Chem Factsheet

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Manufacture of Ethanol

Ethanol, C_2H_5OH, is a simple but extremely important compound manufactured globally on a huge scale. Current annual production of ethanol is in excess of 80 billion litres and this continues to rise. The vast majority of ethanol is made via fermentation with the small remainder synthesised from petroleum-based feedstock. Most of the ethanol created is used as a biofuel; other large-scale applications include solvents and the alcoholic beverage industry.

Fermentation

Typically, sucrose ($C_{12}H_{22}O_{11}$) in sugar cane or beets or corn starch is converted to ethanol using yeast.

1. Enzymes are added to corn starch before fermentation to hydrolyse it to glucose ($C_6H_{12}O_6$).
2. Sugar cane or hydrolysed starch is added to warm water (30-35 °C).
3. Yeast is added to the mixture.
4. Yeast enzymes convert sucrose in the sugar cane into glucose and fructose.
5. The enzyme zymase, present in yeast, converts glucose into ethanol and carbon dioxide in the absence of oxygen.

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

6. The ethanol produced can then be processed and purified depending on how it is to be used:

a. **Distillation and dehydration**
Ethanol used as a fuel must be close to pure (100% ethanol). Yeast begins to die above 12-15% ethanol content and so ethanol produced by fermentation never reaches the desired concentrations. The ethanol solution is distilled to yield an azeotropic mixture of about 95% ethanol and 5% water.

Azeotrope - a mixture of two liquids whose proportions cannot be changed by distillation because the composition of the vapour is identical to the composition of the solution.
The remaining water can be removed using a dehydrating agent.

b. **Sedimentation, clarification and bottling**
For low ethanol content beverages, (e.g., beer) the yeast and other organic matter is left to settle at the bottom of the mixture, the ethanol mixture is run off and a clarifying agent added. This clear solution can then be bottled for distribution and sale.

Cellulosic ethanol is an ever-growing industry in which cellulose (rather than sucrose or starches) is used as the source of glucose. Specialised organisms (e.g., fungi) use enzymes to hydrolyse the cellulose in plant matter to glucose molecules which can then be used in fermentation.

Catalytic hydration of ethene

Ethene, produced via the cracking of petroleum-derived alkanes, can be hydrated ("water added") with superhot steam to yield ethanol in the presence of a catalyst.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

Specific conditions:

Temperature:	300 °C
Pressure:	60-70 atmospheres (6-7 MPa)
Catalyst:	Phosphoric(V) acid, H_3PO_4 (adsorbed on to a porous solid support)
Ratio:	1.0 mole of C_2H_4 to 0.6 moles of H_2O.

A non-stoichiometric ratio (not 1 mole : 1 mole) is used with ethene in excess to prevent the phosphoric acid catalyst being diluted or washed off the support by the steam.

Equilibrium considerations

1. **Temperature**: the hydration process is exothermic and, therefore, yield of ethanol improves as the temperature decreases. However, rate of ethanol production decreases at the same time. The selected temperature of 300 °C provides an acceptable yield at an acceptable rate of production; this is termed a **compromise temperature**.
2. **Pressure**: the forward reaction converts two moles of gas into one mole of gas. Increasing the pressure will shift the equilibrium to the side with fewer moles of gas and therefore increase the yield of ethanol. This explains the high pressure used; higher pressures are not used due to cost (energy and equipment) and safety implications and the increasing possibility of ethene polymerisation.
3. **Catalyst**: does not affect yield of ethanol but increases rate of ethanol production and allows a lower temperature to be used (increasing yield and reducing energy costs).
4. **Removal of ethanol**: ethanol is condensed and removed from the system as it is produced. This prevents equilibrium from being established and the forward reaction is constantly being driven. Any unreacted ethene and steam are recycled back into the main reactor.

Advantages and disadvantages of fermentation

Advantages	Disadvantages
Produced from renewable feedstock, e.g. crops	Slow batch process – may take weeks for conversion of sugars
Initial production of ethanol has a low energy usage	Requires significant labour to harvest crops and run fermentation/ purification processes
Low environmental impact	Low yield
Easy to control batch process	Impure product
	Subsequent distillation is energy intensive
Equipment can be cheap and simple	Land used to grow ethanol crops rather than food crops – may lead to food shortage or price rises
	Moderate atom economy – 51%

The final product is an ethanol-water mixture (as some steam condenses with the ethanol) which then has to undergo distillation and dehydration to produce ethanol in excess of 95% by volume.

Advantages and disadvantages of catalytic hydration

Advantages	Disadvantages
Very fast and continuous flow process	Uses non-renewable petroleum-derived feedstock
High yield of ethanol	
Product is 'pure' (only water as impurity)	Energy intensive
Highly automated – small workforce needed	Complicated and expensive equipment required
Yield and rate of production can be controlled	
100% atom economy	Product still requires distillation

Choice of process

Despite all its apparent advantages, catalytic hydration is used to make less than 10% of the ethanol manufactured globally each year. Considerations as to which process might be employed include:

1. **Availability of resources**: the two largest producers of ethanol, USA and Brazil, are able to produce corn and sugar cane in vast quantities due to the availability of land and appropriate climates. Catalytic hydration requires an established petroleum industry which many countries do not possess.
2. **Environmental impact**: production of ethanol from crops has a lower carbon footprint (per litre of ethanol) than catalytic hydration as the crops remove carbon dioxide from the atmosphere as they grow.
3. **Economics**: depending on resources, energy production and established industries, one process may be more profitable than the other. The batch process of fermentation is simpler and easier to set up than hydration.

Questions

1. State and explain the effect of increasing the temperature on the yield of ethanol during catalytic hydration of ethene.

2. Explain why fermentation gives a low yield of ethanol.

3. Suggest two advantages of making ethanol via fermentation rather than catalytic hydration.

4. Explain why temperatures that give a better yield of ethanol during hydration are not used.

Answers

1. Yield decreases; equilibrium shifts in endothermic direction which is the backwards reaction.

2. Ethanol poisons/kills yeast at fairly low concentrations (e.g. 15% by volume) so fermentation stops.

3. Fermentation uses renewable feedstock, hydration uses non-renewable feedstock.
   Fermentation has lower energy requirements
   Fermentation uses simpler/cheaper technology

4. Better yield is created by lowering the temperature; however, rate of production of ethanol becomes too slow to be economical.

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