Preface

This study guide covers the necessary material required for the VCE Chemistry 3/4 Study Design 2017 - 2021 and is designed to build problem solving skills for students studying VCE Chemistry Units 3/4, to assist them in learning each topic and in preparing for SACs. It consists of two sections, Section 1 containing 8 trial SACs and Section 2 containing 3 trial txaminations. This book comes with a second solution manual. That is, each practice test comes with model solutions and a marking scheme, along with a detailed explanation of the solution to each problem.

The feature that makes this study guide package different is the hyper-detailed solutions to all problems in the solution manual, which is available as a digital download from www.examproguides.com. The majority of current VCE Chemistry practice material is very much question-oriented without any meaningful focus on the solutions to the questions. There is nothing more frustrating than attempting a question, getting it wrong or being stuck, and not being able to make head-or-tail of a skeleton solution set with little-to-no explanation. We have endeavoured to ensure that the detailed explanations in this book will give you a good understanding of how you can get the answer to any of our problems. They will show you how to think when you see a problem how to use logic to get to your answer. They will also show you how to methodically structure your answer so that it is easy for the examiner to follow. In some cases, there will even be coverage of theory to fill in potential knowledge gaps.

The three trial examinations are designed to match the specifications of the new 2017-2021 study design, and are arranged approximately in order of difficulty, with Exam 1 being the easiest and Exam 3 being the hardest. Exam 1 matches the easier end of VCAA's spectrum of difficulty, whereas Exam 3 matches the harder end (even perhaps being a little bit harder than VCAA). Of particular note in this study design is the focus on experimental investigation and the inclusion of "extended answer questions" in the examinations, as per the Examination Specifications provided by VCAA at the time of publishing. Therefore, the trial examinations contain a significant number of questions that require you to draw upon your knowledge of experimental design. They also contain extended answer questions of about 6-10 marks worth; the author anticipates that these questions will be the differentiating questions in the exam - so work on these carefully!

Remember, **Chemistry is a problem-solving based subject** and the best way to study it is through completing lots of problems. This subject can be a richly rewarding study for those who work hard at it. Good luck, and have fun!

Thushan Hettige

Acknowledgements

Table of Contents

UNIT 3 AREA OF STUDY 1, TEST 1

FUELS

Writing time: 90 minutes

Structure of test

Number of questions	Number of questions to be answered	Number of marks
4	4	50

Question 1 (14 marks)

Methane is a chemical that can be used as a fuel to generate electricity. The molar enthalpy of combustion of methane at 25ºC is -882 kJ mol^{-1}.

a. Define the term 'fuel'. 1 mark

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b. Write down a **thermochemical equation**, including states, for the complete combustion of methane. 3 marks

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The molar enthalpy of combustion of carbon monoxide (CO) is -283 kJ mol^{-1}.

c. Write down a balanced equation, including states, for the **incomplete** combustion of methane. 2 marks

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d. Therefore, using the information above, determine the molar enthalpy for the reaction written in part **c**. 2 marks

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e. Compare and contrast the different sources of methane with respect to their renewability and environmental impacts related to sourcing and combustion.　　　　6 marks

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Question 2 (17 marks)

Crude oil is a black tarry fluid containing a mixture of hydrocarbons. It can be refined to separate the hydrocarbons of different sizes. One distillate of crude oil is called **fuel oil**, which is used for electricity generation in some countries like Sri Lanka.

a. Which has the greater energy content per kilogram of fuel, fuel oil or coal? 1 mark

b. Why is it impossible for the energy content of fuel oil to be expressed in kJ mol^{-1}? 1 mark

One substance that is found in fuel oil is hexadecane ($C_{16}H_{34}$), which has a molar enthalpy of combustion of $-10,700$ kJ mol^{-1}.

c. Write down a **thermochemical equation**, including states, for the complete combustion of hexadecane. 3 marks

A 3.50 g sample of pure hexadecane was combusted in excess oxygen.

d. Calculate

    i. the total volume of CO_2 produced at a pressure of 175 kPa and a temperature of 210ºC 3 marks

    ii. the total volume of CO_2 produced at SLC. 2 marks

It has been given that

- methane has a molar enthalpy of combustion of -882 kJ mol^{-1}

- hexadecane has a molar enthalpy of combustion of $-10{,}700$ kJ mol^{-1}.

e. Based **only** on the volume of greenhouse gases emitted per MJ of energy released at SLC, determine which of the two fuels has a lesser environmental impact. 4 marks

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f. Explain whether your answer to part **e** alone allows you to make a firm conclusion as to whether the combustion of biogas or fuel oil has a lesser environmental impact. 3 marks

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Question 3 (10 marks)

Bioethanol is a type of biofuel.

a. Describe what is meant by the term 'biofuel' and explain whether biofuels are renewable or not.   2 marks

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A spirit burner containing ethanol is placed underneath a beaker containing water. The ethanol in the burner is ignited and burnt, which heats the water in the beaker. A diagram of the experimental setup is shown below:
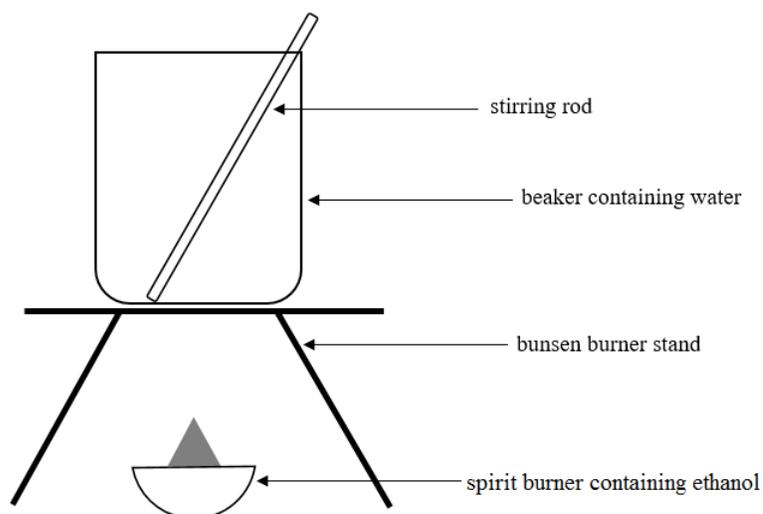
mass of water in the beaker	500.0 g
initial mass of ethanol in burner	22.15 g
final mass of ethanol in burner	20.20 g
initial temperature	24.5°C
final temperature	46.7°C

b. Using the experimental data above, estimate the molar enthalpy of combustion of ethanol.   3 marks

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Data sources quote the molar enthalpy of combustion of ethanol is -1370 kJ mol^{-1}.

c. Explain the discrepancy between the value obtained in part **b** and the quoted value above.   1 mark

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d. Express the quoted molar enthalpy of combustion of ethanol in MJ tonne^{-1}.   2 marks

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e. Write down a balanced equation for the **incomplete combustion** of ethanol.   2 marks

_____

Question 4 (9 marks)

The structures of two molecules are shown below:

Structure A   **Structure B**

a.   Which of the above structures is a component of **petrodiesel**? Explain your answer.   1 mark

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_____

b.   With reference to the above structures, compare the cold flow properties of biodiesel and petrodiesel and
the implications of these properties on the operation of a diesel-fuelled car in extreme cold conditions.   3 marks

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c. With reference to structures A and B, compare the relative hygroscopicity of petrodiesel and biodiesel, and describe the implications of increased fuel hygroscopicity on the operation of a car.   3 marks

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d. Circle the correct responses to the following statement.   2 marks

Compared to petrodiesel, the combustion of biodiesel leads to

        lesser CO production   greater CO production

        lesser nitrogen oxide production   greater nitrogen oxide production

MODEL SOLUTIONS AND MARKING SCHEME

UNIT 3 AREA OF STUDY 1, TEST 1

FUELS

Question 1

<u>**Part a.**</u>

The mark is awarded for a valid definition. Below is an example of a valid definition:

"A fuel is a substance that can be reacted with other substances (often oxygen), leading to the release of energy (usually chemical) that can be harnessed for a specific purpose."
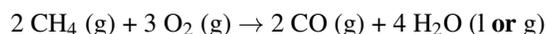
<u>**Part b.**</u>
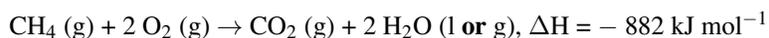
$$CH_4 \text{ (g)} + 2\, O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2\, H_2O \text{ (l \textbf{or} g)}, \Delta H = -882 \text{ kJ mol}^{-1}$$

One mark is awarded for each of:

- correctly balanced equation
- correct states
- correct ΔH value.

Technically, when the molar enthalpy of combustion is given at 25ºC, the state of each chemical have to be the state that it would be in at 25ºC, so water should be a **liquid**. However, in the 2010 VCAA Assessment report, water was given as a gas. Therefore, it is likely that both water as a **liquid** or as a **gas** would be accepted in the VCE context.
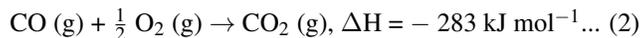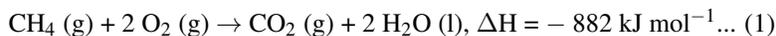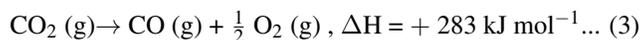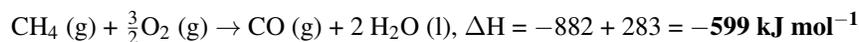
<u>**Part c.**</u>

$$CH_4 \text{ (g)} + \tfrac{3}{2}O_2 \text{ (g)} \rightarrow CO \text{ (g)} + 2\, H_2O \text{ (l \textbf{or} g)}$$

OR

$$2\, CH_4 \text{ (g)} + 3\, O_2 \text{ (g)} \rightarrow 2\, CO \text{ (g)} + 4\, H_2O \text{ (l \textbf{or} g)}$$

One mark is awarded for each of:

- correctly balanced equation
- correct states

Part d.

$$CH_4 \text{ (g)} + 2\, O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2\, H_2O \text{ (l)}, \Delta H = -882 \text{ kJ mol}^{-1}... (1)$$

$$CO \text{ (g)} + \tfrac{1}{2}\, O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)}, \Delta H = -283 \text{ kJ mol}^{-1}... (2)$$

Rearranging equation (2),

$$CO_2 \text{ (g)} \rightarrow CO \text{ (g)} + \tfrac{1}{2}\, O_2 \text{ (g)}, \Delta H = +283 \text{ kJ mol}^{-1}... (3)$$

Adding equations (1) and (3), we get:

$$CH_4 \text{ (g)} + \tfrac{3}{2}O_2 \text{ (g)} \rightarrow CO \text{ (g)} + 2\, H_2O \text{ (l)}, \Delta H = -882 + 283 = \mathbf{-599 \text{ kJ mol}^{-1}}$$

One mark is awarded for each of:

- writing down/identifying equation (2) with its associated ΔH value of -283 kJ mol^{-1}

- the correct answer of **-599 kJ mol**$^{-1}$ (or -1198 kJ mol^{-1} if equation in part **c** has a coefficient of 2 in front of the CH$_4$).

Part e.

One mark is awarded for each of the following:

- identifying the sources of methane as **natural gas, coal seam gas** and **biogas**

- correctly describing the renewability of **only** the sources of methane mentioned in student's answer, so long as it is consistent with the following:

    - natural gas is nonrenewable
    - coal seam gas is nonrenewable
    - biogas is renewable

- identifying **land clearance/habitat destruction** as an environmental impact related to sourcing, for all three sources of methane

- identifying and **describing** a difference in environmental impact between sourcing of coal seam gas vs natural gas (i.e. **fracking**)

- identifying **ONE** other environmental impact related to sourcing or combustion (eg. gas leaks for natural gas and coal seam gas, photochemical smog from nitrogen oxides due to combustion of natural gas or coal seam gas, acid rain from sulfur oxides due to combustion of natural gas or coal seam gas)

- describing and explaining why greenhouse gas emissions are lower for biogas compared to the other two (biogas is carbon-neutral as the CO$_2$ emitted was recently absorbed from atmosphere during growing of crops, could also describe how sewage-derived biogas converts atmosphere-destined CH$_4$ to the less potent greenhouse gas CO$_2$ - leading to a drop in impact from greenhouse gases)

An example answer is shown below:

Biogas is a renewable source of methane, whereas both natural gas and coal seam gas are non-renewable sources of methane.

Environmental impacts (sourcing): Land clearance and habitat destruction are impacts common to all three sources of methane. However, with sourcing natural gas and coal seam gas, there is a significant risk of gas leak, which could be harmful to the community and release significant amounts of methane, a highly potent greenhouse gas, into the atmosphere. Coal seam gas also has the issue related to fracking (the use of fluid to crack the coal seam), including contamination of water in aquifers.

Environmental impacts (combustion): There is little net greenhouse gas emissions for biogas, given that in the growth of the plant material required to produce the biogas, CO$_2$ is consumed by the plants. The amount of this CO$_2$ is near the amount of CO$_2$ released during combustion of biogas. The net greenhouse gas emissions for methane and coal seam gas (both fossil fuels), are significantly higher than that for biogas.
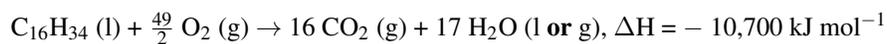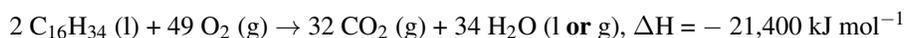
Question 2

Part a.

fuel oil

Part b.

Fuel oil is a **mixture** of different substances (with different molar masses).

Part c.

$$C_{16}H_{34} \text{ (l)} + \frac{49}{2} O_2 \text{ (g)} \rightarrow 16 \, CO_2 \text{ (g)} + 17 \, H_2O \text{ (l or g)}, \Delta H = -10{,}700 \text{ kJ mol}^{-1}$$

OR

$$2 \, C_{16}H_{34} \text{ (l)} + 49 \, O_2 \text{ (g)} \rightarrow 32 \, CO_2 \text{ (g)} + 34 \, H_2O \text{ (l or g)}, \Delta H = -21{,}400 \text{ kJ mol}^{-1}$$

One mark is awarded for each of:

- correctly balanced equation
- correct states
- correct ΔH value.

Part di.

Solution:

$$
\begin{aligned}
n \, (C_{16}H_{34}) \ &= \ \frac{3.50}{226.0} \\
&= \ 0.0155 \text{ mol} \\
n \, (CO_2) \ &= \ 16 \, n(C_{16}H_{34})* \\
&= \ 0.248 \text{ mol} \\
V \, (CO_2) \ &= \ \frac{nRT}{P} \\
&= \ \frac{0.248 \times 8.31 \times 483}{175}* \\
&= \ 5.68 \text{ L}*
\end{aligned}
$$

One mark is awarded for each of:

- correctly using the $CO_2/C_{16}H_{34}$ mole ratio of 16
- correctly using the ideal gas equation (including a depiction of correct numbers used)
- correct answer of **5.68 L**.

Part dii.

Solution:

$$
\begin{aligned}
V\,(CO_2) \;&=\; n\,(CO_2)\times V_m \\
&=\; 0.248 \times 24.8* \\
&=\; 6.15 \; L
\end{aligned}
$$

One mark is awarded for each of:

- correctly identifying the molar volume as 24.8 L

- correct answer of **6.15 L**.

Part e.

methane (CH_4)	hexadecane ($C_{16}H_{34}$)
The amount of methane required to release 1 MJ = 1000 kJ of energy: $$\begin{aligned} n\,(CH_4) \;&=\; \frac{1000}{882} \\ &=\; 1.13 \text{ mol} \end{aligned}$$ Therefore, $$\begin{aligned} n\,(CO_2) \;&=\; n\,(CH_4) \\ &=\; 1.13 \text{ mol} \\ V(CO_2) \;&=\; 1.13 \times 24.8 \\ &=\; \mathbf{28.1\ L} \end{aligned}$$	The amount of hexadecane required to release 1 MJ = 1000 kJ of energy: $$\begin{aligned} n\,(C_{16}H_{34}) \;&=\; \frac{1000}{10700} \\ &=\; 0.0935 \text{ mol} \end{aligned}$$ Therefore, $$\begin{aligned} n\,(CO_2) \;&=\; 16 \times n\,(C_{16}H_{34}) \\ &=\; 1.50 \text{ mol} \\ V(CO_2) \;&=\; 1.50 \times 24.8 \\ &=\; \mathbf{37.1\ L} \end{aligned}$$

Therefore, based on this information, combustion of methane has a lesser environmental impact (CO_2 is a greenhouse gas).

One mark is awarded for each of:

- working out the amount of methane **or** hexadecane required to release 1 MJ of energy (one of these will give the mark)

- working out the volume of CO_2 released upon burning of methane

- working out the volume of CO_2 released upon burning of hexadecane

- stating that methane has a lower environmental impact

Part f.

One mark is awarded for each of:

- stating that the answer to part **e** does **NOT** give sufficient information **AND** giving one reason why (from the list shown below)

- giving one **OTHER** reason (from the list below)

- explaining that biogas is carbon-neutral, and therefore the net CO_2 released from the combustion of methane, as per answer in part **e**, is an overestimate

List of reasons:

- part **e** does not take into account the nitrogen and sulfur oxides that are released, that can cause **acid rain**

- part **e** does not take into account the nitrogen oxides that are released, that can cause **photochemical smog**

- part **e** does not take into account that particulate matter is released with the burning of fuel oil, which can lead to harmful effects in humans

- fuel oil is composed of a mixture of hydrocarbons, not just hexadecane

- any other valid reason

Question 3

Part a.

One mark is awarded for the **definition**.
"Biofuels are fuels sourced from plant material from living or recently deceased plants."

One mark is awarded for stating that **biofuels are renewable AND** explaining that the plant material can be replenished (via photosynthesis) quickly/at a rate similar to which it is consumed.

Part b.

Solution:

$$
\begin{aligned}
\Delta T &= 46.7 - 24.5 \\
&= 22.2\ ^\circ C \\
E_{water} &= 500.0 \times 4.18 \times 22.2* \\
&= 4.64 \times 10^4\ J \\
&= 46.4\ kJ \\
m\ (ethanol) &= 22.15 - 20.20 \\
&= 1.95\ g \\
n\ (ethanol) &= \frac{1.95}{46.0} \\
&= 0.0424\ mol* \\
\Delta H &= \frac{-46.4}{0.0424} \\
&= -1.09 \times 10^3\ kJ\ mol^{-1}*
\end{aligned}
$$

One mark is awarded for:

- correctly determining temperature change **AND** correctly using the $E = mc\Delta T$ formula (or correctly calculating energy absorbed by water)

- calculating the amount of ethanol burnt

- correctly calculating ΔH

Part c.

The mark is awarded for explaining that a significant amount of energy released from the reaction was lost to the environment.
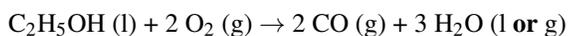
Part d.

Solution:

$$
\begin{aligned}
\Delta H &= -1370 \text{ kJ mol}^{-1} \\
&= -1.370 \text{ MJ mol}^{-1} \\
&= \frac{-1.370}{46.0} \text{ MJ g}^{-1}* \\
&= -0.0298 \text{ MJ g}^{-1} \\
&= -0.0298 \times 10^6 \text{ MJ tonne}^{-1} \\
&= -2.98 \times 10^4 \text{ MJ tonne}^{-1}*
\end{aligned}
$$

One mark is awarded for each of:

- converting from amount to mass (first asterisk)

- correct answer

Part e.

C_2H_5OH (l) + 2 O_2 (g) $\rightarrow$ 2 CO (g) + 3 H_2O (l **or** g)

One mark is awarded for each of:

- correct reactants and products

- correctly **balanced** equation **AND** correct states

Question 4

Part a.

The mark is awarded for **BOTH** of:

- structure **A**

- explaining that structure **A** is a hydrocarbon **OR** that structure **B** contains an ester group/is a methyl ester

Part b.

One mark is awarded for each of:

- at cold conditions, biodiesel is **significantly more <u>viscous</u>** than petrodiesel

- explaining that biodiesel can exhibit stronger dipole-dipole interactions via its **C=O groups**, leading to a greater viscosity

- explaining that in extremely cold conditions, the highly viscous biodiesel can block fuel lines/the biodiesel may not be able to flow

Part c.

One mark is awarded for each of:

- stating that biodiesel is significantly more hygroscopic than petrodiesel

- explaining that the C=O groups in biodiesel allow for hydrogen bonding with water, ensuring that biodiesel can interact with water to a slightly greater extent

- any of:

    - water in the fuel can precipitate rancidification, leading to production of free fatty acids that can corrode the fuel lines

    - water in the fuel can accelerate rusting of fuel lines

    - water in the fuel can promote growth of microorganisms and algae, which can block/clog fuel lines

Part d.

One mark is awarded for circling each of:

- lesser CO production

- greater nitrogen oxide production

DETAILED SOLUTIONS

UNIT 3 AREA OF STUDY 1, TEST 1

FUELS

Question 1

Part a.

This is essentially a definition question, which is largely recall.

"A fuel is a substance that can be reacted with other substances (often oxygen), leading to the release of energy (usually chemical) that can be harnessed for a specific purpose."

You need to know the definition of a fuel; it would be good if you could find a reliable definition from a textbook, for example.

Part b.

A **thermochemical equation** is basically a balanced equation that includes the ΔH value. Therefore, the first step here is to write a balanced chemical equation for this reaction.

So, this is just an example of balancing a combustion eqauation. We have this so far:

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$
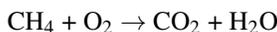
The products of combustion of a hydrocarbon or an organic compound composed of only carbon, hydrogen and oxygen are **carbon dioxide** and **water**.

To balance combustion equations, use the following steps:

1. Balance the **C** atoms first by writing the appropriate coefficient next to the CO_2.

2. Balance the **H** atoms then by writing the appropriate coefficient next to the H_2O.

3. Balance the **O** atoms by writing the appropriate coefficient next to the O_2.
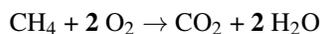
Let's start with **Step 1 (C atoms).**

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$
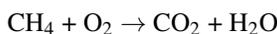
There is one C atom in CH_4. Therefore, there would be only one C atom in CO_2.

Now, for **Step 2 (H atoms).**

$$CH_4 + O_2 \rightarrow CO_2 + \mathbf{2}\,H_2O$$
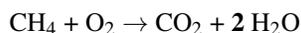
There are **4** H atoms in CH_4. Therefore, you need to have 2 H_2O molecules (each H_2O molecule has 2 H atoms).

Let's go to **Step 3 (O atoms).**

$$CH_4 + \mathbf{2}\,O_2 \rightarrow CO_2 + \mathbf{2}\,H_2O$$

There are **4** O atoms on the RHS (1 CO_2 and 2 H_2O). Therefore, you will have **2** O_2 molecules on LHS.

Now, add states. Methane is a gas at room temperature - oxygen and carbon dioxide are also gases. Water is a tricky one. There are two ways of looking at it:

- the combustion reaction usually releases so much energy that water is evaporated as a gas - by this logic H_2O would be a gas

- the products are cooled back down to 25ºC after the reaction, where water would be a liquid

Conventionally, when we write thermochemical equations for enthalpies of combustion and the quoted enthalpies are given at 25ºC, the states of all species will be the states that they exist at 25ºC. This is because changing the state of the product changes the ΔH value (there is an enthalpy change in the interconversion of water from liquid to gas). The ΔH value given **assumes water to be a liquid**. However, this distinction is usually not discussed in VCE, and VCAA Assessment reports have given water as a gas. Therefore, whilst **liquid** is the technically correct state, either liquid or gas should be accepted at VCE level.

The final step is to assign the correct ΔH value. The question stated that the molar enthalpy of combustion of methane is -882 kJ mol^{-1}, meaning this would be the total enthalpy change if you combusted **1 mole** of CH_4. Now, if we assign a ΔH value to the above equation, this would be the enthalpy change if you react **1 mole** of CH_4 with **2 moles** of O_2. Hence, the thermochemical equation is:

$$CH_4 \text{ (g)} + 2\ O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2\ H_2O \text{ (l)}, \Delta H = -\ 882 \text{ kJ mol}^{-1}$$
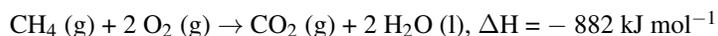
Part c.

This is similar to part **b**, except you need to know that when writing equations of **incomplete combustion**, the products are conventionally **carbon MONOxide (CO)** and **water**. In reality, when you perform incomplete combustion, you produce a variety of products in varying quantities, such as a tiny amount of CO_2, CO, graphite (elemental carbon, C), and when you incompletely combust large hydrocarbons, you can also produce smaller unburnt hydrocarbons by pyrolytic cracking. Anyway, balancing incomplete combustion equations - you use the exact same steps as for part **b**.

So we have the following equation:

$$CH_4 + O_2 \rightarrow CO + H_2O$$

Balancing the **C** atoms - they are already balanced (1 on each side).

Balancing the **H** atoms:

$$CH_4 + O_2 \rightarrow CO + \mathbf{2}\ H_2O$$
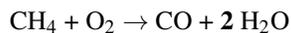
Balancing the **O** atoms: there are 3 O atoms on the RHS, except the only oxygen-containing species on the LHS is O_2 - therefore one could say that you could only add an even number of O atoms on the LHS. We can get around this issue **by using fractions as coefficients**. This is a perfectly acceptable convention to use. Hence, balancing the O atoms and including states, we get -
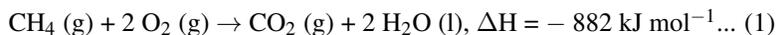
$$CH_4 \text{ (g)} + \tfrac{3}{2}\ O_2 \text{ (g)} \rightarrow CO \text{ (g)} + 2\ H_2O \text{ (l)}$$
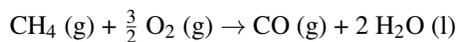
Alternatively, if you do not like fractions, you **can** double the coefficients:

$$2\ CH_4 \text{ (g)} + 3\ O_2 \text{ (g)} \rightarrow 2\ CO \text{ (g)} + 4\ H_2O \text{ (l)}$$
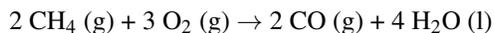
Part d.

This is a rather tricky question. Let's put out the facts on the table. What do we know? We know the thermochemical equation for the complete combustion of methane:

$$CH_4 \text{ (g)} + 2 O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2 H_2O \text{ (l)}, \Delta H = -882 \text{ kJ mol}^{-1}... (1)$$

We are also given that the molar enthalpy of combustion of CO is -283 kJ mol^{-1}. What does this equation look like? Since there are no H atoms in CO, the only possible product in the combustion of CO would be CO_2. Hence, we can write this thermochemical equation:
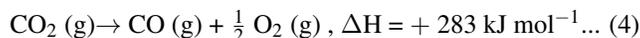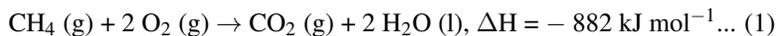
$$CO \text{ (g)} + \tfrac{1}{2} O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)}, \Delta H = -283 \text{ kJ mol}^{-1}... (2)$$
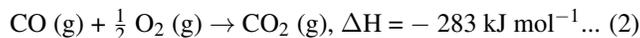
Now, we need to use the above two equations to derive a ΔH value for the following equation:

$$CH_4 \text{ (g)} + \tfrac{3}{2} O_2 \text{ (g)} \rightarrow CO \text{ (g)} + 2 H_2O \text{ (l)}... (3)$$
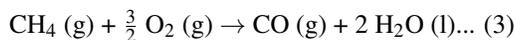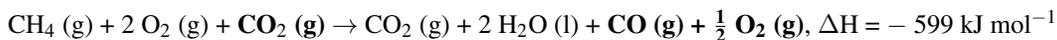
Now, equation (3) most closely resembles equation (1), except we have to somehow get rid of the CO_2 and replace it with CO. Fortunately, we are given a thermochemocal equation that converts between CO and CO_2 - equation (2). However, equation (1) and (2) have the CO_2 on the same side. Hence, we need to reverse equation (2) to get the CO_2 onto the opposite side so we can cancel out the CO_2 by combining equations (1) and (2). Reversing equation (2):

$$CO_2 \text{ (g)} \rightarrow CO \text{ (g)} + \tfrac{1}{2} O_2 \text{ (g)} , \Delta H = +283 \text{ kJ mol}^{-1}... (4)$$
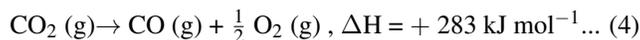
Remember that reversing a reaction equation means you change the **sign** of the ΔH value. Lets put equations (1) and (4) side by side for comparison:

$$CH_4 \text{ (g)} + 2 O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2 H_2O \text{ (l)}, \Delta H = -882 \text{ kJ mol}^{-1}... (1)$$

$$CO_2 \text{ (g)} \rightarrow CO \text{ (g)} + \tfrac{1}{2} O_2 \text{ (g)} , \Delta H = +283 \text{ kJ mol}^{-1}... (4)$$

You can now just add equations (1) and (4) to, in effect, replace the CO_2 with CO. Adding equations means adding ΔH values:

$$CH_4 \text{ (g)} + 2 O_2 \text{ (g)} + \mathbf{CO_2 \text{ (g)}} \rightarrow CO_2 \text{ (g)} + 2 H_2O \text{ (l)} + \mathbf{CO \text{ (g)}} + \mathbf{\tfrac{1}{2} O_2 \text{ (g)}}, \Delta H = -599 \text{ kJ mol}^{-1}$$

Simplifying this equation by cancelling out the CO_2 and $\tfrac{1}{2}$ the O_2:

$$CH_4 \text{ (g)} + \tfrac{3}{2} O_2 \text{ (g)} \rightarrow CO \text{ (g)} + 2 H_2O \text{ (l)}, \Delta H = -599 \text{ kJ mol}^{-1}$$
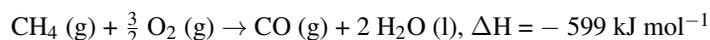
There's your answer!

Part e.

This question is difficult and requires you to think before you write. With these kinds of questions, ensure that you have a good structure and you plan your response.

Let's read the question again:

"Compare and contrast the <u>different sources of methane</u> with respect to their <u>renewability</u> and <u>environmental impacts</u> related to <u>sourcing</u> and <u>combustion</u>."

The first part of this question is - what **are** the different sources of methane? This requires recall!

Remember that methane can be sourced from:

- **fossil fuels**; methane is a hydrocarbon that will be a product of the fossilisation of plant material that has been deceased millions of years ago, and subjected to extremely high pressures via burial. The methane can be present -

    – in **gaseous deposits** under the ground as part of **<u>natural gas</u>**
    – in **liquid deposits**, dissolved in **<u>crude oil</u>** (the methane comes out as association gas after drilling into an oil well - this is very peripheral knowledge and is probably not examinable)
    – in **solid deposits**, mixed in with **<u>coal</u>**, as **<u>coal seam gas</u>**

- **biofuels**; the methane can be sourced from recently deceased plant matter or sewage (where bacteria produce methane as a metabolite) as **biogas**

Now, what are the renewabilities of these different sources of methane? Remember that **fossil fuels** are **nonrenewable**, as the process of fossilisation takes millions of years and is an extremely slow process, whereas **biofuels** are **renewable** as the plants that provide the biomass for the generation of biogas can constantly be grown. Therefore, the fossil-fuel derived sources of methane, being natural gas and coal seam gas, are nonrenewable whereas biogas is renewable.

Let us now focus on the environmental impact related to sourcing the fuel. With respect to coal seam gas and natural gas, both require **drilling** into the ground. To set this up, it is necessary to **clear some land**, which necessitates **destruction of natural habitat** for animals. This could affect ecosystems in negative ways. Even with biogas, biogas derived from biomass may involve clearing up land for the perpetual growth and harvesting of plants for biogas production. This leads to manipulation of natural habitats, which can also have negative ecological effects.

Additional issues with respect to sourcing of fuels include:

- **Gas leaks** in the drilling of natural gas. This leads to significant amounts of methane being released into the atmosphere; methane is a potent greenhouse gas

- **Fracking**. Fracking is a practice that is **sometimes** used to extract methane from coal seams. It involves the pumping of fluid into the coal seam under very high pressures (alongside the drill), leading to the splitting of the coal seam and the subsequent release of methane gas. The issue here is that the fracking fluid, that contains a mixture of chemicals, can seep through the rock and contaminate water from groundwater aquifers that are sometimes used as sources of drinking water.

- **Loss of water from aquifers**. Drilling of methane from coal seams leads to the extraction of a lot of water (called produced water) that is mixed in the coal seam. This depressurises the coal seam, which can cause water from nearby aquifers to seep into the coal seam, potentially removing a source of drinking water for the locals.

How about combustion?

The first thing to talk about are **greenhouse gas emissions**. Carbon dioxide is the typical greenhouse gas. It goes without saying that burning methane from coal seams and from natural gas leads to the evolution of carbon dioxide into the atmosphere.

Biogas is a little different. Yes, the methane from biogas produces carbon dioxide when combusted, whih evolves into the atmosphere. However, keep in mind that we source biogas, at least partially, from biomass (recently deceased plant material). Now, these plants would have recently absorbed carbon dioxide from the atmosphere via photosynthesis, in the synthesis of its structure and large organic molecules, in the course of its life. Therefore, it is believed that the CO_2 evolved from the combustion of biogas is comparable to the CO_2 absorbed from the atmosphere during the production of one of the sources of biogas (biomass).

The burning of natural gas and coal seam gas is associated with some issues. In particular, there is some sulfur and nitrogen which, when combusted, lead to the evolution of sulfur and nitrogen oxides. These can both lead to the production of **acid rain**, and nitrogen oxides in particular can lead to **photochemical smog**. That said, this particular issue is significantly less prominent in the combustion of gas compared to the combustion of coal or crude oil.

Question 2

Part a.

This question is largely recall. However, the general pattern is that the bigger the molecule, the smaller the energy content **per gram of fuel**. The energy content, from **highest** to **lowest** in **MJ/kg**, of each fuel -

- methane (highest)

- petroleum gas

- petrol, petrodiesel, biodiesel, fuel oil (similar to one another)

- **bioethanol**

- coal

The anomaly is **bioethanol** - the presence of the heavy O atom causes the energy content on a mass basis to decrease.

Part b.

For an energy content to be able to be expressed in kJ mol^{-1}, your substance has to have a **known molar mass**. In other words, your substance must be pure with a known formula. However, fuel oil is a **mixture of different hydrocarbons**, whose exact composition cannot be perfectly ascertained.
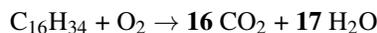
Part c.

A similar method to that shown in **Question 1b** should be followed here.
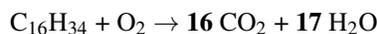Let's start with **Step 1 (C atoms).**

$$C_{16}H_{34} + O_2 \rightarrow \textbf{16}\, CO_2 + H_2O$$
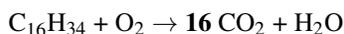
There are 16 C atoms in $C_{16}H_{34}$. Therefore, there would be **16** CO_2 molecules on the RHS.

Now, for **Step 2 (H atoms).**

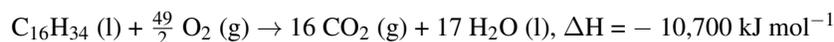$$C_{16}H_{34} + O_2 \rightarrow \textbf{16}\, CO_2 + \textbf{17}\, H_2O$$

There are **34** H atoms in $C_{16}H_{34}$. Therefore, you need to have **17** H_2O molecules (each H_2O molecule has 2 H atoms).

Let's go to **Step 3 (O atoms).**

$$C_{16}H_{34} + O_2 \rightarrow \textbf{16}\ CO_2 + \textbf{17}\ H_2O$$

There are **49** O atoms on the RHS (16 CO_2 and 17 H_2O). Therefore, you will have $\frac{49}{2}$ O_2 molecules on LHS.

Hence:

$$C_{16}H_{34}\ (l) + \tfrac{49}{2}\ O_2\ (g) \rightarrow 16\ CO_2\ (g) + 17\ H_2O\ (l),\ \Delta H = -\ 10{,}700\ kJ\ mol^{-1}$$

Part di.

In this question it is clear that the **ideal gas equation** needs to be used here. Let's have a look at the ideal gas equation:

$$pV\quad =\quad nRT$$

Here, we know the **pressure** to be 175 kPa and the **temperature** to be 210ºC = 483 K. To work out the volume of CO_2 produced, we therefore have to work out the amount of CO_2 produced. How do we do this?

Note that we know the **mass** of hexadecane combusted (3.50 g). We need a relationship between a quantity of hexadecane and a quantity of CO_2. The reaction equation gives this relationship; if **1 mole** of hexadecane is combusted, **16 moles** of CO_2 are produced. Therefore, to exploit this relationship, we need to determine the amount, in moles, of hexadecane:

$$
\begin{aligned}
n\ (C_{16}H_{34}) \quad &= \quad \frac{3.50}{226.0} \\
&= \quad 0.0155\ mol
\end{aligned}
$$

Now that we know the amount of hexadecane, now we can work out the amount, in moles, of CO_2, knowing that it will be 16 times the amount of hexadecane:

$$
\begin{aligned}
n\ (CO_2) \quad &= \quad 16\ n(C_{16}H_{34}) \\
&= \quad 0.248\ mol
\end{aligned}
$$

Applying this to the ideal gas equation:

$$
\begin{aligned}
V\ (CO_2) \quad &= \quad \frac{nRT}{P} \\
&= \quad \frac{0.248 \times 8.31 \times 483}{175} \\
&= \quad 5.68\ L
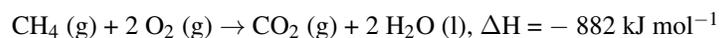\end{aligned}
$$

Part dii.

Remember that SLC means a temperature of 25ºC and a pressure of 100 kPa. The old definition, which was used in VCAA exams from 2016 and earlier, uses a pressure of 101.3 kPa. This was changed in 2017 for VCAA exams, to put them in line with the IUPAC consensus.

At SLC, **1 mole** of gas occupies **24.8 L** of volume. Therefore, sicne we have 0.248 mol of CO_2, the volume of CO_2 produced is

$$
\begin{aligned}
V\ (CO_2) \quad &= \quad n\ (CO_2) \times V_m \\
&= \quad 0.248 \times 24.8^* \\
&= \quad 6.15\ L
\end{aligned}
$$

Part e.

The idea here is just to work out the volume of CO_2 evolved at SLC, if you were to release 1 MJ = 1000 kJ of energy. Let's start with methane - via its thermochemical equation:

$$CH_4 \text{ (g)} + 2\,O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2\,H_2O \text{ (l)}, \Delta H = -\,882 \text{ kJ mol}^{-1}$$
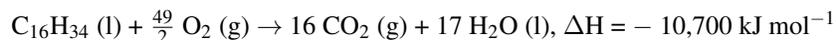
You would want to know how much methane you would need to combust to release 1000 kJ of energy. If you combust **1 mole** of methane, you would release **882 kJ** of energy. Therefore, to work out how much methane is needed to release 1000 kJ of energy:

$$
\begin{aligned}
n\,(CH_4) \quad &= \quad \frac{1000}{882} \\
&= \quad 1.13 \text{ mol}
\end{aligned}
$$

Now, how much CO_2 produced at SLC here -

$$
\begin{aligned}
n\,(CO_2) \quad &= \quad n\,(CH_4) \\
&= \quad 1.13 \text{ mol} \\
V(CO_2) \quad &= \quad 1.13 \times 24.8 \\
&= \quad \textbf{28.1 L}
\end{aligned}
$$

Let us repeat the same exercise for hexadecane.

$$C_{16}H_{34} \text{ (l)} + \tfrac{49}{2}\,O_2 \text{ (g)} \rightarrow 16\,CO_2 \text{ (g)} + 17\,H_2O \text{ (l)}, \Delta H = -\,10{,}700 \text{ kJ mol}^{-1}$$

Working out the amount of hexadecane required to release 1000 kJ of energy, given that combusting **1 mole** of hexadecane releases **10700 kJ** of energy:

$$
\begin{aligned}
n\,(C_{16}H_{34}) \quad &= \quad \frac{1000}{10700} \\
&= \quad 0.0935 \text{ mol}
\end{aligned}
$$

Working out the volume of CO_2 produced:

$$
\begin{aligned}
n\,(CO_2) \quad &= \quad 16 \times n\,(C_{16}H_{34}) \\
&= \quad 1.50 \text{ mol} \\
V(CO_2) \quad &= \quad 1.50 \times 24.8 \\
&= \quad \textbf{37.1 L}
\end{aligned}
$$

The environmental impact referred to in this question is the release of greenhouse gases - namely CO_2. Therefore, based on this data, methane is more environmentally friendly.

Part f.

This requires a significant amount of critical thinking. This is essentially a question on comparing the environmental impact of **biogas** and **fuel oil** in terms of combustion. Let's brainstorm the different environmental issues:

- **Greenhouse gas emissions**: Whilst combustion of biogas and fuel oil both lead to release of CO_2 into the atmosphere, remember that biogas is **carbon neutral** (during the production of the source that gives rise to biogas - biomass - CO_2 is absorbed from the atmosphere).

- **Release of sulfur and nitrogen oxides in combustion of fuel oil**. Remember that sulfur oxides and nitrogen oxides are released upon combustion of coal and crude oil, as these contain sulfur and nitrogen atoms. Sulfur and nitrogen oxides are acidic oxides, and can react with water to form sulfuric and nitric acid, leading to the production of **acid rain**. Additionally, nitrogen oxides can undergo photochemical reactions to produce **ozone (O_3)**, contributing to **photochemical smog**.

- **Release of particulate matter in combustion of fuel oil**. When fuel oil is burnt, this can lead to the expulsion of soot, or particulate matter. When inhaled, this can lead to significantly harmful environmental effects.

The answer to part **e**, therefore, does not capture the true environmental effects of the combustion of biogas and fuel oil. For example, the CO_2 volumes quoted in part **e** do not reflect the sulfur and nitrogen oxides, as well as particulate matter that is released upon combustion of fuel oil. Additionally, the CO_2 volume for biogas is an overestimate of the greenhouse gas effect, because CO_2 would have been removed recently from the atmosphere to produce the biomass that gives rise to biogas.

Question 3

Part a.

This is a definition question. However, you should know that a **renewable** energy source is one that **can readily be replenished in a short period of time via natural processes**. Biofuels are derived from living plant material (or recently deceased), which can be replenished readily by growing new plants.

Part b.

Let's discuss the process that is going on.

Ethanol in the spirit burner is being burnt in oxygen to release significant amounts of energy - thermal energy. **Some** of this energy is being absorbed by the water in the beaker as heat, increasing the temperature of the water. In this question part, we are expected to use this data alone to work out the molar enthalpy of combustion of ethanol. Therefore, we would have to assume that all the energy is being absorbed by the water in the beaker.

So, how much energy has the water absorbed? We know that to increase the temperature of **1 g** of water by **1ºC**, you need **4.18 J** of energy. However, the energy from burning the ethanol caused the temperature of **500.0 g** of water to increase from **24.5ºC** to **46.7ºC** (an increase of 22.2ºC). Hence, how much energy was absorbed by this water in total?

$$
\begin{aligned}
E_{water} &= 500.0 \times 4.18 \times 22.2 \\
&= 4.64 \times 10^4 \text{ J} \\
&= 46.4 \text{ kJ}
\end{aligned}
$$

Assume that all the heat released from the burning of the ethanol is absorbed by the water. If we want to work out the enthalpy of combustion of ethanol, we need to work out the amount of energy released when **1 mole** of ethanol is burnt. How much ethanol was burnt in actuality? Well, initial mass of ethanol in spirit burner was 22.15 g and final mass 20.20 g. Hence,

$$
\begin{aligned}
m \text{ (ethanol)} &= 22.15 - 20.20 \\
&= 1.95 \text{ g}
\end{aligned}
$$

Since we are working out the amount of energy released when you burn **1 mole** of ethanol, we need to work out the amount, in moles, of ethanol:

$$n \text{ (ethanol)} = \frac{1.95}{46.0}$$
$$= 0.0424 \text{ mol}$$

Now, burning **0.0424 mol** of ethanol leads to the release of **46.4 kJ** of energy. How about for **1 mole** of ethanol? Additionally, when energy is released in a chemical reaction, there is a decrease in chemical energy - i.e. the ΔH value is negative. Hence:

$$\Delta H = \frac{-46.4}{0.0424}$$
$$= -1.09 \times 10^3 \text{ kJ mol}^{-1}$$

Part c.

The quoted value suggests that more energy should have been released when the ethanol was combusted. This is easily explainable - a lot of heat would have been lost to the surroundings. Hence, the amount of energy absorbed by the water in the beaker would have been much lower than the energy released by the ethanol. If you assume that the energy absorbed by the water is equal to the energy released by the ethanol, you would get the impression that burning ethanol would lead to the release of not much energy. Therefore, you will get a ΔH value that is less negative, consistent with the data given.

Part d.

Now, this -1370 kJ mol^{-1} number means that if you combust **1 mole** of ethanol, **1370 kJ** of energy has been released. When you convert to MJ tonne^{-1}, you are asking how much energy is released, in MJ, when you combust **1 tonne** of ethanol. First, it would be useful to convert kJ to MJ; 1000 kJ = 1 MJ. Therefore, 1370 kJ = 1.370 MJ. Hence, -1370 kJ mol^{-1} = -1.370 MJ mol^{-1}.

So how do we do this? Since we are converting from a mole unit to a mass unit, we should first work out how much energy is released when you combust any mass of ethanol.

Now, we know that **1 mole** of ethanol weighs **46.0 g**. Therefore, combusting **46.0 g** of ethanol will lead to **1.370 MJ of energy being released**. How about for **1 g**?
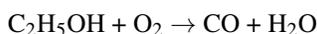
$$\Delta H = \frac{-1.370}{46.0} \text{ MJ g}^{-1}$$
$$= -0.0298 \text{ MJ g}^{-1}$$

Now, 1 tonne = 1000 kg = 1,000,000 g. So we know how many MJ of enery is released when you combust 1 g of ethanol. How about 1,000,000 g?

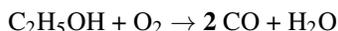$$\Delta H = -0.0298 \times 10^6 \text{ MJ tonne}^{-1}$$
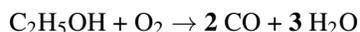$$= -2.98 \times 10^4 \text{ MJ tonne}^{-1}$$

Part e.

Remember, incomplete combustion equations, by convention, mean that CO and H_2O are the products. Let's write the equation:

$$C_2H_5OH + O_2 \rightarrow CO + H_2O$$

Balancing the C atoms - there are **2** on the LHS, therefore there must be a '2' next to the CO:

$$C_2H_5OH + O_2 \rightarrow \textbf{2} \text{ CO} + H_2O$$

Balancing the H atoms - there are **6** on the LHS, therefore there must be a '3' next to the H_2O:

$$C_2H_5OH + O_2 \rightarrow \textbf{2 } CO + \textbf{3 } H_2O$$

Balancing the O atoms - there are **5** O atoms on the RHS, and **1** O atom on the LHS - **do not forget the O atoms in the alcohol!** Now, we must have **4** O atoms on the LHS, therefore we should have a '2' next to the O_2. Putting in states, we get:

$$C_2H_5OH \text{ (l)} + 2\, O_2 \text{ (g)} \rightarrow 2\, CO \text{ (g)} + 3\, H_2O \text{ (l \textbf{or} g)}$$
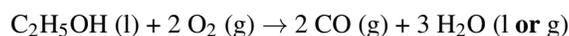
Question 4

<u>Part a.</u>

Biodiesel is made out of **FAMEs** (fatty acid methyl esters). This is basically a methyl ester (ester with a methyl group at the end) derived from a fatty acid. FAMEs look like this:
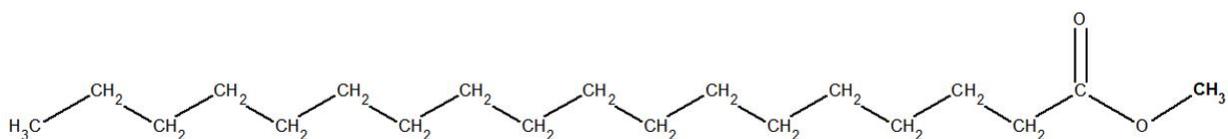
Clearly, structure **B** resembles what is written above - therefore structure **B** resembles biodiesel and structure **A** represents petrodiesel.

<u>Part b.</u>

Cold flow properties of the fuels refer to how these behave in cold climates. The cold flow property of the fuel that you need to know about is **viscosity**.

Viscosity refers to the resistance a fluid has to flow. The higher the viscosity, the harder it is for the fluid to flow. Viscous fluids are **thicker**. For example, oil is a more viscous fluid than is water. You will also find that when you heat oil in a frypan, the oil becomes more 'runny' - i.e. less viscous.

Anyhow, viscosity is a function of two things:

- the intermolecular attractions of the two molecules

- the shapes of the two molecules

If ths intermolecular attractions between the molecules are strong, it is difficult to separate the molecules from one another and therefore the fluid would be quite thick. Additionally, if the molecules are long and thin in shape, they are likely to 'tangle' during the flow of fluid, which inhibits flow.

It is important to know that **biodiesel is significantly more viscous than petrodiesel, especially in cold climates**. This is because biodiesel can exhibit dipole-dipole attractions via C=O double bonds of different molecules, in addition to dispersion forces.

What are the implications? Remember that fuel travels from the fuel tank down narrow pipes (fuel lines) and are injected into the cylinder. If the fuel is very thick, it will be very difficult for the fuel to flow down the fuel line and lead to blockade of the fuel line.

Part c.

Hygroscopicity refers to the ability of the fuel to **absorb water**. Now, both biodiesel and petrodiesel are insoluble in water. However, biodiesel is slightly more soluble in water than is petrodiesel. This is because biodiesel contains C=O double bonds, which can form a couple of hydrogen bonds with water molecules. Therefore, **biodiesel is more hygroscopic than petrodiesel**.

What are the implications of this? When biodiesel absorbs water, the biodiesel is more susceptible to degradation by a process called **rancidification** (you will learn about this later this year). The biodiesel effectively degrades to form smaller fatty acids, which can corrode the inside lining of the fuel tank. Additionally, the water in the fuel can promote the growth of algae and other organisms; this could **block** fuel lines, or possibly promote the rusting of the fuel lines.

Part d.

This is basically recall and based on empirical evidence.