Chem Factsheet

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Ethanol Production

The three major exam boards have different requirements in this context. Hence, they are summarised below to allow you to choose the most relevant sections of this Factsheet for your particular needs.

AQA
- know how ethanol is produced industrially by fermentation
- know the conditions for this reaction and understand the economic and environmental advantages and disadvantages of this process compared with the industrial production from ethene
- understand the meaning of the term biofuel
- know that the term carbon neutral refers to 'an activity that has no net annual carbon (greenhouse gas) emissions to the atmosphere'
- appreciate the extent to which ethanol, produced by fermentation, can be considered to be a carbon-neutral biofuel

EDEXCEL
- apply the concept of carbon neutrality to different fuels, such as petrol, bio-ethanol and hydrogen

OCR
describe the industrial production of ethanol by:
- o fermentation from sugars, i.e. from glucose,
- o the reaction of ethene with steam in the presence of an acid (conc. H_3PO_4) catalyst;

To succeed in this topic you need to:-
- Be familiar with basic organic nomenclature and functional groups.
- Know what is meant by the terms; fuel, combustion, oxidation, fermentation, catalyst, enzyme.

After working through this Factsheet you will:-
- Know and be able to compare and contrast the principle industrial methods of ethanol production.
- Be able to discuss the ideas relating to the use of ethanol as a fuel in terms of sustainability, carbon neutrality and viability.

Introduction
Ethanol can be made either by the hydration of ethene (derived from crude oil) or by fermentation of sugars (obtained from plants that can be replanted). At first sight it would seem to be obvious that the second method is more environmentally friendly, more sustainable and possibly carbon-neutral. However, a fuller consideration of the two processes needs to be made if we are to reach any definite conclusions.

Industrial Hydration of Ethene

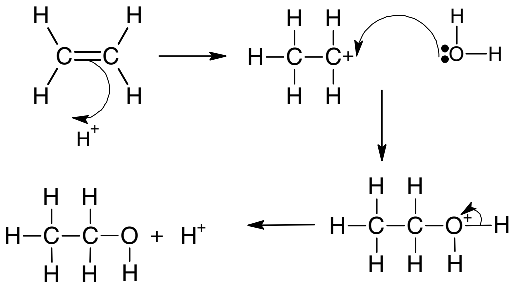
Ethene and steam react together at 300°C under a high pressure of 7 MPa, in the presence of a concentrated phosphoric acid, H_3PO_4, catalyst.

$$CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$$

As the reaction is an equilibrium the high pressure increases the yield (why? – see answers to questions in text (i)

However, the reaction is also exothermic, so the higher the temperature the poorer the yield (why? – see answers to questions in text (ii). It therefore seems odd that such a high temperature is chosen for this reaction (why? – see answers to questions in text (iii).

The catalytic role of the phosphoric acid can be seen in the mechanism below, as it is the source of the hydrogen ions.



i.e. the hydrogen ion's catalytic nature is seen from the fact that it is added in the first stage but regenerated at the end of the sequence. Overall this reaction is referred to as an electrophilic addition – but what is the role of the water in the second stage of the sequence? (why? – see answers to questions in text iv)

Fermentation of Sugar
Fermentation involves the decomposition of sugar into ethanol and carbon dioxide, catalysed by enzymes in yeast. The production of ethanol for use as a fuel is very similar to that employed during wine and beer making.

The sugars can come from a variety of sources including:
- Sugar beet
- Sugar cane
- Molasses (which is a by product of processing sugar cane and sugar beet)
- Starch from wheat, potatoes or maize.

If the source is a starch-containing crop then a hydrolysis step is necessary to breakdown the long-chain starch molecules into glucose before fermentation can be carried out.

Sugar-containing crops are extracted to produce a sugar solution to which the yeast is added directly and fermented at a pH of 4.5 (why? – see answers to questions in text v) and a temperature of about 37°C (why? – see answers to questions in text (vi)).

The mixture remaining at the end of the fermentation process (called mash) typically contains 50-100 grams of ethanol per litre (5-10% w/v) and the ethanol is separated from the mash by distillation.

The product of distillation is not pure ethanol as a mixture of water and ethanol forms a constant-boiling mixture (called an "azeotrope") of about 95% ethanol and 5% water which cannot be separated further by distillation.

The 95% ethanol can be used directly as a fuel and, in many cases, it may be cheaper and simpler to convert engines to run on ethanol fuel than to purify the ethanol further by complicated dehydration processes.

If 100% ethanol is produced by dehydration then this can be added to petrol in any proportion up to 20% ethanol without the need for any engine modification so saving on demand for petrol and also improving the quality of the petrol by raising its octane rating. In a blended fuel the proportion of ethanol is indicated by giving the fuel an 'E' number i.e. E5 contains 5% ethanol, E20 contains 20% ethanol and E100 refers to the azeotrope.

Economic and 'Green' Issues

A 2010 motor car with "E20 Capability" – it can be fuelled by E20 petrol without any engine modification.

Disadvantages of Fermentation:
- The low purity of ethanol produced by fermentation adds to the overall cost of the fermentation process due to all the extra steps and energy inputs needed to purify it.
- By comparison with the addition reaction involved in direct hydration, fermentation has a low atom economy, which is usually a sign of it being a poor process in terms of sustainability. However, the carbon dioxide produced can be used to make fizzy drinks, so improving the overall atom economy of the process.
- The fact that fermentation is a batch process makes it more labour intensive and time-consuming, but the equipment needed is much cheaper than that required for the continuous process of hydration.
- The land needed to grow crops to provide feedstock for ethanol production by fermentation could potentially be used for growing food crops. This could lead to an increase in food prices or even food shortages.

Advantages of Fermentation:
- The much lower temperatures and pressures needed for fermentation make the energy use much lower than for direct hydration.
- It reduces the use of non-renewable fossil fuels
- The low temperatures and pressures also reduce the cost of the equipment needed for fermentation
- The crops needed to produce the sugars for fermentation are renewable resources. This both reduces the need to use and deplete a non-renewable fossil fuel resource and also makes ethanol, from this source, a potentially carbon-neutral biofuel.

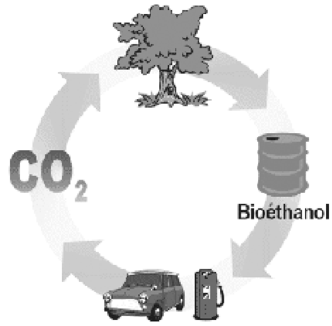
Carbon Neutral Fuel

By definition, a carbon neutral fuel is one that results in zero annual net carbon (greenhouse gas) emissions to the atmosphere. The argument in favour of ethanol, produced by fermentation of sugars, being carbon neutral, is that, overall, the carbon dioxide produced by burning the fuel is exactly matched by the carbon dioxide taken up by the crop plants during photosynthesis while they are growing. i.e.

Photosynthesis = $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

Fermentation = $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

Combustion = $2C_2H_5OH + 6O_2 \rightarrow 6CO_2 + 6H_2O$



Combining fermentation and combustion gives:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

This is the reverse of the original photosynthesis equation and the energy released during combustion is effectively the energy that was originally absorbed during photosynthesis from the sun.

However, these equations don't tell the whole story as there are also other factors to consider. For example:
- Making and operating farm machinery and processing plants
- Making and transporting fertilisers
- Distilling and dehydrating the ethanol
- Distributing the fuel after production

If the energy demands of any of these processes are met by using fossil fuels (e.g. fuel for transport tankers) then the bioethanol produced cannot be considered to be truly carbon-neutral.

If examined in even closer detail, less obvious factors need to be considered. For example, carbon dioxide is also produced during the manufacture of steel and concrete used to build any fermentation site. Similarly, it is released during the production of hydrogen needed for the Haber process to make ammonia necessary to manufacture fertilisers for the successful growing of the sugar-based plants. There are many such factors which contribute to the final conclusion that bioethanol is not truly carbon neutral.

Answers to Questions in Text

(i) By Le Chatelier's Principle, as there are more moles of gas on the left than on the right, an increase in pressure will be counteracted by a shift in position of equilibrium to the right.

(ii) By Le Chatelier's Principle, an increase in temperature is always counteracted by a shift in equilibrium in the direction of the endothermic reaction. As this reaction is exothermic in the forward direction the reverse reaction must be endothermic and hence the equilibrium shifts to the left at high temperatures, so reducing the yield.

(iii) The temperature chosen is a compromise between the low temperature that would be most favourable from the point of view of the yield and the higher temperatures that would increase the rate of the reaction. If too low a temperature was chosen then the reaction would be much too slow so this temperature is chosen so as to give a decent rate without having too adverse an effect on the yield.

(iv) By donating a lone pair from the oxygen to the carbocation formed in the first step, the water is acting as a nucleophile.

(v) Controlling the pH prevents the growth of contaminating bacteria and the yeast enzymes operate at optimum pH without denaturing.

(vi) This is the optimum temperature for the enzyme, lower temperatures would be slower while, at higher temperatures the enzymes would be denatured and the yeast killed.

Practice Questions

1. Ethanol can be manufactured by two different processes. One process uses ethene and the other uses glucose.
   Process 1: $CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$
   Process 2: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
   (a) For each process, name the type of reaction and give a suitable catalyst.
   (b) Give one advantage that **each** process has over the other. [6]

2. Ethanol is an alternative fuel for car engines. Ethanol can be made either by the hydration of ethene or by the fermentation of glucose.
   (a) State what is meant by the term *hydration*.
   (b) Write an equation for the hydration of ethene.
   (c) Write an equation for the formation of ethanol from glucose, $C_6H_{12}O_6$
   (d) Write an equation for the incomplete combustion of ethanol to produce carbon monoxide and water only[4]

3. Industrially ethanol can be produced in one of two ways
   I. The direct hydration of ethene with steam
   $C_2H_4 + H_2O \rightarrow C_2H_5OH$
   II. The fermentation of glucose
   $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$
   (a) State the atom economy for the direct hydration shown in I above [1]
   (b) Calculate the atom economy for the fermentation shown in II above [3]
   (c) Comment on the comparison between these values in terms of what they suggest about the sustainability of each process [3]
   (d) How could the sustainability of the fermentation be improved? Give a specific example to support your suggestion [2]
   (e) Write an equation for the complete combustion of ethanol [2]
   (f) Define the term *carbon neutral* [1]
   (g) Discuss the extent to which the use of ethanol, derived from each of the two possible methods of production, can be considered to be a carbon-neutral fuel [4]

Answers

1. Process 1:
   M1 Hydration ***OR*** (electrophilic) addition (not 'hydrolysis)
   M2 Concentrated H_2SO_4 ***OR*** concentrated H_3PO_4
   M3 100% or high yield ***OR*** (more) pure product ***OR*** fast reaction (ignore unqualified references to cost or to energy use or to the use of a continuous process)

   Process 2:
   M1 Fermentation
   M2 Yeast or suitable enzyme (zymase)
   M3 Renewable source of raw material/sugar/glucose/reactant ***OR*** (uses) cheap equipment (NOT 'glucose' is a renewable energy source; ignore references to carbon dioxide)

2. (a) The addition of water / H_2O

   (b) $C_2H_4 + H_2O \rightarrow CH_3CH_2OH$

   (c) $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

   (d) $C_2H_5OH + 2O_2 \rightarrow 2CO + 3H_2O$

3. (a) 100% (this is the case for any addition reaction, i.e. where there is only a single product).

   (b) $$AE = \frac{\text{Total } M_r \text{ of required product}}{\text{Total } M_r \text{ of all reactant}} \times 100$$

   $$= \frac{92}{180} \times 100 = 51.1\%$$

   (c) The much lower value for the fermentation process suggests that this process is not as sustainable as the hydration. However, this is not the only factor to consider as the hydration depletes a non-renewable resource (crude oil, used to produce ethene) whilst the fermentation depends on a renewable resource (the crop grown to produce the sugars) making the latter more sustainable.

   (d) A use would need to be found for the CO_2 produced, e.g. for the manufacture of fizzy drinks.

   (e) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

   (f) A process is carbon neutral if there is no net annual production of atmospheric carbon (greenhouse gases).

   (g) Ethanol derived from ethene is not carbon-neutral as the CO_2 produced has been 'locked up' as fossil fuel for a very long period of time so is a net addition to atmospheric carbon. Ethanol derived from fermentation is sometimes considered to be carbon neutral as the CO_2 produced appears to be balanced by that taken up by the plants during photosynthesis as they grow. However, this does not take account of the CO_2 produced during processes involved in farming and transportation of the raw materials (if they are powered from fossil fuels).

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