Manufacture of Ethanol

- Ethanol may be produced by either synthetic chemical method or by fermentation.
- Fermentation was until about 1930 the main means of alcohol production.
- In 1939, for example 75% of the ethanol produced in the US was by fermentation, in 1968 over 90% was made by synthesis from ethylene.
- Due to the increase in price of crude petroleum, the source of ethylene used for alcohol production, attention has turned worldwide to the production of alcohol by fermentation.

Manufacture of Ethanol

- Fermentation alcohol has the potential to replace two important needs currently satisfied by petroleum, namely the provision of fuel and that of feedstock in the chemical industry.
- The production of gasohol (gasoline – alcohol blend) appears to have received more attention than alcohol use as a feed stock.
- Nevertheless, the latter will also surely assume more importance if petroleum price continues to ride.

Manufacture of Ethanol

- Governments the world over have set up programs designed to conserve petroleum and to seek other energy sources.
- One of the most widely publicized programs designed to utilize a new source of energy is the Brazilian National Ethanol Program. Set-up in 1975, the first phase of this program aims at extending gasoline by blending it with ethanol to the extent of 20% by volume.
- The United States government also introduced the gasoline programme based on corn fermentation in 1980 following the embargo on grain sales to the then Soviet Union.

Substrates

- The substrate used will vary among countries.
- In Brazil sugar cane, already widely grown in the country, is the major source of fermentation alcohol, while it is planned to use cassava and sweet sorghum.
- In the United States enormous quantities of corn and other cereals are grown and these are the obvious substrates.
- Cassava grows in many tropical countries and since it is high yielding, it is an important source in tropical countries where sugar cane is not grown.

Substrates

- It is recognized that two important conditions must be met before fermentation alcohol can play a major role in the economy either as gasohol or as a chemical feedstock.
  - ✓ **First,** the production of the crop to be used must be available to produce the crop without extensive and excessive deforestation.
  - ✓ **Secondly,** the substrate should not compete with human food.

Fermentation

- The sterilized fermentable sugars are pumped or allowed to flow by gravity into fermentation tanks and yeast is inoculated or 'pitched in' at a rate of 7-15 x 10^6 yeast cells/ml, usually collected from a previous process.
- These broths are inoculated with up to 5% (v/v) of thick yeast broth.
- Although yeast is re-used there is still a need for regular inocula.

Fermentation

- In general the inocula are made of selected alcohol-tolerant yeast strains usually *Sacch. cerevisiae* grown aerobically with agitation and in a molasses base.
- Progressively larger volumes of culture may be developed before the desired volume is attained.
- *When the nitrogen content of the medium is insufficient nitrogen is* added usually in the form of an ammonium salt.

Fermentation

- As in all alcohol fermentations the heat released must be reduced by cooling and temperatures are generally not permitted to exceed 35 - 37°C.
- The pH is usually in the range 4.5 - 4.7, when the buffering capacity of the medium is high.
- Higher pH values tend to lead to higher glycerol formation.
- When the buffering capacity is lower, the initial pH is 5.5 but this usually falls to about 3.5. During the fermentation contaminations can have

Distillation

- After fermentation the fermented liquor or 'beer' contains alcohol as well as low boiling point volatile compounds such as acetaldeydes, esters and the higher boiling, fusel oils.
- The alcohol is obtained by several operations:

➢ First, steam is passed through the beer which is said to be steam-stripped.

✓ The result is a dilute alcohol solution which still contains part of the undesirable volatile compounds.

Distillation

➢ Secondly, the dilute alcohol solution is passed into the center of a multi-plate aldehyde column in which the following fractions are separated: esters and aldehydes, fusel oil, water, and an ethanol solution containing about 25% ethanol.

➢ Thirdly, the dilute alcohol solution is passed into a rectifying column where a constant boiling mixture, an azeotrope, distils off at 95.6% alcohol concentration.

❑ To obtain 200° proof alcohol, such as is used in gasohol blending, the 96.58% alcohol is obtained by azeotropic distillation.

Distillation

- ✓The principle of this method is to add an organic solvent which will form a ternary (three-membered) azeotrope with most of the water, but with only a small proportion of the alcohol.
- ✓Benzene, carbon tetrachloride and chloroform may be used, but in practice, benzene is used.
- ✓Azeotropes usually have lower boiling point than their individual components and that of benzene-ethanol-water is 64.6°C.
- ✓On condensation, it separates into two layers.

Distillation

- ✓The upper layer, which has about 84% of the condensate, has the following percentage composition: benzene 85%, ethanol 18%, water 1%.
- ✓The heavier, lower portion, constituting 16% of the condensate, has the following composition: benzene 11%, ethanol 53%, and water 36%.
- In practice, the condensate is not allowed to separate out, but the arrangement of plates within the columns enable separation of the alcohol. Four columns are usually used.

Distillation

- In practice, the condensate is not allowed to separate out, but the arrangement of plates within the columns enable separation of the alcohol. Four columns are usually used.

✓ The first and second columns remove aldehydes and fusel oils, respectively, while the last two towers are for the concentration of the alcohol.

✓ A flow diagram of conventional absolute alcohol production from molasses is given in Fig. 20.4

Distillation

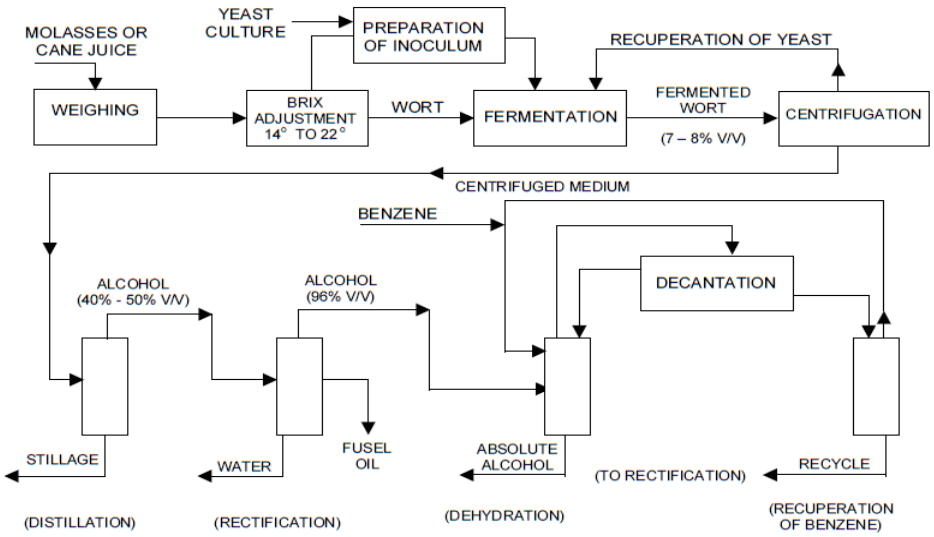

Fig. 20.4 Flow Diagram of Conventional Alcohol Production

Some Developments in Alcohol Production

- Due to the current interest in the potential of ethanol as a fuel and a chemical feedstock, research aimed at improving the conventional method of production has been undertaken, and more will, most certainly, be undertaken. Some of the techniques aimed at improving productivity are the following:

(i) Developments of new strains of yeast of *Saccharomyces uvarum able to ferment sugar* rapidly, to tolerate high alcohol concentrations, flocculate rapidly, and whose regulatory system permits it to produce alcohol during growth.

Some Developments in Alcohol Production

(ii) The use of continuous fermentation with recycle using the rapidly flocculating yeasts.

(iii) Continuous vacuum fermentation in which alcohol is continuously evaporated under low pressure from the fermentation broth.

(iv) The use of immobilized *Saccharomyces cerevisiae* in a packed column, instead of in a conventional stirred tank fermentor. Higher productivity consequent on a higher cell concentration was said to be the advantage.

Some Developments in Alcohol Production

(v) In the 'Ex-ferm' process sugar cane chips are fermented directly with a yeast without first expressing the cane juice.

- The chips may be dried and used in the offseason period of cane production.
- It is claimed that there is no need to add nutrients as would be the case with molasses, since these are derived from the cane itself.
- A more complete extraction of the sugar, resulting in a 10% increase in alcohol yield, is also claimed.

Some Developments in Alcohol Production

(vi) The use of *Zymomonas mobilis, a Gram-negative bacterium which is found in some* tropical alcoholic beverages, rather than yeast is advocated.

➢ The advantages claimed for the use of *Zymomonas are the following:*

(a) Higher specific rates of glucose uptake and ethanol production than reported for yeasts.

✓ Up to 300% more ethanol is claimed for Zymomonas than for yeasts in continuous fermentation with all recycle.

Some Developments in Alcohol Production

(b) Higher ethanol yields and lower biomass than with yeasts.

- ✓This deduction is based on Fig. 20.5 where, although the same quantity of alcohol is produced by the two organisms in 30-40 hours, the biomass of *Zymomonas required for this* level of production is much less than with yeast.
- ✓The lower biomass appears to be due to the lower energy available for growth.

Some Developments in Alcohol Production

- ✓ *Zymomonas* utilized glucose by the Enthner-Duodoroff pathway (Fig. 5.4) which yields one mole of ATP/mole glucose, whereas yeasts utilize glucose anaerobically via the glycolytic pathway (Fig. 5.1) to give two ATP/mole glucose. Its use does not appear to have gained general acceptance.

(c) Ethanol tolerance is at least as high or even higher [up to 16% (v/v)] in some strains of the bacterium than with yeast.

Some Developments in Alcohol Production

(d) *Zymomonas also tolerates high glocuse concentration and many cultures grow* in sugar solutions of up to 40% (w/v) glucose which should lead to high ethanol production.

(e) *Zymomonas grows anaerobically and, unlike yeasts, does not require the* controlled addition of oxygen for viability at the high cell concentrations used in cell recycle.

(f) The many techniques for genetic engineering already worked out in bacteria can be easily applied to *Zymomonas for greater productivity.*

Some Developments in Alcohol Production

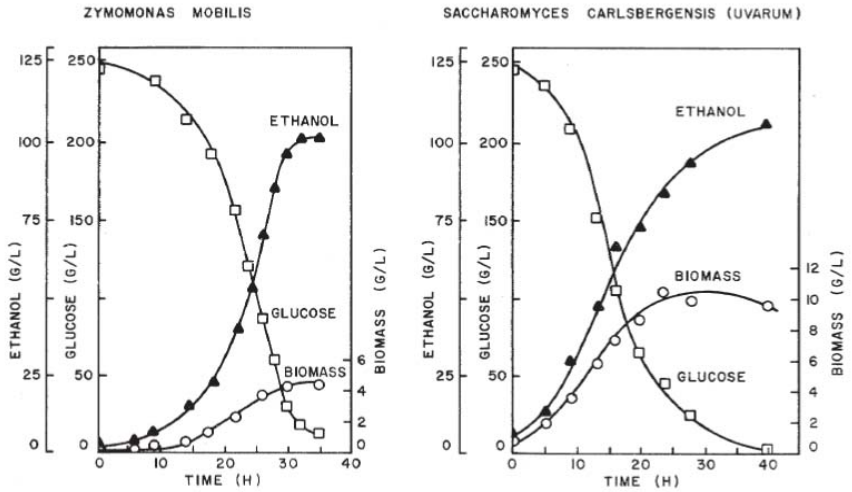

Fig. 20.5 Alcohol Production by Yeast and *Zymomonas mobilis*

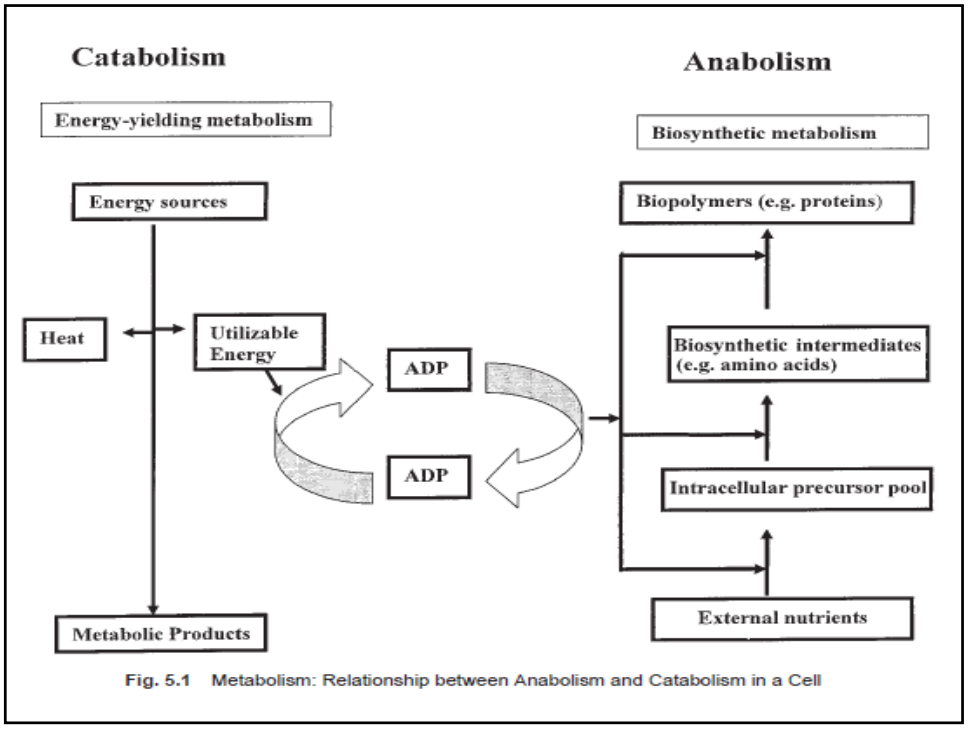

Fig. 5.1 Metabolism: Relationship between Anabolism and Catabolism in a Cell

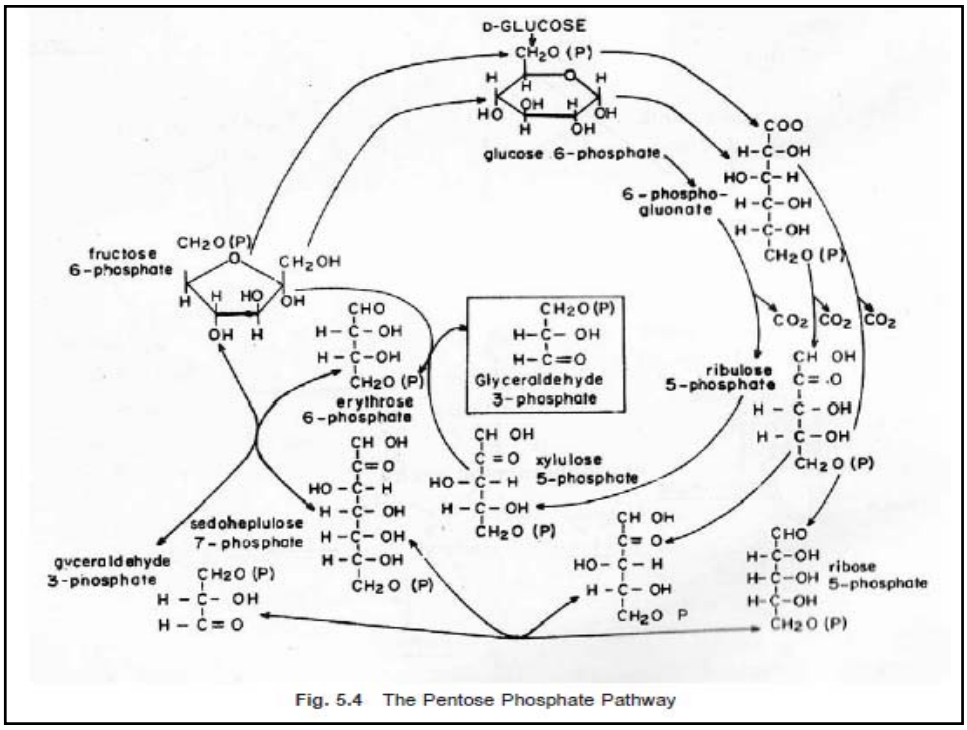

Fig. 5.4 The Pentose Phosphate Pathway