# **OVERVIEW OF ALCOHOL PRODUCTION**

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## USE OF DIFFERENT RAW MATERIALS/FEED STOCKS FOR ETHANOL PRODUCTION

### **Raw Material - Determinants & Imperatives**



### **Raw Materials for Bioethanol**



## **Raw Material Selection Criteria**

- Availability & Cost of Raw Material
- Storage, Handling & Transportation Cost
- Pre-Processing & Capital Cost
- Utility Cost
- Technology Availability
- Plant Location
- Plant Capacity & Annual Operation
- Revenue from Co-products
- Effluent Treatment & Discharge

The feed stocks raw materials are of 3 types

- 1. Saccharine containing Sugar
- 2. Starchy Containing Starch
- 3. Cellulosic Containing Cellulose

#### Saccharine

All saccharine material can be converted to ethanol after their conversion to glucose.



### **Classes of Carbohydrates**

**Monosaccharides** contain a single polyhydroxy aldehyde or ketone unit (e.g., glucose, fructose).

**Disaccharides** consist of two monosaccharide units linked together by a covalent bond (e.g., sucrose).

**Oligosaccharides** contain from 3 to 10 monosaccharide units (e.g., raffinose).

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**Polysaccharides** contain very long chains of hundreds or thousands of monosaccharide units, which may be either in straight or branched chains (e.g., cellulose, glycogen, starch).







# Starch

- Major storage carbohydrate in Plants
- Long straight glucose chains (a1-4)
- Branched every 4-<sup>α1-4 link</sup>
  8 glc residues (a
  1-6)

α1-6 link





#### Saccharine Raw Materials









Sugarcane molasses



Black strap molasses









Cashew apple

Mahua Flowers

Whey

Beet molasses

All saccharine material can be converted to ethanol after their conversion to glucose.

- Sucrose + H2O -----> Glucose + fructose
- Lactose + H2O ----- Glucose + Galactose
- Maltose + H2O ----- Glucose + Glucose

Cellobiose + H2O ----- Glucose + Glucose

S.No.	Saccharine Content	Sugar Content (%)	Yield (Litres/Ton)
1	Sugarcane Juice	35-45	70-80
2	Sugar beet Juice	12-13	60-65
3	Sugarcane molasses	48-49	230-270
4	Beet molasses	48-49	250
5	Black strap molasses	50-51	250
7	Cashew apple	7-8	60-62
9	Mahua Flowers	50-67	225-250

### **Typical characteristics of Indian cane molasses**

S. No.	Particulars	Test values
1	Brix	86.00-90.00
2	Moisture content (%)	15.00-21.50
3	Total suspended solids (%)	3.50-7.00
4	Total dissolved solids (%)	72.00-82.00
5	pH of molasses	4.20-4.50
6	Total reducing sugars (%) by mass	42.00-52.00
7	Total fermentable sugars (%) by mass	40.00-48.00
8	Calcium content (gms/1000 brix)	1.80-2.75
9	Fermentable/Non fermentable ratio (F/N)	1.50-2.00
10	Carbonated ash (%)	8.00-12.00
11	Sulphated ash (%)	11.00-15.00
12	Nitrogen (% of molasses)	0.700-1.200
13	Potassium (% of ash)	15.00-16.50
14	Sodium (% of ash)	0.90-0.95
15	Chlorides (% of ash)	13.00-14.00
16	Phosphates (% of ash)	0.25-0.35
17	Total organic volatile acids (mg/lit.)	2500-7000



#### Corn



Barley



Tapioca

### **Starchy Raw Materials**



Wheat

Sweet potato

**Rice Bran cake** 

Rice



Sorghum

#### INDIAN MILLETS



Pampered Cern!



Potato

Starchy substance too are needed to be converted to glucose after gelatinization, liquefaction and Scarification.



S.No.	Starch Content	Starch Content %	Yield Kg/Ton
1	Corn	74	491
2	Wheat	65	431
3	Rice	80	531
4	Sorghum	75	497
5	Millets	70	464
6	Barley	64	425
7	Таріоса	35	190
8	Potato	20	130
9	Sweet potato	25	150
10	Rice bran cake.	45	230



#### Bagasse







#### Wheat Husk









#### Cellulosic Raw Materials



#### PLANT PART USED FOR ETHANOL PRODUCTION

Cassava	Root
Sweet potato	Root
Sugar Beet	Root ( Juice/ molasses )
Sugar Cane	Stalk (Juice/Molasses/Bagasse)
Sweet Sorghum	Stalk
Paddy	Grain (Husk/Rice Bran Cake)
Corn	Grain/Residue
Sorghum	Grain
Wheat	Grain/Straw
Millets	Grain
Barley	Grain
Rice	Grain/Husk
Mahua	Flowers
Cashew apple;	Juice
Forest plants	Wood waste

**Raw material** 

Mostly Broken Rice, Kinki, Millet and Sorghum or mixed grains are being used as raw material in these distillery units. Under table is about the starch percentage & alcohol yield from various grains.

Raw material	Fermentable Carbohydrate (Starch %)	Alcohol yield (Lit. of alcohol/MT)
Rice	62-67	380-418
Sorghum	62-65	380-410
Wheat	62-65	380-410
Potato	19-20	127-134
Malt	58-59	389-395
Maize	62-65	380-410

#### **Grain Quality**

Starch is present as granules which are embedded in a protein matrix. This matrix is surrounded by cell walls containing a gum called  $\beta$ -glucan. The starch granules are therefore inaccessible and protected from attack by the amylase enzymes that are produced during germination.

During the process however, the cell walls and the protein will be dissolved by other enzymes which are produced naturally as the seed grows.

It must have a low proportion of protein. The lower the protein, the higher the amount of carbohydrate. (Protein levels are measured by measuring nitrogen content, a typical spec being less than 1.8%.)

The grains should be of an even size. That way they are more likely to grow evenly.

The grains should be consistent colour, helping indicate the same variety and lack of damage due to for instance moisture.

The grains should be large. Large are easier to process.

They must be undamaged, free of split or pre-germinated grains and free of disease or pests such as beetles or moths.

They must be free of other cereals or other varieties.

The moisture level must be suitable. If freshly harvested, not more than 18%, and suitable for drying to 12% prior to storage.



# **Composition and classification**

- The third boiling of the sugar syrup yields dark, viscous fluid known as molasses.
- The majority of sucrose from the original juice has crystallized and been removed.
- The quality of Indian molasses is inferior as compared to the molasses available in countries such as Brazil and Australia and also varies widely within the country. The quality of Indian molasses is inferior as in India sugar is produced by double sulphitation method that involves three and half boiling and use of SO<sub>2</sub> for sulphitation.
- Sugarcane molasses is agreeable in taste and aroma, and is primarily used for sweetening and flavoring foods.
- It is a defining component of fine commercial brown sugar.
- Unlike highly refined sugars, it contains significant amounts of vitamin  $B_6$  and minerals, including calcium, magnesium, iron, and manganese.
- It is a major raw material for the production of ethyl alcohol, bakers' yeast and citric acid.

# Characteristics\* of Indian cane molasses

Sr. No.	Particulars	Test values
1	°Brix	86.0-88.0
2	Moisture content (%)	15.0-21.5
3	Total suspended solids (%)	3.5-7.0
4	Total dissolved solids (%)	72.0-82.0
5	pH of molasses	4.20-4.50
6	Total reducing sugars (%) by mass	42.0-44.0
7	Total fermentable sugars (%) by mass	35.0-40.0

**Characteristics/ properties -** How substance appears and behave both chemically and physically

### Composition

Particulars	%
Total solids	83 to 85
Invert/Reducing sugar	12 to 18
Sucrose	30 to 40
Fermentable sugar	50 to 55
Non-sugar organic compounds*	20 to 25
Ash	7 to 10
Moisture	12 to 14

\*includes nitrogenous substances, cane wax, vitamins, etc. Note-Composition of a substance is what the substance is made of

### Classification

Grade	°Brix	TRS (% w/w)	Ash (% w/w)
А	88 to 90	50 and above	12 to 13
В	85 to 88	44 to < 50	14 to 15
C*	83 to 85	40 to < 44	17 to 18

Molasses containing TRS less than that of 'C' grade are considered to be of 'Below' grade.

#### What is good quality molasses?:

As far as Indian molasses is concerned the quality of molasses is usually judged on the basis of

- 1. Fermentable to Non-fermentable (F/NF) ratio. This should be as high as possible but not less than 1,
- 2. The level of contaminants in molasses. On and average the contamination level in molasses is about 103 CFU/g of molasses. Higher level than this results in poor fermentability of molasses,
- 3. Total organic volatile acidity of molasses. For good quality molasses the TOVA should be in the range of 3000-3500 ppm. Higher volatile acidity is an indication of contamination of the molasses and the volatile acids generated retards the fermentation rates,
- Sludge content of molasses- The normal range of sludge content of molasses is 8.0-12.0% (v/v). Higher sludge content results in lowering the effective volume of fermenters and scaling problems in equipment's and distillation columns.

# Types of Fermentation



### Batch fermentation

- All necessary medium components and the inoculum are added at the beginning.
- The products of fermentation, whether intracellular or extracellular, are harvested only at the end of the run.
- The concentration of medium components are not controlled during the process.
- As the living cells consume nutrients and yield product(s), their concentrations in the medium vary along the process.
- The affecting factors, such as pH and temperature, are normally kept constant during the process.
- The optimum concentration of raw materials can be decided only according to the initial concentration.

### Continuous fermentation

- One or more feed streams containing the necessary nutrients are fed continuously.
- The output stream containing the cells, products and residues is continuously withdrawn.
- ✤ A steady state is established for the process.
- The culture volume is kept continuous by maintaining an equal volumetric flow rate of feed and output.
- Need for cleaning is minimized as a continuous culture concentration is maintained in the fermenter.

### Fed-batch fermentation

- ✤ Nutrient or raw material is fed intermittently.
- ✤ After the first filling, the inoculum is added.
- ✤ After a small retention time, filling is continued.
- Fermentation starts right after the first filling and continues along the process.
- ✤ At the end of the process, fermenter is emptied and the product is obtained.
- It is currently the most popular mode of fermentation amongst the distilleries in India.

### Commercial fermentation processes

Alcon process and Tate & Lyle process

- Both the processes are nearly the same and in these processes feed is sterilized only once during the first filling in the fermenter.
- ✤ Feed is given without sterilization.
- ✤ The contents of the fermenter are mixed by pumped recirculation.
- ✤ The settled yeast is recycled and supernatant is sent for distillation.
- Yeast cell concentration is 10 to 45 g/l.

### Commercial fermentation processes

Alcon process and Tate & Lyle process


Melle Bionet process

- ✤ Achieves a reduced fermentation time and increased yield by yeast recycling.
- The yeast cells from the previous batch are centrifuged and 80% are recycled back increasing cell density to 80 billion cells/liter which initiates fermentation immediately.
- The productivity is high and reduced growth makes more sugar available for conversion to ethanol (2 to 7% more).
- Centrifugation is done at pH 2.0 to remove lactic acid bacteria (non-sporulating).
- ✤ Mainly used for ethanol production from sulphite waste liquor.



Semi-continuous process

- Carried out initially as batch, but, afterwards 25% of fermented wash is retained as seed for next cycle.
- The process was described by K.H.K., Japan and has a fermentation efficiency of 88%.
- ✤ Yeast cells can be reused without any mechanical device.
- Reduction in frequency of fresh yeast propagation, thus,
- ✤ Low process water utilization.
- ✤ No increase in fermentation temperature.
- Prevention of microbial control without any energy output.
- ✤ Can be worked out on.
- Fermentation efficiency and ethanol recovery are more than conventional batch fermentation.



Biostil process

- A continuous fermentation system providing high yield of alcohol and reduces effluent volume.
- ✤ An excess amount of yeast instantaneously converts sugar into alcohol.
- Yeast is constantly separated from the fermented wash and recycled in the fermenter.
- It converts almost all sugar that is put into the fermenter through molasses into alcohol.
- ✤ Conversion of minimum 90% of fermentable sugars.
- Yield is 286 litres containing 47.5% fermentable sugars at distillation efficiency of 98.5%.

Biostil process

- ✤ A special feature of biostil is the recycle of weak wash which has been passed through distillation column and exhausted of most of the alcohol.
- Recycling of weak wash reduces the requirement of water needed to dilute the molasses being pumped into the fermenter.
- Schizosaccharomyces pombe yeast is used which tolerates high amount of dissolved solid increased due to the recycling of weak wash.
- ✤ About 60% of wash is recycled, thus, total effluent output is 5 to 6 l/l of ethanol.
- ✤ It uses only one fermenter, thus, drastically reduces the space requirement.
- ✤ It is an infection free process.

Biostil process

- ✤ Formation of glycerol, higher alcohols and fusel oils is suppressed.
- ✤ Yeast propagation is required only during start of the process.
- ✤ No DAP and urea is added.
- ✤ No spent wash, but, only weak beer is recycled.
- ✤ Process water is 25% less than cascade.
- ✤ Cost of ETP is reduced by half.



Cascade process (HiFerm)

- ✤ It utilizes three to five fermenters in series.
- ✤ Wash flows from one fermenter to other.
- The first fermenter is used partly for growth and the remaining exclusively for alcohol production.
- \* This is done by adding part of substrate in first fermenter and sparging it with air.
- Sugar concentration is maintained at relatively low level and oxygen is provided via air.
- ✤ In the other fermenters, remaining substrate is added and carbon dioxide sparged.

Cascade process (HiFerm)

- It raises sugar content and ensures that no oxygen is present, thus, providing ideal conditions for ethanol production.
- ✤ Ethanol content of wash is 8.5 to 9.0%.
- It provides low steam consumption, reduced effluent volume and suppression of microbial activities.
- Since, fermentation is distributed over several fermenters, gas evolved per fermenter as well as foaming is reduced.
- ✤ Lot of time is saved in filling the fermenters, cleaning, etc.

Cascade process (HiFerm)



Vogelbusch

Encillium process

- ✤ Molasses is diluted in a mixer tank and pasteurized by heating to 90°C.
- ✤ Now it is cooled at 30°C and introduced into the first of the few fermenters.
- ✤ Air is constantly supplied to the fermenter.
- The overflow from the first fermenter along with some additional molasses is fed to the next fermenter.
- ✤ The broth from the second fermenter is distilled to separate ethanol.
- The yeast is retained in the fermenters and overflow stream from the end fermenter is totally free from yeast.

Encillium process

- The temperature is maintained at 30 to  $32^{\circ}$ C.
- The process includes molasses treatment and clarification plant consisting of primary clarifier, a secondary clarifier and heat exchangers, etc.
- The process of clarification involves diluting the molasses with hot water at 90°C in 1:1 proportion.
- ✤ This diluted molasses is then preheated by outgoing wort.
- ✤ It is further heated to 85°C by live steam and clarified in primary clarifier.



286 litres of recovery for A grade molasses and 90% fermentation efficiency

# DIFFERENT TYPES OF COLUMNS USED FOR DISTILLATION PROCESS

# Distillation

- 1. Analyzer Column
- 2. Degasifying Column
- 3. Pre Rectification cum stripper column
- 4. Extractive distillation column
- 5. Recovery Column
- 6. Rectifier cum Exhaust Column
- 7. Simmering Column
- 8. MSDH column



### Analyzer Column

•In this column preheated fermented wash is stripped off from all

volatile components, including ethyl alcohol.

•From bottom, spent wash is drained and sent to ETP.

•This column generally has a degasser section on the top, which

removes all dissolved gases in the fermented wash.

•This column is generally operated under vacuum to eliminate the

chance of scaling and reduce energy requirement.

•The vapors (45% to 55% ethanol vapors) of this column are

condensed and fed to prerectifier column.



#### Pre-rectifier Column

•In this column the heavier alcohols (fusel oil) are

separated and collected from top middle draw.

•It is operated under vacuum.

•The main product is drawn off from the top side of

the column.

•Bottom product of the column is called spent lees.



#### Rectifier Column

This column operates under elevated pressure.
Rectified spirit, the first alcoholic product, is drawn from this column.

•The bottom product, spent lees, is used in the process of fermentation.

•Fusel oil and technical alcohol are also drawn from this column.



### Extractive Distillation Column

•In this column DM water is used as an extractant to dilute the rectified spirit.

•Water is added to change the relative volatility of the undesirable components to obtain a product clear of smell.

•Water is added in the ratio of 1:9.

•It is operated at atmospheric pressure.

•Bottom product is fed to the simmering column for further concentration.



### Simmering Column

•This column is operated under high reflux and vaccum

•Methanol, diacetyl and mercaptans are separated from

the top of the column.

•The final product, i.e., extraneutral alcohol (ENA) is

obtained as bottom product.

#### Recovery Column



•Fusel oils along with the condensates of analyzer and

ED column are fed to this column for concentration.

•A technical alcohol is taken out from the top of the

•Fusel oils are drawn off from upper trays

•Bottom lees is drained off.

•It is operated at atmospheric pressure.

•Consists of a simple column and two sieve columns packed with zeolite.

•RS is fed to the column for concentration and heating.

•The superheated vapour is fed to one of the sieve columns for adsorption of moisture.

- •When the first sieve column gets saturated, the second is under operation.
- •The first sieve column is cleared of the accumulated moisture by vacuum.

•Ethanol (99.6%) is obtained from the sieve column and is cooled.

# Contd...

Molecular Sieve Dehydration System

Molecular sieve technology works on the principle of pressure swing adsorption.
Molecular Sieve is nothing but synthetic Zeolites typically 3 Angstrom Zeolites. This materia
has strong affinity for water.
•They adsorb water in cold condition and desorbs water when heated. This principle is used to
dehydrate ethanol.
•The crystalline structure of zeolites is complex and gives this material the ability to adsorb o
reject material based on molecular sizes
•The molecular sieve adsorbents developed for vapour phase, Ethanol dehydration are meta
a lumino-silicate with effective pores size opening of 3 Angstrom.
•During dehydration of ethanol, the water of hydrolysis fills the cavities or pores in the
molecular sieve. The potassium form of molecular sieve has pore size of 3 Angstrom, the critical
diameter of water molecules is 3.2A and Ethanol is 4.4 A.

### Contd...

- In vapor phase, the gaseous water molecules are strong dipoles. They are drawn in to the pores and condense at the wall of pores, while ethanol being bigger in size passes through the bed without getting in to pores of molecular sieve.
- The life of molecular sieve is 5 to 7 years.
- · RS is fed to the column for concentration and heating.
- The superheated vapour is fed to one of the sieve columns for adsorption of moisture.
- When the first sieve column gets saturated, the second is under operation.
- The first sieve column is cleared of the accumulated moisture by vacuum.
- Ethanol (99. 6 %) is obtained from the sieve column and is cooled.

### Molecular Sieve Dehydration System



# Flow diagrams Related to Process, Distillation and MSDH





