified juice can accomplish the complete removal of the salts, amino acids and betaine. Although the resulting juice purities are high and much less molasses results, complete removal of the salts is not economical and is too expensive. Trials being made in Holland with a desugaring process which desalts molasses, based on a study by QUENTIN[116, 131], appear promising. In 1956 a unit was set up in Italy for the desugaring of 100tons of molasses; the removal of the salts with anion and cation exchangers raised the purity from 64 to 92% [116, 132].
Suitable cation exchangers have been applied in many European sugar factories since 1950 to remove calcium from the juices to protect the evaporation equipment from incrustation[60]. The sodium cation exchanger takes up calcium ions and sodium ions go into solution.
In contrast to the combined cation and anion exchange in the desalting process, the calcium-sodium exchange has practically no effect on the *amount* of molasses, only the chemical composition of the molasses is changed. In place of the calcium ions, which can be removed almost completely, the molasses contains an equivalent amount of sodium ions. The effect of this deliming of thin juice has a subordinate significance on the composition of the molasses.

Process employing solvents. Methods for extracting sugar from molasses by means of solvents (acetic acid, for instance) never became popular on account of the high processing costs. None of these methods are studied in pilot plants. The principle of these processes is to affect the system: sugar-salts-water through the action of anhydrous organic solvents. About 35 years ago FRIEDRICH and RAJTORA were granted a patent for treating concentrated molasses with glacial acetic acid and benzene at 40°C; about 80% of the sugar could be recovered in a crystalline form. The 'Usines De Melle' mixed heated molasses with glacial acetic acid followed by the addition of anhydrous ethyl acetate. The principle of reducing the solubility of sugar has received interest in recent years. ANDRES[116] reports that welldeveloped crystals of sugar precipitate after addition of methanol. The B.M.A. in Brunswick was granted a patent on a similar process. A technological difficulty is the complete removal and recovery of the added chemicals.

(ii) ***Chemical conversion of the molasses sugar***

Among the processes purely for chemical conversion of the sugar in molasses, the production of lactic acid has technical significance. Sugar of molasses is converted into lactic acid in the presence of excess lime by subjecting the material to a high temperature for a sufficient time, preferably under pressure. The yields are distinctly lower than in the fermentation process; the highest yield is 43.3% lactic acid on sugar. The quantity of lime is used in the ratio of 3 mols CaO to 1 mol saccharose; the reaction is done in autoclaves at 210-230°C over a period of 2 hours[116, 130].

(iii) ***Biochemical utilization of molasses sugar***

Biochemical processes of using molasses are technically and economically highly important. Table 56 presents a condensed summary of products obtained technically from molasses. The significance of molasses as raw materials for these instances will be discussed individually.

(iv) Other uses of molasses

Aside from the use of molasses in stock feeds to be discussed later, the description of the use of molasses cannot be complete without mentioning that many practical suggestions have been made for putting molasses to practical uses. A separate section will outline processes for isolating and extracting nonsugar components. Today individual nonsugars are produced industrially only from the molasses vinasses; this is made feasible by the absence of interfering carbohydrates and the higher concentration of nonsugars, partly as a consequence of the necessity to reduce the organic matter of these waste solutions before they can be discharged in public waters. Special attention has to be given to betaine and glutamic acid. No practical interest has been aroused by processes designed to isolate leucine, isoleucine, asparagine, glycocoll, valine, alanine and the vitamins; these vinasses contain too little of these materials to render their commercial isolation profitable[116].

TABLE 56

SURVEY OF THE BIOCHEMICAL PROCESSES OF UTILIZING MOLASSES[4]

Organisms	Fermentation products from molasses (*1 mol, **2 mol, ***3 mol hexose)	Chief products
Anoxidative fermentations		
Yeasts	(*) $2C_2H_6O + 2CO_2$	Ethyl alcohol
	(*) $C_3H_8O_3 + C_2H_4O + CO_2$	Glycerine
	(**) $C_4H_{10}O + C_3H_6O + 5CO_2 + 4H_2$	Butanol, acetone
Bacteria	(*) $C_4H_8O_2 + 2CO_2 + 2H_2$	Butyric acid
	(*) $2\,C_3H_6O_3$	Lactic acid
	(**) $C_4H_{10}O_2 + 2C_2H_6O + 4CO_2 + H_2$	2, 3-Butyleneglycol (2, 3-butanediol) and ethyl alcohol
	(***) $4C_3H_6O_2 + 2C_2H_4O_2 + 2CO_2 + 2H_2O$	Propionic acid
Oxidative fermentations		
Yeasts	Feed yeasts, Nutrient yeasts, Fat yeasts, Bakers yeasts — not defined stoichiometrically	Yeast cellular substance
Bacteria	(* + $2O_2$) $2C_2H_4O_2 + 2CO_2 + 2H_2O$	Acetic acid
	(** + O_2) $2C_6H_{12}O_7$	Gluconic acid
	(** + O_2) $2C_3H_6O_3 + 2C_2H_4O + 2CO_2 + 2H_2O$	Dioxyacetone
Molds	(** + $3O_2$) $2C_6H_8O_7 + 4H_2O$	Citric acid
	(** + O_2) $2C_6H_{12}O_7$	Gluconic acid
	(* + $3O_2$) $C_4H_4O_4 + 2CO_2 + 4H_2O$	Fumaric acid
	(** + $9O_2$) $C_2H_2O_4 + 6H_2O$	Oxalic acid

(b) Fermentation of Molasses

(i) ***Production of alcohol from molasses***

The end syrup from the manufacture of sugar was introduced 150 years ago by ACHARD in the distilling industry. BALLING[61] gives the beginning of the industrial utilization of beet molasses for alcohol production around 1830. Up to about 1880 the only industrial use of molasses was in the manufacture of alcohol, a process carried out in molasses distilleries. Alcohol is also produced from molasses combined with the manufacture of yeast (yeast aeration spirits).

It is possible to alter greatly the relative yields of yeast and alcohol. The yields shown in Table 57 can be obtained concurrently from 100 kg of normal beet molasses.

When molasses is to be fermented to alcohol, the sugar content should be high. Raffinose, which amounts to 0.5 to 2% in beet molasses, is broken down into fructose and melibiose by yeasts which contain the enzyme saccharase. Melibiose in turn is broken down by some yeasts (*e.g.* bottom yeasts) into glucose and galactose. Raffinose is broken down completely by the bottom yeasts; top yeasts ferment only one-third of the raffinose. The alcohol and yeast industry, using beet and cane molasses, is concerned with the suitability for alcohol fermentation or for the production of yeast.

TABLE 57

YIELDS OF YEAST AND ALCOHOL FROM 100 KILOGRAMS OF BEET MOLASSES[4]

kg of pressed yeast (27% dry substance)	Alcohol (100%)* (l)	Efficiency** (η)
90–100	0	99–110
80	5	103
70	10	107
60	13	105
50	16	103
40	20	104
30	24	105
25	26	105.5
0	30–32	—

* With respect to the quality of the pressed yeast, too high yields of alcohol (over 15%) are disregarded.
** % yeast × 1.1 = a; % alcohol × 3 = b; $a + b$ = efficiency.

The concept 'nonsugar substances' is different in the fermentation industries from that in the sugar industry. Invert sugar and also raffinose are included in the term sugar. But invert sugars as raw materials for fermentation do not apply to certain nonfermentable reducing materials which are included in the determination of total sugars. The determination of total sugars includes reducing compounds, which have the effect of simulating higher sugar content, but which are not fermentable or to only a limited extent.

TABLE 58

MOLASSES FROM RAW CANE SUGAR REFINERIES[4]

Source of molasses	Brix	Saccharose (%)	Red. substances (invert sugar) (%)	Total sugar (%)		
				Sum of 2 and 3	Saccharose	Difference of 4 and 5
	1	2	3	4	5	6
English refinery (raw cane sugar)	—	39.65	25.51	65.16	63.6	1.56
German refinery (Cuba raw sugar)	80.3	40.78	15.47	56.25	55.48	0.77
Louisiana (raw sugar)	80.0	32.0	30.0	62.0	60.5	1.5
German refinery (Cuban molasses)	84.4	35.6	20.7	56.3	53.4	2.9

The examples in Table 58 show remarkable differences between 'total' sugar and the sum of saccharose arid reducing substances; these differences have to be considered in judging the yeast-producing or fermentation properties The standardized sugar determinations are more or less inaccurate with respect to molasses. By the presence of different kinds of sugars and optically active nonsugars, the polarization is not without a certain error. This is likewise true of the chemical methods of determining reducing sugars in view of the non-fermentable reducing substances. A practical appraisal of the value of a molasses fermentation is the biological determination of its alcohol productiveness. Cuban molasses (No. 4 in Table 58) was found in the laboratory to yield 30.75 litres of alcohol per 100 kg or 57.58 liters/100 kg total sugar (column 5, Table 58); the yield was about 0.42 litre below the minimum yield.

The nonsugars in molasses do not exert enough influence on the fermentation to warrant special attention. Only a portion of the amino acids in molasses is consumed in the yeast metabolism to form fusel oil; the quantity of fusel oil is proportional to the quantity of dry yeast substance formed. The yield of fusel oil can be reduced by adding ammonium salts, as the yeast is able to cover its nitrogen requirement more easily from ammonium salts than from the deamination of the amino acids.

The fermenting process of molasses has undergone various changes over the years:

A) process with a mash (absorption or mashing-in process);
B) partial mashing process;
C) feeding-in process;
D) process with return of yeast (MELLE process).

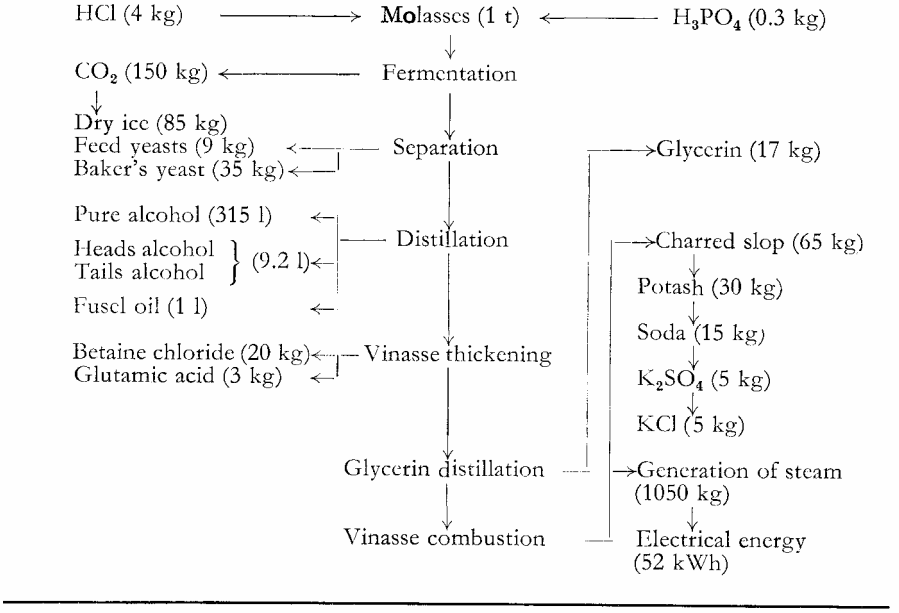
Recent developments have been featured by efforts toward:

A) increasing the yield of alcohol;
B) continuous fermentation;
C) utilization and recovery of the by-products:

Apparatus and equipment employed will not be discussed nor will the individual processes of molasses fermentation.
If the operating conditions are good about 64 litres of alcohol are obtained from 100 kg of sugar processed molasses (*cf.* Table 56). A schematic review of the yields of the principal and by-products resulting from the manufacture of alcohol from molasses is presented in Table 59.
Some of the components of molasses are recovered from the molasses slops after removing the alcohol.
Through the coincidence of a number of unfavorable circumstances in molasses fermenting factories, certain batches may result in what is known as 'saltpeter fermentation.' This is characterized by the evolution of dark brown fumes of nitrogen dioxide from the fermenting mash; bacterial reducing processes are responsible for this reaction. The bacteria introduced with the dilution water or present in the molasses participate in the fermentation and in addition to organic metabolic products may yield hydrogen.

TABLE 59

REVIEW OF THE PRINCIPAL AND BY-PRODUCTS OF MOLASSES FERMENTATION



This reduces the nitrites in the mash to nitrites and nitrous acid, whose decomposition leads to NO_2. Since nitrogen dioxide is a very effective yeast poison, the alcoholic fermentation is stopped. This 'saltpeter' fermentation occurs only in factories where large amounts of diluted molasses solutions are made and stored for lengthy periods in anticipation of continuous or periodic addition to the fermenting tanks. This infection can be avoided by proper sanitation methods in the fermentation room and by using vigorous 'starter' yeast. Reference should be made also to molasses which are difficult to ferment, a condition repeatedly reported in the literature.

The causes include: primary or secondary infections in the mashes and abnormal relationships in composition, *e.g.*, the presence of volatile fatty acids, excessive amounts of caramel substances and excess of raffinose.
Practically no new information concerning the testing of molasses on resistance to fermentation has come to light since the previous century; methods for determining growth substances are of recent date. A method proposed during the previous centum- has been retained in the literature without change[62,63] even though there is difference of opinion on its indicative value. If the high amounts of volatile acids are the reason for and a lowered yield of alcohol, the molasses solution can be made distinctly acid and boiled to remove these interfering substances.
Experience has demonstrated that molasses which have been 'sterilized' for pure fermentation likewise give a lowered yield of alcohol or yeast, depending on the boiling time and pH. It appears that the problem of slow fermentation of molasses has not received proper attention in recent investigations. In earlier times interferences in molasses distilleries were often conveniently ascribed to the resistance of the molasses to fermentation, but the fault was many times poor yeast management and inadequate cleanliness.

(ii) ***Production of glycerin from molasses***

In normal alcoholic fermentation, about 3% of the weight of the sugar is converted into glycerin, which thus represents theoretically a by-product. In weak alkaline solution the fermentation can be guided in such a manner that glycerin and acetaldehyde are the predominant products, together with alcohol and carbon dioxide. This relation, discovered in 1916 by NEUBERG, CONNSTEIN and LUDECKE, has been developed into a technical process which in Germany became known, principally during World War I, as the 'Protol' process and in Austria as the 'Fermentol' process. At that time, it added monthly about 1000 tons of crude glycerin to the defence economy[116].
Alcoholic fermentation normally splits sugar into approximately equal parts of carbon dioxide and alcohol, with slight amounts of succinic acid and glycerin, when the fermentation proceeds in weakly acid to neutral surroundings. Fermentation by yeast in alkaline medium shows the following deviations

A) the yeast does not multiply at all or to an insignificant extent;
B) the formation of carbon dioxide is decreased to 40% or lower to the benefit of other products of the fermentation;
C) the formation of alcohol decreases and increasing amounts of acetaldehyde and glycerin are produced, roughly in proportion to the quantity of sodium sulfite added.

The latter has been found to have a beneficial effect in the glycerin production. The added sodium sulfite maintains a marked alkaline reaction and the yeast can tolerate considerable amounts of it. The yeast can be used repeatedly provided appropriate intermediate fermentation to rejuvenate the yeast has been employed. The amount of sodium sulfite to be introduced has to be limited because of its decelerating action on the fermentation, the quantity is kept below 40% of the weight of the sugar.
Theoretically one mol of glycerin should be formed for each mol of acetaldehyde produced:

$$C_6H_{12}O_6 \rightarrow CH_3CHO + CO_2 + CH_2OH.CHOH.CH_2OH$$

In practice only 36% of the weight of the sugar can be recovered as glycerin compared to theoretically 51%. Acetaldehyde appears in the so-called 'sulfite' fermentation in the form of a bisulfite addition compound. This is not entirely stable; the decomposed portion is reduced by hydrogen, producing a corresponding amount of ethyl alcohol.
After fermentation, according to KRETZSCHMAR[64], the normal mashes contain around 3% glycerin, 2% alcohol, and 1% acetaldehyde bound to sulfite. The volatile materials are distilled off and the Protol slops worked up. Sulfite is precipitated as $CaSO_3$ by adding calcium chloride, filtered and washed. The filtrate is concentrated under vacuum to 50-60% crude glycerin. The purification loss is 25-30% of the glycerin content of the fermented mash.

In contrast to glycerin solutions obtained from colorless sugar solutions, notable for their clarity and freedom from impurities, the alkaline fermentation of beet and cane molasses yields glycerin solutions highly contaminated with coloring matters and undesirable impurities.
KRETZSCHMAR[64] describes a purification process used by the Glycerine Corporation of America, New York, consisting of the following steps:

(1) removal of the yeast from the fermented mash;
(2) acidification of the filtrate;
(3) removal of the volatile components by distillation;
(4) concentration by continuous evaporation or distillation;
(5) dialysis under controlled conditions;
(6) precipitation of iron from the diffusate;
(7) treatment with ion exchangers to remove other impurities
(8) concentration of the diffusate.

The details of the operation are: A fermented alkaline molasses mash is filtered, made weakly acid, and the volatile materials distilled off in copper stills. The still residue is further concentrated to one-half its volume and neutralized with a 10% solution of potassium bicarbonate. After heating to 75°C the solution is passed through a series of dialyzing cells, arranged in such a manner that the direction of flow is counter to that of a stream of water which is likewise at 75°C; the cellulose semipermeable membranes are kept entirely covered with liquid. The iron is precipitated from the diffusate by adding sodium sulfide. The diffusate is passed through an ion exchanger charged with a synthetic resin and absorption agent. The diffusate is finally decolorized by means of active carbon.
The continuous series dialysis has great advantages; the glycerin is stripped from the membrane areas on the diffusate side; the insoluble nonsugars are kept in Suspension and clogging or settling on the membranes is thus avoided. The resulting solution of glycerin is clear and light enough in color to be used as a plasticizer for transparent materials (cellulose hydrate, etc.), casein, all kinds of papers, including glazed papers, for leathers, cosmetic and pharmaceutical products, and the preparation of synthetic resins.
Proposed processes for extraction of glycerin from the fermentation slops of molasses by various accumulation procedures will be merely mentioned.

(iii) ***Preparation of rum from beet molasses***

The biochemical utilization of molasses sugar has witnessed in Germany in the preparation of rum from beet molasses the combination of acidulation processes with alcoholic fermentation. Manufacture of rum is typically and traditionally indigenous to the cane sugar regions. Cane molasses and the products resulting from the manufacture of cane sugar are mainly employed for the rum mashes (see Table 110). The first attempts to manufacture rum from European raw materials (beet juice, beet molasses, and effluents from beet sugar manufacture) date back a half-century. On the basis of bacteriological studies of the acidulation and fermenting methods commonly employed in cane sugar areas, different raw materials were subjected to appropriate microbial acidulation and esterification in order to produce a ‘German’ rum. The designation for the resulting product has been accepted by competent authorities because of the qualities exhibited by this product. According to the text of a patent, dated 1939, on the preparation of ‘German’ rum, molasses solutions are used which have been inverted by acids. These solutions are after partial inversion, firstly treated with alkali in the gold and then heated for at least 30 minutes to 90°C. The pH is adjusted at 5.2-5.6, the solution is diluted to 18-20 brix and fermented with the addition of different nutrient materials. Under normal economic circumstances there is no need to restrict the use of imported rum; genuine cane rum is far superior to all imitations not only with respect to price, but primarily as to quality. A comparison (Table 60) of the analytical data derived from many samples of ‘German’ rum with genuine original ‘cane’ rums shows that the German product never reaches the average values for the ester content of cane products, but according to experts the aroma can approach a blend of imported rums.

(c) Manufacture of Yeast from Molasses

(i) General considerations

The introduction, about 40 years ago, of beet molasses as the principal raw material for the production of yeast resulted in a fundamental change in this industry.

TABLE 60

ANALYTICAL DATA FROM GENUINE ORIGINAL RUM AND 'GERMAN RUM'[4, 66]

(According to WÜSTENFELD–HAESELER; values in mg per 100 ml pure alcohol)

Type of rum	Volatile acids as acetic acid	Esters as acetic ester	Aldehydes as acetal-dehyde	Furfurol	Fusel oil	LUSSON–GIRARD number*
Overseas	21–426	37–2390	0.3–92	0.1–26	26–440	239–1142
German (1914–1922)	13–101	190–373	3–50	0.1–5.3	20–217	345–552

* LUSSON–GIRARD number (impurity coefficient) is the sum of acids, esters, aldehydes, furfurol and higher alcohols referred to 100 ml pure alcohol; it serves, along with the taste test, for judging the quality of the varieties of rum.

Yeast production till that time had been based on the use of grains. The use of molasses introduced a fundamentally altered manufacturing process; it initiated a development that led to a certain standardization of the manufacturing processes. Molasses and cheaper inorganic nutrients, aeration, the feeding system, yeast culture, and the separator station as well as the yeast filtration constitute distinguishing features of the modern methods of producing yeast.

In contrast to the relatively constant and usually even stoichiometrically tangible microbial metabolic products, it is an innate feature of yeast production that it cannot be treated in summary fashion as alcohol production, because yeast is a living organism and a complicated substance. The problems involved in the utilization of molasses for the production of yeast cannot be reviewed apart from the yeast cell and its physiology. The special importance of molasses as raw material for yeast was mentioned in the previous review of the formation and composition of molasses.

This molasses application in no way alters the fact that molasses is regarded by the sugar industry as a waste product. It is understandable why the sugar manufacturers are not interested in altering their processes to produce a by-product, which is of minor value, with a composition especially suitable for another industry. Certain steps within the usual sugar manufacturing process resulting in an improvement in the molasses quality can be looked on as a realizable objective. A substantial contribution is made by careful attention to all filtrations of the sugar products to will be as free as possible from suspended materials and by relieving the yeast manufacturer of a part of the clarification problems. Similarly, prompt cooling of the freshly centrifuged cane molasses before storage is of direct interest to the processing industry, because of the reaction, which results in the conversion of fructose to non-fermentable reducing materials which are of little or no value to the yeast organism.

Of all industries processing molasses the manufacture of yeast makes the highest demands on the quality of commercial molasses. The rating of molasses is based on analytical data. The primary factor for the value of molasses and its grading for the industry is the sugar content. No matter how low the price for which a molasses may be bought, it is always expensive if no commercial yeast can be made from it by the usual procedure.

Yeast manufacturers everywhere prefer beet molasses to cane molasses, and they use a mixture of the two varieties of molasses rather than cane molasses alone. This preference is based on the composition. The usual constituents of beet molasses produced in Germany are given in Tables 2-4 and 52. Cane molasses is seldom processed for yeast in Europe. Disregarding refinery cane molasses obtained from imported cane sugar, Spain is the only European country regularly processing cane molasses; the cane sugar region in southern Spain is the only European area where this crop is still raised. The U.S.A. is among the countries continually utilizing both beet and cane molasses.

Among the beet molasses the compositions of raw sugar, white sugar, and refinery molasses are similar (compare Tables 3 and 4). They are practically equivalent with respect to chemical constituents, but not with regard to the content of colloidal materials, suspended matter and color. Furthermore, these different molasses may contain relatively slight amounts of other nonsugars, such as volatile acids, nitrates, sulfites and/or microbiological infections, which are unfavorable to the utilization of the molasses. Several questions regarding the fundamental differences in the nutrient materials content of the various Beet molasses have not yet been answered.
The prejudice against refinery molasses has its basis in the fact that they are the final repository of all the mistakes and maltreatments that may have occurred during the manufacture of the raw sugar. The refinery molasses is directly related to the molasses in the raw sugar: a good molasses can only be expected from a refinery provided with a good sugar. This means that questionable products may also be found among raw sugar molasses. Moreover, refinery beet molasses is sometimes confused, with respect to quality, with molasses produced in the refining of cane and beet sugars, *i.e.* those having an abnormally dark color and low nitrogen content. If procedures are used to lighten the molasses color and to supplement the nitrogen a usable baker's yeast can likewise be produced from cane sugar and refinery molasses.

(ii) ***Harmful factors***

The quality of the yeast may never be affected unfavorably by the molasses used in its manufacture. Any molasses which requires a special pre-treatment beyond the ordinary routine, *i e.* any stop which may be called expensive, is regarded as having little economic justification in the yeast factory.
The deleterious factory in molasses include: excessive content of sulfurous acid, nitrates, volatile acids, abnormally dark color, colloidal and suspended matter and serious infection.
(α) *Sulfurous acid in molasses*. The danger that the sulfite content of molasses, resulting from the use of SO_2 in the sugar manufacturing process, will cause difficulties in the yeast factory is due to the fact that the optimal decolorizing effect in the thin juice (referred to 100 brix) requires, according to HILDEBRANDT[67], a SO_2 content of 0.03-0.05%. To obtain a molasses satisfactory with regard to its sulfur dioxide content, not more than 0.003-0.004% SO_2 may be present in the corresponding thin juice or syrup. With average SO_2 contents of 0.0205 or 0.0282% in molasses the highest sulfur dioxide values of German beet molasses of 1934/35 were below 0.125% SO_2, given by CLAASSEN as the highest tolerable amount of SO_2 for yeast manufacture. That the rating of the SO_2 content in molasses was formerly not at this level is shown by the decision rendered at Magdeburg on January 4, 1933, by the Sugar Arbitration Board[4], in which the complaint of a yeast factory, objecting to 0.45% sulfur dioxide in a large shipment of molasses, was denied. This decision was based on the fact that the molasses could be judged as normal and genuine, since at that time no regulations had been established by the trade regarding the highest permissible content of sulfur dioxide, and consequently the molasses in question did not contravene the terms of the contract.
The significance of the SO_2 content of molasses with respect to the manufacture of pressed yeast was later taken into account in the molasses specifications by fixing the maximum allowable content at 0.15% SO_2. According to LAFAR[4] the fermentation activity of various kinds of yeast is impeded when the sulfur dioxide content reaches approximately 6.8-9.2 mg/litre. The question as to the limiting concentration harmful to yeast, *i.e.* how far and in what amounts SO_2 in molasses has an unfavorably effect on the growth of yeast cannot he answered by a single numerical value; this limiting figure is below the value at which fermentation is prevented. Differences in clarification, dilution and aeration can lead to quite different limiting concentrations of SO_2, in the molasses or molasses wort that are still tolerable for the production process. The experiences gained under specific conditions are not of general validity.
CLAASSEN[4] states that 0.125% SO_2 in molasses is not harmful in yeast manufacture, KARCZEWSKA[30] reports that this figure may go up to 0.3%, whereas DREWS[4] Claims that 0.02% sulfur dioxide is definitely harmful, and SCHMIDTER[4] states that as little as 0.011% is deleterious.
The presence of sulfurous acid in molasses does not inevitably lead to difficulties under all conditions. On the other hand, change of color of the yeast and odor of hydrogen sulfide are typical quality disorders likely to make themselves evident when molasses containing sulfurous acid are processed. Such effects, as a rule, can be avoided by minor modifications in the clarification process.

The removal of sulfurous acid by the usual hot acid defecation method can be intensified by adding such strong oxidizing agents as sodium chlorate, converting the sulfites into sulfates. The mixture is thoroughly stirred and heated to 80-95°C.

(β) *Nitrates and nitrites in molasses*. In yeast factories brown fumes of nitrogen oxides are sometimes evolved from molasses. This rather rare occurrence, which was last observed in several South German molasses, takes place during the hot acid defecation after the molasses has been acidified to about pH 5.0 and heated above 70°C.

The generation of nitrous gases is due to the decomposition of the nitrites present, formed by reduction of nitrates originally present in the beets or formed in processing. In addition to altered beets or beets grown on nitrate-rich soil, microbiological activity is responsible for the nitrite content of molasses[20]. Sugar beets from different countries contain different amounts of nitrate nitrogen, in fact -based an beets- 0.164% to 0.342%

N_2O_5 were found in French, Hungarian and Russian Beets, and 0.01% N_2O_5 in beets grown in Bohemia, whereas German beets of the same time contained hardly any N_2O_5[20]. Traces of nitrite were found in the crude juice and 0.004-0.01% nitrite nitrogen in the molasses. Under laboratory conditions 100 g of a first massecuite, which was acidified and boiled, yielded more than 170 ml of a gas which contained 52.3% CO_2 and 38.0% nitrogen oxides[20].

(γ) *Volatile organic acids in molasses*. The free volatile acids occurring in molasses are generally present in slight amounts, so that they do not impair the culture of the yeast. If the molasses is acidified at boiling, volatile acids such as acetic, formic and butyric are evolved. Considerable quantities of these volatile fatty acids affect the growth of the yeast unfavorably. The growth and activity of yeast is reduced by 0.005% butyric acid in the wort[4], while 0.1% butyric acid stops the fermentation completely. The proportion of the volatile acids may not exceed 15-20% of the total activity to maintain the activity of the yeast[4]. There is no satisfactory explanation of the influence of acetic and formic acid on the yeast activity under the conditions for producing pressed yeast. The normal value for the total volatile acid content in molasses is given as 0.1-0.3%[30]; beet molasses from California was found to contain 1.92%, and a sample from Colorado contained 3.54%. For a satisfactory yield and grade of yeast, molasses containing 0.35-1% volatile acids must be subjected to a special preliminary treatment.

Difficulties encountered in the manufacture of yeast and alcohol from molasses led to detailed investigations, directed especially to the determination of acetic and butyric acid; these studies were conducted in the laboratories of the Dansk Gaering Industrie[68].

Butyric acid content in molasses mash of 0.15% (corresponding to 0.60% in the molasses) is considered to be the critical level; greater concentrations of butyric acid led to complete interruption of alcohol fermentation. A lower content of butyric acid was accompanied by an improvement of the fermentation; the normal fermentation rate was attained when the mash contained 0.08% butyric acid (*i.e.* 0.32% in the molasses). The great divergence in the fermentation obtained under strictly comparable conditions with ‘normal’ molasses and with one containing 1.23% acetic acid and 0.96% butyric acid is impressive. The distillate from the inferior molasses containing the volatile organic acids was added to the ‘satisfactory’ molasses and the latter fermented. The impairment of the fermentation then corresponded to that observed with the molasses containing the volatile acids from the beginning. ‘Normal’ molasses, treated subsequently with fatty acids, exhibited likewise the impairing action of the volatile organic acids, and *vice versa,* a normal fermentation picture was shown by molasses from which these acids had been removed.

TABLE 61

VOLATILE ACIDS IN DANISH BEET MOLASSES[4, 68]

Molasses No.	Formic acid (%)	Acetic acid (%)	Propionic acid (%)	Butyric acid (%)	Valeric acid (%)
1	0.3	0.6	0.3	0.4	0.0
2	0.2	0.5	0.2	0.5	0.0
3	0.4	0.7	0.1	0.5	0.1
4	—	1.0	traces	0.6	0.1
5	—	0.9	traces	0.0	traces

Differences were found with various strains of yeast with respect to their resistance to the interference of butyric acid. The molasses Nos. 1-4 given as examples in Table 61 impaired the fermentation, whereas molasses No. 5, which was free from butyric acid, lay in the region of 'normal' quality[68].

The Danish sugar industry was not entirely satisfied with these findings[66]. With respect to the distillation method of DIERSSEN and co-workers[68] for the determination of butyric acid in molasses it has to be remembered that SO_2 in molasses and also formalin, which is sometimes present, affect the results and make the determination inaccurate. No upper limit can be established for the permissible content of butyric acid in molasses because the restraining action of butyric acid in the fermenting or yeasting of molasses is related to the quantity of acetic acid present and it also depends an the SO_2 content. Since a collective influence is present, no absolute statements can be made about the exact harmful amount of each of the undesired acids in the case of an industrial molasses. Except for fermentations conducted under carefully controlled conditions, little has been done in the study of this complicated problem.

(iii) ***Coloring matters in molasses***

The importance of coloring matters of molasses with respect to their effect on the quality of the produced yeast is difficult to state exactly. No general statements can be made about the composition and amounts of the molasses coloring matters. This is not surprising in view of the complexity of the pigmenting compounds of molasses, which are chiefly caramel substances, melanoidines and iron-phenol compounds and are related to the molasses colloids. Molasses from different years and factories seldom have the same color.

A light-colored molasses may indicate that it contains much SO_2. As a result of an intense sulfuring of the juices, this assumption can be checked by analysis.

Certain relationships between the colors of crude sugar, white sugar and refinery molasses have become evident from the averages of many years (*cf.* Table 4), but no reliable rating of an individual molasses can be derived from the color determination of the molasses. As a rule, very dark molasses must be pretreated; efforts must be made to remove impurities and colloids as well as caramelized and humic-like substances as completely as possible. If the color components of molasses are designated as humic-like, this points to the colloidal nature and heterogeneous composition of aromatic complexes, which through oxidation to brown amorphous products have a similarity to the humus substances in the soil. Melanoidines, for instance, are classified in many instances among the humic-like materials. According to POLLAK[70], the humic nonsugars are particularly involved in the color of the produced yeast. POLLAK explains this as due to the exchange of the amino acid oxygen of the yeast; colored 'radicals' of the humic nonsugars are taken up by the yeast and precipitated in the yeast substrate, whereas the amino acids of the coloring matter are transformed into yeast protein; a certain proportion of the coloring matter is included in the yeast cells. Unless special measures are taken, a 'humin' content of 0.6% in the molasses impairs the growth of yeast[30]. If only 'caramel' substances are involved it has been found that yeast grown in sugar solutions containing added caramel is as light in color after thorough washing as that produced in pure sugar solutions.

TABLE 62

THE COLOR OF YEASTS OBTAINED FROM MOLASSES OF VARIOUS EXTINCTIONS

(From values furnished by the Institut für Zuckerindustrie, Berlin[4, 71])

Type of molasses	1924/1925 No.	1924/1925 Extinction coefficient of molasses	1924/1925 Color of yeast	1925/1926 No.	1925/1926 Extinction coefficient of molasses	1925/1926 Color of yeast
Raw sugar	1	31.0	brown	10	25.1	white with yellow tinge
	2	23.5	trace lighter than 1	11	25.0	light brownish
	3	19.0	light brown	12	20.5	trace darker than 11
White sugar	4	16.7	light brownish	13	18.5	whitish with a tinge of yellow, about the same as 10
	5	12.9	somewhat darker, more yellow than 4	14	21.5	light brownish
	6	44.6	brown	15	22.7	brownish grey darker than 14
Refinery	7	35.0	light brownish	16	24.1	yellowish, slightly darker than 10
	8	37.5	brown–grey	17	39.3	somewhat more reddish than 16
	9	38.8	midway between 7 and 8	18	30.3	trace darker than 17

Molasses arranged according to the color of the yeasts grown from them (from light toward dark); the extinction coefficients of the molasses in parentheses.

1924/25: 7 (35.0); 9 (38.8); 8 (37.5); 3 (19.0); 4 (16.7); 5 (12.9); 2 (23.5); 1 (31.0); 6 (44.6).
1925/26: 10 (25.1); 13 (18.5); 16 (24.1); 17 (39.3); 18 (30.3); 11 (25.0); 12 (20.5); 14 (21.5); 15 (22.7).

Aside from the fact that the caramel pigments act in the analysis as reducing substances affecting the determination of sugar, they tend to increase the difficulty of normal fermenting of molasses and they contribute to the need for clarification steps. Furthermore, an unusually intense washing of the yeast constitutes an additional operational burden. A very dark molasses is always a disadvantage from the standpoint of presenting subsidiary problems.

The caramel content of a beet molasses from California was 1.49 %, that of one from Colorado was 0.9%. Normal procedures cannot produce satisfactory yeasts from molasses that contain 2.3 to 2.4% caramel.

The preparation of a clear molasses wort is from a technological point of view a complex problem. KARCZEWSKA[30] states that a turbidity as low as that corresponding with 0.08% colloids in the molasses or molasses wort has a harmful effect on the growth of yeast. Poorly clarified worts lead to an after-darkening of the produced yeasts and in fact, because of precipitation, coagulation and adhesion, undesirable impurities cling to the yeast cells and are centrifuged off and pressed out along with the yeast, thus producing oxidative reactions leading to after-darkening. The color of yeast cannot be related in a simple way to the color of the molasses; it is affected to varying degrees by a number of factors. The extinction coefficients or color concentration of the molasses cannot be used satisfactorily for predicting the color of the yeast. Variations in color within a single type of molasses as well as the differences between the types of molasses do not exert a predictable effect on the yeasts made from these raw materials. SPENGLER[71] compared the color of yeasts grown under uniform aerating conditions and filtered under vacuum, employing molasses of different colors. The color in each case was matched and recorded by means of water colors, since it is not possible to make a direct comparison of yeasts grown under parallel conditions in different experiments. A decisive factor was the agreement of the shade after drying on paper with that of the original moist yeast (Table 62).

The molasses from the 1925/26 season all yielded lighter yeasts than those from the preceding German beet crop. The molasses from which the three relatively lightest yeasts were made were for 1924/25 three refinery molasses, and for 1925/26 one raw sugar molasses, one refinery molasses and one refined sugar molasses. It was evident that the molasses color and the color of the yeast made from this molasses have no functional connection, but this is not the same as stating that the coloring substances in molasses have no influence whatsoever on the color of the yeast produced. Molasses colloids are closely related to the color of the molasses. The color and the amount of colloids, which in part are carriers of the color of the molasses, are of fundamental importance with respect to the ability to be clarified of the molasses and hence to the quality of the yeast.

(iv) ***Molasses colloids and suspended materials***

Certain compounds included among the nonsugars of molasses interfere with the manufacture of yeast. Molasses cannot be used in its original condition for this purpose. The properties of the colloidal and suspended nonsugars have already been discussed in connection with the composition of molasses. For pressed yeast colloids and suspended materials must be removed as completely as possible, *i.e.* the molasses must be clarified. As little as 0.008% of molasses colloids have an unfavorable effect in the making of yeast. The second objective of the preliminary treatment of molasses is the extensive removal of the microflora.

(v) ***Micro-organisms in molasses***

Statements regarding the kinds and extent of the microflora in molasses are quite divergent (*cf.* Table 9).

Findings that molasses contain 29 to 500 million germs per gram[13] differ substantially from statements that beet molasses contains around 10,000 to 5 million micro-organisms per gram[30]. Only those germs deserve special attention which multiply during storage of the molasses or which can cause complications in the fermentation process. Molasses have been graded in three classes with respect to quality according to the content of microorganisms (Table 63).

TABLE 63

QUALITY GRADING OF MOLASSES ACCORDING TO THE GERM CONTENT[4, 30]

Quality grades	Germs/g beet molasses	Processing to pressed yeast
I	up to 100,000	simple and easy
II	up to 1 million	special pretreatment
III	up to 5 millions	no normal yield of a full-value yeast

A molasses, biologically seriously contaminated in the sense of yeast manufacture, is characterized by the fact that among the large number of organisms present in the molasses, one species is dominant and, as a 'pest' to the yeast, affects the normal growth and or the quality of the yeast.

Infections of wild yeasts and acid-forming bacteria are especially to be feared. The development of these micro-organisms is connected with loss of sugar and organic nitrogenous materials and with the production of various undesired metabolic products. There is no essential difference in the fungus flora of molasses which are 'easy' or 'difficult' to ferment.

Among the organisms several *leuconostoc* strains are of practical interest, because they can introduce the formation of the greatly feared and extremely bothersome 'frog spawn' or dextran fermentation, which in recent years has gained technical importance[72]. There is not much danger of this infection in a modern yeast factory, but it has not been excluded; molasses fermenters still retain a vivid picture of its evil effects.

The dissolved dry substance in molasses consists not only of sugar, but contains a considerable amount of nonsugars, as in the case of molasses; the vital activity of osmophilic yeasts becomes possible at a low water content of 25-30%. Cases are recorded in the literature in which one variety of yeast, *Saccharomyces mellis* (formerly *Zygosaccharonzyces mellis acidi),* can tolerate sugar concentrations up to 70-80%. Molasses with a density of less than 76.3 brix are regarded as not being stable when stored.

A refinery cane molasses, which had lost its entire sugar content in several weeks storage through microbiological action, was found to contain two groups of micro-organisms, namely, fission fungi and osmophilic yeasts that were not further characterized[73]. These organisms were inoculated into sterilized cane molasses and their action was observed in two independent experiments (Table 64).

TABLE 64

CHANGES IN THE SUGAR CONTENT OF CANE MOLASSES PRODUCED BY OSMOPHILIC YEASTS[4, 73]

Sample	After 18 days at 25°C			After 21 days at 22°C		
	Invert sugar (%)	Total sugar as invert (%)	Brix	Invert sugar (%)	Total sugar as invert (%)	Brix
Control mixture (not inoculated)	21.1	55.6	77.6	18.1	46.6	78.0
After incubation with inoculating culture of:						
Schizosaccharomycetes	21.3 (+ 0.2)	52.9 (− 2.7)	77.0 (− 0.6)	19.0 (+ 0.9)	45.7 (− 0.9)	—
Undefined osmophilic yeast	28.0 (+ 6.9)	53.2 (− 2.4)	75.7 (− 1.9)	23.7 (+ 5.6)	44.8 (− 1.8)	—

The figures between brackets show the differences from the value of the control mixture.

The invertase of the yeasts gave an increase in the invert sugar content of the molasses, with a loss of about 4% of the total sugar present.

(vi) ***Removal of 'harmful' constituents by clarification of the molasses***

Crude molasses may contain components which are harmful to or interfere with the manufacturing process or the preparation of yeast. The processing of molasses, which contain downgrading factors, is connected with losses and increasing costs. The lowering of the quality extends from increase in color to loss of storing ability, and smeary consistency of the yeast. As a rule, a more or less extensive pretreatment of the molasses is a necessity; the objectives being:

A) clarification (removal of suspended matter, colloids, coloring materials, volatile acids, nitrites and sulfites);
B) disinfection (reducing or elimination of the fungus flora).

Since these two goals can usually be attained in a single procedure, and since the clarification effect is most obvious, this pretreatment of the molasses is referred to as the clarification process. The choice of the pretreatment depends on the kind and condition of the molasses involved and on the working conditions and special circumstances in the factory.

TABLE 65

TREATMENT OF MOLASSES OR MOLASSES SOLUTIONS FOR CLARIFICATION AND DISINFECTION

Treatment	Thermal	Physico-chemical	Chemical	Mechanical
Action	germ-weakening or germ-killing and coagulation	coagulation through shift of pH	precipitating, formation of insoluble compounds	removal of suspended materials
Process	heating	addition of acids or alkalis	addition of superphosphate, water glass, tannin, Al salts, etc.	sedimentation, decanting or filtration or centrifuging
Examples:				
Hot acid clarification molasses solution about 15–20 brix	heating to about 90 °C	addition of sulfuric acid to pH 4.5	addition of 1–2% superphosphate on basis of weight of molasses	decanting of the clear solution
Centrifugal clarification after heating to about 40 °C	heating to near 100 °C	no acid	no additives	separation (*cf.* Table 66)

Cane molasses are fundamentally much more difficult to clarify than beet molasses, and consequently are not popular with yeast manufacturers. The existence of a whole series of clarification methods, some differing in their essential features, indicates that the clarification of molasses is not simple and easy and consequently cannot be carried out by a standard procedure. A number of clarification methods can be employed singly or in combination for the coagulation, flocculation and removal of the undesirable substances from molasses (Table 65). The methods most commonly used are:

A) the hot-acid procedure;
B) centrifugation (centrifugal clarification).

Although the acid content of molasses is rather high in the hot-acid clarification, only a small percentage of the sugar is inverted by this pretreatment. The amount ranges between 5 and 10%, because the free acids are organic acids of the molasses, liberated by the added sulfuric acid. The remaining 90-95% of the molasses saccharose is inverted when the starter yeast is introduced[100]. Centrifugal clarification is characterized by its simplicity; it saves space, steam and time and can be carried out with very slight losses. These advantages outweigh its objectionable feature, namely, that this process is not quite so safe as the hot-acid clarification method, since after-precipitations may occur during the yeasting. Table 66 provides some information about the molasses clarification separators on the market[29].

TABLE 66
MOLASSES CLARIFICATION SEPARATORS
(According to OLBRICH[29])

Manufacturer	Type	Design Open	Design Closed	Output (kg molasses/h)	Mud chamber (l)	Mud capacity of drum (kg molasses)	Power requirement of the separator (kW or HP)*	Drum (rev/min)
1	2	3	4	5	6	7	8	9
Westfalia	Mel. A 3000	×	—	300–500	10.5	1800–3000	1.8 HP	6000
Westfalia	Mel. A 5000	×	—	500–800	15.0	3000–4500	2.5– 2.8 HP	6000
Westfalia	Mel. A 8000	×	—	800–1200	20.5	5000–8000	3.5– 4.0 HP	5500
Westfalia	KG 2006	—	×	250–400	6.0	1500–3000	2.5– 3.5 kW	8500
Westfalia	KG 4006	—	×	500–800	12.5	3000–5000	3.5– 5.0 kW	7000
Westfalia	KG 8006	—	×	1000–1500	20.5	5000–8000	5.5– 6.5 kW	6500
Westfalia	KG 10006	—	×	1200–1800	60.0	15000–25000	7.5– 9.0 kW	4500
Westfalia	SIG 10006	—	×	1500–4000	continuous removal of mud; disk drum with nozzles		10.0–14.0 kW	4500
Westfalia	SDD 9011	—	×	up to 2000	13.0	adjustable periodic removal up to 250 kg/h	± 9.0 kW	4500
De Laval	3	×	—	800–1200	18.0	up to 8000	3.5 HP	
De Laval	L 2930 S	—	×	800–1200	18.0	up to 8000	3.4 kW	6150
De Laval	K 21230 S	—	×	1200–1800	65.0	up to 30000	5.2 kW	4200
De Laval	PX 20930 S	—	×	1000–2400	hydraulic intermittent mud discharge through ejection slots		5.5 kW	5600
De Laval	QX 2930	×	—	1000–2400	continuous removal of mud; disk drum with nozzles		3.3 kW	4600
De Laval	QX 21030	×	×	2000–5000			9.6 kW	6100
Titan	Superjector NS 71	—	×	600–1000	13.0**	hydraulic intermittent discharge through ejection slots	8.5 HP	6000
Titan	Superjector NS 150	—	×	1500–2500	23.0**		20.0 HP	5200

* Since it is customary to give the data in horsepower or kilowatts, the figures furnished by the suppliers were retained because the conversion is not difficult (1 HP = 0.736 kW or 1 kW = 1.36 HP).
** These data refer to the drum capacity; the actual mud chamber is smaller and, for instance, is 7.4 l in the case of the Superjector NS 71.

The amount of molasses that can pass through the separator chambers before complete clogging occurs depends on the suspended solid content of the molasses which is, for beet molasses, around 0.3-0.5%. The performance characteristics (kg molasses/h) can vary widely (Table 66, column 5). The centrifugal clarification also demonstrates that the low specific heat of molasses has practical significance. In Table 67, 1 kg of molasses at 10°C was diluted with 1 kg of water at 80°C, resulting in a solution at 54.7°C. In the reverse instance, with molasses at 80°C and water at 10°C, the temperature of the mixture is 38.7°C.

TABLE 67

DEMONSTRATION OF THE PRACTICAL SIGNIFICANCE OF THE SPECIFIC HEAT OF MOLASSES[4]

Molasses (80 brix, 48 pol resp., $Q = 60$)			Water			Solution of 1 kg molasses and 1 kg water (40 brix, $c_m = 0.78$)	
Temp. (°C)	Spec. heat c	Heat capacity (cal/kg)	Temp. (°C)	Spec. heat c	Heat capacity (cal/kg)	Heat Capacity (cal/kg)	Temp. $\frac{\text{cal} \cdot \text{kg} \cdot {}^\circ\text{C}}{\text{kg} \cdot \text{cal}} = {}^\circ\text{C}$
10	0.5251	$0.53 \cdot 10 = 5.3$	80	1	80	$\frac{5.3 + 80}{2} = 42.65$	$42.65 : 0.78 = 54.7$
80	0.6317	$0.63 \cdot 80 = 50.4$	10	1	10	$\frac{50.4 + 10}{2} = 30.2$	$30.2 : 0.78 = 38.7$

In order to obtain the most efficient removal of the suspended solids, the concentrated molasses from the flow-through sterilizer, diluted with cold water before entering the clarification centrifuge, has to be cooled. As shown by Example 2 in Table 67, 1 kg of water is required for 1 kg of molasses at 80°C for a concentration of 40 brix, which is regarded as optimal for centrifugal clarification. At higher dilutions, the salts, which are predominantly present in the molasses in the non-dissolved state (mostly lime salts), go into solution and so escape being removed in the separator bowl.
If the factory water is at 10, 15 or 20°C the temperature of the molasses, which has been diluted to around 40 brix, will be approximately 39, 42 or 45°C when it enters the separator. With respect to the completeness of the separation of sludge, the best centrifugal performance in molasses clarification is attained below the starting temperature of the fermentation, for instance around 25°C[29]. It is not possible to control this temperature at the required concentration by means of the dilution water alone. For controlled cooling a special cooling device will have to be installed ahead of the separator.

(vii) ***Valuable properties or components***

The grading of molasses with respect to their suitability for the making of yeast should not be confined to the disadvantageous and harmful features. Attention must also be paid to the characteristics and components of the molasses which are favorable and valuable in the growing of yeasts. These include the buffering capacity of the molasses and the growth and nutrient materials.

Buffering capacity of molasses. In spite of the fact that the buffering power of different molasses seems to be rather uniform (see Table 30), the question is still open as to the extent to which this finding holds for individual molasses under the conditions maintained in the yeast factory. The comparability of the molasses given in Table 30 shows that the initial pH values differed by as much as 3.01 pH units and the molasses concentrations do not correspond to the conditions in the yeast factory. In addition, in the interest of accuracy, it is recommended that 0.1 *N* solutions be used instead of *1 N* acid or 1 *N* base for the sake of comparison with data in the available literature.

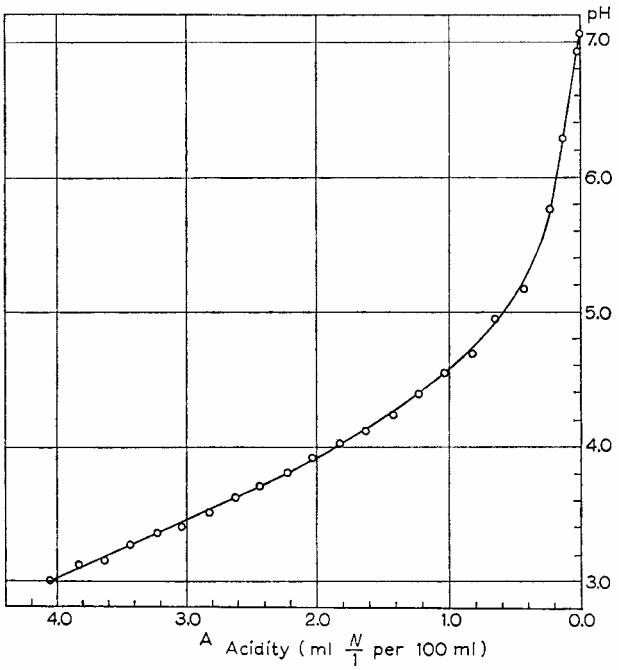


Fig. 11 7. Buffering power of molasses in the pH range 3.0–7.07 at 25-fold dilution (*cf.* note to Table 68).

The buffering power of molasses is of practical interest to the yeast manufacturer only in an acid milieu. The determination of the buffering action should be conducted with regard to the needs of the practical operations. Molasses is subjected to hot-acid clarification and diluted 25-fold. Each 50 ml portion is treated with 0.1 N acid or base, added 1 ml at a time and the resulting change in the pH is determined electrometrically. The acidities are entered as abscissas and the corresponding pH values as ordinates. Fig. 11/7 and Table 68 show the buffering effect of molasses determined in this manner over the pH range 3.0 to 7.07.

This buffering action is typical. Beet molasses, no matter what their origin, differ only in degree but not in the nature of their buffering effects; the buffering of beet molasses shows only slight variations caused by differences in the amounts and compositions of the nonsugars, but without irregularities or sudden pH changes.

The extent and pattern of the buffering capacity shown by widely different beet molasses reveal noticeable differences. No conclusions may be drawn in this respect from the molasses quotients (*Q*). Molasses No. 8 in Table 69 has the highest nonsugar content (*Q* = 59.5) and the highest buffering capacity. Molasses No. 1, with the lowest nonsugar content, does not exhibit the lowest buffering effect. Only slight differences in buffering power were found in general.

There are no beet molasses which are poorly buffered in the Sense of showing irregular action. Earlier reports indicating the contrary[31] have to be discarded. A distinction between ‘mild’ and ‘dangerous’ or ‘difficult’ beet molasses, based on the buffering pattern, have no validity. In contrast with beet molasses, cane molasses (Table 69, No. 9) is extremely inferior in buffering capacity, but the buffering is of the uniform pattern, *i.e.* uncoordinated deviations due to varying weight relationships between the participating substances and which lead to changes in the fundamental character of the buffering behavior do not occur.

In connection with the regular picture of the buffering in molasses (Table 68 and Fig. 11/7), it is an important consequence of the chemical nature of the nonsugars that the buffering action increases the lower the pH; it decreases around the neutral point. The addition of 2 ml of 0.10 *N* hydrochloric acid to a molasses with an initial pH of 5.18 shifts the pH by 0.48 units, but the addition of 2 ml of 0.10 N base changes the pH to 6.94, *i.e.* a shift of 1.76 pH units.

TABLE 68

BUFFERING POWER OF A MOLASSES SOLUTION OF 3.5 BRIX IN THE pH RANGE FROM 3.0 TO 7.07[4]

Solution added	Addition (ml *N*/10 per 50 ml)	Acidity* (ml *N*/l) per 100 ml	Acidity* (ml *N*/l) per 20 ml	pH	Reaction difference in pH units per ml (column 1)
	1	2	3	4	5
N/10 NaOH	2.15	0.00	0.000	7.07	—
	2.00	0.02	0.004	6.94	1.17
	1.50	0.12	0.024	6.29	—
	1.00	0.22	0.044	5.77	0.59
No addition	—	0.42	0.084	5.18	0.00
N/10 H_2SO_4	1.00	0.62	0.124	4.95	0.23
	2.00	0.82	0.164	4.70	0.25
	3.00	1.02	0.204	4.55	0.15
	4.00	1.22	0.244	4.38	0.17
	5.00	1.42	0.284	4.25	0.13
	6.00	1.62	0.324	4.12	0.13
	7.00	1.82	0.364	4.02	0.10
	8.00	2.02	0.404	3.92	0.10
	9.00	2.22	0.444	3.80	0.12
	10.00	2.42	0.484	3.70	0.10
	11.00	2.62	0.524	3.62	0.08
	12.00	2.82	0.564	3.52	0.10
	13.00	3.02	0.604	3.41	0.11
	14.00	3.22	0.644	3.36	0.05
	15.00	3.42	0.684	3.27	0.09
	16.00	3.62	0.724	3.16	0.11
	17.00	3.82	0.764	3.11	0.05
	18.00	4.02	0.804	3.02	0.09
	18.10	4.04	0.808	3.00	—

* For comparison purposes, the acidity is referred to the consumption of ml *N* acid or *N* base per 100 ml solution and in fact on pH 7.07. Normally, however, in the fermentation plant and yeast technology, the degree of acidity or basicity (°Sr, °S, °ac, °Delbrück) is taken as the consumption (in ml) of *N*/1 alkali which shifts the acidity of 20 ml solution (see column 3) but not as here to 7.07, but to the 'neutral point' of glazed litmus paper of the 'Institut für Gärungsgewerbe', Berlin (pH 5.6–5.7). However, for the determination of the buffering in molasses this end point is not as favorably situated as the neutral point pH 7.07.

The graph (Fig. 11/7) reveals that molasses solutions are strongly buffered in the region 3.0-5.0; the buffering is much weaker in the fermenting region (pH 5-6). The example of buffering given in Table 70 is for pure molasses solution (approximately 3.5 brix).

When it is desired to appraise or compare the buffering capacity of various molasses, the pH range in question has to be specified. If buffering is defined as the change in acidity (ml 1 *N)* which changes the pH from 3.0 to 7.07, then this range will adequately include all conceivable changes in pH that may be encountered during the production of yeast. Table 71 shows the buffering occurring under these conditions as observed in molasses diluted 25-fold (see likewise column b in Table 69, molasses No. 5).

The division into sectors makes it possible to state that the buffering action between pH 5 and pH 6 is twice as great as between pH 6 and pH 7. In the region below pH 4, where the detrimental effect of high acidity on yeast starts, the buffering is almost six times as great as in the pH 5-6 region. The uniformly decreasing course of the buffering curve is shown more distinctly if a study is made on molasses solutions at various dilutions. There is practically no change in pH when a molasses is diluted with water to 1%[11]; pH shifting is more pronounced when the buffer concentration falls with increasing dilution. The buffer values of the solutions are related to each other, with respect to their buffering capacity in proportion to their concentrations. Within the separate pH segments the buffering values of the molasses solutions from 5-fold to 50-fold dilution are in the ratio of 1 : 10, and for 25-fold to 50-fold dilution the ratio is approx. 1 : 2 (nee Table 69, columns a, b and c). In terms of magnitude, the buffering of beet molasses at a dilution of 1 : 15 corresponds approximately to the buffer ratio in normal 12% beer wort.

It has been established that für the concentrations and pH regions that are significant for practical yeast production, solutions of 'normal' beet molasses, as well as beet molasses unusual with regard to the nonsugar content, show no fundamental differences in buffering (Table 69).

TABLE 69
BUFFERING IN MOLASSES AT VARIOUS CONCENTRATIONS[4,32]

Type of molasses	No.	Partial regions of buffering*								
		pH 3.0–4.0			pH 4.0–5.0			pH 5.0–6.0		
		a	b	c	a	b	c	a	b	c
Raw sugar and white sugar	1	8.90	1.90	1.04	6.85	1.21	0.62	2.29	0.39	0.27
	2	8.25	2.06	1.06	6.25	1.18	0.60	1.75	0.38	0.26
	3	9.51	1.99	1.12	5.96	1.03	0.58	2.12	0.35	0.20
	4	10.16	2.22	1.12	7.95	1.44	0.63	2.50	0.52	0.26
	5	10.54	2.22	1.17	7.05	1.26	0.56	1.90	0.38	0.26
Refinery	6	9.63	2.28	1.16	6.81	1.26	0.57	1.62	0.34	0.23
	7	9.40	2.05	1.07	6.80	1.32	0.60	2.15	0.47	0.22
	8	11.45	2.23	1.28	7.35	1.33	0.66	2.55	0.41	0.28
Cane	9	3.77	0.82	0.43	2.25	0.51	0.27	1.00	0.26	0.16
		Approx. total buffering (exclusive of cane molasses)								

* a, b and c respectively refer to molasses dilutions of 1 : 5, 1 : 25 and 1 : 50.

Total buffering*						Analytical nature						
										Nitrogen		
pH 6.0–7.0			pH 3.0–7.07						Biol. alcohol productivity (ml)	Total (%)	Assimilated (%)	Alkalinity (acidity) of 100 g in ml N/10 acid (case)
a	b	c	a	b	c	Brix	Pol	Q				
0.63	0.20	0.11	18.67	3.70	2.04	78.5	53.1	67.6	32.8	1.52	0.52	11.50
0.50	0.18	0.16	16.75	3.80	2.08	82.4	52.2	63.3	30.2	1.50	0.51	10.25
0.64	0.17	0.08	18.23	3.54	1.98	79.6	50.2	63.1	30.0	1.95	0.57	11.50
0.55	0.18	0.15	21.16	4.36	2.16	79.5	49.8	62.6	28.6	1.74	0.52	7.25
0.55	0.18	0.25	20.04	4.04	2.24	78.6	48.8	62.1	29.1	2.03	—	6.00
0.52	0.18	0.10	18.58	4.06	2.06	82.4	51.0	61.9	29.8	2.01	0.65	9.75
0.55	0.23	0.16	18.90	4.07	2.05	80.4	49.8	61.9	29.8	1.55	0.43	1.40
0.65	0.11	0.08	22.00	4.08	2.30	80.0	47.6	59.5	28.6	2.12	0.59	3.75
0.50	0.18	0.14	7.52	1.77	1.00	79.4	—	—	36.8	0.23	—	(4.70)
			19.3	4.0	2.1							

During the aeration process the acid relationships in the milieu provided by the molasses change in accordance with the concentration of the solution, the physiological state of the nutrients, and the prevailing growth conditions. Details of the resulting buffering relationships may be found in publications on yeast manufacture. The yeast yield should not be related exclusively to the sugar content of the molasses; an inadequate supply of growth and trace substances and nutrients affect the growth and development of the yeast. With respect to sugar in molasses, in practice for each batch of yeast around 16 kg of reducing substances will be present in the wort for each 1000 kg of molasses sugar used[100]. These reducing materials which are not assimilated originate from metabolic processes of the yeast.

Growth material content of molasses. The content of growth substances in cane and beet molasses was discussed in connection with the composition of molasses (see Tables 34-37 and 39). The supply of growth substances in the molasses is not sufficient in all cases for attaining the highest yields or for insuring the complete development of the yeast.

Before the structure of the organic growth substances was unravelled, they were designated as Bios I, II and III, following the discovery of one phytohormone, called 'Bios'. It is known today that Bios I is identical with the sexivalent cyclic alcohol meso-inositol, Bios II is identical with biotin and Bios III is pantothenic acid.
Pantothenic acid is known to be sensitive to some of the steps of the clarification process. When studies were made of the stability of vitamin B_1 (thiamin), B_6 (pyridoxin) and niacin (nicotinic acid) under the conditions of the hot acid clarification, they showed practically no differences such as in clarified and untreated samples[74]. Reports that these vitamins are adversely affected or destroyed during the clarification cannot be accepted.

TABLE 70

pH SHIFT IN DIFFERENT pH REGIONS IN A MOLASSES SOLUTION OF 3.5 BRIX

pH region	Buffering	pH shift through increasing or lowering the acidity by 0.2 ml *N*/1 per 100 ml (or by 0.04 ml *N*/1 per 20 ml)
3.0–5.0	vigorous	by 0.1 pH unit
5.0–6.0	decreasing	by 0.8 unit from pH 6.0 to 5.2
6.0–7.07	slight	traverses the entire region

TABLE 71

MOLASSES BUFFERING IN SEVERAL SECTORS OF THE pH REGION FROM 3.0 TO 7.07 (25-FOLD DILUTION)

pH	ml *N*/1
3.0–4.0	2.22
4.0–5.0	1.26
5.0–6.0	0.38
6.0–7.07	0.18
3.0–7.07 (total buffering)	4.04

There is evidence that the alkali-sensitive vitamin B_1 decreases during storage. Molasses kept too long in a tank is not as good for the production of yeast because of this gradual loss of vitamin B_1 content. Remainders of old molasses should be scrutinized from this point of view.
The number of growth-promoting factors is not uniform in any given case and depends on the kind of yeast used. Yeast is strongly heterotrophic with respect to growth substances, *i.e.* yeast can suffer an extensive loss of its ability to synthesize growth substances and therefore becomes dependent on the addition of these materials. Yeast reacts very vigorously to such added materials. It is fairly certain that most yeasts require inositol, pantothenic acid and biotin, sometimes combined with thiamin and pyridoxin. Since these growth substances are limiting factors, it is revealing that no satisfactory yields of yeast are obtained when the source of the carbohydrates is more or less the crystalline deposit taken from the bottom of molasses storage tanks. Yeasts grown with a deficiency of nutrient substances not only give low yields, but have also defects in their quality. When pantothenic acid is deficient the yeast tends to liquefy and to autolyze, and easily produces hydrogen sulfide. A shortage of inositol results in a lowered leavening power. From a technological standpoint there need be no fear of lack of inositol except in high-test molasses; this growth substance is present in ample amounts in all other kinds of molasses (*cf.* Table 22) and exists in a stable form. Table 72 gives a review of the growth substance requirements. The amounts of growth substances required to produce maximum yields of yeast from molasses are presented in Table 36.

TABLE 72

GROWTH SUBSTANCE REQUIREMENT OF VARIOUS STRAINS OF SACCHAROMYCES CEREVISIAE AND OTHER YEASTS[4]

Growth substances	Yeast strains: *Saccharomyces cerevisiae*		Various yeasts		
	3	10	38	163	
Biotin	3	10	36	78	Number of strains according to the growth substance requirement
Pantothenic acid	3	10	14	30	
Aneurin, thiamin	1	9	15	33	
Inosite	1	6	4	15	
Pyridoxine	(0)	0	6	13	
Nicotinic acid	—	—	6	13	

The knowledge available about growth substances in molasses and the related problems in the culture of yeasts is still quite incomplete. The investigations published on the role of growth substances in the growth of the yeast are numerous since yeast is a favored model subject for the study of the life functions of micro-organisms. No other micro-organism has been explored as thoroughly as yeast with respect to the action of the growth substances.

Growth substances cooperate in the formation of the yeast cell material. The part played by the vitamins thiamin and riboflavin in the fermentation and respiratory coenzymes is known; nicotinic acid amide, together with adenylic acid, ribose and phosphoric acid are constituents of the cozymase. Pantothenic acid, which cooperates in the acetylation process, is a constituent of the coenzyme A, the constitution of which has not yet been established.

Attention should also be directed to certain amino acids which are significant with respect to growth. These are β-alanine, glutamic acid, lysine, and methionine. The amino acids have a cooperative relationship with the activity of the vitamins. In a stuck of amino acid nutrition of yeast with reference to biotin deficiency, aspartic acid especially showed an ability to activate the growth of the yeast[75]. Complete knowledge of all the growth materials of yeasts will obviously not be available until far in the future.

Trace substances in molasses. The investigation of the significance of trace elements in the growth of yeasts is in its early stages. The identity of the trace materials found in molasses is fundamentally related to the habitat of the sugar beet; trace elements are essential to the successful raising of sugar beets. Not many exact facts are known in this field. Quantitative statements made about the restricted and regular microconstituents of molasses or about their accidental occurrence are not more numerous than the statements made about the 'normal' supply of trace elements in molasses or about the essential needs of yeasts grown under aerobic conditions. It is known that as well as certain amounts of iron, a definite action on the growth of the yeast is exerted by traces of zinc and copper. On the basis of the weight of the yeast about 20 y/% of zinc and 1 y/% of copper are essential for maximal yields[76]. The amounts of copper and zinc given in Table 33 as contained in molasses are more than adequate for the peak yield, taking into account a 25-fold dilution. Traces of lead, tin, iodine, boron, cobalt and manganese are reputed to be of importance to the nutrition of the yeast. The problem of molasses as a source of trace elements essential for obtaining the highest yields of yeast has as yet received limited attention.

Nutrient content of molasses. There must be available to the yeast, in an adequate amount and in a nutritive form, *i.e.* in a diffusable and assimilatable condition, all the substances necessary for the formation of cell substance, and also for satisfactory growth, when the highest yields of yeast are desired. The nutrient requirement of yeast can be deduced from the composition of the yeast substance (Table 73).

TABLE 73

COMPOSITION OF THE YEAST DRY SUBSTANCE

(According to WHITE[4, 37])

Constituent	%
Ash	6–8
Glycogen	1–30
Fat-soluble fraction (real fats, steroids, lipoids, etc.)	1–2.2
Yeast gums	up to 4
Yeast cellulose	up to 5
Proteins and nitrogenous bases, etc.	44–67

The principal elements, C, H, O and N make up more than 94% of the dry yeast substance (Table 74). In the form of organic compounds these essential elements are mainly found in the carbohydrate-nitrogenous yeast substance, disregarding the small amount of fat-soluble materials. The inorganic constituents of yeast are contained in the yeast ash.

The complete utilization of the sugar as the chief component of molasses is the primary objective in the manufacturing process and its yield goal.

This is the basis for appraising the nutritive value of the other constituents of molasses. Any deficiency with regard to sugar has to be compensated by additions. It is obvious that molasses becomes more valuable in proportion to its content of important components other than sugar.

In considering the sugar content of molasses it is necessary to distinguish between total sugar and 'fermentable' sugar. The difference may amount to several percent and is dependent on the kind of molasses supplied for processing. The raffinose content may alter and also the components, which have a reducing action but are not fermentable, may vary. In molasses fermenting plants interest is directed, because of the need to raise the yield, to the utilization of Melibiose which remains alter the partial cleavage of raffinose; the Melibiose is decomposed further by means of prepared beer yeast autolysate. The fermentable portion can amount to as much as 10% of total sugars in cane molasses, and to 5% of the total sugar content in high test molasses[55].

TABLE 74

ANALYSIS OF YEAST DRY SUBSTANCE

(According to values by WHITE[4, 37])

Constituents	% found	Average % found
Carbon (C)	45.0–49.0	47.0
Hydrogen (H)	5–7	6.0
Oxygen (O)	30–35	32.5
Nitrogen (N)	7.1–10.8	8.5
Total ash	4.7–10.5	6.0
Phosphate (as P_2O_5)	1.9–5.5	2.6
Potassium (as K_2O)	1.4–4.3	2.5
Calcium (as CaO)	0.005–0.2	0.05
Magnesium (as MgO)	0.1–0.7	0.4
Aluminum (as Al_2O_3)	0.002–0.02	0.005
Sulfate (SO_4)	0.01–0.05	0.03
Chloride (Cl)	0.004–0.1	0.02
Iron (as Fe_2O_3)	0.005–0.012	0.007
Copper (Cu)	0.001–0.01	0.002
Silicon (as SiO_2)	0.02–0.2	0.08

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TABLE 75

THE NUTRIENT REQUIREMENT OF YEAST WITH REGARD TO THE NUTRITION PROVIDED BY VARIOUS KINDS OF MOLASSES

(According to OLBRICH[4])

Constituent	Average content 100 g yeast dry substance (from Table 74) (g)	Requirement (g) for 27 g yeast dry substance	Amount obtained from molasses (g)			Deficit of demand from column 2 (g)		
			Beet molasses (from Table 2, 3 and 33)	Cane molasses (from Table 54)	High test molasses (from Table 54)			
	1	2	3	4	5	3a	4a	5a
N	8.5	2.295	(1.7)	(0.7)	(0.1)			
(a) of 40% assimilated portion:			0.68	0.28	0.04	1.615	2.015	2.255
(b) of 20% assimilated portion:			0.34	0.14	0.02	1.955	2.155	2.275
P_2O_5	2.6	0.702	(0.06)	(0.9)	(0.3)			
of 50% assimilated portion:			0.03	0.45	0.15	0.672	0.252	0.552
K_2O	2.5	0.675	3.9	3.6	0.9*	+ + +	+ + +	(+ + +)*
MgO	0.4	0.108	0.16	0.07	0.02	+ + +	0.038	0.088
CaO	0.05	0.0135	0.26	0.5	0.1	+ + +	+ + +	+ + +
Cu	0.002	0.00054	0.001	—	—	+ + +	—	—

* The potash content of high test molasses is given also as 0.2–0.7% K_2O, the MgO content as 0.12–0.25%, and that of P_2O_5 as only 0.03–0.22% (see Table 105).

A sugar fermented by yeast will also be assimilated by it, but yeast is also capable of assimilating carbohydrates which it cannot ferment. The question is still open to doubt as to whether, under aerobic culture conditions, raffinose or Melibiose can be assimilated to produce cell substances.
In auxanogram, the pressed yeast cannot assimilate the Melibiose as it lacks the enzyme Melibiose. It may be assumed, therefore, that the unfermentable sugars-at least in part-are not capable of forming yeast substances.
In practice an exact knowledge of the yeast nutrient materials provided in the molasses is assumed to be a sound foundation for a profitable operation; nutrient substances, which are absent or only present in an insufficient quantity for a satisfactory growth, must be added in an appropriate form or supplemented to an adequate degree. Particular molasses being used must be analyzed to learn to what extent it is capable of covering the nutrient demand of the yeast.
If a yield of 100 parts of pressed yeast (27% dry substance) from 100 parts of molasses is taken as a basis, the nutrient demand of a yeast with the average characteristics given in Table 74 is shown in Table 75 (column 1). The compositions of beet and cane molasses (and also of high test molasses) show fundamental differences that are of importance to the alimentation of the yeast. All molasses have a shortage of nitrogen and phosphoric acid, with more or less extensive differences between the different types of molasses (Table 75) and with respect to the variations in individual cases of industrial molasses. Potassium and calcium are present in excess. High test molasses may occasionally have a deficit of potassium (*cf.* note to Table 75). Some cane molasses and high test molasses may show a deficit of magnesium and similarly a critical examination of the Mg-content of beet molasses is in order, as was pointed out in Table 22. A paucity of magnesium must always be kept in mind when beet molasses are involved.
It is known that only that part of the available nutrient is of value for the manufacture of yeast which is present in a state that can be used by the yeast. The measure of the utilizability of the nutrients is the assimilation factor, *i.e.* the amount of a specific material which is present in the finished yeast or which represents the difference of the non-assimilated part. The assimilation factor is highly important for calculating the amounts of nutrients to be added. Laboratory experiments show that 50%, of the molasses phosphate is easily and completely assimilated by the yeast. The yeast manufacturer is particularly interested in the molasses nitrogen from this standpoint.

Nitrogen assimilation factor (NAF). BERGANDER[77] set up the following hypothesis concerning the question as to which nitrogenous materials of molasses are of interest in the growing of yeast:

(I) Inorganic and higher molecular organic compounds are assimilated completely and readily, if the N-bearing group takes the place of a free H-atom in the molecule. Lower aminocarboxylic acids are completely assimilated but with difficulty.

(II) Nitrogen compounds are not assimilatable if:

(a) the N-bearing group takes the place of on hydroxyl group in organic or inorganic compounds;
(b) all the free H-atoms of the ammonia molecule are substituted by organic radicals (as in betaine and choline). An inadequate supply of nitrogen in the molasses has led to many studies and observations in an effort to promote the growth of yeast by extensive use of the molasses nitrogen along with additions of nitrogen, but simultaneously by limiting the amount of nitrogen added to the amount essential for satisfactory growth. The proper dosage of nitrogen during growth greatly influences the characteristics of the yeast, such as its keeping properties, its temperature- and shipping-characteristics, and also its leavening power and its stability in a volume of baked goods. The yield of yeast is affected strongly by the kind and amount of nitrogen added.

For the nutrition of yeast glutamic acid and aspartic acid are the most important nitrogenous compounds. Others having some significance are leucine, isoleucine, glycocoll, valine, γ-aminobutyric acid, alanine, tyrosine, proline, phenylalanine, cystine, serine, lysine, arginine, histidine. Tables 12 and 14 should be consulted concerning the quantities of these amino acids present in beet molasses.
It is necessary to distinguish between *assimilated* and *assimilatable* nitrogen

TABLE 76
THE ASSIMILATION OF MOLASSES NITROGEN BY YEASTS
(According to CLAASSEN[4,78])

No.*	Origin of the molasses		Assimilatable % of total					
			In the main fermentation I			In the secondary fermentation		
		Total N (%)	Increase	Metabolism	Sum	Increase	Metabolism	Sum
	1	2	3	4	5	6	7	8
1	Raw sugar factory (Rhineland)	1.37	35.4	4.5	39.9	2.2	4.4	6.6
2	Raw sugar factory (Rhineland)	1.37	40.3	4.3	44.6	4.4	2.3	6.7
3	White sugar factory (Rhineland)	1.52	45.5	5.0	50.5	7.4	2.4	9.8
4	White sugar factory (Rhineland)	1.20	46.0	4.6	50.6	2.8	2.4	5.2
5	Refinery (Rhineland)	1.61	34.8	3.8	38.6	3.2	4.0	7.2
6	Raw sugar factory (Silesia)	1.92	39.0	4.1	43.1	3.0	1.8	4.8
7	Raw sugar factory (Pomerania)	1.70	34.5	3.9	38.4	1.6	1.7	3.3
8	Raw sugar factory (Hannover)	1.90	37.7	4.2	41.9	3.0	2.0	5.0
9	Raw sugar factory (Brandenburg)	1.70	35.6	4.0	39.6	1.5	2.0	3.5
10	Raw sugar factory (Brandenburg)	1.92	37.9	4.0	41.9	3.2	1.8	5.0
11	Raw sugar factory (Anhalt)	1.80	42.5	4.5	47.0	0.9	1.8	2.7
12	White sugar factory (Rhineland)	1.81	42.1	4.4	46.5	3.5	2.0	5.5
13	White sugar factory (Rhineland)	1.74	43.6	4.8	48.4	1.6	2.1	3.7
14	Refinery (Anhalt)	1.80	36.1	3.9	40.0	4.3	1.8	6.1
15	Refinery (Saxony)	1.83	35.5	3.9	39.4	5.7	2.4	8.1
16	Refinery (Saxony)	1.83	35.9	4.0	39.9	8.3	1.8	10.1
17	White sugar factory (Rhineland) with molasses desugaring	1.36	33.6	4.3	37.9	2.0	2.4	4.4

* Nos. 1–5 refer to 1924/25; Nos. 6–17 refer to 1925/26.

nitrogen / nitrogen — Altogether: Increase	Altogether: Metabolism	Altogether: Sum	% of the molasses: Increase	% of the molasses: Metabolism	% of the molasses: Sum	Non-assimilatable (%)	Remarks
9	10	11	12	13	14	15	16
37.6	8.9	46.5	0.51	0.12	0.63	0.74	Fermenting with pitching yeast
44.7	6.6	51.3	0.61	0.09	0.70	0.64	Fermenting with shipping yeast
52.9	7.4	60.3	0.80	0.12	0.92	0.60	—
48.8	7.0	55.8	0.59	0.09	0.68	0.52	Molasses from decayed beets
38.0	7.8	45.8	0.61	0.13	0.74	0.87	Raw sugar from Central Germany
42.0	5.9	47.9	0.81	0.11	0.92	1.00	—
36.1	5.6	41.7	0.61	0.09	0.70	1.00	—
40.7	6.2	46.9	0.78	0.11	0.89	1.01	—
37.1	6.0	43.1	0.63	0.10	0.73	0.97	—
41.1	5.8	46.9	0.79	0.11	0.90	1.03	Culture process
43.4	6.3	49.7	0.78	0.11	0.89	0.91	Diffusion process
45.6	6.4	52.0	0.83	0.11	0.94	0.88	—
45.2	6.9	42.1	0.79	0.12	0.91	0.83	Single sample
40.4	5.7	46.1	0.73	0.10	0.83	0.97	—
41.2	6.3	47.5	0.76	0.11	0.87	0.96	Fermenting with pitching yeast
39.9	10.1	50.0	0.73	0.18	0.91	0.92	Main fermentation: pitching yeast After fermentation: shipping yeast
35.6	6.7	42.3	0.49	0.09	0.58	0.68	Anomalous molasses

The assimilated portion is smaller than the assimilatable nitrogen value; it refers to the actual nitrogen uptake of the yeast. The determination of the assimilatable nitrogen, which cannot be carried out directly, requires optimal experimental conditions and includes the nitrogen again excreted in the metabolic processes, which in the aeration process amounts to around 8% of the nitrogen content of the yeast produced[78].

CLAASSEN determined the assimilatable nitrogen in two successive charges (Table 76). After the first growth he removed the yeast and again aerated the wort, which contained the remaining nutrient materials as well as fresh starter yeast. The only source of nitrogen was the residual nitrogen from the first fermentation. The yeast from the second growth was definitely undernourished and could not be qualified as standard commercial yeast; it had, however, taken up a certain amount of molasses nitrogen from the residual wort. By comparison of the two fermentations, CLAASSEN calculated assimilatable nitrogen (columns 11 and 14), this being the sum of the increment-N of both yeasts (columns 9 and 12) as well as of the metabolic-N of both worts (columns 10 and 13). This is instructive, but it does not apply to the conditions prevailing in the yeast factory, where the interest lies in the nitrogen assimilated under normal conditions, *i.e.* in the nitrogen present in the yeast substance, which eventually has a direct bearing on the quality of the baker's yeast. To the extent that yeast nitrogen is derived from the raw material, it is a direct measure of the utilized portion of the total molasses nitrogen. There is a great need for a simple and reliable procedure for determining the assimilated nitrogen in molasses. In addition to the biological method for determining, the nitrogen assimilation factor (NAF) of molasses, chemical analysis is becoming important. The principle of the method is that following protective acid hydrolysis of the molasses solution, the usable nitrogen is measured as amino nitrogen by the VAN SLYKE procedure. Under proper conditions[4] reproducible values are obtained which agree with the data obtained by the biological method (Table 78, columns 4 and 5).

The following comments can be made about the determination methods: the classical biological method is awkward and time-consuming with respect to the preparation and performance as well as in the calculation of the nitrogen balance. The values given in Table 76, column 3 and in Table 78, column 4, were obtained biologically. The method demands exact maintenance of uniform experimental conditions to obtain sufficiently reproducible values. The assimilation of nitrogen is influenced by the absolute amount and specific substrate concentration of the nitrogen supply and it is affected by the degree of aeration, the pH and temperature pattern during the growth of the yeast as well as by the kind and condition of the starter yeast[78]. Even if these factors are given careful

consideration, the experimental conditions can at best approximate the factory conditions, since a part of the molasses nitrogen is taken up as 'starvation' nitrogen. The NAF value measured in the laboratory has been found by comparison with large scale operations to be not reached under ordinary conditions because the yeast, at least in part, is more prone to take up inorganic nitrogen. It has been proposed that in assimilation tests more inorganic nitrogen be made available to the yeast, and that this, with the nitrogen of the starter yeast, has to be subtracted from the nitrogen content of the yeast produced to calculate the nitrogen balance. The influence of the supplementary nitrogen can in this way be taken into account with respect to the utilization of the molasses nitrogen. This corrected biological determination of nitrogen has not been adopted for standard laboratory use. The assimilation factor is the upper determining factor, which may not be exceeded in the calculation of the required nutrient material, it is preferably assumed to be lower. This is also the case for the NAF values obtained by the chemical method. The value of the present NAF determination is limited; it should serve as a first orientation. The study of the produced yeast in the factory and the corrections resulting from the nutrient balance cannot be dispensed with in actual practice.
A rapid biological method for determining the NAF in molasses has to be mentioned[4,79].

TABLE 77

NAF VALUES BY A RAPID BIOLOGICAL METHOD

(According to STUCHLIK and associates[4, 79])

Origin of molasses with respect to yeast factory	Polarization	Total nitrogen (%)	N-Assimilation Factor (NAF) determined by a	
			Biological method (%) on 100 l scale (trial method)	rapid procedure (laboratory method)
Trencin I	53.8	1.658	0.632	0.643
Trencin II	51.0	1.560	0.594	0.590
Trenc.-Teplá	51.6	1.509	0.589	0.574
Olomouc-Pavlovice	51.6	1.359	0.425	0.419
Kolin	47.6	1.304	0.430	0.385
Michalovce	49.4	1.849	0.634	0.562
Plzen	50.6	1.655	0.631	0.609
Krásne Brezno	48.7	1.389	0.405	0.351
Liban	51.4	1.559	0.458	0.449
Teplice-Lázne	51.4	1.651	0.519	0.520
Olomouc Hejcin	51.2	1.498	0.433	0.432

The procedure includes the use of an excess of yeast as well as a saccharose supplement to insure the rapid removal of the assimilatable nitrogen from a comparatively small, accurately weighed sample of molasses under moderate aeration; the NAF of the molasses is determined from the difference between the total nitrogen of the molasses and the residual nitrogen of the wort freed of yeast. The results obtained by this method agree well (Table 77) with those of the feeding-in procedure on a 100-l scale. The chemical method represents an acceleration and simplification of the classical method for determining the NAF; it is not subject to the disadvantages of the biological method. The agreement of the values obtained from the two methods (Table 78, columns 4 and 5) is the result of the peculiar composition of the N-components of molasses. Betaine is not attacked during the protected hydrolysis and the composition of the hydrolysate is affected hardly at all by the small quantity of protein present. The primary and secondary degradation products of the other nitrogenous constituents of molasses yield VAN SLYKE nitrogen in accordance with the content of free amino acids.

TABLE 78

NAF VALUES OF VARIOUS BEET MOLASSES[4]

No.	Sugar (%)	Density (brix)	Nitrogen (%)			
			Kjeldahl method	Biological method	Van Slyke method	
					Hydrolyzed molasses	Original molasses (without decomposition)
	1	2	3	4	5	6
1	49.1	76.6	1.64	0.68	0.72	0.27
2	50.3	81.4	1.80	0.77	0.79	0.31
3	49.4	78.4	1.53	0.55	0.54	0.24
4	51.0	81.4	1.86	0.83	0.83	0.28
5	48.3	80.6	1.57	0.54	0.51	0.24
6	49.4	79.9	1.55	0.53	0.56	0.24
7	49.4	80.0	1.47	0.52	0.53	0.21
8	49.2	82.0	1.59	0.54	0.57	0.24
9	52.1	—	1.69	0.71	0.75	0.30
10	50.8	81.1	1.72	0.72	0.73	0.33

The older as well as the recent literature warns repeatedly against overestimating the value of the N-assimilation factor of molasses. This factor gives no assurance of the excellence of the yeast and it often fails with distinctly N-rich molasses. There exist no regularities in the relations between NAF and total nitrogen of molasses. Molasses with high total nitrogen and comparatively low NAF is frequently encountered.

Cane molasses are poor in nitrogen and the content of utilizable nitrogen is mostly around 0.1%. In a solidified cane molasses sample the nitrogen assimilation value was only 0.01%. Considerable variations are found in beet molasses with NAF values up to more than 0.8%. In practice the yeast technologist makes his calculations on the basis that beet molasses contains around 0.3-0.6% utilizable nitrogen. The utilization factor of beet molasses averages 0.4% nitrogen. WHITE[37] maintains that the nitrogen requirement for the yeast production can be largely covered by inorganic nitrogen, and he believes it to be impractical to count on more than 10-20% of useful nitrogen of the total nitrogen of the molasses. It has to be remembered that it is known that yeasts employed in the feed yeast process (*Torula* species) are able to consume up to 80% of the total nitrogen of the molasses. The type of clarification has hardly any effect on the usability of the molasses nitrogen. Changes in the degree of aeration during the growth of the yeast result in no significant differences with respect to assimilation of the majority of the molasses nitrogen. Proposals to raise the assimilation value[4]-such as bacterial disintegration of the molasses nitrogen, especially bacterial degradation of betaine-have no practical significance. It was found that the utilizability of the molasses nitrogen is increased by 5% by lactic acid fermentation. Yeast produced with molasses inverted with mineral acids showed a remarkable increase in leavening power, a result that may be attributed to concurrent hydrolysis of the N-components of the molasses with consequent enhancement of the NAF value. However, this procedure is quite expensive.

TABLE 79

N CONTENT AND NAF VALUES OF MOLASSES FROM SUGAR FACTORIES WITH AND WITHOUT ION EXCHANGE FACILITIES FOR THE DELIMING OF THIN JUICES

(According to WEBER and BECKER[60])

No.	Origin of molasses	Exchange process	Season	% N on basis of 78 brix	% assimilated N of total N (column 5)	NAF
1	2	3	4	5	6	7
1	Pomerania	without	1925	1.67	38.4	0.64
2	Lower Saxony	without	1925	1.88	41.9	0.78
3	Rhineland	without	1937	1.70	38.8	0.66
4	Holland	with	1949	1.74	47.0	0.82
5	Dormagen	with	1950	1.59	40.7	0.65
6	Dormagen	with	1954	1.66	39.9	0.66

The question remains whether or not the changes in the composition of molasses, brought about by deliming thin juices by cation exchangers, and which is fundamentally limited to the replacement of calcium by sodium, are of any importance and whether or not the N-constituents and the NAF are significantly involved (Table 79).

Results of years of study of the nitrogen content and the NAF values of molasses from sugar factories, with or without facilities for removing calcium salts from thin juices by ion exchange, together with analyses furnished by more than half of all the West German sugar factories, give a representative cross-section of the molasses composition. It shows that there is no fundamental difference between the two groups of molasses. In some years there was a slight drop in the nitrogen content of the molasses from factories employing ion exchangers as compared with factories without ion exchange facilities, but the reason for this decrease has not yet been determined. In 1951 the difference was 0.15%; no difference was found for 1954 (Table 80).

TABLE 80

COMPARISON OF THE N CONTENTS AND NAF VALUES OF MOLASSES FROM SUGAR FACTORIES WITHOUT AND WITH ION EXCHANGE FACILITIES FOR THE DELIMING OF THIN JUICES

(According to WEBER and BECKER)

	Factories without ion exchangers				Factories with ion exchangers			
		% N				% N		
Season	Number of factories	Total N calc. on basis of 78 brix	Assimilatable N as % of total N	NAF	Number of factories	Total N calc. on basis of 78 brix	Assimilatable N as % of total N	NAF
1948	9	1.50	40.8	0.62	—	—	—	—
1949	44	1.67	48.7	0.81	—	—	—	—
1951	27	1.67	41.8	0.70	13	1.52	40.4	0.62
1952	12	1.74	40.6	0.70	14	1.60	41.2	0.66
1953	20	1.68	39.8	0.67	15	1.64	39.4	0.65
1954	12	1.61	43.6	0.70	24	1.61	44.2	0.71

The average decrease in the nitrogen content of the ion exchanger molasses during the years of study was 4.8%. The percentage of assimilatable nitrogen remained practically unchanged. In relation to the total nitrogen content, the NAF value of molasses from juices that had been subjected to cation exchange treatment averaged 0.03 % below the value of the molasses from juices that had not been treated. These small differences are within the usual limits of variation. No differences in yield or quality of yeast were observed in the yeast factory when these two kinds of molasses were given parallel treatment. It appears certain that the use of exchangers in the calcium-sodium cycle for the

removal of calcium from the thin juices has no harmful effect on the quality of the corresponding molasses with respect to the production of yeast.

(d) Production of Citric Acid from Molasses

In contrast to the microbiological production of citric acid through fermentation of waste carbohydrates, chiefly from cane or beet molasses by means of suitable strains of mold (*Aspergillus niger* and *Aspergillus wentii*), the method for producing citric acid from citrus fruits (the only process up to 1920) and pineapple wastes (used in Hawaii) is becoming more and more of minor economic importance. As to the system of processing, distinction has to be made between top and bottom fermentation. In Europe most of the fermentation citric acid has till recently been produced by top fermentation, this being the oldest and the classic method. The operation is divided into two main processes, the actual fermentation and the processing stages. Under sterile conditions, molasses solutions (around 15-18 brix) supplied with nutrient and growth substances give yields of 60-80% of sugar in molasses; the yield can be as high as 90%. The concentrations of citric acid in the mash are about 15-20%. The fermentation is conducted at 30-35°C in flat dishes or pans with an area per unit of several square meters. These are placed over each other and housed in fermentation rooms, which have to be disinfected by vaporization (usually with formaldehyde) and are ventilated during the fermentation with conditioned sterile air of a relative humidity of 45-60%. The pans are charged with mash to a height of 10 to 15 cm and inoculated at the fermentation temperature with spores, which have been prepared in the laboratory either in the form of powder or as a suspension. The fungus blanket closes after 2-3 days, and a total of 50-80 kg of fungus mycelial dry substance per ton of citric acid will have formed. The formation of the acid from the sugar in solution is ended after 7-11 days. The cost of the equipment and the difficulty of carrying out the operation with a minimum of labor led WEHMER as early as 1912 to make trials with bottom fermentation in the production of citric acid[104], a problem which could not be regarded as being solved satisfactorily from a scientific and practical standpoint until recently. Since the mycelial structure of the submerged culture differs from that of the surface culture, it is not recommended to use the same strains of mold for both processes.

For the bottom or submerged fermentation process the molasses solution after sterilization is pretreated with an inoculation of spores or precultures, stirred with an agitator and aerated at the same time. Air or even pure oxygen or mixtures of the two are blown, finely dispersed, into the substrate to maintain a suitably high concentration of oxygen. As a rule defoaming agents must be added. The fermentation is complete after 3-8 days. CLEMENT[105] and MARTIN AND WALTERS[106] made studies of the fermenting of beet molasses to citric acid. The latter two investigators developed a pure aeration process in a fermenting tower, in which the maximal formation of acid was reached after only 68 hours.
Both processes have disadvantages; in the case of the top fermentation these are long fermentation time, the space required for the pans, the great expenditure for structural materials (high quality steel, pure aluminium, synthetic resins) capable of withstanding the low pH of 2, and labor costs; the bottom process usually gives varying and lower yields (65-75% citric acid based on the sugar), sensitivity to variations in the composition of the raw material, high requirements as to design and plant construction, and continuous supervision and control. A general decision on the development of the industry in favor of the deep tank process cannot be reached until uniform yields and reliability in the pretreatment of the raw material and the technological operations are assured. The construction of large-scale technical fermenting plants started in 1951 in the U.S.A. for the bottom process.
Details concerning the isolation of the strains of the molds and the bacteriological methods of selection used, the composition and the variation of the nutrient substrates, as well as the precise operating conditions employed, are considered to be trade secrets of the citric acid manufacturers, although these processes can be used and studied without encountering such complicated and difficult problems.
In both processes as applied commercially, the citric acid is recovered from the fermented mashes via precipitation of the insoluble calcium salt, which is decomposed with sulfuric acid into citric acid and calcium sulfate. The filtrate is concentrated, purified (activated carbon filtration) and the product recrystallized.

As a rule, the main raw material, molasses, is subjected to intense pretreatment. Variations in the composition of the molasses ash, especially in the content of trace elements, make themselves evident in the fermentation; investigators report that the bottom fermentation is more susceptible to such adverse influences than top fermentation. The sensitivity of the *Aspergillus* strains in their ability to produce citric acid requires close control of the added nutrient and trace materials, and makes thorough purification and pretreatment of the raw materials imperative. In addition to treatment by ion exchangers, supplementary to purification processes by means of precipitation, clarification and filtration, with or without active carbon and treatment with hydrogen peroxide, the molasses may also be treated with potassium ferrocyanide (around 2-3 g $K_4Fe(CN)_6$. 3 H_2O per kg of molasses) to precipitate the excess of iron in the molasses. The success of the fermentation with regard to citric acid yield is influenced by the substrate concentration of the various elements and their mutual concentration relationships. Molasses contains an excess of potassium and assimilatable nitrogen. Phosphates, magnesium and trace materials may have to be introduced. A good fermentation requires certain minimum and maximum concentrations of heavy metals (iron, zinc, copper, manganese and molybdenum). The iron content in the substrate must preferably be kept below 1 mg/l. When molasses is being processed, the fermentation has to be initiated by adjusting the mash (by means of hydrochloric acid) to an initial pH between 5.7 and 6.3. When extensively purified saccharose or invert sugar solutions are used the starting pH should be adjusted to 1.8-2.5, which is the best value for reducing the danger of infection. No citric acid is formed in molasses mashes when the initial pH is below 4.5. This pH range is traversed smoothly once the acid formation has started and a pH of approximately 2.4 is reached in the end fermentation.
Numerous improvements for increasing the yield and for accelerating the fermentation process have been developed, although these are frequently only applicable to a particular strain of mold or to a special substrate.
The economic importance of citric acid is evident from the demand which extends over various industrial fields. The total consumption of citric acid, whose world production in 1957 was estimated at 50,000 tons per annum, is distributed, according to statistical data for 1954[107], as follows:

60% food and beverage industry (confectionery, soft drinks, essences, marmalades, ices, baking powder, manufacture of dried milk, etc.);
15% chemical industry (synthetic resins, plasticizers);
10% textile and leather industry;
5% pharmaceutical industry;
5% refining of metals;
5% miscellaneous.

In the U.S.A., whose capacity is around 50% of the world production, 40% is used in foodstuffs, 30% by the pharmaceutical industry, and the remaining 30% for miscellaneous purposes[104].

(e) Production of Itaconic Acid from Molasses

The presentation in Table 56 does not include the production of itaconic acid from molasses; its increasing technical importance warrants a brief discussion[80]. The industrial production of itaconic acid, whose dimethyl and dibutyl esters as well as two esters of citric acid are manufactured by Pfizer & Co. of Brooklyn, N.Y., is based on the fermentation of molasses. Five compounds are involved which hitherto have been accessible to only a limited extent. Among them is the readily reactive itaconic acid (methylene succinic acid, HOOCC (: CH_2- CH_2)COOH) for the applications of which more than 60 patents were granted from 1940 to 1955. Now that it can be produced on a large scale, there is every reason to believe that it will find widespread use. Because of its reactivity, itaconic acid is suitable for:

A) preparation of high molecular thermoplastics through polycondensation;
B) the subsequent hardening of there thermoplastics by polymerization;
C) replacing fumaric or maleic acid in the manufacture of alkyd resins;
D) use in its esterified form for the separate or joint polymerization with vinyl monomers by peroxides for the production of transparent materials.

Itaconic acid and its derivatives supply a field of modern chemical technology which ranges from ion-exchange resins (cation exchangers) and rubberlike materials, through soil conditioners, viscosity improvers for lubricating oils, etc., hardening and plasticizing agents, to synthetic resins with most varied properties, such as those which because of their ability to withstand the high temperatures due to friction, are suitable for use in the construction of aircraft designed for supersonic speeds.
The production of itaconic acid from sugar by means of *Aspergillus* itaconicus has been known since 1931. Either top or bottom fermentation may be employ ed for producing itaconic acid on the industrial scale. The fermentation of molasses is carried on with bottom fermentation through the action of *Aspergillus terreus.* This mold is grown in a molasses solution at 35°C under slight pressure. The vessels are made of stainless steel. Inorganic nutrients (including nitrogenous salts) are added during the fermentation. Mechanical stirring is employed and the aeration is done by means of sterile air blown in through a system of jets. The concentration optimum for the formation of itaconic acid is determined by titration. The fermented liquor is drawn off, filtered over vacuum filters and concentrated in multiple effect evaporators. When the concentrated solution is cooled, the crude itaconic acid precipitates. The latter is centrifuged, washed with water, redissolved, and heated with active carbon. The solution is filtered through frame filter presses. The pure acid is precipitated from the clear solution, centrifuged, and dried. The final product is in the form of a colorless crystalline powder.

(f) Production of Butanol and Acetone from Molasses

The method for obtaining butanol and acetone by the fermentation process is determined by the raw materials used. In addition to its use in the original processing of corn, molasses was from 1936 to 1941 the only raw material used as a starting material in the U.S.A., where it served for the production in 1941 of 49,000 tons of butanol and 25,400 tons of acetone. The particular micro-organisms introduced determine whether special additives (for example corn meal, rice bran) must be used or whether the usual supplement of nitrogen and phosphate is sufficient for the direct fermentation. The modern fermentation process operates on beet and cane molasses as well as on high test molasses.

Compared with the fermentation of raw materials rich in starch, molasses offers the following advantages for the butanol-acetone fermentation: easy sterilizability of the mashes; higher yields of butanol at the expense of the ethanol formed concurrently; less infection because of lower fermentation temperature; fermentation of higher concentrations of sugar in a shorter time; simpler cleaning of the fermentation tanks; simpler appliances and distillation columns; and a more favorable price of the sugar in molasses. The yields and the relative amounts of the fermentation products are dependent on many factors, such as the strain of the bacteria, the composition of the mash and the type of molasses. About 1 kg of total solvents is obtained

TABLE 81

YIELD BALANCE OF THE BUTANOL-ACETONE PRODUCTION FROM HIGH TEST MOLASSES[4, 81]

Raw material	Amount (kg)	Product	Amount (kg)
Sugar cane molasses	100	Butanol	11.5
Total dry substance	81.5	Acetone	4.9
Saccharose and invert sugar	57.0	Ethanol	0.5
Crude protein	3.1	Carbon dioxide	32.1
Ash	6.2	Hydrogen	0.8
		Dry vinasse (6 kg crude protein, 6 kg ash)	28.6

from 2.6 kg of high test molasses; the yield is 28-33% on sugar, as shown in Table 81[108].
The molasses is diluted to a sugar content of 5-7%, phosphates (0.3% of the sugar) are added, the solution is sterilized and fermented at 28-32°C with a graded selective culture (0.5-3.0% of the main mash) of the saccharolytic *Clostridium*. The pH at the start of the fermentation is 6.7 and in the course of 16 h the pH falls to about 5.6.

This degree of acidity is maintained by adding ammonia from time to time as needed. Some of the water used for diluting the molasses can be advantageously replaced by spent wash. This substitution results in better utilization of the nutrient materials, higher buffering action, decreased foaming, and improved yields.
The dried slop yields a valuable feed supplement (about 21-37% crude protein material containing 40-80 mg/kg of lactoflavin). This dried vinasse has been recommended for use as a binding material for foundry use. When incinerated, this vinasse leaves an ash with a high potash content[108].

(g) Production of 2,3-Butanediol from Molasses

2,3-Butanediol (2,3-butylenediol, dimethylene glycol) occurs in three stereoisomeric forms, namely:

A) levorotary D (-)-2,3-butanediol ;
B) dextrorotary L (+)-2,3-butanediol;
C) optically inactive meso-2,3-butanediol.

All three of three configurational forms can be produced by fermentation, but there are differences with respect to the kind of ferment used, the fermentable substrate, and in the resulting fermentation by-products which are formed to greater or lesser extents.
The only interest of the process is its use for molasses. Certain molasses ferment well when inoculated with the *Aerobacter*, but only when the organism is acclimatized beforehand. Strains of aerobic molds produce mainly meso-2,3-butanediol and some L (+)-2,3-butanediol. The yields are 36-39% *i.e*. 72-78% of the theoretically possible amounts. A higher total concentration of glycol in the fermented mash is reached, if the sugar concentration is kept around 6% by periodic addition of molasses.
When beet molasses is fermented with *Aerobacter aerogens* or *Pseudomonas hydrophyla,* ethanol, acetoin and lactic acid are formed along with the 2,3 butanediol. The ripe mash is freed of ethanol by distillation and the concentrated syrup contains 20% of the diol. The latter can be distilled with steam at 2.8 atmospheres into a packed column. After being washed with water in a scrubbing column, a diol-water mixture containing 24% diol is obtained.
By adding sodium hydroxide and concentrating, it is possible to obtain dimethylene glycol (98% pure) at a cost that is commercially feasible provided sufficient capacity can be obtained. It may be used as a solvent for oils, fats, waxes, resins, varnishes, lacquers, cellulose derivatives, etc.; because of its hygroscopic properties it can also he used as a drying agent. It finds use in many manufacturing processes such as the preparation of printing inks and pastes, dyes, soaps, synthetic perfumes, ointments and detergents, wood and leather stains, etc. This compound, which was put on the market in 1951 by the Celanese Corporation of America, has become a competitor of such long established materials as ethylene glycol, glycerin and other glycols[4].

(h) Production of Dextran from Molasses

Dextran is a bacterial polysaccharide similar to starch; it is a polyglucosan and hence is made up of glucose structural units. It first came to the attention of the beet sugar industry as an unwanted by-product, which often developed in the sugar juices and clogged the filters. This ‘frog spawn-like’ slime was analyzed by SCHEIBLER[117] and as early as 1869 he found it to be a poly-saccharide $(C_6H_{10}O_5)_n$. Its marked similarity to the dextrins and its high optical rotation led him to name these hydrophilic materials ‘dextrans’. The importance of the dextran fermentation underwent a radical change. Previously it was an infection phenomenon, which was much feared and which constituted a serious technological problem (‘fermentation gum’) in the sugar industry and in the molasses processing plants, but now it has become a commercially applied process[72].
The ‘wild’ dextran fermentation hardly occurs anymore in modern sugar factories because the juice is not cooled during the manufacturing process and the growth of the microflora is greatly repressed by sulfuring. Traces of dextran can still be found in sugar and in molasses.
Under favorable conditions the dextran fermentation can spread widely and produce considerable damage in a short time after it starts in molasses.

Diluted batches of molasses or molasses residues must never be left in storage tanks, since dextran fermentation can proceed even at a relatively high osmotic pressure and at pH values below 8. The fouling of pipes and filters, which may become clogged completely, is especially troublesome. Diluted molasses used in yeast factories is not immune if the solution is allowed to stand around. Most disinfectants, with the exception of formalin, are not very effective because *Leuconostoc,* being enveloped by gelled dextran, is very resistant not only to heat, but also to chemical action.
In 1941 INGELMAN[118], in cooperation with the Swedish Sugar Association, began a series of studies on the colloids of the sugar beet. He found that his attempt to detect tiny amounts of dextran by a serelogical reaction was unsuccessful. Since dextran produced no antibodies, the idea was advanced of using dextran as a plasma substitute since apparently there would be no danger when it was injected into the blood stream. This suggestion awakened wide interest. Since 1948 there has been a growing number of papers dealing with the production of dextran and its use in various fields.
This fermentation phenomenon, which proceeds with formation of dextran and which is known as 'frog spawn', is due to a series of microorganisms *(Leuconostoc mesenteroides, L. dextranicum, L. citrovorum, Betacoccus vermiform, Phytomonas tumefaciens, Streptococcus bovis).* Among these *L. mesenteroides* and *L. dextranicum* are regarded as the best producers of dextran. It is also possible to synthesize dextran biologically from certain dextrins by strains of acetous bacteria such as *Acetobacter capsulatum.* In comparison with the varieties of *Leuconostoc,* the other dextran-formers have little or no technical importance. Different mucilage formers are found in the sugar factory, but they do not produce dextran. Instead the product is laevin, a polyfructosan, for which no commercial use has been discovered. Immobile gram-positive diplococci, about 1 μg in diameter, which can occur in long chains, are characteristic of *Leuconostoc mesenteroides* grown on pentoses. Although they do not form spores, most of these micro-organisms are quite resistant in the dormant stage because they are encapsulated by dextran. The dextran-producing coccus *Leuconostoc mesenteroides* normally resides on all kinds of decaying plant parts. During its growth it forms an exocellular enzyme which polymerizes the glucose portion of cane sugar, the fructose portion of the sucrose being set free. Dextrans, produced by various strains of *Leuconostoc,* differ in the extent of their branching. The dextran chains are made up of about 200,000 glucose units, corresponding to a molecular weight of approximately 40 millions.
The dextran bacteria grow in solutions of the monohexoses, but they produce notable amounts of dextran only in saccharose solutions containing growth substances and mineral salts along with trace materials. HASSID and DOUDOROFF[119] suggest the following reaction:

$$\underset{\text{saccharose}}{(\text{glucose-}1\text{-fructose})_n} \rightarrow \underset{\text{dextran}}{(\text{glucosan})_n} + n\ \text{fructose}$$

Accordingly, only the glucose moiety is consumed for the formation of dextran when the saccharose is broken down; the fructose is partly assimilated and partly liberated and can be recovered from the fermentation liquor. It is notable that dextran cannot be produced successfully if glucose is used alone or mixed with fructose. Its presence as a constituent of saccharose is essential.
Small amounts of mannitol and lactic acid result as by-products. The mannitol can be recovered from the fermented liquor by evaporation after the dextran has been removed. The lactic acid, which causes the pH to fall from 7 to around 4 during the course of the fermentation, can be precipitated as its zinc salt. If selected strains of *Leuconostoc* are used, not much carbon dioxide is produced. The fermentation is of the submerged type and is conducted at 20 to 30°C with gentle stirring since the oxygen demand in the formation of dextrans is very slight. The liquor gradually thickens and in several days a gelatinous more or less coherent mass results. The higher the temperature the lower the yield.
For the technical production of dextran, molasses has until now not been used successfully. Molasses contains too many impurities (colored nonsugars, salts) which are transferred to the dextran, requiring uneconomical purification methods. Therefore, the dextran manufacturer's use exclusively as raw material raw sugar and white sugar, under addition of trace elements, to obtain a microbiologically pure, clinically applicable dextran quality.
Salt free molasses could be taken into consideration for the production of technical dextran. This, however, depends on the fact whether there would be a greater demand for technical dextran of a lower quality.

(i) Other Uses of Molasses

A long and remarkable list would result if all the suggestions and attempts to use molasses that have appeared in patents, papers, etc. were enumerated. Apart from the uses discussed in the previous sections, there have been but few of the suggested uses or possibilities that have attained any practical significance. Some examples are: use of molasses in shoe polishes, rat poisons, fly killers, adhesives; as a fuel and in road paving materials. (Compare the utilization of cane molasses as discussed on page 680.)

The commercial exploitation of molasses is especially obvious in the efforts to widen the use of molasses in human diets. Although, as a tax-free end-product, molasses was sold in Germany during the past few years at 135 D.M. ($35.00) per ton, the same weight, when retailed in small packages for dietary use, brought no less than 3800 D.M. Molasses to be used in brewing must be pretreated by cleansing and clarification steps. Partial cleansing is adequate for molasses that is to serve as an additive of up to 12%; this is accomplished by acidifying and boiling for at least 90 min. If larger proportions of molasses are introduced, the purification must be much more thorough. Definite conditions must be maintained with regard to pH, temperature and concentration. Following the hopping, the molasses wort is clarified which is best done by filtering. Since molasses contains too little assimilatable nitrogen, it is necessary to add ammonium phosphate to the clarified wort. Molasses seems better suited for top fermentation; light beers result which differ hardly at all from the beers prepared from pure malt.

The salty taste of molasses does not appear on high dilution and the molasses taste can be removed easily by treating the molasses with activated carbon. Since beet molasses has an alkaline reaction, it can be adjusted to the pH most suitable for boiling with hops by adding sour whey. If the mixture contains around 0.8-1% molasses sugar it is possible to produce a beer-like beverage with a natural drive by cask fermentation.

Attention should be directed to the fact that, under proper conditions, beet molasses can be a source of B-vitamins, produced by *Bacillus megatherium,* for instance.

(j) Isolation and Production of Nonsugars from Molasses Vinasse

(i) ***Composition of molasses vinasse***

Nitrogenous substances are not made directly from molasses, but rather from the vinasse (slops). It is necessary to distinguish between the molasses vinasse resulting from the manufacture of alcohol (fermentation slops, molasses alcohol or distillery slops) and the vinasse derived from desugaring plants. The compositions of these two types of molasses vinasse differ considerably (Table 82).

The figures presented are based on dry substance of desugaring slops from the Dessau plant, concentrated to 41° Bé, with a polarization between + 1.6 and + 5.0°, or on dry substance with a polarization from + 2 to + 6.4°. This rotation is not due to saccharose; the inverted vinasse gives a higher dextrorotation. Optically active nonsugars are responsible for the rotation. The content in the desugarized vinasse of raffinose, of arabinose (from the degradation of pectin), of glutamic acid and other amino acids, and especially of products derived from sugars formed during the fabrication and during the desugaring of the molasses, is responsible for the optical activity. Only a small amount of saccharose was present in desugarized vinasse from Dessau; the saccharose content in the dry vinasse was less than 1%.

TABLE 82

COMPOSITION OF MOLASSES VINASSES FROM THE MOLASSES FERMENTING AND FROM THE MOLASSES DESUGARING PLANT[84]

Fermenting plant vinasses			*Desugaring plant vinasses**		
Constituent	% form molasses fermentation	% form potato fermentation	Property	Original vinasse	Substance
Water	92.2	94.3	Specific gravity	1.0862	—
Dry substance	7.8	5.7	Brix	20.5	100
From the dry substance:			Dry substance (%)	19.1	100
Ash	1.9	0.7	Water (%)	80.9	—
Digestible organic substances: crude protein	1.0	0.6	Ash (%)	6.62	34.66
Digestible organic substances: crude fat	—	—	Organic nonsugars (%)	12.48	65.34
Digestible organic substances: crude fiber	—	—	Alkalinity (CaO) (%)	0.16	0.83
Digestible organic substances: N-free extractives	3.6	2.2	Pol (direct)	+ 1.0	+ 5.2
Non-digestible organic substances	1.3	2.2	Pol after inversion (I_{20})	+ 1.2	+ 6.3
Starch value	3.7	2.6	Reducible substances after inversion (as saccharose) (%)	1.75	9.16
Albumin	0.3	0.5			
Desugaring vinasses fermented with pressed yeast yielded:					
			Alcohol (g)	0.54	2.83
			Pol (%)	− 0.8	− 4.2
Reducible materials (as saccharose)				0.28	1.57
Fermentable reducible substances $= \frac{\text{alcohol}}{0.49}$				1.11	5.6

* From the molasses desugaring factory Dessau by the Stronia process.

The vinasses from different desugaring processes have varying compositions. Slops from desugaring processes differ fundamentally in composition from the vinasse from molasses fermentation; compounds containing nitrogen and phosphoric acid (P_2O_5) are added to the molasses mashes; these are present in the fermentation slops in the form of yeast substance or metabolic products of yeast. The small amounts of molasses albuminous materials are almost entirely hydrolyzed during the desugaring. Desugaring slops[82] contain more amino acids than those originally present in the molasses (Table 83).

TABLE 83

DISTRIBUTION OF THE TOTAL NITROGEN CONTENT (EXCEPT NITRATE NITROGEN) IN DESUGARING VINASSES[4, 82]

Constituent	Analyses (%)		
	1947	1948	1949
Amino acid N	39.8	39.9	38.5
Betaine N	40.5	40.2	44.2
Ammonia N	1.5	1.9	1.3
Other iodine-precipitable N	4.5	4.4	3.2
Undefined N	13.7	13.6	12.8

TABLE 84

COMPOSITION OF CONCENTRATED MOLASSES VINASSE IN THE DRY SUBSTANCE OF GERMAN MOLASSES FERMENTING PLANTS

(According to KOSACK)

No.	Total N (%)	N (%) Amino acids	N (%) Betaine	Betaine (%)	Glycerin (%)	Total ash (%)	Insoluble (%)	K_2CO_3 (%)	KCl (%)	K_2SO_4 (%)	Na_2CO_1 (%)	KCl + K_2SO_4 calc. as K_2CO_3	Total K salts calc. as K_2CO_3
1	4.03	0.27	1.81	15.1	5.52	23.43	1.59	12.05	2.62	3.55	3.62	5.24	17.29
2	3.92	0.42	1.53	12.81	6.65	23.63	2.05	7.26	6.51	3.72	4.09	8.98	16.24
3	3.91	0.39	1.84	15.36	6.21	22.61	2.07	7.26	5.67	3.58	4.03	8.10	15.36
4	4.33	0.41	1.97	16.45	5.01	23.19	1.43	9.60	4.30	3.00	4.86	6.17	15.77
5	4.18	0.37	1.82	15.50	5.10	22.68	1.78	8.63	5.97	2.32	3.98	7.37	16.00
6	4.19	0.27	1.69	14.11	5.71	23.58	2.14	11.10	2.26	4.83	3.25	5.94	17.04
7	3.93	0.30	1.65	13.79	5.90	23.94	2.20	12.65	2.20	3.97	2.92	5.19	17.84
8	4.69	0.32	1.55	12.94	5.37	25.45	1.51	11.32	2.40	5.74	4.48	6.77	18.09
9	4.25	0.28	1.70	14.20	6.24	22.73	1.78	9.80	2.68	3.03	5.44	4.88	14.68
10	4.28	0.33	1.59	13.28	4.82	25.38	1.52	13.31	2.40	4.64	3.51	5.90	19.21
11	4.01	0.35	1.96	16.37	6.04	22.10	1.70	9.85	3.70	2.25	4.60	5.22	15.07
12	4.36	0.44	1.84	15.78	5.28	20.95	2.46	11.32	2.45	1.98	2.74	3.84	15.16
Average	4.17	0.35	1.75	14.64	5.65	23.30	1.85	10.34	3.60	3.55	3.96	6.13	16.50

Thin molasses slop is concentrated to 38-42° Bé for further processing (*cf.* Table 96). Variations in the composition of concentrated molasses, thick slops and the average values obtained are presented in Table 84.

(ii) ***Production of glutamic acid and betaine***

The production of glutamic acid is the only process of technical and economic importance in the utilization of the concentrated slops for the isolation of nitrogenous nonsugars in molasses. The process consists of the following steps:

A) hydrolysis (with caustic soda, lime, or with hydrochloric or sulfuric acid) of the pyrrolidone carboxylic acid to glutamic acid;
B) concentration of the solution for crystallization of the inorganic salts;
C) removal of the salts (filters or centrifuge);
D) adjustment of the solution to pH 3.2 for the gradual precipitation of the glutamic acid as fine crystals;
E) removal of the crystals of glutamic acid;
F) the filtrate can be processed to obtain betaine.

If sodium glutamate is produced the glutamic acid obtained is dissolved in sodium hydroxide and the solution is decolorized with active carbon. Sodium glutamate of more than 99% purity is obtained by recrystallization.

According to U.S.A. Patent No. 2,510,980 (JACOBS and FITSCH, 1950), ion exchangers can be used for adsorbing the pyrrolidone carboxylic acid. After removing the salts in a first ion exchange treatment, the glutamic acid is converted into its anhydride, pyrrolidone carboxylic acid, by boiling the solution. The cationic amino acids are removed in a second cation exchanger treatment and the pyrrolidone carboxylic acid is retained in an anion exchanger, from which it is recovered. The glutamic acid is made from the pyrrolidone carboxylic acid by hydrolysis.

The direct production of betaine or of betaine hydrochloride in combination with the production of glutamic acid from molasses vinasse is simple, but the slight demand has limited the practical interest in this product.

In beet molasses betaine is present to about 5 %, and to about 12% in the fermented or desugared molasses (with 80% dry substance). According to AMELUNG[110], there are several methods of obtaining betaine. When concentrated molasses vinasse is used, it is treated with an excess of concentrated hydrochloric acid or gaseous HCl (about 50 parts of concentrated HCl or the corresponding amount of HCl per 100 parts thick vinasse) and stirred in the warm for several hours. The alkali chlorides, which crystallize first on cooling (especially KCl), are removed and the mother liquor is concentrated and cooled.

The portion which crystallizes out consists predominantly of betaine hydrochloride. Yields of 70-80% are obtained by fractional crystallization and purification with activated carbon. The betaine can also be extracted by treating the thick slop with equal parts of ethyl or methyl alcohol and heating; the alcohol extract contains up to 50% betaine in the dry substance. After distilling off the alcohol, the method described is used to isolate the betaine (as its hydrochloride) from an aqueous solution. A simpler and different method is to use ion exchangers which retain the betaine and the inorganic cations present in the vinasse or molasses. When the exchange filter is regenerated with diluted hydrochloric acid, the betaine goes into solution and the extract is concentrated. The evaporation residue is extracted with hot absolute alcohol to isolate betaine hydrochloride. The yields are around 50%, of the betaine present[111].

(iii) ***Processing of vinasse carbon***

The utilization of molasses includes the recovery of its salt content. The first method is to work up the salts which crystallize out during the preparation of glutamic acid from molasses. The oldest technical use of vinasse, which is the preparation of charred slop from concentrated vinasses, can also be employed. The weight of charred vinasse is approximately 9-12% of the weight of the molasses[83]; its content of potassium carbonate averages 45%. The composition of the ash varies considerably (Table 85) according to the nature of the molasses or vinasse, the ashing procedure used and the design of the combustion furnace. The content of potassium sulfate depends on whether sulfuric acid or hydrochloric acid was used in the acidification. The organic materials of the vinasse are destroyed during the combustion. The porous charred material is ground in ball-mills, leached with water, and the salt solution is filtered and concentrated.

TABLE 85

COMPOSITION OF VARIOUS CHARRED VINASSES[4]

No.	K_2CO_3 (%)	KCl (%)	K_2SO_4 (%)	Na_2CO_3 (%)	K_2S + $K_2S_2O_3$ (%)	Water (%)	K_3PO_4 (%)	$CaCl_2$ (%)	Insoluble (%)	Loss (%) (*resp.* K_2SiO_3)	Total (%)
1	35.0	19.3	7.2	17.1	—	2.9	—	—	18.0	0.5	100.0
2	58.9	15.2	4.3	15.1	0.5	6.0	—	—	—	—	100.0
3	37.7	20.8	3.1	30.8	7.6		—	—	—	—	100.0
4	47.7	—	15.98	3.86	0.23	11.27	0.81	10.19	11.47	—	
5	30–35	18–22	6–8	18–20	—	—	—	—	15–25	—	
6	36.50	21.26	13.24	7.10	0.34	2.69	0.24	—	18.29	(0.34)	100.0

The by-products are removed by fractional crystallization and the crude potassium carbonate obtained is subjected to a special purification process.

The average yield, using the charring process, is 6% potassium carbonate, 2% potassium sulfate, 1% potassium chloride and 1% sodium carbonate, on the basis of the weight of the original molasses.

(iv) ***Production of distillation gases by carbonization***

A special carbonization process is used to utilize the nitrogenous materials of the vinasse: the thick molasses vinasse is dry-distilled, and in addition to the char, there results a mixture of gases and vapours (Table 86) which is purified in dust and tar chambers.

During the carbonization, ammonia is split from the amino acids, and trimethylamine from the betaine; the trimethylamine is 'cyanized' by 'super-heating', *i.e.*, decomposed into methane and hydrogen cyanide:

$$\underset{\text{betaine}}{CH_3\text{-}COO^-\\ |\\ N(CH_3)_3} \xrightarrow[700\text{–}800^\circ\,C]{\text{dry distillation}} \underset{\text{trimethylamine}}{N(CH_3)_3} \xrightarrow[1000\text{–}1100\ ^\circ C]{\text{super-heating}} \underset{\text{hydrogen cyanide}\\ \text{methane}}{HCN + 2\ CH_4}$$

The gases are cooled and the ammonia removed by scrubbing with 20% sulfuric acid; the resulting ammonium sulfate is recovered. The hydrogen cyanide is removed by passing the gases through a bubble-plate water column. The purified waste gases are burned to generate steam for the thickening of the vinasse. The dissolved hydrocyanic acid is concentrated under vacuum and worked up into sodium (potassium) cyanide by absorption in concentrated NaOH(KOH).

TABLE 86

COMPOSITION OF THE DISTILLATION GASES IN THE CARBONIZATION OF MOLASSES VINASSE[4, 80]

(1. prior to the cyanizing by overheating, 2. later)

1.	Hydrogen, CO_2, CO, H_2, CH_4 and heavy hydrocarbons, N_2, NH_3 and lower amines (methylamine, trimethylamine)
2.	7 to 10% HCN, 5 to 8% NH_3, 8% hydrocarbons, 12% H_2, 18% CO, 24% CO_2 and 24% N_2

About one quarter of the vinasse nitrogen can be recovered as hydrogen cyanide and one quarter as ammonia; the remainder of the nitrogen is lost. In another process, 25% of the nitrogen is obtained as ammonium sulfate and 35% as sodium cyanide[84]. The commercial feasibility of there processes is determined by the demand for, and prices of, cyanides.

(v) ***Biological utilization of molasses vinasse***

In addition to the indirect processing of molasses via vinasse, the biological utilization of the vinasse has to be mentioned. Section 49 of the German Fodder Law states that molasses vinasse is 'the residue of the processing of molasses for alcohol and is not suitable for feeding purposes'. Different proposals have been presented for the feeding of concentrated molasses vinasse. Certain conditions have been set up regarding the materials to be used as carriers for the molasses vinasse. The following figures are given regarding the composition of concentrated vinasse (*cf.* Table 94). The values refer to % dry substance:

crude protein (N X 6.25),	24.7;
pure protein,	5.4;
crude fat,	5.15;
N-free extract,	38.85;
sugar (by the tariff method),	3.36;
organic materials,	68.69;
starch value,	38.4.

More details will be given in the Section 'Feeding of molasses.'

(vi) ***Yeasting of molasses vinasse***

The utilization of non-concentrated molasses vinasse for the preparation of Torula or feed yeast requires some discussion. Molasses vinasse obtained from the molasses fermentation plant is practically free of sucrose and hexoses and also contains no pentoses. The conduct of the Torula yeasting process (*Torulopsis utilis*) differs from the production of *Saccharomyces* yeast from molasses. The usual standards for the determination of yeastable substances is not applicable for Torula.

There are no simple methods which can be applied to practical operations for determining the C-sources in the vinasse involved in the growth of the yeast, nor for measuring the yeast substance metabolic products derived from the fermentation. The possible quantity of yeast sedimented by centrifuging from known volumes has to be determined by experience[85]. At the beginning of World War II, ILLIG[123] was the first to report on the use of molasses vinasse as substrate for the production of Torula yeast to be used as feeding material. The present process is as follows: the molasses slop is fed continuously into a tank provided with a stirrer; there has to be ample aeration and the specified concentration is carefully maintained. The period of growth has been worked out empirically, and at

the end the product is worked up in the usual manner. Superphosphate extract is used as the source of P_2O_5, and any insufficiency in nitrogen requirement is covered by adding ammonium sulfate.
The manufacture of Torula yeast from vinasse entails a high consumption of sulfuric acid. The organic acids liberated from their salts in the acidification with sulfuric acid (and also the glycerin resulting from the alcoholic fermentation) are assimilated by the Torula yeast. The yeasting process is constantly steered toward the alkaline side; the continual pH adjustment consumes a considerable amount of acid.
In the two-stage process there is a greater assurance of an extensive use of the raw materials than in the one-stage process, in which the molasses vinasse as well as water and nutrient solutions are fed continuously into the same vat, from which the yeast mash is drawn off for separation. However, the yield per vat is less in the two-stage process.
The molasses vinasse, which contains at the start about 10 g of dry yeast substance per litre with a concentration of 6.5-7.0 brix, is worked up in a two-stage separation. The first separation contains 40-50 g yeast solid per litre; the second separation contains 150 g yeast solid per litre. The yeast product is washed and dried in a roller drier. The dried commercial product contains 90-94% dry substance.
The final sedimentation yeast recovered from the fermentation (about 3 g per litre) is not added to the manufactured fodder yeast; the yield amounts to 19-20 kg of dark dry yeast per cubic meter of vinasse.
When food yeast is produced, the sedimentation yeast is removed from the vinasse prior to the yeasting; this fraction is used as fodder yeast. The yeast obtained in this way from molasses vinasse is pale yellow; the protein content of the dry substance is 55%.
The yeasting of vinasse by means of Torula or Candida offers no technical difficulties today. As to yields, it has been confirmed[86] that 10-15 kg of dry yeast can be expected per 1000 litres of thin vinasse, corresponding to 5-7 kg of crude protein.

(vii) ***Myceliation of molasses vinasse***

The use of molasses vinasse as substance for the mass production of fungus mycelia by means of *Oospora* fungi through the biosynthetic process was described by FABEL[124] and confirmed by BERGT[86]. The processes patented by the Biosyn Company[125] conduct the formation of mycelia as bottom fermentation under vertical 'rhythmic layering' with concurrent aeration of the mycelial mass, making use of such raw materials as diluted or undiluted hardwood or softwood sulfite spent liquors, hydrolysates, cellulose or pentoses containing materials or wheys. The Biosyn process allows small plants, which cannot afford the installation of proper yeasting equipment, to carry out the myceliation of molasses slops. The production of mycelia is not dependent on the operation of aeration systems and separators; a few tanks with suction or rotary filters are sufficient. The mycelia obtained can be worked up in a number of ways[86]. The crude protein content of the dried mycelial substance corresponds to that of dry yeast. Up to 10 kg of the dried material can be obtained from 1 cubic meter of thin slop on a technical scale, *i.e*. approximately 5 kg of crude protein.
SPECHT[126] conducted a series of experiments to specify the optimum conditions of the submerged culture of *Oospora lactis*. The surface process can be used for growing this organism in molasses vinasse; the shaking process as well as the submerged aeration method can be employed. It was found that the *Oospora* strains employed made poor use of the reducing substances provided by the substrate.

The clear molasses vinasse filtrate used has the following approximate average composition:

reducing sugar (as glucose)	2.24 g/l
nitrogen	5.1 g/l
P_2O_5	0.14 g/1
concentration	10.5-11.0 brix
pH	5.1-5.2

The strains of *Oospora* were grown in stages from: malt wort → agar culture *via* molasses vinasse-agar → molasses vinasse → nutrient solutions. By growing *Oospora lactis* by the surface method with and without additives (Table 86a) and through analyses of the mycelia and the nutrient solutions, data were obtained which showed that good yields can be attained only by adding ammonium sulfate and superphosphate.

The carbohydrates and the carbohydrate building units contained in the molasses vinasse and utilizable by the organism can be taken for granted; no consideration need be given to increasing the amounts of these essential materials.

In alcoholic fermentation the yeast takes up a considerable part of the assimilatable nitrogen of the molasses (30-40%); but the nitrogen in molasses vinasse is present chiefly as non-assimilatable betaine nitrogen. For example, in Table 86a only 6.8 % of the total nitrogen content of molasses vinasse I has been assimilated. The addition of phosphate increases the assimilation of nitrogen (vinasse II), but vinasse nitrogen is taken up with difficulty.

TABLE 86a

YIELDS OF MYCELIA OF OOSPORA LACTIS FROM MOLASSES VINASSE IN THE SURFACE PROCESS WITH AND WITHOUT ADDITION OF NUTRIENT MATERIALS

(According to SPECHT[126])

Constituents	Molasses vinasses		
	Without additives	With 0.2% superphosphate	With 0.15% ammonium sulfate and 0.2% superphosphate
	I	II	III
Initial N(g/l)	4.86	4.86	5.19
Initial P_2O_5 (g/l)	0.151	0.52	0.52
Residual N (g/l)	4.53	4.33	4.50
Residual P_2O_5 (g/l)	0.036	0.271	0.169
Atro* mycelia yield (g/l)	4.7	6.5	9.5
N content of mycelia (%)	6.91	7.30	7.6
P_2O_5 content of mycelia (%)	2.51	3.80	3.65
Mycelia N (g/l)	0.325	0.52	0.72
Mycelia P_2O_5 (g/l)	0.113	0.246	0.346
Assimilated N as % of total N of molasses vinasse	6.8	10.7	—

* Atro = absolutely dry.

Decisive improvement occurred after inorganic nitrogen was added, not only with respect to the myceliar nitrogen content, but also in the yield of mycelia (vinasse III), which amounted to 9.5 g of dry mycelia per litre of vinasse. Table 86b gives an analysis of the dry mycelia obtained in a 3-day surface procedure. The growth of *Oospora mycelia* is increased in the shaking culture (shaking apparatus with 100 movements per min). The growth period was shortened by a day in comparison with the surface method. With continuous shaking the yield after two days at 26-27°C was, in round numbers, 8 g or more of dry mycelia per litre of vinasse. The submerged culture required a pregrowth under uninterrupted shaking (for instance in 4 generations). The fifth generation was grown in a standard apparatus for small scale fermentations equipped with a ceramic aeration candle, the so-called FINK apparatus[127]. Three litres of vinasse were inoculated with 10%, of preliminary culture and aerated at 26-28°C over a period of 18 h with addition of minimum amounts of a defoaming agent. The following schedule was followed:

Volume of air (l/h)	Time (h)
200	2
450	1
150	5
50	10
	Total 18

The final pH was 8.0. As a result of the rapid growth, the quality of the 9.4 g of dry mycelium obtained was excellent. Table 86b gives a comparison of the composition of the fungus mycelium obtained with that of the mycelium resulting from top fermentation.

TABLE 86b

COMPOSITION OF THE DRY MYCELIUM OF OOSPORA LACTIS FROM MOLASSES VINASSE[126]

Constituent	% from dry mycelium	
	in the surface process (after 3 days)	in the submerged aeration process (after 18 h)
Water (4 h at 125 °C)	2.51	5.6
Nitrogen (KJELDAHL)	7.63*	8.59*
Crude protein	47.68*	53.70*
P_2O_5	3.47*	4.27*
Fat (according to SMEDLEY–MACLEAN[128])	10.87*	5.04*

* Absolutely dry.

In further studies on submerged fermentation a laboratory fermenter made of aluminium was used; it could be kept at a constant temperature. Yields of 11 g/l of vinasses were obtained in 18 h under constant stirring and aeration. The air was introduced into the nutrient solution at the rate of 40 l/h by means of a rotary aerator; the liquid was agitated by means of a stirrer at the rate of 420 rev/min. The nutrient salt addition in all processes was found to be adequate using 0.15% ammonium sulfate and 0.2% superphosphate per 100 g of molasses vinasse. It was found recommendable to keep the temperature at 28-29°C. The pH of the nutrient solution should be 5.0-5.3 at the start.
Table 86c gives some analytical data obtained with the laboratory fermenter, for the atro-mycelium yields, the mycelium nitrogen, the mycelial phosphoric acid, the reducing substances and pH of the nutritive solution. Practically all the cultures were free from infections.

TABLE 86c

COURSE OF THE SUBMERGED MYCELIATION OF MOLASSES VINASSE[126]

Organism	Time (h)	Nutrient solution pH	Red. substances as glucose in the nutrient solution (g/l)	Yield of atro-mycelium (g/l)	Yield of mycelium N (g/10 l)	Yield of mycelium P_2O_5 (g/10 l)
Oospora lactis 56	0*	5.2	4.21	0.85	0.156	0.086
	6	5.4	—	0.99	0.93	0.51
	12	7.6	3.90	6.46	6.80	3.62
	16	8.2	3.71	10.21	8.21	3.65
	18	8.5	3.62	11.08	8.50	3.66
	24	8.8	—	10.31	7.02	3.90
Oospora lactis var. fragrans	0*	5.2	3.28	0.083	0.078	—
	18	5.5	3.13	1.25	1.14	0.516
	24	6.4	2.93	5.37	5.55	2.80
	28	7.1	2.80	4.38	4.30	2.16

* Seed.

Under the conditions of the laboratory fermenter, the fermentation was complete after 18 h in the case of *Oospora lactis;* after 24 h there was a decrease in the yield of atro-mycelium and the mycelial nitrogen, while the mycelial phosphorus was still increasing. There was a notable rise in pH at the end. The yield of atro-mycel was satisfactory with 11 kg vinasse per cubic meter which is higher than in any other processes studied.
Oospora fragrans produces only about half the amount of atro-mycelium after 24 h. The yield fell off markedly after 28 h. The rise of the pH was slow during the growth. An esterlike aroma became distinctly evident during the myceliation and persisted in the nutritive solution as well as in the centrifuged mycelium.

6. The Use of Molasses in Cattle Feed and other Feed Products

(a) General Remarks

In terms of soil management, sugar beets yield the highest nutritional value per unit area. It is one of the most demanding of all crops and its requirements include soil, climate, fertilizers and cultivation. It contains high-value organic materials, trace elements and mineral substances. Since one of the fundamentals of proper animal husbandry is to employ home-grown feeds to a considerable extent, special attention should be paid to the feeding of cattle with the by-products of beets. Comparable advantages accrue to the agriculturist when proper use is made of the beet products from the fermenting of these materials. Only a part of the contents of the beets is removed during the manufacture of sugar, *i.e.*, only the substances built up by the assimilation of carbon dioxide from the air concurrent with the absorption of water and various elements from the soil. All the other constituents of the beets taken up from the soil will be found for the most part in the defecation filter mud, but mainly in the form of leaves, dried pulp and molasses. The more completely these nutriments are consumed by the animals in the agricultural cycle: soil-crop-animal digestive tract--manure-soil, the more ideal is the animal economy and the more perfect the use and conservation of the land.

At a yield of 35 metric tons of beets per ha, about 4% of the weight of the sugar beets appears as molasses (1.4 metric tons) which consists of 25-30% organic and inorganic nonsugars. Accordingly, about 0.35-0.42 metric tons of salts and organic nonsugars are removed per ha of beet fields with each crop. If the grower is concerned with replacing this loss he cannot do this by merely feeding leaves and pulp to his cattle and by applying defecation skum to the field. A considerable portion of the valuable substances withdrawn from the soil, *i.e.* minerals and trace elements, combined with vitamins, etc. go into the molasses, which is being used in increasing amounts in stock feed. The portion of the yearly supply of molasses available for the preparation of mixed feeds, especially for drying of and mixing with pulp, as well as for the steadily increasing direct feeding of molasses, is shown in Table 87. The latter applies to the conditions prevailing in the United States and in West Germany.

TABLE 87

PORTION OF THE ANNUAL CONSUMPTION OF MOLASSES FOR FEEDING AND FOR THE FEED INDUSTRY[4]

Season	German Federal Republic			U.S.A.
	Manufacture of mixed feed products (%)	Drying on pulp and direct feeding (%)	Total feeding of molasses (%)	feeding of molasses (%)
1950/51	4.6	15.2	19.8	—
1951/52	6.5	13.4	19.9	57.1
1952/53	7.8	27.6	35.4	56.6
1953/54	8.9	23.8	32.7	72.0
1954/55	9.0	32.2	41.1	68.0
1955/56	13.1	31.4	44.5	65.0

(b) Molasses as Stock Feed

How does molasses work out as stock feed[4,87]? The value of molasses as feed is based mostly on its sugar content (around 50%). In comparison with the carbohydrates in concentrated form, molasses contains a small amount of protein, but it provides also a certain amount of nonprotein nonsugars which have some nutrient value especially for ruminants. In general, molasses should be added to feed when it is essential to compensate for an excess of protein. Molasses has a high mineral content, but it usually lacks adequate calcium and phosphorus. These must be taken into account when preparing mixed feeds and they should be supplied by suitable supplements (*e.g.* lime) or by a proper combination of feeding materials. The figures given in Table 88 apply approximately to the nutritive substance content of molasses and molasses feeds. The high potash content makes it necessary to limit the daily intake of molasses by cattle to 1½-2 kg per head.

TABLE 88

NUTRIENT CONTENT OF MOLASSES AND MOLASSES PULP[4]

Feed product	Dry substance (g/kg)	Digestible protein (g/kg)	Starch (units/kg)
Molasses	790	28	475
Molasses pulp (dried)	900	54	520

TABLE 89

CONTENT OF TRACE MATERIALS IN HAY AND MOLASSES[4, 35]

Micronutrient	Amount found in hay* (p.p.m.)**	Amount found in molasses (p.p.m.)	Ratio hay: molasses
Cobalt	0.04	0.6	1 : 15
Boron	15.0	3.0	1 : 0.2
Iron	160.0	115.0	1 : 0.7
Copper	5.0	4.9	1 : 1.0
Manganese***	200.0	18.0	1 : 0.1
Molybdenum	0.35	0.2	1 : 0.6
Zinc	50.0	34.0	1 : 0.7

* The hay came from a farm in the Black Forest region; it was infected with the Hinsch disease.
** p.p.m. = parts per million (γ/g; mg/kg; g/t).
*** Because of the acid character of the soil in all cases, the manganese content is especially high.

A notable feature of the use of molasses in feeds is its content of trace elements, which are essential to the health of the living organism. These trace elements include together with cobalt, boron, iodine, copper, manganese, molybdenum and zinc, which are present in amounts that are about equal to the amounts found in hay[35]. The cobalt content of molasses is more than seven times that of good quality hay and around 15 times that of cobalt-poor hay (Table 89).
Accordingly, the supplementary feeding of molasses is especially indicated and favorable when the fodder is deficient in cobalt. Though it is not yet known to what extent the cobalt of plants becomes accessible and is actually used when the fodder is ingested, the cobalt supplied by the molasses may be completely assimilatable by the animal.
A malady known as 'witches pestilence' in North Germany and as 'Hinsch disease'* in certain parts of the Black Forest region afflicts dairy cattle and sheep.

*The Symptoms of the Hinsch disease show themselves in dairy cattle during the time of barn feeding, especially between Christmas and Easter after dry summers. Because of increased cobalt requirement, young animals up to their second year are particularly susceptible, so that some farms have never been able to bring the calves to maturity an home-grown feed alone. The problem in certain Black Forest farms is a matter of cobalt. Healthy and diseased farms may be rather close to one other since the deficiency of cobalt is frequently limited to rather sharply-bounded regions, predominantly where granite occurs as a soil-forming rock, and also if the 'Hinsch farms' have only high, exposed grazing areas which sometimes have no more than several centimeters of black earth above the underlying rock. The lower limit is usually accepted as 4 γ Co/g soil.

It is due to a deficiency of cobalt, and the animals exhibit their unusual cravings by licking rocks, etc. This disease occurs in many countries around the world and has been given a variety of names. It is known as 'daising' in Scotland, 'salt sickness' in Florida, 'grand traverse' in Michigan, 'Denmark disease' in Australia (from the West Australian district of Denmark), or 'enzootic marasmus', in New Zealand it bears the name 'coast disease', 'brush disease', or 'Morton's disease' (after a place of this name), and 'pine disease' in Canada and England, and 'nakaturuitis' in Kenya.
Since beet molasses contains relatively muck cobalt, it is used as a palliative in persistent cases, as a cure in mild attacks, and in all cases as a precautionary measure against the results of cobalt deficiency. The dairy requirement of adult dairy cattle (1 mg Co) can usually be met by a supplementary feeding of 1-2 kg of molasses since the cobalt content of this material usually exceeds 0.5 mg/kg. Furthermore, the purely dietetic action of the molasses aids in alleviating the gastric and intestinal disturbances resulting from a deficit of cobalt. The essential production of vitamin B_{12} in the paunch of ruminants, which may have been stopped or destroyed, is brought back to normal by administering cobalt in this way. The importance of the micro-nutrients with respect to their physiological action in the animal body should not be judged exclusively by the quantities in which they occur in molasses. This is shown by the effect exerted by the extremely low cobalt content, which compensates for a deficiency in the feed. By means of radioactive cobalt isotopes it was shown that cattle cannot store cobalt and require fresh administration of this element after a week.
One of the distinctive features of molasses that gives it a special place in the feeding of all animals is its acceptable taste. In addition to its dietetic action, molasses offers the possibility of being mixed with feeds that are not ordinarily accepted by animals or that are eaten unwillingly, or that have a lower nutritive value but which can be made more palatable and more nourishing by molasses addition. In the United States and in the Union of South Africa it becomes more common practice to mix molasses with over-mature, ordinarily rejected pasture grass or hard dry grass; in fact the fields are occasionally not mowed, but instead are sprayed with molasses and then opened to the cattle. Feeding with molasses not only arouses the appetite, and increases the uptake of food in the digestive tract, but also, in the case of cattle, keeps the gastric and rumen flora in a good state of growth during the winter while the animals are kept in the barns.
Molasses is valuable, because, compared with practically all other feeds; it balances the protein and starch relationships and makes a harmonic feeding program possible. Not only is excess feeding of protein avoided in this way, but the milk and butter fat yields are increased. The abundance of food in the spring leads all too easily to serious feeding errors. If 80 kg of green fodder is assumed as the daily ration per cow, this ration will be adequate for a good milk production, as shown in Table 90.
The feeding of proper amounts of molasses will result in a balanced and high quality forage allowing the cows to produce the optimum amount of milk.

TABLE 90

PROTEIN CONTENT AND STARCH UNITS IN GREEN FODDER

Type of fodder	kg milk according to the content of:	
	Protein	Starch units
Young pasture grass	40	20
Young green fodder:		
(a) alfalfa	40	16
(b) red clover	30	17

Since the fat content of milk is largely a matter of heredity, the possibilities of influencing the quality of the milk are admittedly different, but it is possible to smooth out the periodic variations in the milk fat content.
Various feeds (for instance, bran, brewery residues, slops, certain trade wastes and young green fodder) sometimes have an unfavorable effect on the fat content of the milk. It is repeatedly observed that the fat content of the milk averages above 4% when the animals are kept in the barn during the winter months, whereas a yield of 3.5% is considered good in the summer. When molasses is used as a supplement to green feeding, this carbohydraterich material not only balances the protein but also raises the milk fat content. In this connection, FINGERLING observed that the content of milk fat was increased when 5-15% of molasses was added to concentrated feeds[4].

The molasses can deliver to the animal organism trimethylamine, derived from betaine; this is not harmful but under some conditions it may give an off-taste to the milk. This effect can be eliminated or reduced by feeding after milking and by allowing a period of 8 h to intervene between milkings. Many reports of feeding experiments with molasses in summer and winter have been published. These involved dairy cattle, beef cattle, sheep and pigs. Certain precautions must be observed when feeding stock with molasses. The high sugar content and the presence of irritant substances in molasses (betaine, potash) exert a laxative action if too much molasses is fed to the animals. Diarrhea can be prevented by feeding materials simultaneously which have a constipating effect, *e.g*. dried pulp (high pectin content). Furthermore, an upper limit to the amount of molasses to be fed per day must be adhered to; in particular, molasses should not be given to animals far advanced in pregnancy, and young animals should be restricted to small amounts. It is especially important that the feeding of molasses be begun gradually and slowly. Small amounts are given at the start and can be increased daily.

The evaluation of molasses as feed material should be based primarily on the carbohydrate content. The content of protein is very small and the fifteen different amino acids occurring in molasses are also present in relatively low amounts (*cf.* Table 14).

Additions of nitrogenous materials can increase considerably the value of molasses as feed for ruminants. As early as 1919, VÖLTZ recognized that the material flora in the rumen of such animals build up 'crude protein' from simple nitrogen compounds. MILLAR, in 1942, was the first to use ammonia as a nitrogen source and STILES (1951) took out a patent an the preparation of 'ammoniated molasses', in which a combination between ammonia and reducing sugars is brought about at 130-135°C under pressure[116]. However, slight amounts of imidazole and pyrazine compounds are formed and these have a toxic effect. WIGGINS (1956) showed that they can be rendered harmless by acidification. Excellent results were obtained in the United States by feeding ruminants with combined urea-molasses or, to a limited extent, by supplying ammonia molasses. Experience has shown that cattle can be brought to the marketing stage by feeding predominantly agricultural products which had hitherto been regarded as worthless (corn cobs) provided the proper nitrogen-molasses combination is supplied as supplementary feed. The active development of the rumen flora provides a continuous and plentiful supply of micro-organisms to the digestive tract, and after these organisms have died they are digested by the host animal and utilized in the form of essential amino acids which are indispensable. The nitrogenous compounds, such as urea and ammonium salts, are made palatable by the molasses. Optimal conditions for the initiation and maintenance of an intensive rumen culture are in fact not created until the animal has available the combination of the sugar and mineral salt content of the molasses on one hand, and the added nitrogenous compounds on the other. By feeding ruminants with urea-molasses, whose preparation has been subjected to strict control conditions, there results a significant relief of the concentrated feed market in favor of the non-ruminants.

Disadvantages include the fact that the nonprotein containing nitrogen compounds are not utilized by calves up to the age of 12 weeks because of the still deficient development of the rumen flora, and up to 12-16 weeks the utilization is limited; these compounds are digested only by calves over 4 months old. Furthermore, a certain decrease in the digestibility of other feeds, especially protein, was observed when this type of molasses feeding was practiced. According to the findings of DAVIS and associates[88], industrial by-products and other feed-stuffs treated with ammonia could not be utilized to the same extent by the rumen microbes as the nitrogen from urea and from native protein. It is not possible to draw more detailed conclusions because as yet the chemical nature of the products formed from the addition of nitrogenous compounds to feeding materials or industrial by-products is scarcely known. Attention is called to the possibility of toxic reactions, which can manifest themselves as nervous symptoms when comparatively small amounts of ammonia-molasses are fed. Urea is toxic in larger amounts; for instance, death followed in 2½ h after 750 g of urea had been given to milk cows in drinking water.

Swedish studies have shown that 200 g of urea can he supplied per head each day for high milk production; the protein requirement for milk being met 50% by the added urea, whose protein value is set at 50% of the nitrogen content. Parallel trials with urea rations (25 g digestible protein +17 g urea), compared with digestible pure protein (50 g), gave approximately the same milk production. According to German findings, the nitrogen requirement for the production of 7-8 kg of milk per day can be supplemented by a quantity of urea reaching up to 50% of the protein value.

REID[89] reports that feeds which contain urea lead to a gradual change in the utilization, in fact at times sugar and cellulose lag behind starch as a substrate if they are used without roughage, whereas a favorable effect is achieved by using a combination of sugar and cellulose. With control animals, whose protein requirement was met by Soya bean meal, peanut flour or fish meal, in addition to the rations consisting of grains, calves older than 4 months, 40-70% of whose protein requirement was furnished in the form of urea, attained only 82-88% of the comparative weight. Since the value of the urea addition to the diet resides less in the 'fattening' effect than in growth, normal growth can be combined with fattening provided 25% of the protein requirement is supplied in the form of urea-nitrogen. The proportion of urea in the feed is given as 3%, while it makes up 1% of the total feed of dairy cattle.
BELASCO[90] investigated, in artificial rumens, the action of ammonium compounds as nitrogen sources for the rumen flora in contrast to urea molasses. He measured the bacterial activity from the breakdown of cellulose as well as from the amount of urea or ammonia left unconsumed. Under similar conditions, the degraded fraction was 65% in the case of urea, 64% for ammonium carbonate, and 74% for ammonium lactate. Ammonium succinate gave the same favorable results as ammonium lactate.
As a whose, it seems to be established that urea is better suited than ammonia as nitrogen source and that in both instances the most favorable ratios are still to be determined.
Molasses and molasses feeds can replace successfully a part of oats when feeding horses. Molasses exhibits a particularly favorable effect on the general health of horses, and because of its advantageous dietetic action it greatly reduces the danger of colic. Daily rations of 2-3 kg of molasses (according to the work output) seem proper[91]. The former German Imperial Remounting Authority included a supplement of molasses in the feeding directions for their horses, and Scandinavian animal insurance companies are said to have set up corresponding regulations. As may be gathered from numerous German military instructions, feeding of stock with molasses brings considerable advantages, namely:

A) economical high grade feed;
B) nutrient compensation for the excess of protein of green fodder with addition of crude fiber;
C) making palatable raw feed and lower grades of farm products;
D) increased production of milk and its fat content;
E) nutritive balancing of a uniform and high grade feed in the preventive action against fertility disturbances in breeding;
F) saving of oats in the horse barn and prevention of colic;
G) saving of cracked corn and vegetable and grain feeds in swine food;
H) prevention and fighting against certain deficiency diseases;
I) closure of the gaps in the natural agricultural cycle: field-animal stomach-field and the related resulting better use of manure so that the minerals, trace elements and other materials indispensable to high yields are returned to the soil.

(c) Direct Feeding of Liquid Molasses

The feeding of molasses takes various forms and proportions. When fed directly, the molasses is usually offered after it has been diluted with water. The diluted molasses should not be used for drinking purposes but only in combination with raw feed. It is best to pour or to sprinkle the molasses solution over the fodder in the manger or trough. The molasses sticks to the feed materials so that it cannot be picked out of the mixture by the animals. If the distribution is uniform, the rationing can be accomplished with sufficient accuracy if the total amount of molasses to be fed each day is diluted in a tub with water. There are different opinions about the amounts of water recommended for diluting the molasses. For example, the ratio of water to molasses may be 4-6 **:** 1 or 2-4 **:** 1, or even 1 **:** 2. The main criterion is that the solution must allow good mixing with hay, chopped materials, raw feeds, etc.[91] Small mechanical devices are available for aiding in the preparation of molasses feeds, *e.g.* for mixing diluted molasses with chopped straw[39, 44]. In the case of silage it is desirable that the molasses, which should be as concentrated as possible, is well distributed. The desired uniform division is

achieved by using a blower chopper, connected with a small geared pump, provided the molasses is warmed to around 70°C or is diluted 1 : 1 with water.
The difficulties formerly attending the transport of molasses from the factory to the feeding centers have now been overcome and the use of molasses is no longer burdened with troublesome circumstances either with respect to handling or buying. Original molasses can now be purchased in Germany in units of various sizes:

rolling hoop barrels	capacity 200 1(260 kg) or 100 1(130 kg)
profile or seamed barrels	capacity 160 1 (200 kg) or 80 1 (100 kg)
molasses cans	capacity 80 1 (100 kg)

The molasses can be withdrawn from these various types of containers by simple molasses pumps or through spigots which can be pounded or screwed in.

(d) Molasses Mixed Feed

The mixed feeds that were customary when direct feeding of molasses was still unknown in animal husbandry are still available on the feed-market. Despite their relatively higher price, the demand for molasses mixed feeds has grown. A wide variety of materials are used in the commercially prepared molasses mixtures and molasses mixed feeds.
To avoid the common confusion about the kinds of pulp which were used in the past and which have to be considered chiefly as molasses carriers or which are offered in molasses mixed feeds, the standard designations of the varieties of pulp are given in Table 91.

TABLE 91

NOMENCLATURE OF THE DIFFERENT KINDS OF PULP[1, 87]

Kind of pulp	Definitions
1. Fresh pulp	Sliced sugar beets.
2. Sugar (beet) pulp	Dried, fresh, up-to-standard slices of sugar beets.
3. Steffen pulp	Scalded, sugar-bearing pulp (12–20% sugar content).
4. Wet pulp Diffusion pulp	Unpressed diffusion pulp (6% dry substance content).
5. Press pulp Green pulp	Pressed diffusion pulp, 'Expressed pulp' (14–18% dry substance).
6. Dry pulp	Dried pressed pulp.
7. Molasses pulp	Pressed pulp, to which (to about 20% of the dry material) has been added molasses; the pressed pulp–molasses mixture is dried together. (Dried molasses pulp.)
8. Molasses pulp	Dry pulp, which subsequently is mixed with molasses (about 35% of the dry material); molassified dry pulp. (Dry pulp molasses, molasses dry pulp.)
9. Mineralized dry pulp	Mineralized molasses pulp.
(a) Terno pulp	Lime molasses pulp, *i.e.* pressed pulp mixed with molasses and saturation filter cake and then dried.
(b) Sepa patent pulp	Improved terno pulp, *i.e.* after separate precipitation of the organic matter and the phosphoric acid followed by thickening (2nd stage by means of separators) sludge obtained by continuous filtering is treated with molasses, the mixture homogenized and sprayed onto the pressed pulp. The mixture of pressed pulp, sludge, and molasses is dried.
(c) Molasses slop pulp	Dry pulp mixed with molasses slops and dried molasses thick pulp (Table 95); also with additional mixing in of filter cake.

The molasses carriers most commonly employed include the press pulp or green pulp and dried pulp. The wet pulps are pressed (press pulp) and then uniformly mixed with warm molasses and dried. The finished material is called molasses pulp. It is also possible to work up dry pulp, immediately after pressing, with molasses to produce (dry) molasses pulp, *i.e.* molassified dry pulp. Although molasses pulp is about the same as molassified pulp with respect to appearance and keeping qualities, the former is preferred.

The reason is that volatile nonsugars with an unpleasant taste or odor are driven off when the press pulp is mixed with molasses and dried; furthermore it may be that the animals prefer such prepared pulp because it has been partially caramelized.

If, in addition, the press pulp is dried, after being mixed with a certain percentage of carbonation sediment filter cake (corresponding to a maximum of 5% calcium carbonate) mineralized molasses pulp or lime molasses pulp result, called terno pulps. The phosphorus deficiency can be overcome by incorporating a technical phosphate, such as a mixture containing 3.5% calcium carbonate and 1.5% calcium phosphate.
In general, when preparing terno, pulps molasses and carbonation filter cake are added to the press pulps, the filter cake being taken directly from the first filter presses. The system of manufacture of mixed cattle feed emphasizes the value of the comparatively high lime content in that it saves the cattle grower a supplementary feeding of dietary calcium. The content of organic matter in filter cake is small. A new working process was inserted in the Sepa patent pulp.
The organic nonsugars and the phosphoric acid in the raw beet juice are precipitated separately and thickened in two stages. The second thickening stage is conducted in separators, and hence the name 'Sepa' pulps. The resulting sediment is filtered off continuously and mixed with molasses. This mixture is homogenized and sprayed on press pulp. The resulting homogeneous mixture of press pulp, clarification sediment and molasses is drum-dried. The manufacturer lays great stress on the preservation of the protein materials; and a concentrated feed results which possesses the advantages of the terno pulps. Feeding experiments on cows in the experiment stations of the South German agricultural schools have given good results with a marked increase in the y[i]eld of milk and milk fat content. The constituents of the Sepa pulp are: 70% dry pulp; 24% molasses; 6% calcium phosphate and carbonate; and 18% sugar.
The complete processing of molasses into molasses pulps have relieved many beet sugar factories over the whole world of the need to provide separate storage facilities for the molasses, and to dispose of molasses, which prior to the direct feeding of molasses was sometimes a problem.
If no special drying of the finished feed mixture exists it is recommended[101] that the materials be mixed with hot molasses as concentrated as possible (at least 78 brix). The temperature of the molasses should not exceed 80°C, since otherwise the feed cools too slowly and subsequent heating may readily occur in the stored and piled mixture. When mixing with malt sprouts or similar materials which cannot withstand high temperatures without browning, or which have an acid reaction, the temperatures should always be kept lower than 80°C. The molasses intended for mixing should not be heated by live steam jets; closed steam coils should be used, since mixed feeds prepared in this way with molasses thinner than about 78 brix are less stable and readily ferment, especially in summer[101].
The finished mixed feed must be cooled before it can be bagged or stored in silos. Molasses feed spoils fast with a too high water content, with a very bad effect on the cattle.
Other kinds of molasses mixed feeds are prepared by mixing molasses with beer and wort residues, malt sprouts, palm kernel extraction wastes, corn and milo starch residues, wheat and rye brans, flax-seed capsule litter, oat and spelt (German wheat) shells. These materials are permitted by the regulations of the national or state laws governing feedstuffs and conform to the current provisions of the feeding materials ordinances. These provisions were made necessary to prevent the excessive use of molasses carriers of the lowest possible or of no value. Such carriers in many cases were without nutritive value (peat moss*, wood meal, saw dust) and sometimes were actually harmful.
Table 91a gives analytical data for peat molasses manufactured in the northwestern pasture area of Germany[129].

* Since molasses contains no crude fiber, the indigcstible crude fiber portion of peat molasses is a little higher than that of hay. However, while molasses balances the relatively high protein content in the case of hay, the correspondingly valuable constituents are lacking in peat.

TABLE 91a

COMPOSITION OF MOLASSES PEAT[129]

Constituent	% in 20% peat–80% molasses	% in 30% peat–70% molasses
Nitrogenous substance	7.81	7.59
Crude fat	0.26	0.40
Crude fiber	6.88	10.37
Nitrogen-free extractives	51.67	58.67
Total sugar (saccharose)	38.05	36.34

The high molasses feeds contain 30-40% molasses and the proportion by weight is limited to 2 or 3 parts of the permissible impregnated carriers. To a great extent, molasses is used in various kinds of mixed feeds, which contain 5-15% and only occasionally more molasses.
The Standard table given in the German Feedstuff Law permits the following amounts of added molasses:

calf feeds	5 %
calf nutrition meals	5 %
goat mixed foods	10 %
dog biscuits	10 %
dairy cattle feeds	15 %
milk-producing feeds	15 %
cattle fattening feeds	20 %
horse mixed feeds	30 %

Molasses is favored in the preparation of these feeding materials as it aids in the shaping of the product (briquettes or crumbled form). A mixture of 75% beet pulp and 25% molasses can be pressed into solid briquettes under a pressure of 120-150 atmospheres. The addition of molasses decreases losses due to dust and therefore is an economy measure. Some kinds of feed are made more friable or are loosened by adding molasses. The presence of molasses not only improves the storage, transportation and measuring of the mixed feeds but also improves their stability with respect to many of the components which are of importance from a nutritional standpoint, *e.g.* the sensitive vitamins, whose stability is improved by the molasses in mixed feeds.
New applications are illustrative of the modern methods of preparing feeds containing molasses. Green fodder, such as alfalfa, is mixed in a suitable manner with molasses, whose hygroscopicity serves to withdraw the water from the plant cells. The mixture is dried. Another new application is that agar or gelatin is added so that the cooling molasses solidifies into a gel-like mass, which can be handled conveniently.
A special fattening feed, including molasses, was prepared by mixing pressed beer yeast with molasses in the proportion of 1 : 1. The mixture, which can be stored and transported in barrels, is not stable indefinitely when it contains around 50% dry substance, but is stable enough for practical purposes and has been found good for fattening hogs[92].
A remarkable way of using molasses is its application as preservative for small trash fish and for fish wastes (25% molasses and 75% herrings) used as a supplementary food on silver and blue fox farms[4].

(e) Molasses as Additive to Silage

In addition to the direct feeding, *i.e.* by mixing it into the basic fodder or into commercial feeds, molasses has special importance as a safety additive in the preparation of fermented feeds, the so-called silage. Sugar-containing food supplements increase the concentration of fermentable carbohydrates and provide the indispensable nutrients to the lactic acid bacteria, so that they grow rapidly and produce adequate amounts of lactic acid. The occurrence of acetic, and above all butyric, acid infection can be prevented as well as undesirable decomposition of protein. In addition to the advantageous fermentation, a favorable ratio of protein and starch units is also achieved. Depending

on the kind of forage plants and increasing with their protein content, 1-4 kg of molasses is needed per 100 kg of green fodder. For use as a silage adjunct the molasses must be as uniformly distributed as possible over the green fodder. The material to be soured is sprinkled in layers during filling of the silo with the molasses, which should be diluted as little as possible. If a suitable atomizing or spraying apparatus is available the particles of green fodder can be coated with a molasses film; relatively simple additional equipment is needed to adapt a blower feed chopper to finely distribute the molasses during the filling of the silo. It is important that the chopped or shredded material should be packed tightly to have a minimum of air and no ventilation. The consequences of failures cannot be rectified by the added molasses. The cash outlay per cubic meter of silo volume for the security supplement is approximately 20% of the cost of 100 kg of molasses. It may be calculated that 50% of the nutrient value of the molasses will be retained in the silo feed.
The palatability of the fermented feed is enhanced by the molasses, a point of interest since the winter and summer vetches are often not accepted at once by the cattle on account of the bitter materials in these green feeds.
The feeding values to the cattle industry can be fully utilized by sensible supplementary feeding with molasses; it is in the interest of animal husbandry to incorporate molasses to a greater extent in feeding management.

(f) Feeding of Molasses Vinasse

In addition to the importance of feeding liquid molasses or molasses dried on carrier materials, reference should be made to the attempts to feed molasses vinasse[4, 93]. It was a customary practice, more than a 100 years ago in Germany, to feed molasses thin slops, when -as a result of the increased capacity of the molasses fermenting plants- the large volume of slops could no longer be consumed for feeding locally especially in view of the relatively low amount tolerated daily by the animals. Shipping of thin slops to considerable distances is not profitable. At most, the feeding of molasses slops retained no more than a local interest. However, during World War I, the feeding of molasses vinasse was resumed and led to new knowledge of, and practical experience with, pure molasses slops and mixed slops derived from the processing of raw materials containing starch. At that time VÖLTZ showed that nitrogenous compounds present in molasses vinasse (amides, for instance) could be rendered usable by ruminants, provided sugar-bearing feeds were supplied simultaneously. This finding was the basis of the increased use in the United States of urea-molasses.
The data supplied by VÖLTZ regarding the crude nutrient materials, digestible nutrients, and starch value units in molasses thin slops and in thickened molasses slops are given in Table 92.

TABLE 92

CRUDE NUTRIENTS, DIGESTIBLE NUTRIENTS AND STARCH VALUES IN MOLASSES VINASSES (THIN AND THICK SLOPS)[4]

Molasses solutions	Ash (kg)	Organic substance (kg)	Crude protein (kg)	N-free extractives (kg)	Starch value (kg)
100 *kg molasses thick slop* + 75% *dry substance*:					
I. Crude nutrients	18.2	56.8	18.3	38.5	30
II. Digestible nutrients	—	36.4	8.4	22.5	
100 *kg molasses thin slop* + 7.8% *dry substance*:					
I. Crude nutrients	1.9	5.9	1.9	4.0	3.1
II. Digestible nutrients	—	3.8	0.9	2.3	

The starch value of 100 kg of dry substance from a molasses vinasse was 30.6 kg in sugar-free feeding; this was raised to 42.8 kg if sugar-containing feed was supplied simultaneously. (In comparison, the starch value of 100 kg of commercial molasses is 48 kg or about 60 kg per 100 kg of molasses dry substance.)

In view of the high potassium content, which has to be regarded as harmful, VÖLTZ gave the weights shown in Table 93 as the maximum amounts to be fed per day per 1000 kg of body weight.
After an interruption of around 20 years, the matter of feeding molasses slops has been again studied since 1950 with the interest centered on concentrated molasses vinasse, known as 'thick slop'. The latter was prepared in the molasses fermenting plants by boiling down the 'thin' slops for purposes of chemical processing, but these liquors were studied recently from the standpoint of their food value and appropriate feeding form.

TABLE 93

DAILY RATIONS OF MOLASSES SLOPS[4]

Type of animal	Thick slop (75% dry substance) (kg)	Thin slop (kg)
Nursing and pregnant animals	none	none
Horses	none	none
Milk cows	up to 1	up to 10 times the amount of thick slop fed
Pulling oxen, sheep	up to 2	
Fattening cattle	up to 2.5	

The weight of molasses thick slop or concentrated vinasse is about 35% of that of the original molasses. The fact that it had not hitherto been introduced as a nutrient material is ascribed by various workers to its composition (Table 94). With a relatively low starch value of 22.5% (Table 95), molasses thick slop is certainly not a concentrated food. Furthermore, the high ash content (above 20%) is notable; around 75% of this is made up of potassium salts, which may have a bad effect on the animal organism if ingested in considerable amounts. However, the early notions that the high potassium sulfate content of molasses vinasses has a powerful laxative action and that it is a heart poison in large amounts are now regarded as incorrect.

TABLE 94

COMPOSITION OF MOLASSES THIN SLOPS AND MOLASSES THICK SLOPS[4]

Constituents	Molasses Thin Slop (%)	Molasses thick slop	
		(%)	% dry substance
Water	91.00	29.10	—
N-free extractives	3.96	31.19	38.85
(including sugar)	(0.3)	(2.37)	(3.36)
Crude protein	2.22	17.51	24.7
Ash	2.82	22.20	31.31

Because of the high content of betaine, which can be utilized neither by the animal organism nor by the yeast, the pure protein content of molasses vinasse is low in comparison with crude protein (Table 95). Since there is no question of a direct feeding of molasses thick slops, the latter is suitably mixed with carrier materials and mixed feeds for commercial products (for instance, molasses (thick) slop pulp). In addition to pulp, carbonation filter cake is also sometimes used in preparing such feed mixtures (mineralized molasses vinasse pulp).

TABLE 95

COMPOSITION OF MOLASSES SLOPS AND DRY PULPS AS WELL AS MOLASSES SLOP PULPS

(According to REINDEL[4])

Constituents	Molasses thick slop (%)	Dry pulp (%)	Molasses slop pulp (%)
Water	29.10	9.24	14.20
N-free extract	27.54	60.83	52.50
(including sugar)	(2.37)	(9.32)	(7.60)
Crude fat	3.65	0.68	1.42
Crude protein	17.51	7.96	10.35
Pure protein	3.82	7.90	6.88
Digestible albumin	2.83	4.10	3.80
Crude fiber	—	16.57	12.40
Ash	22.20	4.72	9.09
Starch value	22.5*	52.25	44.8

* Without evaluating the amide.

Since satisfactory results were obtained in feeding trials, the following summation can be made:

A) Stable 'molasses thick vinasse pulps' may be prepared without drying by mixing of thick slops with molasses in equipment as used for the preparation of molasses mixed feed. When the vinasse content is high or when superior sugar pulp or STEFFEN pulp is used it is recommended to dry the mixture to obtain better keeping qualities.

B) The objections to the high potash content of the molasses vinasse with regard to its effect on the health of the animals as published in the past went too far. Greater amounts of thick slop can be fed in place of the maximum daily rations suggested by VÖLTZ with no ill effects. The quantities of vinasse prescribed by VÖLTZ can be exceeded by 50% without hesitation.

C) The molasses thick pulps are readily accepted by the animals provided the daily ration is not too high. The digestibility is said to be good and the feeding value corresponds roughly to that of dried beet pulp (dried pulp).

These findings have advanced the utilization of molasses thick pulps considerably, but the problem of improving this protein-poor food to a state comparable with that of potato vinasse is still unsolved. The molasses thick pulps cannot meet present feed requirements because the limit that must be observed in the amount that can be safely ingested per day prevents the supplying of enough protein. Probably the use of molasses thick pulps as feeding material may be aided by efforts parallel to the studies which led to the use of urea-molasses.

7. Standardization of Molasses in the International Molasses Trade

The conditions for the sale of and payment for molasses that are more or less in force in all countries will be illustrated by the practices employed in West Germany and, with slight modification, in the East German region. Although these stipulations no longer have any 'official' status with respect to transactions within West Germany, they are still retained in general as guiding principles.

(a) Sales and Payment Conditions for Beet Molasses

(1) The basic price of beet molasses applies to healthy merchandise containing at least 47% total sugar, calculated as saccharose and determined with MÜLLE R's solution, and having a density of 76.3-78.3° Bg or brix. The total sugar is determined by the method of SPENGLER, TÖDT and SCHEUER.
(2) The density should be ascertained by the dilution method to be 1 **:** 1 by testing with a hydrometer at 20°C.
(3) For reasons of storage stability, molasses that is more acid than corresponds to a pH of 6.8 (limit of error ± 0.1) should not be delivered.
(4) When mixed molasses (cane molasses and beet molasses) is sold, the proportions in which they are mixed must be stated with an accuracy of ± 5% in the broker's note.
(5) The following molasses are not considered as commercial molasses:

(a) molasses with less than 76.3 brix (or about the same ° Bg, corresponding to 40.5° old Baumé degrees (Table 96));
(b) molasses with pH less than 6.8 (± 0.1);
(c) molasses with less than 47% total sugar calculated as saccharose;
(d) molasses with more than 0.15% sulfur dioxide, determined iodometrically.

The commercial specifications fix the minimum sugar content, but do not stipulate any upper limit. This is set in Germany by the Sugar Tariff Law (Zuckersteuergesetz, September 26, 1938) Section 3, Paragraph 2: 'Beet sugar (cane sugar) effluents, beet juices (beet syrup, beet tops and beet wastes) and other beet sugar solutions and mixtures of those products, which have a degree of purity (sugar content in the dry material) of less than 70 parts per hundred, are not subject to the sugar tax.'
Sales agreements sometimes include the 'invert clause' which specifies that the price is to be lowered if the invert sugar content is above 0.25% to a maximum of 1%. Any invert sugar content up to 0.25% is disregarded in beet molasses; from 0.25-1%, the total invert sugar content is multiplied by 5 and the result is made the basis of a decrease in the selling price. Special agreements are made when molasses with more than 1% invert sugar are being sold. This lowering of the selling price stems from the changes such molasses have suffered in the sugar factory, changes which are disadvantageous in the production of yeast. The invert sugar itself is utilized without disadvantage. Other consumers do not set such high requirements. Buyer and seller come to a special agreement when they deal with molasses that are not within the usual commercial range. The selling price is f.o.b. tank cars at the loading dock of the sugar factory.
The commercial specifications in West Germany do not completely agree with those in forte in East Germany. In the latter area, the sugar factories do not have any disposal rights. The sales agreements are negotiated prior to the season on the basis of the yield of molasses anticipated by the government authorities. During the season of 1954/55 there was a possibility that, as an exception, direct contracts could be concluded between the sugar factory and the molasses processing plants. Among the molasses consumers, only the fermentation industry came into this category, since the use of molasses as a feeding material is essentially illegal in East Germany. The molasses involved was priced at 60 German Marks per ton by order of the governmental bureau in charge of the food industry, which fundamentally conforms to the sales conditions in the West German Republic, but specifies that the density be at least 76.2 brix. Each percentage point above 48° polarization is rewarded by a supplementary payment of 1.25 German Marks per ton, and each percent below 47° polarization is penalized with a decrease of 1.25 German Marks per ton.

The Brix readings, which are referred to 20°C, can practically be equated with Balling degrees, which differ merely in the reference temperature (17.5°C). The conversion of Balling degrees into hydrometer degrees of the Baumé scale and into specific gravities has been compiled in Table 96, which accordingly provides a handy and comprehensive conversion table for the molasses trade.

TABLE 96

CONVERSION OF SACCHAROMETER DEGREES (°BALLING) INTO HYDROMETER DEGREES (°BEAUME) AND INTO SPECIFIC GRAVITIES AT 17.5°C

(According to OLBRICH[29])

°Bg	°Bé Old	°Bé New	Spec. grav.	°Bg	°Bé Old	°Bé New	Spec. grav.	°Bg	°Bé Old	°Bé New	Spec. grav.	°Bg	°Bé Old	°Bé New	Spec. grav.	°Bg	°Bé Old	°Bé New	Spec. grav.
0	0.0	0.0	1.000*	21	11.6	11.8	1.088	41	22.4	22.9	1.185	61	32.9	33.5	1.296	81	42.8	43.6	1.423
1	0.6	0.6	1.004	22	12.2	12.4	1.092	42	23.0	23.4	1.190	62	33.4	34.0	1.302	82	43.2	44.1	1.429
2	1.1	1.1	1.008	23	12.7	13.0	1.097	43	23.5	24.0	1.195	63	33.9	34.5	1.308	83	43.7	44.6	1.436
3	1.7	1.7	1.012	24	13.3	13.5	1.101	44	24.0	24.5	1.200	64	34.4	35.1	1.314	84	44.2	45.1	1.443
4	2.2	2.3	1.016	25	13.8	14.1	1.106	45	24.6	25.0	1.205	65	34.9	35.6	1.320	85	44.7	45.5	1.449
5	2.8	2.8	1.020	26	14.4	14.6	1.111	46	25.1	25.6	1.211	66	35.4	36.1	1.326	86	45.1	46.0	1.457
6	3.3	3.4	1.024	27	14.9	15.2	1.115	47	25.6	26.1	1.216	67	35.9	36.6	1.332	87	45.6	46.5	1.464
7	3.9	4.0	1.028	28	15.4	15.7	1.120	48	26.1	26.7	1.222	68	36.4	37.1	1.338	88	46.1	47.0	1.471
8	4.4	4.5	1.032	29	16.0	16.3	1.125	49	26.7	27.2	1.227	69	36.9	37.6	1.345	89	46.5	47.4	1.478
9	5.0	5.1	1.036	30	16.5	16.8	1.130	50	27.2	27.7	1.233	70	37.4	38.1	1.351	90	47.0	47.9	1.485
10	5.6	5.7	1.040	31	17.1	17.4	1.134	51	27.7	28.2	1.239	71	37.9	38.6	1.357	91	47.5	48.4	1.492
11	6.1	6.2	1.045	32	17.6	17.9	1.139	52	28.2	28.8	1.244	72	38.4	39.1	1.364	92	47.9	48.9	1.499
12	6.7	6.8	1.049	33	18.2	18.5	1.144	53	28.8	29.3	1.250	73	38.9	39.6	1.370	93	48.3	49.3	1.506
13	7.2	7.4	1.053	34	18.7	19.0	1.149	54	29.3	29.8	1.255	74	39.4	40.1	1.376	94	48.8	49.8	1.514
14	7.8	7.9	1.057	35	19.2	19.6	1.154	55	29.8	30.4	1.261	75	39.9	40.6	1.383	95	49.3	50.3	1.521
15	8.3	8.5	1.061	36	19.8	20.1	1.159	56	30.3	30.9	1.267	76	40.4	41.1	1.389	96	49.7	50.7	1.528
16	8.9	9.0	1.066	37	20.3	20.7	1.164	57	30.8	31.4	1.273	77	40.8	41.6	1.396	97	50.2	51.2	1.536
17	9.4	9.6	1.070	38	20.8	21.2	1.169	58	31.3	31.9	1.278	78	41.3	42.1	1.403	98	50.6	51.6	1.543
18	10.0	10.2	1.074	39	21.4	21.8	1.174	59	31.9	32.5	1.284	79	41.8	42.6	1.409	99	51.1	52.1	1.550
19	10.5	10.7	1.079	40	21.9	22.3	1.179	60	32.4	33.0	1.290	80	42.3	43.0	1.416	100	51.6	52.6	1.558
20	11.1	11.3	1.083																

* In practice, the following rough approximation is ordinarily used for converting new °Bé into °Bg: new °Bé × 1.8 = °Bg. For instance, 6.8°Bé × 1.8 = 12.08°Bg. This rule has no more than an orienting value for values above 50°Bg.

(b) The Sampling of Molasses

Even the most accurate laboratory studies lose much of their value and do not achieve their objective if the samples do not represent the precise condition of the particular specimen at the time the sample is taken. The peculiar circumstances encountered in the case of molasses have led, in Germany, to the promulgation of strict regulations governing the sampling of this commodity. Directions for the guidance of licensed samplers of molasses, in force from July 1, 1931, include the following:

(i) ***Calculation of overage above* 78 *brix***

In case the supplying sugar factory enters a claim for overages (above *78* brix), it should notify the recipient of this fact on the same day if possible, and at the latest on the day after the departure of the molasses tank or other container.

(ii) ***Arbitration analyses***

If one of the parties demands an arbitration analysis, the sealed samples intended for the analysis should be submitted at once by the parties involved to a chemist who is recognized as being able to conduct arbitration analyses. Basically, the involved parties should agree on a chemist who has been approved for arbitration analyses. The calculated mean from two samples is decisive for the results. The party whose claim differs most from the arbitration analyses is not considered for price settlement between seller and buyer.

TABLE 97

MOLASSES PRODUCTION OF THE WEST GERMAN REPUBLIC[4, 94]

No.	Season	From beet processing and refining of raw beet sugars (t)	From added imported sugar (t)	Molasses yields on beets[5] (%)
1	1946/47	99,160	—	3.19
2	1947/48	103,308	9,416	4.21
3	1948/49	144,107	30,059	3.55
4	1949/50	188,959	31,629	4.38
5	1950/51	272,464	23,009	3.94
6	1951/52	302,577	10,249	4.22
7	1952/53	280,974	17,921	4.29
8	1953/54	369,999	3,198	4.08
9	1954/55	363,806	16,423	3.93
10	1955/56	372,670	16,768	4.25
11	1956/57	336,594	36,663	4.10
12	1957/58	443,063	2,274	4.22

(c) *General Economic Relations of the Molasses Market*

The production of molasses has constantly risen in the West German Republic (see Table 97) because of the extension of the acreage devoted to sugar beets and also because of more intensive methods of cultivation. The present production of molasses in West Germany is about 350,000 tons, which amounts to approximately 58% of the production in the former German Reich. The proportion of the annual yield of molasses from the refining of imported raw sugar has decreased.
The stock on hand and the amount produced each year make up the quantity of molasses that is distributed to various consumers (see Table 98).

TABLE 98
MOLASSES BALANCE OF THE WEST GERMAN REPUBLIC[4,94]

Molasses balance	1950/51 (t)	1951/52 (t)
Amounts on hand and in production:		
(a) Stocks of sugar factories on September 30	5,324	4,859
(b) Production		
(1) from beet processing and refinery raw sugar	272,464	302,577
(2) from imported raw sugar	23,009	10,249
(c) Imported	—	—
Total (a + b + c)	300,797	317,685
Deliveries and consumption:		
(1) Yeast factories	134,408	128,424
(2) Molasses fermentation	11,236	31,166
(3) Tornesch*	8,004	6,549
(4) Citric acid manufacturers	13,647	13,373
(5) Mixed feed factories	13,947	20,795
(6) Export	53,928	53,488
(7) Desugaring	1,998	6,129
(8) Other users	13,023	11,931
(9) Sugar factories (for drying and mixing into pulps, etc. and delivery in liquid state to beet growers)	45,747	42,583
Total	295,938	314,437
Final stock on hand or excess (September 30)	4,859	3,248

* Fermentation Plant and Chemical Works of Tornesch Co., Tornesch in Holstein.

1952/53 (t)	1953/54 (t)	1954/55 (t)	1955/56 (t)	1956/57 (t)
3,248	5,316	6,421	5,403	5,425
280,974	369,999	363,806	372,670	336,594
17,921	3,198	16,423	16,768	36,663
—	—	—	18,479	39,264
302,143	378,513	386,650	413,320	417,946
147,126	159,132	113,529	134,289	164,128
15,044	15,953	8,344	8,998	26,752
—	—	—	—	—
9,544	18,290	16,358	21,837	20,327
23,668	33,583	34,629	53,973	45,535
—	17,292	34,634	3,408	—
9,185	24,349	15,080	26,851	15,992
8,974	13,238	34,263	28,709	22,558
83,286	90,255	124,410	129,830	118,102
296,827	372,092	381,247	407,895	413,394
5,316	6,421	5,403	5,425	4,552

The proportion of the molasses consumed by the fermentation industry, which in Germany is limited practically to the manufacture of yeast, alcohol and citric acid, was approximately 50% of the total consumption of molasses in the West German Republic up to 1953/54 (Table 99) and has shown a falling tendency since then.

TABLE 99

PROPORTION OF THE GERMAN MOLASSES SUPPLY USED ANNUALLY BY THE FERMENTATION INDUSTRY[4]

User	Until 1927/28 (%)	1950/51 (%)	1951/52 (%)	1952/53 (%)	1953/54 (%)	1954/55 (%)	1955/56 (%)
Pressed yeast factories	up to 40	44.7	40.0	48.7	42.4	29.4	32.5
Molasses fermentation plants	10	3.7	9.8	4.9	4.2	2.2	2.2
Citric acid factories	—	4.5	4.2	3.1	4.8	4.2	5.3

The absolute increase in the annual supply of molasses stemming from the growing of more beets contributed to a price development in the West German Republic that was disturbing at first (Table 100). A fair molasses price is of great importance to the earning capacity of the sugar factories. Uncertain speculations as to the amounts of molasses that will result from the campaign are the reasons for the unsettled prices in the molasses market when supply and demand prevail. Through systematic advertising and certain other outlays, the sugar industry has assured itself of an effective regulating factor in the feeding of molasses in various sectors of agriculture. As a result, since 1956 there has been an increase in molasses prices not only in Germany but also in the world market (Table 100). At a price of 12.50 German Marks per 100 kg molasses, the sugar present in the molasses is valued at 25 German Marks per 100 kg, whereas bagged sugar (excluding the beet subsidy and taxes) could bring the sugar manufacturer about twice this amount.

However, the fob factory prices are not the actual cost prices for the processors. There must be added the agent's fee (up to 0.50 Mark per 100 kg), freight and siding charges; in some cases also rent for tank cars and demurrage, and also the monthly extra charges (for instance, 0.10 Mark per 100 kg for storage per month). Depending on the location and other circumstances, these costs will add up to between 5 and 25% of the fob factory price of the molasses.

TABLE 100
DEVELOPMENT OF MOLASSES PRICES FROM OKTOBER 1950 TO 1956
(From Proceeds of sale in D.M./cwt for deliveries in tank cars fob sugar factory[4,94])

Month	1950/51		1951/52		1952/53	
	a	b	a	b	a	b
October	8.94	8.85	13.89	—	10.80	—
November	10.93	9.50	14.99	—	10.59	—
December	10.02	—	16.40	16.60	11.08	11.03
January	10.77	11.50	17.35	17.00	11.38	—
February	11.58	11.75	—	—	14.00	—
March	12.30	—	—	18.00	14.33	—
April	14.00	14.49	19.38	—	14.20	12.60
May	—	14.49	17.00	17.00	—	—
June	14.18	—	—	—	15.00	—
July	14.00	—	14.00	14.00	—	14.38
August	12.40	12.00	13.00	13.00	13.00	—
September	—	11.50	13.10	13.10	13.28	—

a refers to Lower Saxony and b to Rhineland.

1953/54		1954/55		1955/56	
a	b	a	b	a	b
14.00	—	7.00	7.00	11.55	11.75
11.17	—	7.00	7.00	11.75	11.98
—	10.37	7.00	7.00	12.86	12.96
8.85	9.46	7.50	7.50	14.17	14.00
9.00	9.50	11.60	11.25	17.00	16.00
9.50	9.50	11.60	12.50	17.50	17.50
9.75	9.70	11.50	12.50	18.00	—
9.75	9.70	11.50	12.50	18.00	18.00
9.75	10.00	11.60	12.50	18.00	18.50
9.75	10.00	11.95	11.50	18.00	—
9.75	9.60	12.00	11.50	18.00	18.50
8.35	—	—	—	18.00	17.50

The conditions in the molasses market in the United States show that the effect of the use of molasses in animal feeds extends into the world market price, and that the German conditions as discussed previously are no more than a reflection of a universal trend.

TABLE 101
PRICES FOR BLACKSTRAP MOLASSES FOB TANK CARS IN NEW YORK FROM JANUARY 1947 TO OCTOBER 1956[4, 56]
(1 U.S.A. $ = 4.20 D.M.)

Month	(D.M./100 kg)									
	1947	1948	1949	1950	1951	1952	1953	1954	1955	1956
January	15.00	30.00	12.37	6.49	29.60	27.17	8.92	10.14	9.41	12.05
February	15.00	30.00	7.87	6.49	29.60	25.54	9.23	9.73	9.41	12.98
March	15.00	30.00	7.29	6.49	29.60	23.21	9.90	9.41	10.04	12.98
April	16.63	30.00	7.06	6.49	29.60	21.66	10.14	9.73	10.14	12.98
May	19.22	30.00	6.69	6.81	29.20	19.06	10.14	9.73	10.14	13.14
June	18.15	27.93	6.69	8.84	29.20	17.03	9.81	9.73	10.14	13.38
July	17.64	21.57	6.69	11.36	29.20	15.61	9.73	9.73	10.14	13.38
August	18.09	20.68	6.69	14.23	29.20	13.99	10.14	9.73	10.14	14.04
September	18.86	19.47	6.69	16.83	29.20	11.68	10.30	9.53	10.14	14.60
October	20.84	17.19	6.69	21.29	28.79	9.02	10.14	9.33	10.45	17.03
November	24.64	16.28	6.69	25.02	27.17	8.21	9.96	9.33	10.54	21.20
December	27.67	16.28	6.57	26.37	27.17	8.52	10.06	9.33	11.05	23.52
Average for the year	18.89	24.17	7.33	13.06	28.96	16.73	9.87	9.64	10.15	15.09

The Agricultural Marketing Service of the United States Department of Agriculture, Grain Division, Washington, D.C. issues a molasses report giving the course of the molasses supply and its utilization, along with the molasses prices in the United States during the preceding period. Since the producing centers are so far apart, price-setting centers have arisen such as New Orleans in the South and New York City and Albany on the eastern seabord. In general, there has been no stability of the molasses prices in the years since 1954. Contributing to this was the difference in price (from January to October 1955) between New York (9.50-10 German Marks) and New Orleans (8-8.50 Marks) per 100 kg of molasses, *i.e.* an average difference of about 1.59 Marks as opposed to 1.20 Marks in the same period of the preceding year[56]. The course of the price of American molasses, shown in Table 101, has been converted, for comparison purposes, into the units commonly used in Western Europe (gallons/litres/ kilograms/ dollars/ German Marks) as used in Tables 97-100. It should be noted in this connection that the prices were controlled until March 1947. There is a steady decrease in the amount of European molasses sold on the American market. Germany and France were the chief sources of foreign beet molasses for the U.S.A. in the post-war period; this amounted to approximately 84,000 tons in 1954.
Table 102 provides information about the sources and utilization of molasses in the U.S.A..

TABLE 102

MOLASSES BALANCE OF THE U.S.A. FROM 1952–1956[1, 56]

Molasses balance	Molasses supply (1000 t)				
	1952	1953	1954	1955	1956*
A. *Own production*:					
Hawaii**	197	249	243	259	256
Puerto Rico**	269	171	192	228	180
From beets	171	197	233	259	269
Cane sugar factories on the mainland	269	254	238	254	197
Refinery molasses	186	186	166	171	209
Hydrol	93	98	93	93	87
Citrus fruits	47	36	47	41	41
Total own production	1232	1191	1212	1305	1239
B. *Imports*:					
Cuba***	963	1507	1051	1206	1203
Mexico	114	166	197	223	154
Dominican Republic	145	135	124	181	164
Other countries	311	315	394	326	302
Total imports	1533	2123	1766	1936	1823
C. *Exports*	26	78	57	47	5
Total supply (A + B − C)	2739	3236	2921	3194	3057
	Molasses utilization (1000 t)				
	1952	1953	1954	1955	1956*
Ethyl alcohol***	823	932	295	427	466
Potable spirits and rum	11	16	10	16	16
Butanol and acetone	41	129	150	186	176
Feed products	1554	1833	2103	2170	2051
Yeast, vinegar and citric acid	274	285	311	337	362
Edible molasses and miscellaneous	36	41	52	62	72
Total utilization	2739	3236	2921	3196	3143

* Estimated values.
** Only the amounts sent to the American Mainland.
*** Including high-test molasses.

About ten times as much molasses is used in the U.S.A. as in West Germany. In the last five years, the yeast industry and the manufacture of acetic and citric acid together consume around 10% of the yearly supply of molasses, and the production of alcohol, which stands in second place, after the feeding of molasses, accounts for 10-30%. The rapid increase from about 55 to 70% in the use of molasses for feeding purposes is notable and also the importation of very considerable amounts (for

instance, 0.4 million tons in 1954) of high-test molasses, which for the greater part is fermented into alcohol.

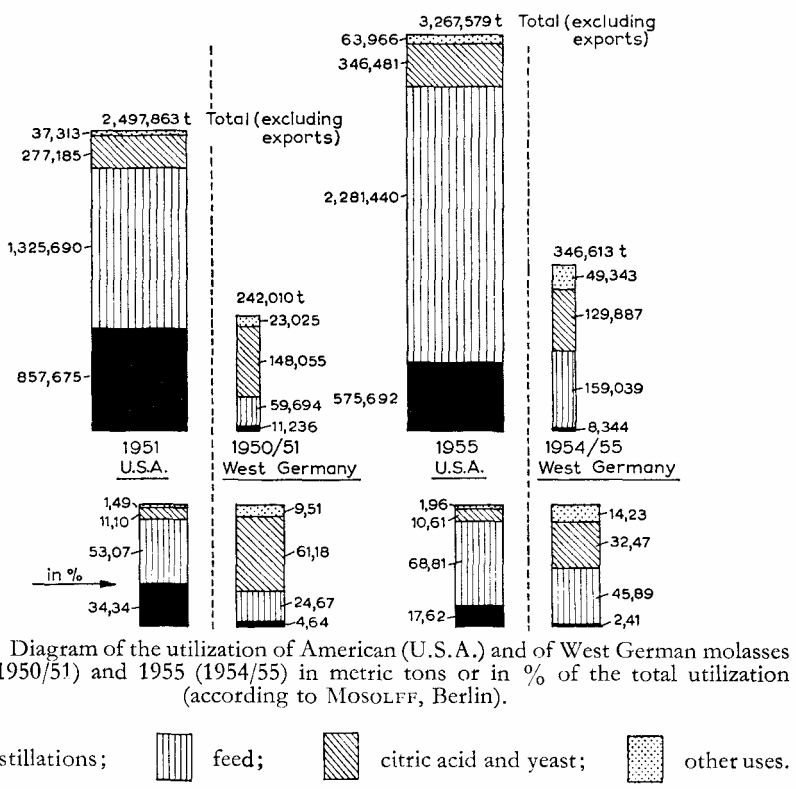


Fig. 11/8. Diagram of the utilization of American (U.S.A.) and of West German molasses in 1950 (1950/51) and 1955 (1954/55) in metric tons or in % of the total utilization (according to MOSOLFF, Berlin).

After a decrease of almost one-third from 1953 to 1954, the alcohol industry again raised its demand for molasses by 8%, and this rise was likewise seen at first in the quantity of molasses consumed in the manufacture of acetone and butanol.

A comparison of the structure of the utilization of molasses in Germany and the United States during 1951 and 1950/51 and also for 1954/55 is informative; the data give interesting insights into the lines along which the American and German molasses markets are developing (Fig. 11/8). During this period the proportion going into feeds in the United States rose from about 53% in 1951 to 70% in 1955. The proportion of the total quantity of molasses going into fermentation outlets fell from more than 34% in 1951 to around 18% in 1955. The other sectors of molasses utilization stayed at about the same levels. In the West German Republic the proportion of molasses put into feeds increased from 25% (1950/51) to around 46% (1954/55). The proportion disposed of in fermentation industries in the same period fell from 4.6% to 2.4%, and likewise the amount consumed in the manufacture of citric acid and in the production of yeast fell from 61% to about 37% in 1954/55.

(d) Consideration of the Molasses Market from the Viewpoint of the Industrial Consumer

The crude product plays the principal role in the computation of manufacturing costs in all industrial uses of molasses. The determination of the value of molasses as a starting material can be ascertained by a comparison with other raw materials serving similar purposes. The evaluation of molasses from the standpoint of various groups of users can also be enlightening. When making such a study, it must not be overlooked, however, that grains and potatoes, for instance, are original products and foodstuffs. In contrast, molasses is a waste product which is not suited to nutrient purposes and, in addition, the possibilities of using it for other purposes are limited.

The exact meaning of the term ‘molasses quality’ is quite questionable, since it carries different connotations in different circles. The fermenter considers primarily the sugar content; the yeast technologist is especially interested in the nitrogen content as well as how much the nitrogen is

assimilatable, and finally, the molasses is judged from its value as a feeding material in case where it is to be fed to animals. To all consumers of molasses, however, a batch of molasses is in general more attractive in price and therefore more advantageous if its concentration is as high as possible.
On the other hand, different molasses are spoken of as being essentially of the same value if one and the same molasses is delivered to one customer at 81 and to another at 77 brix, because the contents agree when recalculated on the basis of a dry substance content of 78 brix. This conversion is of importance in scientific studies, but it may not be applied, and is of no practical value, when dealing with the consumers of molasses.
Molasses is compared in the first place with such materials as are ordinarily accepted by fermenting industries as raw materials (Table 103). The raw material costs were based on saccharose (column 5 in Table 103).

TABLE 103

EVALUATION OF MOLASSES AND STARCH CONTAINING MATERIALS AS RAW MATERIALS[4]

Raw materials	Starch content (%)	Market price of raw material (D.M./100 kg)	Raw material evaluation for use in: Manufacture of spirits: Starch content as disaccharide equivalent[1] (%)	Manufacture of spirits: Price per kg saccharose or equivalent (D.M.)	Feeding: Biological starch value[2] (kg/100 kg)	Feeding: Price for biological starch value (D.M./kg)
1	2	3	4	5	6	7
Sorghum	60	42.00	63.3	0.66	74.2	0.56
Rye	57	38.00–40.00	60.2	0.63–0.66	71.3	0.53–0.56
	54		57.0	0.67–0.70		0.36–0.41
Potatoes	18	7.20–8.10	19.0	0.38–0.43[3]	19.7	0.27–0.32
		5.40–6.30		0.28–0.33[4]		
Molasses	—	19.38	48.0	0.40	47.6	0.41
		12.00		0.25[5]		0.26
		8.85		0.18		0.19

[1] Monosaccharide : disaccharide : polysaccharide is 100 : 95 : 90.
[2] Sum of all feed values through evaluation of the constituents as starch values, such as: pure starch, N-free extract and crude fiber sometimes 1 : 1; digestible protein 1 : 0.94; digestible fat 1 : 2.
[3] Price per kg of starch in industrial potatoes is D.M. 0.40–0.45.
[4] Price per kg of starch in industrial potatoes is D.M. 0.30–0.35.
[5] Purchase prices of molasses for the years 1950–1954 (*cf.* Table 100), *not* cost prices.

When it is considered that under prevailing conditions the price of potatoes has reached the allowable limit for the manufacture of potato starch and for the fermenting of potatoes (price per kg of starch in industrial potatoes is $ 0.11), the peaks in the price of molasses in the past years are disquieting. The assumption that molasses is the cheapest of all raw materials applies only to those periods when the fermenter finds that the price of industrial potatoes is not falling or when the price of molasses is not rising. Furthermore, it should be noted that the cost price to the purchaser of molasses is about 5 to 25% above the price fob sugar factory (*cf.* Tables 100 and 101). If for feeding purposes the molasses sugar is calculated according to the biological value (Table 103, columns 6 and 7), the relation between potatoes and molasses remains practically the same as in the evaluation for the manufacture of alcohol. The value of molasses as feeding substance should be judged on this basis. Rising prices of molasses are not warranted in the interest of the feed industry. The proper valuation of molasses as raw material for the manufacture of yeast must likewise be based on the price level which is applicable to the fermenting industries and to the production of feed materials. Consequently, the efforts which were made to introduce a separate molasses price for the yeast industry should be discouraged. The justification was based on the following arguments[96]:
In addition to saccharose, there are also nitrogenous materials in molasses, in fact the assimilatable nitrogen amounts to 0.3-0.8%. Since a good quality of yeast in high yields cannot be grown without organic nitrogen, it is imperative, in case no molasses nitrogen is available; to rely on equivalent nitrogen such as is present in malt sprouts. From the standpoint of composition, the soluble malt sprout nitrogen, like that derived from molasses, consists predominantly of amino acids and to a slight extent

of acid amides. On the basis of this parallelism it is possible to draw conclusions regarding the value of the utilizable molasses nitrogen (Table 104).

TABLE 104

VALUATION OF ASSIMILATABLE MOLASSES NITROGEN[4, 96]

Valuation	1928 R.M.	1955 D.M.
100 kg malt sprouts	16.50	23.50
Less spent residue value* of 45 kg dry residue (100 kg dry residue R.M. 6, or D.M. 8.50)	2.70	3.80
1.4 kg assimilatable malt sprout nitrogen	13.80	19.70
i.e. 1 kg malt sprouts nitrogen	10.00	14.00
Corresponding value of the assimilatable N of 100 kg molasses (NAF 0.7)	7.00	9.80

* Spent residue here denotes the extracted remainder of malt sprouts.

The following calculation illustrates this procedure. The molasses nitrogen value is added to the sugar value (for instance, molasses polarizing 48°)determined from the feed industry starch value of the molasses of, for example, 0.25 German Mark/kg (0.20 Reichsmark/kg), *i.e.* 12.00 German Marks/ % kg (9.60 R.marks/ % kg). The molasses value (fob sugar factory) should then, for example, be 21.80 German Marks (16.80 R.marks) to the yeast maker.

Where this multiple pricing system could lead becomes evident if the other possibilities are envisioned, namely if additional calculations have to be made for the other components of molasses which are of importance to the growth of yeasts, *e.g.* potash, magnesia, phosphoric acid, trace elements and growth substances. The same procedure could even be applied with respect to the various buffering capacities shown by different molasses. The uncertainties of this method of appraising molasses gives it little appeal to the molasses consumers who look upon molasses as a waste product which they have elevated into the position of a useful raw material.

Finally, attention must be directed to the other extreme, namely that the price of molasses has been officially set and fixed at 6 Marks per 100 kg in East Germany, where furthermore it has been declared illegal to use molasses in stock feeds.

The molasses market is subject to price management to prevent comparatively few sugar factories exerting a marked effect on this market. The sugar factories have a distinct advantage, when dealing with the yeast manufacturers, in that the latter have few possibilities of using other materials instead of molasses. The molasses-consuming industries consider that the sugar manufacturers are employing a price fixation by delivering an increasing proportion of molasses partly as molasses pulp to the beet growers who have other sources of stock feed. This has created a greater demand for these by-products, with the result of higher prices for molasses for the industrial users. It is innate in the situation that the interests of the sugar industry are not those of the yeast makers and other molasses consumers; the sugar manufacturers are primarily interested in putting the sale of molasses on a firm basis and seeing that the price is as favorable as possible to the seller. However, the importation of molasses should not be viewed by the local sugar industry as an unwarranted importation of taxfree sugar. The officially sanctioned price agreements applying to locally produced sugar have not as yet been extended in any country to cover the price of sugar in molasses.

8. Differences between Beet and Cane Molasses

(a) Composition

The chief components which are found in the same state in both beet and cane molasses, differ in the typical weight relationships of the substances contained (*cf.* Table 2). The chapter by HONIG, *Principles of Sugar Technology,* Vol. I, 1953, p. 686 should be consulted regarding the composition of cane molasses.

As compared with beet molasses, cane molasses in general have a lower content of nonsugar substances and ash. On the other hand, their total sugar content is higher (Table 105). This often is above 50% in commercial cane molasses, but it is not chiefly saccharose as in beet molasses since as much as one third to half may be invert sugar.

TABLE 105

DIFFERENCES IN THE COMPOSITION OF BEET AND CANE MOLASSES

Constituents (%)	Beet molasses[37]	Cane molasses[5]	Cane refinery molasses[37]
Dry substance	78–85	77–84	78–85
Total sugar as invert sugar	48–58	52–65	50–58
C	28–34	—	28–33
N	0.2–2.8	0.4–1.5	0.08–0.5
P_2O_5	0.02–0.07	0.6–2.0	0.009–0.07
CaO	0.15–0.7	0.1–1.1	0.15–0.8
MgO	0.01–0.1	0.03–0.1	0.25–0.8
K_2O	2.2–4.5	2.6–5.0	0.8–2.2
SiO_2	0.1–0.5	—	0.05–0.3
Al_2O_3	0.005–0.06	—	0.01–0.04
Fe_2O_3	0.001–0.02	—	0.001–0.01
Total ash	4–8	7–11	3.5–7.5

Normal Brazilian molasses contain a total of 46-49% sugar but for transport and commercial purposes these molasses are 'sugared up' so that the total sugar content may then reach almost 60% (*cf.* Table 55). A remarkably high proportion of the reducing substances are not fermentable and of no value for yeast production; this may amount to as much as 10% of the total sugar content of cane molasses. Biological determination of the alcohol yield (see Table 58) will readily reveal the biochemical value of cane molasses.

Formerly it was the practice to designate the reducing substances which were not amenable to yeast production as 'glutose'. In 1897 DE BRUYN and VAN ECKENSTEIN asserted that this was a chemical compound of the 3-ketohexose type. After about 30 years this conclusion was corrected and it was shown that 'glutose' in molasses is actually a mixture of various compounds based on fructose anhydrides and including caramel substances, nitrogen-containing reducing compounds and melanoidines[4, 45].

The high and varying amounts of invert sugar found in different molasses are due mainly to the reducing sugars in the raw material, sugar cane, and only to a small extent to inversion of saccharose during the sugar manufacturing process and while the molasses is in storage. The microflora, which multiply with marked vigor under the tropical conditions, are involved to a very small extent in the formation of invert sugar. In contrast to beet molasses, cane molasses are almost always strongly infected; furthermore, it always shows an acid reaction (see Table 54). The sugar in molasses is transformed by bacteria, yeasts and molds which give rise to very varied degradation and metabolic products, whose natures and amounts differ widely from case to case. In this connection we should keep in mind the various oligo- and polysaccharides, organic acids, mixtures of the 'glutose' type, and also the numerous compounds between carbohydrates and nonsugar substances, which appear in part as coloring matter. These substances collectively are responsible, to a certain extent, for the difficulties encountered in the defecation procedures (*cf.* Table 65) for preparing cane molasses for the manufacture of baking yeasts, and which result in the expenditure of increased time, work and money. Ordinarily it is not difficult to defecate beet molasses, whereas a satisfactory defecation of cane molasses can be very difficult. The data available on the composition of cane molasses make it clear that we may expect, even less than in the case of beet molasses, that cane molasses possesses certain predeterminable values or that certain constituents will be present in prefixed amounts. The definition of a 'normal cane molasses' is hardly feasible.

Cane molasses contains no raffinose; betaine is a typical component of beet molasses only. Glutamic acid (partly in the marked form of pyrrolidone carboxylic acid) is present in the greatest amount as compared with all other amino acids in beet molasses; the principal amino acid in cane molasses is aspartic acid. The total nitrogen content of cane molasses is low and, in particular, the assimilatable nitrogen, which is essential to the growth of yeasts, is barely one quarter of the amount found in beet

molasses (*cf.* Tables 54 and 75). Among the nitrogen-free nonsugar materials, cane molasses possess a remarkable constituent, namely aconitic acid, whose commercial production will be mentioned later. The amount and composition of the ash of cane molasses are affected by the cane variety, the conditions under which it was grown (climate, soil) and by the methods employed in the sugar factory. In general, cane molasses produces less ash than beet molasses (*cf.* Tables 3, 54, 55 and 106). Cane molasses have a higher content of SiO_2, CaO and P_2O_5 than beet molasses. Salts are known to affect the solubility of the sugar. In fact, the uncrystallizability of the sugar in final molasses is due to the solubility-enhancing effect of the salts[134, 135, 131].

TABLE 106

COMPOSITION OF PURE ASH OF A CANE AND A BEET MOLASSES

Constituents	Cane molasses containing 5.4% ash (%)	Beet molasses containing 7.2% ash (%)
K_2O	35.6	69.0
KCl	14.4	—
NaCl	5.0	—
Na_2O	—	12.0
CaO	16.8	5.5
MgO	3.0	0.3
P_2O_5	2.6	0.6
Fe_2O_3	—	0.2
SO_3	8.7	2.0
SiO_2	13.9	0.4
Chlorine	—	10.0
Total	100.0	100.0

If, as is the case in beet molasses, it is assumed that to each part of K_2O there are there parts of organic potassium salts, then about 15% organic potassium salts corresponds to the potash content of molasses I in Table 107, and to around 12% in the case of molasses II of this table.

TABLE 107

COMPOSITION OF JAVA CANE MOLASSES AND THE RELATION OF THE ORGANIC POTASSIUM SALTS TO SACCHAROSE AND GLUCOSE[102]

Constituents	Cane molasses from Java (%) I	II
Water	22.1	22.8
Saccharose (by inversion polarization)	33.9	31.5
Invert sugar	18.9	20.3
Ash	10.15	8.66
K_2O	approx. 4.95	approx. 3.9
Organic potassium salts (calc. from K_2O)	approx. 15.0	approx. 12.0
Organic nonsugars	14.15	16.84
Purity	43.5	40.7
Per 100 *saccharose*:		
Total nonsugars	74.1	80.9
Invert sugar	55.7	64.4
Ash	32.3	27.5

Accordingly, Java molasses contain the following amounts of organic potassium salts:

	I	**II**
per 100 total Bugar (saccharose + glucose)	28.2	23.2
per 100 saccharose	44	38
per 100 glucose	79	59

In contrast, 'normal' beet molasses contains 40 parts of organic potassium salts per 100 saccharose (as total sugar).
Table 108 contains a compilation of the results of crystallization experiments with Java molasses.

TABLE 108

SOLUBILITY OF SUCROSE IN CANE MOLASSES FROM JAVA AT 45°C[102]

	Java molasses I			Java molasses II		
Sample No.	Q	Solubility value	Saturation value	Q	Solubility value	Saturation value
1	44.1	1.59	0.64	44.1	1.67	0.67
2	42.2	1.72	0.69	41.3	1.80	0.72
3	38.0	1.74	0.70	39.2	1.93	0.77
4	35.5	1.89	0.76	38.9	1.86	0.75
5	36.6	2.06	0.83	38.5	1.99	0.80
6	38.8	2.55	1.02	40.5	2.21	0.89

The saturation figures were around 0.7 for both molasses. The lowest sugar solubility was reached at a purity of 35.5 (molasses I) or 39 (molasses II).
A special feature in regard to the composition of the minor components is the difference in the biotin content of beet and cane molasses. Because of the high biotin content of the latter (see Table 36) an addition of cane molasses of up to 20% to the biotin-poor beet molasses works out very well in the manufacture of yeast to obtain the highest yields. The amount of pantothenic acid in refinery cane molasses is usually far below the limit of growth materials to be observed for maximum yields of yeast.
According to German agreements, the mixed molasses placed on the market must state the ratio in which the beet and cane molasses are present with an accuracy of ± 5%.
As might be expected from the low content of nonsugars in cane molasses, their buffering action is distinctly lower than that of beet molasses (*cf.* Table 69). Similarly, the values for the elevation of the boiling point are below the temperatures found with beet molasses (see Table 50). In comparison with a normal beet molasses with the same water content, CLAASSEN[102] found that the viscosity, as determined from the outflow time in the viscosimeter, is markedly higher for cane than for beet molasses (Table 109).

TABLE 109

VISCOSITY BEHAVIOR OF A BEET AND A CANE MOLASSES HAVING THE SAME WATER CONTENT ACCORDING TO THE OUTFLOW TIME FROM THE VISCOSIMETER[102]

	Outflow time (sec)	
Temp. (°C)	Beet molasses	Cane molasses
20	167	639
30	56	188
45	15	36
70	4	6

(b) Utilization

(i) ***Fermentation of cane molasses***

The disinclination of yeast manufacturers to use cane molasses and their preference for beet molasses are due to the fact that the characteristics and components of the two kinds of molasses which are important to the growth of yeasts are precisely those which prove themselves unfavorable in the case of cane molasses. However, the divergent utilization of the two varieties of molasses involves still other considerations. The possibilities of using cane molasses in the countries in which it is produced are limited. In addition, the utilization of cane molasses has certain features which are peculiar to this kind of molasses.

Manufacture of alcohol from cane molasses. *A* considerable part of the cane molasses is fermented to alcohol. The fermenting processes ordinarily employed are the same as those usually applied in the fermentation of beet molasses. Special operating conditions have to be maintained if good yields of alcohol are to be obtained under tropical conditions, which present more difficult manufacturing environments.
For instance, in fermentation operations in Brazil the high outside temperature poses a constant threat of infection both to the stored molasses and during the fermentation itself. The chief sources of danger reside in inadequate cooling of the fermenting vats and in not providing proper guards against infection. Besides the materials ordinarily employed for preventing infection during the fermentation, namely sulfurus acid, formalin, fluorides, more and more importance is being attached to new materials for warding off harmful wild infections during the fermenting of cane molasses. One of these preparations is called Emulsan AL (97); it is an alcoholic solution of the sodium derivative of pentachlorophenol (specific gravity 1.08; pH 6.5-7.2). The quality of the molasses also plays a role here, as serious infection of the molasses intended for fermenting can be dealt with only by an experienced operating staff.

Manufacture of rum from cane molasses. The word 'rum' comes from the Sanskrit 'roma', *i.e.* water. Rum is produced mainly from cane molasses and from the residues and waste products of cane sugar manufacture. The rum mash intended for the fermentation is prepared from three components, whose quantities may vary (Table 110). These ingredients are:

A) 'skimmings', *i.e.* the sugar-containing foam obtained by skimming off the foam which forms when the cane juice is boiled, and to which are added sugared water and crushed sugar cane;
B) original cane molasses which has been subjected to a souring process for several days and then diluted with water to 17-22° Bg;
C) 'dunder', *i.e.* spontaneously bacterially soured cane molasses slops from the fermentation plant. This is important for producing the characteristic rum esters.

TABLE 110

EXAMPLES OF THE COMPOSITION OF RUM MASHES[66]

Constituents	Mash from Martinique (%)	Mash from Jamaica (%)
Skimmings	—	30
Cane molasses	12	10
Water	28	20–50
Dunder	60	10–40

The mashes are fermented with yeast for 6-12 days and then distilled in simple stills to yield crude and fine grades of rum. The specific quality of the rum obtained (*cf.* Table 60) is determined primarily by the starting materials and by their preliminary treatment in the mashing stage. However, added materials also have a certain effect. Such additives include clover, acacia bark, custard apples, pineapples, etc. The attempts to manufacture rum from products of beet sugar manufacture have met with no more than limited success (see Table 60).
(γ) Manufacture of arak from cane molasses. In many regions producing sugar cane, molasses and rice are the principal starting materials for the production of arak. (The word comes from the Arabic *araq, i.e.* juice.) In some regions it is customary to add certain materials to the mash, such as palm wine, which is the fermented juice of the sugar palm, also known as 'toddy' and which is sometimes prepared by the addition of cashew fruits. Details of the process will not be described here except to point out that the methods for making arak are more varied and considerably more complicated than those employed for rum. As to the cane molasses used, it is reported, for instance, that in Java the molasses are final blackstrap molasses of low purity and -in contrast to the sugar- rich light brown Jamaica cane molasses are darker colored and more viscous[66, 84].

(ii) ***Recovery of aconitic acid from cane molasses***

Among the notable materials found in cane molasses there is, besides oxalic acid, the 1, 2, 3-propenetricarboxylic acid better known as aconitic acid. Very small amounts of this acid are also present in sugar beets.

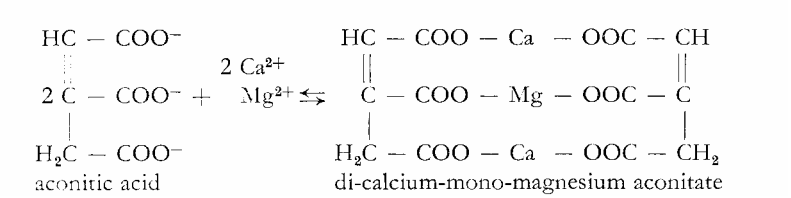
The sugar content falls with rising amounts of aconitic acid. Because of the short growing season, the content of aconitic acid in the cane may reach 0.1-0.2% particularly in the subtropical regions, so that the corresponding molasses may contain as much as 3-7% in the dry substance.

Since 1944/45 this high content of aconitic acid has served as the basis for the production of this material in Louisiana, either as a by-product in the manufacture of sugar or as an initial or intermediate product in the processing of molasses. Cane molasses is also used for this purpose as also is the second run-off from raw sugar mills at around 89 brix, which after the removal of the aconitic acid is returned to the sugar factory for a third crystallization.

It is hoped that the use of ion exchangers will lead to a more advantageous processing of molasses containing less than 3% of aconitic acid. The aconitic acid, obtained as its dicalcium magnesium salt, is used in the preparation of plasticizers for synthetic products based on high molecular esters.

When the aconitic acid is to be precipitated, the molasses is brought to optimum conditions for precipitation and separation of the precipitate (50-55 brix; pH 6.5-6.8). The molasses is heated to 80°C and lime and calcium chloride are added in graduated amounts. The crystallization period is 2 h at a temperature of 88°C.

Occasionally, unknown factors exert inhibiting effects on the formation of the crystals of aconitic acid, and lead to unsatisfactory yields (below 40%) despite a 'normal' content of aconitic acid in the raw material. The 'usual' yield from this process is around 42% of the aconitic acid content of the molasses[98]. A primary consideration in the precipitation is that suitable amounts of Ca^{2+} and Mg^{2+} ions are available, but excesses must be avoided. Louisiana molasses contain the stoichiometrically requisite magnesium in sufficient amounts.



The crude fine aconitate crystals are recovered by means of filters, separators, and continuous centrifuges, dried on endless steel belts, and packed after crushing.

According to Indian reports, the aconitic acid can be extracted, after acidifying, with ethyl acetate, or, according to a U.S.A. patent, weakly basic exchangers may be used[116, 133].

(iii) ***Other uses of cane molasses***

If the amount of cane molasses was temporarily so great that it could not be consumed either for commercial purposes or for feeding, it was formerly the practice to employ it as a fertilizer on the sugar cane fields, especially for light soils[102]. Cane molasses has been used also as fuel and for the manufacture of road pavings in tropical countries.

The following data were obtained from 51 combustion trials with 200,000 tons of cane molasses used for generating steam:

H_u original molasses	2521	kcal
H_u referred to combustible material in the molasses	3714	kcal
Amount burnt each hour	1440	kg
CO_2-content (in dry flue gas)	14	%
Temperature of flue gas	314	°C
Thermal efficiency	64.8	%
Stack losses	19.8	%
Undetermined losses (hearth losses, radiation, etc.)	15.4	%

Regarding the successful use of molasses in road building, it may be pointed out that when mixed with coal tar and asphalt, and with the addition of sulfuric acid, the molasses sugar combines with the Phenol components of the other materials on heating to give plastic-like self-hardening condensation products.
Because of complete dehydration and corresponding pretreatment, the molasses used for this purpose has a plastic dough-like consistency. Furthermore, for the most part, cane molasses can be employed in the ways described above for beet molasses.

(c) Storage of Molasses, especially Cane Molasses

To restrict the chemical changes that are favored under tropical conditions, the freshly centrifuged cane molasses should be cooled as much as possible before being placed in storage. Difficulties are known to arise sometimes when the sediments have to be removed from tanks that have not been cleaned for a long time, since these deposits become caked and adhere so firmly that chipping tools are required to loosen them.

(i) ***Decomposition and destruction of stored molasses***

(α) *Behavior during storage of molasses.* Stored beet molasses seldom shows unusual behavior. Its alkalinity and the low atmospheric temperature favor its keeping qualities. The following instances can serve as warnings of the serious consequences of uncleanliness or local rises in temperature. These occurrences might also have happened with cane molasses, in which, however, the reactions are faster and more vigorous as a rule.

TABLE 111

DIMENSIONS OF MOLASSES STORAGE TANKS[59, 112]

Dimensions	Examples			Catastrophe tank in		
	1	2	3	Tank in Berlin —N 65	Boston, Mass. 1919	Germany 1932
a	b	c	d	e	f	g
Capacity (m^3)	250	500	1,000	800	10,000	880
Capacity* (t)	350	700	1,400	1,120	14,000	1,230
Height (m)	4	5	6	8.0	15	7.8
Diameter (m)	9	11.3	14.6	11.0	—	12.0
(or circumference) (m)	—	—	—	—	(86)	—
Bottom thickness (mm)	7.5	8.5	9.5	15.0	—	12.0
Wall thickness (mm)	7.0	8.0	8.0	**	—	9.0
Weight (t)	13	—	—	*ca.* 20	—	—

* With a molasses density around 1.35–1.45, *i.e.* 38–45 new °Bé (*cf.* Table 96), the volume of 1 ton of molasses is about 690–740 l. The calculation was made on the basis of an average value of 715 l/ton, *i.e.* a concentration of about 78 brix (or °Balling).
** The tank consists of 4 rings, each 2 m high, with a wall thickness (mm) decreasing from bottom to top in the following order: 15.0, 12.0, 10.0 and 8.0. The thickness of the sheet metal roof, on which a vapor vent is set, is 7 mm.

A German molasses tank (Table 111, column g) which had not been cleaned for 15 years, exploded in 1932 and burst into flames[112]. Two investigations, instituted from different directions, agreed that micro-organisms had been active, but otherwise the explanations were divergent. The first expert believed that fermentation gases (probably methane and hydrogen) that had been generated over the years had been trapped by the hardened molasses until explosive pressures were built up. The other expert attributed the formation of gas to fermentation acids (lactic, butyric, acetic and others) which had slowly corroded the iron of the storage tank with generation of hydrogen. The bottom of the container, which after the explosion was found to have bulged out as much as 1.10 m, showed corroded patches 5-6 sq. m in area. Parts of the plates 2-3 mm thick could be easily pushed out of this portion of the bottom. Although the iron plates had been washed with water in the factory and then had stood in the rain for a long time, it was still possibly to dissolve the iron with the cold water

leachings from the corroded bottom plates. Since the hardened molasses prevented the escape of the hydrogen, the increasing pressure led to slight ruptures in the stems. When the gas escaped through these openings, the pressure fell and air entered the tank.
The report stated that the friction at the escape sites had resulted in an increase in temperature, which, in combination with the contact action of the finaly divided iron oxide, which was found at the hydrogen-exit site, had initiated a gas explosion which struck into the tank and destroyed it. This case shows that the explosion of the hydrogen-air mixture followed from the suction action of the decrease in pressure. This inexcusable accident could have been prevented if the tank had been thoroughly cleaned of the molasses residues at not too infrequent intervals.
In another instance, an operating catastrophe (Eppeville-Ham, France) was due to excessive heating of the stored beet molasses[103]. In March 1949, three months after the close of the campaign, a spell of unusually cold weather thickened the molasses so much that it was impossible to pump it from the tank. Steam, at about 143°C, was therefore injected to reduce the viscosity. The perforated steam pipe was placed just above the bottom of the tank and the molasses in this region was heated to around 80 or 90°C. Some days later the molasses remaining in the tank began to decompose vigorously, a phenomenon ordinarily observed only in cane molasses (*cf.* Table 112). The total loss of all the remaining molasses was prevented by immediately flooding the molasses with water. In addition to the unusually high heating of the molasses, it was assumed that another factor contributing to the accident was the high glucose content which was abnormal for beet molasses. It was attributed to the especially dry season of 1948.
In another instance, beet molasses taken from an open stone container was observed to be exceptionally free-flowing. On examination it was discovered that about one quarter of the 320 tons of molasses that had been stored had turned into a compact black charcoal-like mass[114]. This carbonization was ascribed to the action of micro-organisms, which possibly had brought about a decomposition accompanied by the formation of hydrocarbons, carbon dioxide, and hydrogen. During the period in question, the atmospheric temperatures ranged from 10.4 to 29.7°C. The molasses had come from the processing of highly discolored beets which were decaying and thus the molasses had been obtained under conditions of manufacture that were completely abnormal.
(β) *Explosions in molasses storage* tanks. An admonitory instance of the consequences of the use of too thin plates (Table 111, column f) is presented by the collapse of a molasses tank at Boston in January 1919. It was facetiously dubbed 'the worst mess of the century' in the daily press. The tank (capacity 14,000 tons) was filled to the brim with Puerto Rican molasses; when the explosion occurred the tank blew apart and the molasses spread over the surrounding streets at a speed of 1 km/min (37.3 miles/h) and under a pressure of 25 tons. This flood of molasses caused the death of 21 persons and many horses were also drowned. An action was brought against the owners of the fermentation plants who in rebuttal caused three tanks erected by themselves to be exploded to prove that only 'an anarchist bomb' could have been responsible for the disaster. However, the plans on file in the office of the building authorities showed that the plates used in the construction of the tank were too weak. The suit, which cost more than a million dollars, was finally settled out of court in 1925.
Explosions of tanks containing cane molasses are fairly common. Ten such occurrences were recorded in the literature between 1922 and 1939 in Egypt, two in Hawaii in 1953, two in Puerto Rico (1952, 1953) and one in India (1953).
The detailed report of the explosion at Central Fajardo, Puerto Rico (1953) revealed that a highly concentrated molasses (*cf.* Table 112) had been heated so that it could be pumped; when it entered the tank its temperature was about 55°C[103].
In general, the critical viscosity region of cane molasses is 81-85 brix. This means that an increase of no more than several tenths in the concentration results in a marked rise in the viscosity[4, 41]. The molasses that was stored at Central Fajardo had a concentration of almost 88 brix (*cf.* Table 112).
On the day of the accident, two tanks (capacity 7500 and 5000 m^3) were charged with 3500 and 3000m^3 of cane molasses; one of the tanks blew up in the afternoon. The contents of the other tank bubbled vigorously and ran over. Gases and vapours with a penetrating odor were evolved and spread over the neighbourhood. The walls of the tank were cooled with streams of water for three days to protect the steel of the tank, but this precaution did not stop the chemical action in the tank, which could not be emptied. After a week the contents of the tank had turned to a fairly solid dark brown to black mass. Since other tanks showed similar behavior during this time, their contents were run into the ocean to remove the direct danger of another explosion. The dark mass in the bubbling tank

showed no further change at first, but after about four months there was a renewed evolution of gases and vapours. The next day the material in the tank burst into flames. The fire was extinguished with water. The molasses stored later had a concentration of 84.5 brix and gave no trouble; the temperature in the tank never exceeded 40°C.
In their report an the happenings at Central Fajardo, FROMEN and BOWLAND[103] compared three similar previous cases hoping to gain some insight into the general causes of the rapid deterioration and destruction of cane molasses in storage.

It is certain that high molasses concentrations (from 85 brix upward) and high storage temperatures (from 45°C) can promote the decomposition of molasses, though the conditions applying to each batch of molasses are not known and the 'critical' or 'safe' limits cannot be stated. The 'safe' storage temperature for one molasses may be in the danger zone of another (*cf.* in this connection the discussion of the storing of high-test molasses on page 474). In addition, the quantity of molasses stored and the length of the storage period undoubtedly plays a part in these events. The prevention of sudden decomposition reactions is possible provided the storage tanks are properly equipped (circulation devices, ventilation equipment, remote thermometer system), so that the temperature can be checked and regulated and the heat drawn off when the temperature rise arouses concern.
Since almost all instances of the destruction of molasses because of rapid violent reactions have involved a temperature rise as the initiating or cooperating factor, supervision and constant inspection of the stored molasses can serve as precautionary measures to combat the trouble and to prevent losses incurred by an extensive deterioration of the molasses.

(ii) ***Theories of the decomposition of molasses***

According to present theories of the decomposition of molasses, the cause and course of the changes in the composition occurring during storage reside in purely chemical reactions. One theory is based on a reaction between lime and the reducing sugars. It states that at a suitable temperature, the decomposition accompanied by the formation of foam with production of carbon dioxide represents a continuation of the reaction between the reducing sugars in the molasses and the unstable organic substances, which have previously been formed in the purification process from the excess of lime present and the reducing sugars.

TABLE 112

COMPARATIVE SIGNIFICANT DATA ON THE RAPID DETERIORATION AND DESTRUCTION OF BLACKSTRAP MOLASSES IN STORAGE

(According to FROMEN and BOWLAND[103])

Information	*Fajardo*, Puerto Rico	*Olokele*, Hawaii	*Plata*, Puerto Rico	*Ermant*, Egypt
Date of accident	June 5, 1953	July 15, 1953	May 2, 1952	March 20, 1938
(1) Approx. amount of molasses destroyed (gall)	1,714,000	198,600	640,000	1,000,000
(2) Growing and grinding season weather conditions	exceptional drought	exceptional drought	exceptionally rainy	hot and dry
(3) Cane:				
(a) Prevalent variety	POJ–2878	37–1933	POJ–2878	POJ–105
(b) Analysis:				
(i) Pol	13.0	15.9	11.8	12.5
(ii) Apparent purity	78.0–80.0	86.0–87.0	80.0–81.0	80.0–83.0
(4) Manufacture process	defecation	defecation	defecation	sulfi-defecation
(a) Special difficulties encountered	in clarification	none	in clarification	none
(5) Final massecuite temperatures:				
(a) As discharged from pan (°F)	155–160	152–164	148–152	occasionally over 170
(b) In crystallizer after cooling (°F)	100	93	100–110	122
(c) Reheated for purging (°F)	130–133	135	as high as 170 (est.)	122
(6) Final molasses temperatures (°F):				
(a) Leaving the centrifugals:				
(i) High	122	125	—	126
(ii) Low	110	100	—	118
(iii) Approx. average	115	110	150–160	122
(b) After heating with steam:				
(i) High	160	170	did not	194
(ii) Low	130	125	heat molasses	143
(iii) Approx. average	143	140	directly	160
(c) When entering storage:				
(i) High	145	165	155	194
(ii) Low	125	120	140	140
(iii) Approx. average	130	135	145	150
(d) During violent reaction	215 (est.)	203	217	187

Information	*Fajardo*, Puerto Rico	*Olokele*, Hawaii	*Plata*, Puerto Rico	*Ermant*, Egypt
(7) Viscosity of final molasses (S.U.V. at 130°F)	62,400	—	—	—
(8) Composition of molasses entering storage:				
(a) Brix	87.8	89.1	91.4	98.4
(b) Real solids by desiccation	81.4	83.5	85.5	84.5
(c) % sucrose (Clerget)	35.2	33.3	37.6	38.1
(d) % reducing sugars	23.9	19.9	21.8	9.3
(e) % total sugars	59.1	53.2	59.4	47.4
(f) % total nonsugars	22.3	30.3	26.1	37.1
(g) % ash (sulphated)	8.1	10.7	8.0	18.0
(h) % organic nonsugars	14.2	19.6	18.1	18.6
(i) Ratio reducing sugars to O.N.S.	1 : 0.59	1 : 0.98	1 : 0.83	1 : 2.00
(j) pH	6.0	5.3	—	6.6
(k) % total nitrogen	0.85	0.54	1.39	—
(9) Storage conditions:				
(a) Type of storage tank	steel	stone	steel	metal
(b) Number of tanks involved in tabulation comparison	2	1	1	2
(c) Approx. capacity each tank (gall)	1,500,000 2,000,000	250,000	1,500,000	330,000 820,000
(d) Method of filling storage tank	from below	from below	from above	from above
(e) Method of emptying storage tank	from below	from below	from below	from below
(f) Temperature control equipment in tank	none	none	none	none
(g) Facilities for circulating stored molasses	none	none	none	none
(h) Ventilation facilities in tanks	ample	none	none	ample
(i) Average length of storage period before accident (weeks)	4.8 5.2	6.9	5.0	2.9 9.6
(j) Approx. amount of molasses destroyed (gall)	790,000 924,000	198,000	640,000	250,000 750,000
(k) Approx. ambient temperatures (°F)				
(1) Day	86	105	95	77–113
(2) Night	69	100	77	38–59

The other theory is based on the reaction between amino acids and reducing sugars, which leads *via* N-glycosides to the melanoidines and which is accompanied by the evolution of gas, especially carbon dioxide. This reaction is known as the MAILLARD reaction. It is the basis of the fact that 15-50% of the total nitrogen content of cane molasses is present in a form which cannot be assimilated by yeasts. However, it is also possible that both theories apply in explaining the phenomena of the decomposition of molasses, and only different factors characterize a chain reaction or a complicated system of reactions.

By working carefully, it is possible to delimit from the rapid and explosive types of decomposition of destruction two milder forms of decomposition phenomena which proceed gradually and lead either to loss of sugar because of destruction of saccharose or which involve particularly the invert sugar content of the molasses. The loss of reducing sugars is ordinarily connected with a concurrent increase of non-fermentable reducing substances.

From the literature, FROMEN and BOWLAND have deduced that the activity of micro-organisms is not the cause of the deterioration of molasses since no metabolism of the microflora can take place at concentrations above 75 brix. This viewpoint, which certainly holds for the violent decomposition processes, is probably not correct as a general statement, since otherwise the activity of osmophilic organisms (yeasts, fungus molds, anaerobic sporeforming bacteria) would be disavowed (*cf.* Table 64). The explosion of a German storage tank in 1932 should be remembered in this connection; it was certainly caused by micro-organisms.

WINDISCH of Berlin (unpublished studies) has investigated the influence of osmophilic organisms and has found that substrate concentrations above 75 brix can be tolerated and that the metabolism does not entirely cease. The number of papers dealing with the problem of the *biochemical* changes in concentrated molasses is limited. In 1944, OWEN[115] reported the dependence of the metabolic activity of the various groups of organisms he studied on the concentration of molasses (see Table 113). The micro-organisms used had been isolated from syrup, molasses and sugar.

TABLE 113

INFLUENCE OF THE CONCENTRATION ON THE METABOLISM OF THE MICROFLORA IN MOLASSES

(According to OWEN[115])

Density (brix)	Type of microbial action	Predominant effect on sugar content	Rate of activity
75–80	Biochemical	Sucrose inverted	Very slow
70–75	Mould fungi	Sucrose inverted	Rapid with heavy inoculation
60–72	Yeast	Inverted sugar fermented	Slow change except at lower levels
50–62	Bacteria	Sucrose converted into gum	Slow except at lower levels

The endless range of variations in the characteristics of the innumerable species and strains of the micro-organisms involved obviously sets a limit to every schematization. In contrast to alkaline and cold-stored beet molasses, this applies especially to the conditions under which cane molasses are stored. At the usual storage temperatures (30-40°C) and at the ordinary pH range (4.5-6.5), and with the usual content of organic and inorganic nutrients, every molasses in storage provides, to some degree, a model field on a large scale for the conflict between the growth of the microflora present in the particular case and the high concentration of the substrate. Initially, the microflora consists of anaerobic bacteria, whose spores have withstood the manufacturing process.

TABLE 114

LOSSES IN SUGAR CONTENT OF MOLASSES DURING STORAGE[73, 103]

Analysis	Cane molasses from Fajardo, Puerto Rico			
	Destruction of stored molasses by sudden decomposition, 1953	Slow decomposition after long storage 1953	1954	Decomposition of molasses by culture of osmophilic yeasts (*cf.* Table 64)
1	2	3	4	5
Brix	87.8	86.2	86.9	77.6
Organic N (%)	0.804	0.736	1.022	—
CaO (%)	0.952	0.973	0.999	—
Ratio of:				
(a) CaO : reducing sugars	0.039 : 1	0.039 : 1	0.041 : 1	—
(b) Organic N : reducing sugars	0.035 : 1	0.029 : 1	0.043 : 1	—
Storage temperatures (°C)	45–63	38–41	38–42	25
Total sugar content (%)				
(a) At start of storage	59.1	59.6	59.0	55.6
(b) At end of storage	27.2*	56.0	55.0	52.9 53.2
(c) Total loss	— 31.9**	— 3.6	— 4.0	— 2.7 — 2.4
Storage period (weeks)	4.8	9.5	19.5	2.5

* The analyses come from the resting period between the first and second reaction of the molasses destroyed in Fajardo (direct polarization, −6.0; saccharose (Clerget), 0.47%; reducing sugar, 26.73%).

** The slight loss in total sugars from the first to the second reaction is notable. Of course the commercial loss was total. The calorific value determined of the carbonized material was far below the calorific value of carbon, actually in %: water content, 18.70; volatile combustible materials, 38.37; carbon, 34.11; ash, 8.87; caloritic value as substance, 7.843.2 B.T.U./lb.; calorific value as dry substance, 9.647.2 B.T.U./lb.

There are also present normal unavoidable infections such as yeasts, molds and bacteria of the most varied kinds. Among these will be organisms whose vegetative forms tolerate temperatures above 80°C.

The metabolic processes of osmophilic organisms may participate in the gradual decrease of the sugar content and in the formation of invert sugar while the molasses is in storage. The extent of the deterioration is related to numerous circumstances that surround the particular case.

Table 114 gives instances of rapid and sudden deterioration and sudden decomposition, examples of gradual deterioration and of microbial degradation, and of some of the various possibilities leading to losses in stored molasses.
The findings obtained through the use of pure cultures with respect to the behavior of osmophilic micro-organisms in concentrated heterogeneous substrates such as molasses cannot of course be applied simply to all communities of organisms which may possibly be introduced into molasses or which may reside there naturally. The proven hydrolysis of saccharose and the demonstrated loss of total sugar in laboratory studies show that the gradual alterations in the composition of molasses while in storage are not due necessarily to purely chemical reactions alone, rather these changes result at least in part from the activity of micro-organisms. It may be stated fundamentally that the chemical reactions of most importance during the storage of molasses are, as a rule, those for which HONIG has set up standard values for the instances of the usual slow changes in the composition of molasses, and which are valid for 6 months storing at 30°C (Table 115).

TABLE 115

CHANGES IN CANE BLACKSTRAP MOLASSES DURING 6 MONTHS STORAGE AT 30 °C
(According to HONIG)

Constituents	Reduction (%)		
	Low	Average	High
Clerget sucrose	0.2	0.5	> 1
Reducing sugars	0.1	0.7	> 1.5
Total sugars	0.3	1.2	> 2.5
Increase in non-fermentable reducing substances	0.3	0.6	> 1.5

The loss of saccharose, reducing sugars and total sugar is invariably accompanied by an increase in non-fermentable reducing substrate. Ordinarily the increase in the latter is most rapid during the first three months of storage. The formation of this unfermentable material is accompanied by the evolution of carbon dioxide and it is inversely related to the height of the storage temperature.

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