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Workshop on Fermentation Alcohol for Use as Fuel and Chemical Feedstock in Developing Countries Vienna, Austria, 26 - 30 March 1979

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> > by

A.G. Nedi++

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LIMITED ID/WG.293/16 ABSTRACT 8 February 1979 ENGLISH

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Workshop on Fermentation Alcohol for Use as Fuel and Chemical Feedstock in Developing Countries

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ABSTRACT

FERMENTATION ALCOHOL INDUSTRY IN EGYPT IN THE LAST THREE DECADES"

by

A.G. Nadi**

Cane blackstrap molasses is the only and most economical starting material for industrial alcohol fermentation in Egypt. Its analysis reveals that it is a suitable medium. Two large scale modern distilleries, are owned by the Egyptian Sugar and Distillation Company, with total plant capacity of 66 million litres of alcohol. There is a surplus of pure and industrial alcohol for exportation. Some technical problems encountered like scaling in the mash column, flocculation of yeast, purification of carbon dioxide which were solved in our distilleries, are mentioned. It is planned to invest the slops for manufacturing fodder yeast and to reduce its B.O.D.

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The Starting Materials for Alcohe. in Egypt

In Egypt the starchy and cellulosic materials are not economically available for alcohol fermentation. The cane blackstrap molasses is the only and most economical starting material which is produced by the Egyptian Sugar and Distillation Company, in quantities of 350,000 tons/season (1978). Two distilleries and one chemical factory are owned by the company, where several different processings are used for manufacturing ethyl alcohol, carbon dioxide, fodder yeast, vinegar, glacial acetic acid, acetone, butanol, ethyl and butyl acetate.

Also molasses is used locally in other factories for the production of baker's yeast and blended feeds for cattle and other farm animals, while the remainder is exported fresh yearly.

Best molasses will be available in Egypt in 2-3 years, when the new project of the beet sugar factory being put in operation, which belongs to the new Delta Sugar Company.

At the end of the next decade the cane and best molasses production may exceed to 500,000 tons/year.

The alcohol yield from blackstrap molasses fermentation amounts to approximately 87% of the theoretical on the basis of the fermentable sugars which rates at about 48% on molasses.

The following figures, condensed from many analyses show the approximate composition of the Egyptian cane blackstrap molasses (3,4,5) and that it is a suitable fermentation medium.

- a) $Water^{(4.5)}$ 19.0 22.0%
- b) Sugars^(4.5)

Total Sugars	50.0 - 55.0 %
Sucrose	33.7 - 40.2 %
Reducing sugar	14.5 - 17.2 %
Aldose sugar as glucose	10.5 - 13.2 %
Non-fermentable sugar	3.5 - 5.0 %

Sucrose alone amounts to about 70% of the sugars and the reducing sugars constitute about 30% of the total sugars. 70% of these reducing sugars are aldoses and the rest are ketoses.

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Paper chromatography revealed three main constituents, sucrose, glucose, fructose and two minor constituents, arabinose, melezitose.

c) Aconitic acid⁽⁵⁾ 5.9 - 6.4%

Aconitic acid is the main organic acid present in the Egyptian blackstrap molasses and is higher than the values of aconitic acid reported for molasses of other countries.

The paper chromatographic studies made for detection of other acids indicated the presence of citric, malic and tartaric acid in very small amounts.

d) Nitrogenous compounds^(4,5)

Total nitrogen	0.7 - 1.10%
Inorganic nitrogen	0.06- 0.11%
Proteins	2.40- 4.75%

Analysis with ion exchange resins showed that about 70% of the nitrogenous substances of cane molasses behave like amino acids. In fresh cane molasses amino acids constituted about 40% of the nitrogenous substances. This ratio drops to about 11% on storage under manufacturing conditions in the open pools erposed to air. This drop is attributed to the carbonyl amino reaction between the amino acid fraction and the monosaccharides. thus producing brown matter not retained by ion exchange resins, that 13 reducing the amino acid fraction and leaving the protein content almost constant. Small amounts of amino acids were revealed by paper chromatography, aspartic acid, cystine, lysine, asparagine, glycine, alanine, valine, tyrosine, leucine, isoleucine, phenylalanine.

e) Lipids⁽⁴⁾ 0.220 - 0.227%

f) Vitamins: The Egyptian blackstrap molasses is found to contain high amounts of both partothenate (30.9 mcg/g) and biotin (609.0 mcg/g). It was found that the higher the temperature of storage of molasses, the lower the amount of pantothenate. On the other hand, an increase in the available form of biotin content had been observed during the storage period at all temperatures of storage.⁽³⁾

g)	Ash ^(4,5)	12.80 - 15.00%
	Calcium	1.12 - 1.37%
	Potassium	3.60 - 4.60%
	Phosphorus as P205	0.38 - 1.78%
	Iron	0.020- 0.024%

Manganese

0.800 - 2.000

Utilization of Fermentation Alcohol in Egypt

80% of the straight run distillation is pure ethyl alcohol and the remainder is impure alcohol.

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The final balance between pure and denatured alcohol is controlled by the market needs, where they are distributed as follows:

1) Pure alcohol 95° G.L.

a) About 4 million litre: are utilized by the Egyptian Sumar and Distillation Commany in the following plants: Two plants for vinemar production using the surface and submerged fermentation processes. 80% of this vinemar is utilized in glacial acitic acid production. Two perfumeries for eau de cologne, perfumes and cosmetics. One esterification plant producing ethyl acetate solvent.

b) About 9 million litres of pure alcohol 95° G.L. are utilized mainly for fortification of alcoholic beverages, ether production, chemical and pharmaceutical industries, hospitals, chemical laboratories.

2) Specially denatured alcohol 95° and 90° G.L. About 3 million litres of specially denatured alcohol are utilized mainly for particular industries or purposes such as: Solvent for dyes, thinners, curing of all forms of tobacco, insecticide, germicide and mothrepelants, inks and printing, show polishes shellad varnishes, spirit varnishes, furniture polishes, lacquers for wood and metals and in chemical laboratories.

- Completely denatured alcohol 90°C.I.
 About 14 million litres are used as fuel for heating and lightening purposes.
- A) Absolute alcohol 99.5° G.L.

While it is reported that in Egypt alcohol is used as motor fuel, it is not yet applied, although it has been found that additions of absolute alcohol in proper proportions (20-30%) to the petrol impaired favourable properties to the fuel, so much so that even countries with sufficient supplies of native petrol are using petrol mixed with absolute alcohol.

However small quantities of absolute alcohol are produced in another company for laboratories and research work.

5) <u>Fuel oil</u>

This by-product of alcohol distillation is used mainly in the evaluation of the fats in milk, and as a colvent for lacquer. Its production ranges from 1,000 - 16,000 litres/year.

6) Alcohol for export

After covering the local needs, there is surplus of pure alcohol 95° amounting to 10 - 15 million litres available for export for heverages or for new product utilization, otherwise for exchange alcohol from petrochemical synthesis.

It was found out that this surplus of alcohol, cannot be used as starting material for ethylene and polyethylene synthesis, as the economical basis quantity should be 200 - 300 million litres of alcohol at least.

Some Applied Technologies

1) Modification of the alcohol fermentation to produce alcohol and fodder yeast in one sligle process

In 1949 a large-scale modern distillery started up using blackstrap molasses as starting material. The diluted molasses was fed gradually to the yeast starter in the fermenters. The fermented mash was distilled in continuous stills to separate and rectify the alcohol. The carbon dioxide evolved during fermentation was collected, purified and liquified.

In 1967 it had been planned by the Egyptian Sugar and Distillation Company to modify the process to produce alcohol and fodder yeast in one single process, by Vogelbusch.

The diluted molasses without treatment was clarified by centrifugal clarifiers. The yeast was encouraged to multiply in the fermenters by partial aeration and added nutrients. After running the mash into the yeast separators, the yeast cream separated was washed and drum-dried, producing fodder yeast with 50% protein. The clarified mash was distilled for alcohol production. Each 100 kg monosachaccharides produce 53.5 litres of alcohol 100% plus 7.6 kg of fodder yeast 90% dry ma ter with 50% prot(in.

The nutritives used are ammonium phosphate, super phosphate, urea. The duration of each fermentation cycle is 14 hours. The annual production of fodder yeast, besides the alcohol reaches 2,500 - 3,000 tons.

As it was found difficult to obtain fodder yeast with 50% protein unless more nutrients than calculated were used, experiments showed that production of fodder yeast of 40% protein was the most economical process concerning nutrient consumption and other factors of costs.

2) Scaling in the mash columns

Scaling is well known to persons engaged in alcohol industry using blackstrap molasses, thus chemists and distillers from the past tried to remedy it. These scales consisting of sulphate mainly, are hard and stick firmly to the plates of the mash column. So hammering and even chiselling are necessary to dislodge scales leading to damages of the plates.

Chemical descalers, inhibitors and molasses pretreatment were applied to reduce or prevent the scale problem, gave the following results (Nadi et al unpublished).

a) The effect of injecting technical chemical descalers in the feed mash did not give constant significant results, and were too expensive.

b) The closed circuit circulation of hot 10% trisodium phosphate + 10% NaOH at 70 - 80° C for several hours removed the hard scales 1 - 2 mm thick, blocking the bubble cap slots of the plates of some segments of the first - running column, after 3 years of continuous operation.

c) The thermal and chemical clarification of Egyptian molasses.

Mean analysis of the scales

Loss on incineration	24.5%
Ca0 %	30.7%
so ₃ %	44.2%
Si 0 ₂	0.3%
Fe ₂ 03	0.2%

From this analysis it is obvious that the hard scaling is caused due to calcium sulphate salts.

The optimum cordition for the clarification adopted and the results obtained on the factory scale are tabulated as follows:

- Brix of the dilute molasses	$40 - 42^{\circ}$ Brix
- Chemical added, needed for the fermentation	sulphuric acid
and for adjusting the pH	superphosphate
	and ammonium sulphate
- pH	▲ 4.5
- Temperature and retention time	$\pm 95^{\circ}$ for 1 hour
- Time of decantation	2 hours
- Losses in the clarification	0.3 - 0.5%
- Percentage of calcium removed	+ 65%
- Clarification efficiency tested by	-
centrifugal tubes at 3,000 r.p.m.	± 65 č
- Improvement in the efficiency of fermentation	+ 31
-The frequency of scale formation in the mash column:	-
a) Without preclarification	15 - 45 dave
b) With preclarification	± 200 days

From the data of the above table, the reduction or eliminination of the scaling problem calls for a thermal and chemical clarification of the Egyptian molasses. In our factory, the preclarification is economically feasible despit: the higher steam consumption as the production of alcohol is coupled with fodder yeast. There is an improvement of the yeast recovery and fermentation efficiency, besides reducing the scaling problem and costs for cleaning and renewal of the mash columns.

3) Flocculation of yeast

According to the Vogelbusch process the selected pure yeast was formerly propagated once a week in the laboratory and the plant through 5 stages. The yeast cream separated from the fith stare, called for simplicity the first generation, was used for seeding 2 fermenters daily for one week. The yeast cream separated from these 2 fermenters, called second generation, was also used as starter for the daily commercial production of alcohol and carbon dioxide; fodder yeast was obtained from drving the third generation yeast cream.

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The first generation yeast was non-flocculent (powdery), the third generation yeast was strongly flocculating, the second generation yeast possessed characteristics intermediate between these two extremes.

Causes, measuring and problems relating to flocculation are mentioned in many references. $(f_{1},7)$

The problem of flocculation found a remedy by modifying the process of fermentation as follows (Madi et al unpublished).

a) Daily inoculation by the laboratory-selected pure yeast instead of the weekly inoculation. This leads to a jess flocculent second generation for the production of fodder yeast instead of the strongly flocculating third generation yeast.

b) The thermal and chemical pretreatment of molasses (Madi et al. unpublished) helps in reducing the problem to extinction.

Purification of carbon dioxide produced during the fermentative production of fodder yeast and ethyl alcohol by Saccharomyces cerevisiae (8)

Paper chromatographic studies showed that the impurities present in the carbon dioxide produced during the fermentative production of fodder yeast and ethyl alcohol by Saccharomyces cerevisiae were mainly acetaldelyde and butyraldehyde (2,4). Dinitrophenyl hydrazine (2,4 - DNP) reagent is sensitive to these impurities and they are precipitated as hydrazones.

The rate of flow of water used for washing and purifying carbon dioxide was increased for both washers in operation. The results obtained showed that the amount of hydrazone impurities decreased with increase of washing water.

Therefore, by increasing the rate of washing water approximately all the soluble volatile compounds, including acetaldehyde and butyraldehyde, were removed from the carbon dioxide gas.

The other impurities were trapped by potassium permanganate scrubber and active charcoal towers to obtain pure carbon dioxide gas.

5) Problem of cooling in tropical region

It was found that spray - ring water cooling is suitable only for fermenters having a capacity up to 20 m³. For larger fermenters, internal coils and other surface extending media or external heat plate exchangers are the best procedures for cooling.

PLANS FOR THE NEAR FUTURE

It is planned to invest the distillery slops (stillages), amounting $1,500 \text{ m}^3/\text{day}$ which contain basides the organic matter, 1.0 - 1.5% total reducing sugar, represeting an organic pollution due to its high B.O.D.

Vogelbusch before 1960, Bookers 1975, and the Egyptian Sugar and Distillation Company, studied the feasibility of treatment and investment of this stillage.

The 1975 studies included 5 systems for this investment:

- 1) Evaporation to thick syrup to be used as a blend in animal feed.
- Evaporation to thick syrup followed by incineration for the production of crude potassium sulphate to be used as fertilizer.
- 3) Refining the crude potassium sulphate for the production of refined potassium salts for chemical indus ries e.g. dyeing.
- 4) Using the stillage as a medium for fodder yeast production.
- 5) The effluents from the previously mentioned fodder yeast production are concentrated, then incinerated to produce crude potassium salts (which are purified) to raise the economy. Studies are now concentrated on producing fodder yeast from the stillage, as it had been initially considered the best potential method for B.O.D. reduction, besides producing 6,000 tons of fodder yeast/year.

Comparative studies on SCP production from molasses and slops showed that the slops can be used for producing fodder yeast either directly or as a diluent for molasses, and that the best strain was Candida tropicalis, and that the yield obtained from the yeast grown on the slops was 54.9% of the sugar consumed (9).

CONCLUSION

The Egyptian blackstrap molasses is the most economical starting material for alcohol fermentation. The complete analysis of the molasses shows that it is a suitable medium for alcohol fermentation and the production of fodder yeast, baker's yeast, acetone and butanol.

Gyllenberg H.G. and Pintimen P. (1973) concluded that the allocation of funds to the soft applications of microbiology as local fermentations are more promising then processes dependent on "harder" technology. But according to the technical poblems mentioned in the paper "soft" alcohol technology cannot be realized solely by obtaining the latest modern plant or gaining experience during the short period of the start-up and commissioning of the imported equipments, as effective technology includes also the following.

- 1) Sufficient information and knowledge about
 - the raw materials available and the obstacles which may hinder resource utilization;
 - the different processes and the different factors affecting the fermentation and distrillation techniques;
 - the engineering of the alcohol industry concerning materials of construction, handling, manufacturing, workmanship, corrosion and erosion inhibitors, etc.;

2) Application of this technical information and knowledge using auitable materials, machinery, tools, personnel in adapting the processes that suit the local conditions.

3) Flexibility for modifications based on applied research to overcome the encountered problems that usually arise due to change in the environmental conditions.

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