HYDROGEN STORAGE AND FUEL PROCESSING STRATEGIES

Callum Richard Campbell

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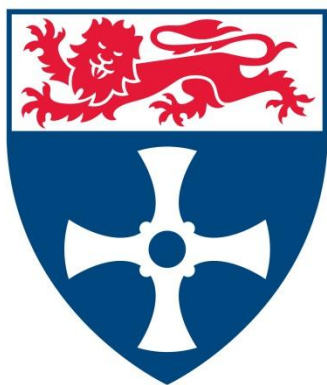
School of Chemical Engineering and Advanced Materials

Newcastle University

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Abstract

It is widely recognised that fossil fuels are finite, and alternatives should be investigated to secure future energy supplies. Much research is directed towards hydrogen as a fuel, but the gas is unmanageable without an effective storage and distribution strategy.

This work investigates the Methylcyclohexane-Toluene-Hydrogen (MTH) system of hydrogen storage with a view to providing vehicular fuel or storing energy produced by intermittent producers. Stable liquid-hydrocarbon hydrogen storage enables hydrogen distribution using the existing fossil fuel network, eliminating the need to build a new fuel infrastructure.

A literature survey is carried out covering the area of Liquid Organic Hydrogen Carriers (LOHCs). A study of the technoeconomic bottlenecks which would prevent the widespread use of the MTH system is conducted to direct the project research efforts, which reveals that the vehicular on-board dehydrogenation system must be reduced in size to be practical. Process intensification is attempted by dehydrogenating methylcyclohexane in the liquid-phase, which is experimentally demonstrated in this work (an original contribution). However, to be feasible for a vehicle, the liquid-phase dehydrogenation system demands a specific window of conditions, with hydrocarbon vapour pressure, enthalpy of reaction and equilibrium constant all being important factors. No window is possible to satisfy all conditions for the MTH system, which renders this vehicular system infeasible. Alternative liquid carriers are investigated to solve the problem, but no clear candidate carrier is found without using highly experimental and costly molecules.

This leads to a new investigation of other applications for the MTH system. MCH for power to a Scottish whisky distillery is investigated, followed by an investment appraisal of the distillery system. The system is technically feasible but attracts a high capital expenditure (almost £16M) and operational cost (£2.4M annually) which is uncompetitive with alternative options such as biomass fuels.

Finally, possible future work in the field of LOHC technology is considered.

For my grandparents.

Ian Campbell, whose footsteps I am honored to follow.

Isobel Campbell, who I know would be incredibly proud

of her grandson, and who is missed every day.

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CRC, February 2014

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Chapter 1   Introduction

The research contained in this work is essentially a study of energy. Energy in context of the everyday can be characterised in terms of human needs, such as heat, light or movement. The Technology Strategy Board, UK, recently designed a piece of online software to help companies function more effectively in terms of their resource use, their outputs *etc*[1]. As part of this, they tried to compile the major factors in building a sustainable future and categorised them into one of three categories: Essential needs; Social/Political Factors; Environmental Boundaries. This notion is illustrated by the diagram given as Figure 1-1.
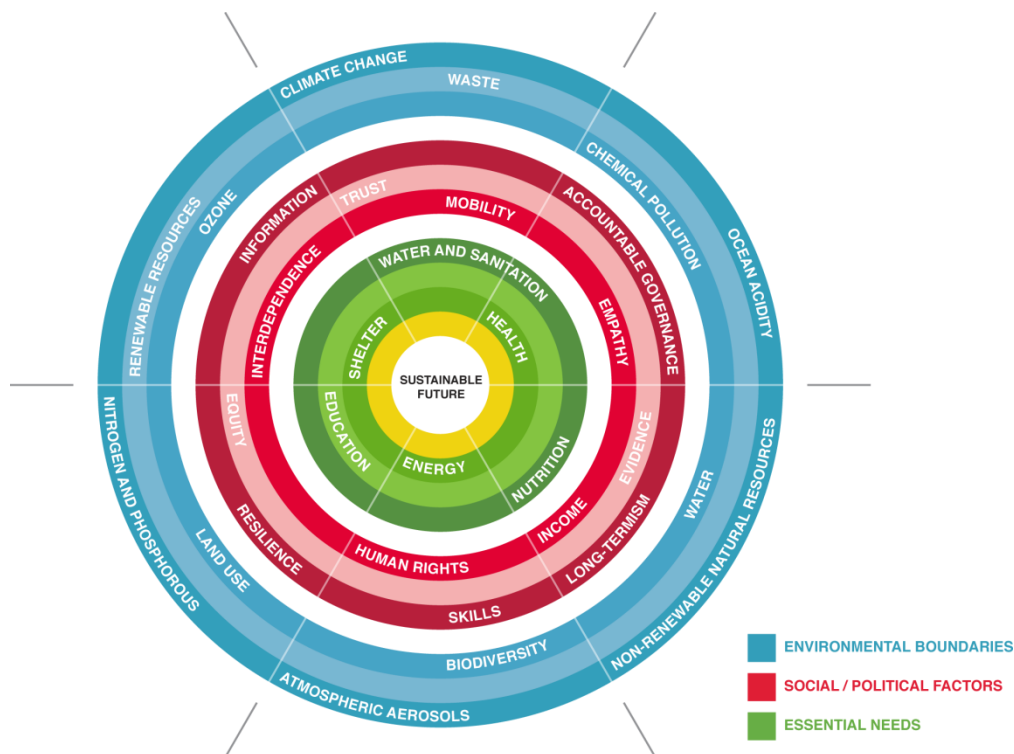
Figure 1-1: Life factors as categorized by the UK TSB

As Figure 1-1 shows, energy is a factor of paramount importance in the design of a sustainable future for human beings, characterised here as an "Essential Need". Energy provides heat for cooking and space heating, transport, light and is the central factor of all of our technology. Clearly, if humanity is to thrive, energy must be available to those who need it for generations to come.

However, the present day has revealed threats to the continued supply of energy. The following section will describe some of these threats. Following this, a description of some of the solutions to our current energy problems is given.

1.1   Global Energy – Threats and Problems

1.1.1 Climate Change

Global warming describes the climate change caused by the release of greenhouse gases caused by the combustion of fossil fuels by humans. Although the attribution of climate change to anthropogenic emissions is hotly debated, the evidence for climate change is compelling. As early as 1955, there were suggestions *"that the apparent "warming up" of the world's climate may be attributed to mankind "contaminating the Earth's atmosphere faster than Nature can clean it""*[2].

Since then, a great deal of work has been carried out to investigate the causes and effects of climate change. In 2013, the Intergovernmental Panel on Climate Change (IPCC) published its fifth assessment on climate change[3]. They determined that from 1951 to 2010, the mean global surface temperature is likely to have been raised by 0.5 – 1.3 °C. Furthermore, it is *"extremely likely"* that more than half of this rise due to anthropogenic emissions. It also shows evidence that the rise in mean global surface temperature will continue into the future. It could be argued therefore that it is the responsibility of the human race to curb its harmful emissions as quickly and effectively as possible while still meeting the needs of the current and future generations.

1.1.2 Scarcity of Supply

The above arguments concerning climate change are in some way academic. Humanity will not be able to rely on fossil fuels in the long-term, even if associated emissions had no ill effects. Since 1965, new discoveries of crude oil have decreased on average by 3.5% per annum[4], and at the current rate of consumption, the equivalent of only an estimated 45 years' worth of global energy remains[5]. It would serve humanity well to have an alternative fuel infrastructure in place before the supplies of fossil fuel begin to wane.

1.1.3 National Independence

A parliamentary report[6] shows that for most of the period of 1980 – 2004, the UK was a net exporter of energy. However, in 2004, the UK became a net importer of energy, which is trend set to continue. This is illustrated by Figure 1-2. This means that the UK's energy supply is only as certain as political relationships with suppliers overseas. It would be desirable, therefore, to have a domestic form of energy which is not based on the geographical location of fossil fuel discoveries, and hence would reduce or eliminate reliance on other countries.

UK imports and exports of energy
thousand tonnes of oil equivalent
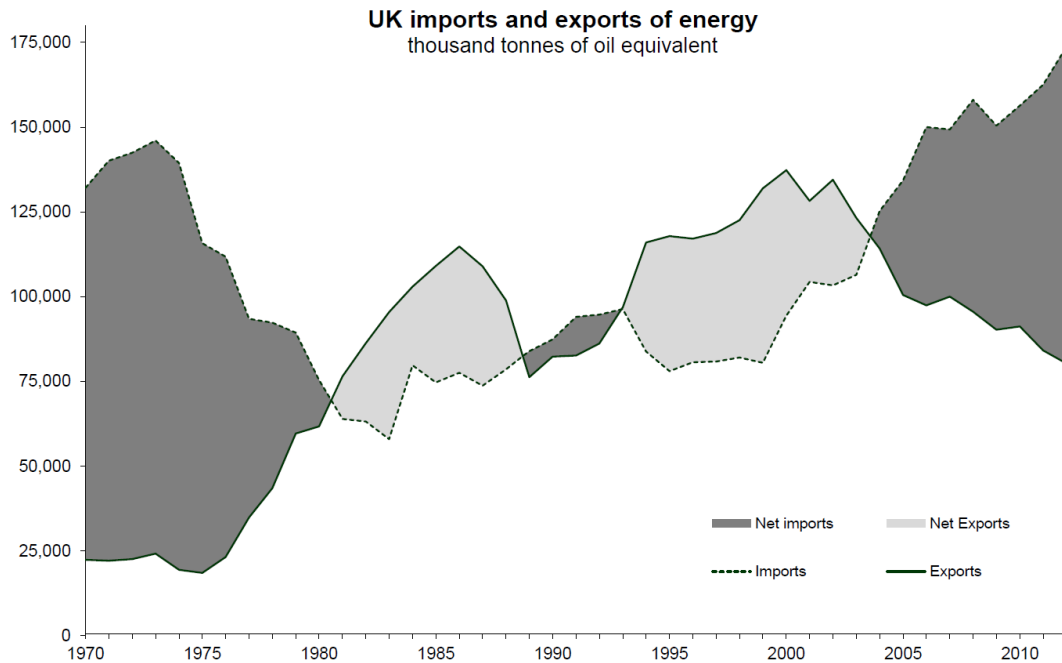
Figure 1-2: Graph to reflect the status of the UK as a net energy importer since 2004

1.2   Energy Solutions

The obvious question is "How can we overcome these issues with our current energy situation?". Intense research efforts have revolved around studying ways to solve these problems. These efforts can be broadly split into two categories:

- Prolonging fuel supplies – making fossil fuels last longer by discouraging unnecessary usage or using less fossil fuel to achieve the same goals by increasing efficiency
- Alternative energy – finding new sources of energy with a view to eventually discarding fossil fuel sources altogether.

1.2.1 **Prolonging Fuel Supplies**

All sectors of energy use have put some energy saving measures into place. Domestically, legislation has driven the adoption of energy saving light bulbs, which provide light at a fraction of the wattage associated with traditional filament bulbs. In addition, there has been much social emphasis on improving insulation in homes to avoid wasted heat, with governmental incentive being put in place for those who cannot afford to make the improvements[7].

In industry, resource efficiency has become an increasingly hot topic. In recent years increasing levels of legislation has limited the amount of greenhouse gas emissions that industry can expel into the atmosphere. This, and the potential for cost-saving with more effective and efficient processes,

has led to a surge of research in the resource-efficiency sector[8]. Many publications in this field cite the need to take a holistic approach to supply chains in order to optimise systems, rather than a reductionist approach of increasing the efficiency of single machines, components *etc*.

An industry in particular where improvements have been made is the automotive sector. Technological advances have brought cars with energy saving features to the market. These features include regenerative braking, modern tyres improving fuel efficiency, hybrid vehicles and engines which shut off or run with only one cylinder when the car is still.

1.2.2 Alternative Energies

Fossil fuels are a convenient energy source because they can be used exclusively to provide energy for all of humanity's needs, as well as producing important materials as part of the process (polymers *etc*). At the current level of technology, it would be challenging to say the same for any other fuel. However, nature does not replenish the world's fossil fuel stocks on a human timescale, so energies which do must be sought.

Alternative energies replace conventional energy in four distinct sectors[9]: power generation; hot water and space heating; transport fuels; off-grid (rural) energy.

The following is a non-exhaustive list of alternative fuels, with a description of the needs which these fuels could fulfil.

1.2.2.1 Solar energy

Solar energy describes the use of the heat and light from the Sun which comes into contact with the Earth. Solar energy is already used passively by all life on Earth, enjoying the warm climate that the Sun's energy supplies. Sunlight is also key to photosynthesis, which permits the growth of plant life and the oxygenation of the surface atmosphere. Researchers are now focussing on harnessing this energy more intelligently.

Of all the possible technologies for harnessing solar energy, photovoltaic (PV) is the most visible in popular media. Photovoltaics is a method of generating electrical current from solar radiation using photovoltaic cells. In 2012, PV contributed 93.0 TWh annually to global electricity, a contribution of 0.41% of global electricity[10].

1.2.2.2 Geothermal energy

Geothermal energy is heat which is generated by the radioactive emissions of the Earth's core. Warm water from underneath the Earth's crust can be used directly for space heating. An example of such a project was carried out by Newcastle and Durham universities in 2011[11, 12], where a geothermal water source was pumped to the surface to provide hot water for space heating. A more common use for geothermal energy is electricity generation, where steam from below ground is used to drive steam engines for power generation.

1.2.2.3 Wind energy

Wind energy is the harnessing of natural airflow to generate mechanical or electrical power. Turbines are deployed in high-wind areas which rotate when caught in the wind's airflow, generating power. Electricity generated in this fashion can be fed to the local power grid for distribution to homes/businesses.

1.2.2.4 Biomass

Biomass describes the use of materials derived from living or recently living organisms. Uses for biomass are the production of biofuels, direct combustion to give heat and conversion of biomass materials to chemicals. For example, a recent paper[13] shows how the production of pyrolysis oil from biomass can yield chemical commodities such as alcohols and polyols.

1.2.3 Hydrogen

1.2.3.1 Hydrogen Production in Brief

Hydrogen is linked to the above alternative energy sources not as a power source in itself, but as an energy buffer, which can be produced using the power sources above.

Conventional hydrogen is produced from fossil fuel sources. Natural gas (methane) can be reformed in steam to give hydrogen and carbon monoxide. This is shown in Figure 1-3.

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
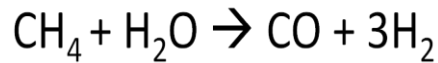
Figure 1-3: Steam reforming of methane

The product mixture yielded in Figure 1-3 is known as synthesis gas (or syngas), because it often used for the synthesis of methanol directly. However, the hydrogen can also be extracted for use as a fuel or as a chemical feedstock.

Further hydrogen can be extracted from syngas by using excess steam. This can react with the carbon monoxide in syngas as shown in Figure 1-4, which illustrates the water-gas shift reaction.

$$CO + H_2O \rightarrow CO_2 + H_2$$
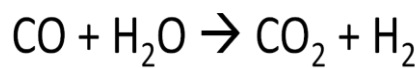
Figure 1-4: Water shift gas reaction

This is the commercial route for hydrogen synthesis.

Hydrogen can also be produced by electrolysis of water. This involves the passing of an electric current through water in the presence of an appropriate anode and cathode to decompose water, yielding hydrogen and oxygen gases. This is illustrated in Figure 1-5.
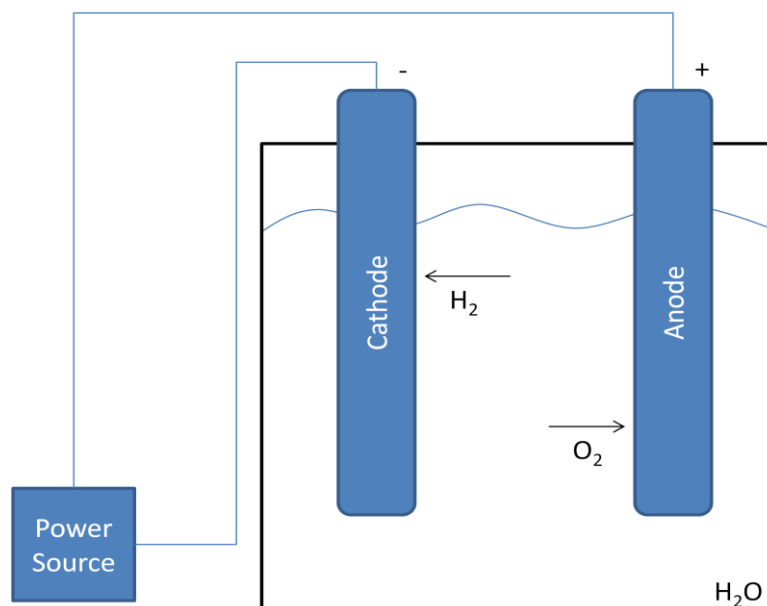
Figure 1-5: Simple representation of water splitting by electrolysis

For renewable hydrogen production, the power source can take the form of any of the sources of electricity discussed in Section 1.2.2.

1.2.3.2 Hydrogen uses

The hydrogen produced as above has a host of uses. Hydrogen is a major chemical commodity for many processes, such as ammonia synthesis, fossil fuel processing, steel making and food manufacturing. Also receiving much attention is the possibility of hydrogen as a fuel for vehicular and domestic applications.

Hydrogen certainly has the potential to act as a fuel in many or all aspects of human fuel needs. It is the most energy dense fuel in existence by mass, with a higher heating value of 141.8 MJ/kg, and burns cleanly, giving a combustion product of only water in the ideal case. However, hydrogen is also extremely buoyant and difficult to manage. It has a very low energy density by volume at atmospheric pressure, and is difficult to contain, especially with its ability to cause embrittlement in some metals. If hydrogen is to reach its potential as a fuel, and if the "hydrogen economy" is to be realized, then a hydrogen storage solution is called for.

1.3 Hydrogen Storage Solutions

The search for a convenient hydrogen storage solution forms the basis of this work. More precisely, Liquid Organic Hydrogen Carriers (LOHCs) are studied. These are unsaturated organic molecules which can be hydrogenated to yield the saturated analogue of the unsaturated carrier. This stable liquid can be stored indefinitely and transported easily, in whole or in part using the existing fossil fuel distribution infrastructure. LOHC technology is particularly appropriate for a vehicular application due to their physical similarity to the liquid fuels used for vehicles today.

A literature search is performed to examine the existing work on hydrogen storage solutions. This is followed by an examination of the barriers which stand in the way of using an LOHC system, in particular the MTH (Methylcyclohexane-Toluene-Hydrogen) system, as a widespread approach for storing hydrogen as a vehicular fuel. The identification of these bottlenecks directs the remainder of the project, leading the work towards a theoretical and experimental examination of the MTH system. Due to the failings of the MTH system, alternative LOHC systems are also subsequently examined, as are alternative applications outside the automotive sector for the MTH system. This leads to a design project of a Scottish whiskey distillery powered by MTH technology. Finally, the opportunities for future work with LOHC technology are discussed.

Chapter 2   Literature Survey

2.1 The Future of Global Energy

Please note that the following section is based on a conference publication by the author, which can be found by the reference:

C. R. Campbell, *"Hydrogen Storage and Fuel Processing Strategies"*, Proceedings of the International Conference for Sustainable Energy Storage 2011, Belfast, February 11, 2011

The environment is of greater concern today than at any time in human history. Nature has offered humanity a concentrated energy carrier in the form of fossil fuels, which led us to the industrial revolution and has enabled us to evolve technologically ever since. With developing countries now on the heels of the West with their own technological revolutions, the environment has never faced such a great anthropogenic threat. Global warming threatens to impose severe weather conditions and a changing environment for humanity and the animal kingdom alike. In addition, and for the global warming sceptics, fossil fuels are a finite resource which is being rapidly depleted. Since 1965, new discoveries of crude oil have decreased by an average of 3.5% per annum[4]. At the current rate of consumption, an estimated 45 years' worth of fossil fuel energy remains[5]. It is also important to mention that fossil fuel use creates UK dependence on foreign sources, and it would be desirable to instead use a fuel which can be produced on home soil, increasing UK independence. With these factors in mind, it is unclear what the landscape of the future of global energy looks like. There has been much investment in recent years to address this problem, with many kinds of alternative fuels being tested and scrutinized all over the world. The fuel or blend of fuels which hold the answer is unclear.

One energy storage solution which presently attracts much attention is the use of hydrogen as an energy buffer. Hydrogen can be used as a means of transporting and storing energy in chemical form, and at the point of use where the energy is reclaimed by oxidation, the only by-product is water. Hydrogen as a fuel possesses one of the highest energy densities per mass, however, it is also the lightest element, and in elemental, gaseous form is extremely light (*i.e.* buoyant in air) as well as flammable, so is difficult to manage, store and transport. An intelligent hydrogen storage solution should be sought in order to make hydrogen a viable energy carrier.

2.2 Hydrogen Storage Strategies

The following criteria should be sought when searching for a method of hydrogen storage[14]:

- High hydrogen content per unit mass and unit volume

- Limited energy loss during operation

- Fast kinetics during charging

- Low self-discharge during standstill

- High stability with cycling

- Low cost of recycling and changing infrastructure

- Moderate safety concerns in regular service or during accidents

No single solution can fulfil all of these criteria, so we must seek the solution which offers the best compromise between these factors.

Compressed hydrogen gas (CHG) is usually stored at a pressure of 350 bar – 700 bar, and at these high pressures, it is necessary to contain the gas in a heavy reinforced container. These containers are expensive and their weight is a disadvantage for a mobile application. Container included, the vessels contain approximately 11 wt% hydrogen[14], and volumetrically contain 14.9 mol H_2/L (700 bar). This volumetric hydrogen content is moderate, and for automotive applications may render this solution unsuitable – for example, 200 L of 700 bar CHG gas would offer a range of only 186 miles (calculated from [15]).

Cryogenic liquid hydrogen (LHG) may be more suitable for the mobile application – it can be stored at atmospheric pressure, and has a higher volumetric hydrogen density of 34.7 mol H_2/L. This would give a car the range of 186 miles with only 86 L of hydrogen, a 57% reduction in volume compared to 700 bar CHG. However, hydrogen liquefaction is energy intensive, occurring at a temperature of around 20 K[16], and requiring 33% – 40% of the gross energy content of the liquefied hydrogen. Further losses occur during transport and storage due to warming and expansion of the LHG, which can only be partly prevented by the use of insulated, high pressure tanks[14]. These losses would increase as the period of vehicle disuse extends (*e.g.* business trips, holidays).

For both of these storage techniques, safety is a barrier to commercialisation as the gas escapes from the system readily. Even without ignition, gaseous hydrogen leaks can destroy a civil structure *e.g.* a garage due to severe overpressure[17], and although CHG technology has been researched and significantly improved over the years due to the evolution of Types I – IV storage tanks, safety remains a critical issue, including the pressurisation of hydrogen at the plant, as well as the danger of leakage in a road traffic accident[15] (also a critical factor for LHG).

A further hydrogen storage alternative is the use of solid metal hydrides, in which hydrogen is reversibly chemi- or physisorbed onto a (supported) metal surface. The metal hydrides can be described by one of two categories depending on the heat input required for hydrogen liberation:

- low temperature (<150 $^{\circ}$C)

- high temperature (>150 $^{\circ}$C).

For the low temperature category, hydrogen content by weight is typically <2% (most often La- or Ti-based alloys[14]). This figure is often surpassed by the high temperature category of metal hydrides, which have a typical hydrogen weight percentage of 3 – 7% (often Mg-based alloys), but it is difficult to decrease the desorption temperature and pressure requirements of these materials[14], so the process is energy intensive.

Recharging the depleted fuels is a further issue, not only in the sense of chemistry (which can often be complex), but also in heat management[18]. Exothermic hydrogenation of the solid material releases heat which must be controlled. If hydrogenation took place on-board a vehicle (the generally accepted route for solid hydride storage materials), the refuelling process would need to be slow to allow cooling. The heat generated through hydrogenation is wasted, and therefore energy efficiency suffers. The refuelling process could be made quicker by refrigeration, but this increased energy input would further decrease energy efficiency, and hence the profitability of the filling station. Further drawbacks include the necessity of heating the entire block of material to liberate hydrogen, and the fact that it is unattractive to have a heated block of reactive material present in the case of a road traffic accident[18].

Finally, there is currently no mechanism for measuring how depleted the hydrogen stock in the hydride fuel tank has become. A mechanism to indicate when the vehicle must be refuelled is necessary for the vehicle user.

Regardless of the disadvantages of solid hydrogen storage, they still have potential to bring storage conditions closer to ambient conditions (temperature and pressure), as well as the conditions required for hydrogen charging and discharge than either CHG or LHG, therefore reducing the net energy and material consumption required in comparison with the pure hydrogen storage techniques[19].

Advanced solid materials may present the solution to the issues with solid hydrogen storage techniques. Research into solid hydrogen storage materials has been stimulated in recent years by the arrival of specialist materials such as Metallic Organic Frameworks (MOFs) and other purpose-designed materials which possess a high surface area[19]. MOFs are crystalline materials which consist of inorganic metallic components which are linked together by physical connection to organic ligands[20]. These materials feature many favourable properties such as very high surface areas, tuneable pore size for gas storage, and an internal surface which can be designed to the user's requirements. These innovative materials may present a solution to some of the problems encountered by the classical solid hydrogen storage materials, but they are a young technology (first reported in 2003[20, 21]), and must be investigated further before a practical, application based solution can present itself.

Often neglected is the possibility of using the liquid counterpart to metal hydrides, Liquid Organic Hydrogen Carriers (LOHCs). These have a typical hydrogen content of 6 wt% − 8 wt%[18], which is lower than 700 bar gaseous hydrogen or advanced metal hydrides, but is nonetheless competitive. An unsaturated organic molecule is hydrogenated for storage and transport, and then dehydrogenated at the point of need, at which time the carrier is removed and stored for recycling. By design, LOHCs are stable and easy to handle under atmospheric conditions with no specialist equipment.

To compare with the figures above, using the MTH system as an example, MCH contains 6.2 wt% H_2, and has a competitive volumetric hydrogen density of 23.3 mol H_2/L, so to achieve the aforementioned vehicle range of 186 miles, 127 L of MCH is required (recall that this compares to 200 L of CHG and 86 L of LHG).

To compare with fossil fuels, approximately 28 L of conventional fossil fuel petrol would be required to cover the same benchmark distance of 186 miles.

LOHCs also have the advantage of being in a liquid state at atmospheric temperature and pressure, giving them very high stability and meaning they can be stored indefinitely in simple, light steel

containers[18] (on-board a vehicle, this would be similar to a standard petrol/diesel tank). Many LOHCs present similar safety concerns to petrol or diesel, which are widely known and accepted. They can be pumped into a vehicle using a conventional liquid fuel pump, with the only difference being the need to reclaim the depleted fuel, so the public never come into contact with hydrogen gas directly. Hydrogen is liberated from the organic material in small aliquots, and so the amount of free hydrogen present in the system at any one time is small. Perhaps the greatest advantage of the LOHC concept is the distribution infrastructure – as organic liquids, LOHCs can be distributed using the same infrastructure as fossil fuels with only minor changes, whereas the storage solutions mentioned above would invariably require major structural overhauls, perhaps including high pressure or liquid hydrogen pipelines/tankers, which would necessitate large capital expense.

To summarise, Table 2-1 shows how each of the aforementioned storage solutions fare against the criteria set out at the start of the section.

Table 2-1: Analysis of hydrogen storage methods according to criteria set out by Conte, 2004[14]

Criteria	Compressed Gaseous Hydrogen	Liquefied Cryogenic Hydrogen	Metal hydride	Liquid Organic Hydrogen Carrier
Hydrogen content by mass (%)	11	Unavailable	1 – 7	6 - 8
Hydrogen content by volume (mol H_2/L)	14.9	34.7	2 - 6[22]	14 – 32 (23.3 for MCH)
Energy loss during operation	Low	Low	High due to heating block of solid material	Mid-range due to endothermic dehydrogenation
Kinetics during charging	Fast	Unavailable	Condition dependent	Condition dependent

Criteria	Compressed Gaseous Hydrogen	Liquefied Cryogenic Hydrogen	Metal hydride	Liquid Organic Hydrogen Carrier
Self-discharge during standstill	Limited	High	None	None
Stability with cycling	Unavailable (variable container stability)	Unavailable (variable container stability)	Variable, unpredictable[18]	96% Carrier Recovery Rate for MTH system[23]
Cost of recycling and changing infrastructure	High	High	High	Low
Safety concerns in regular service or during accidents	High	High	Mid-range	Low

It is clear that although LOHCs are not the "silver bullet" of hydrogen storage, they do present a strong case against the alternatives. It is certainly worth investigating this solution further.

2.3 Liquid Organics as Hydrogen Carriers

The idea of using MCH as a rechargeable organic hydrogen carrier is not recent. Sultan and Shaw first studied the MTH system as an energy carrier in 1975[24]. Since then, volumes of work have been carried out investigating the potential of LOHCs for a variety of applications.

2.3.1 LOHCs for Seasonal Energy Storage

LOHC systems are attractive for seasonal storage of energy. Energy requirements (domestic, commercial, industrial) vary throughout daily, weekly and seasonal timescales. Energy storage can balance these inconsistencies, *e.g.* energy from a wind turbine generated at night when demand is low can be stored and put through the grid the following day when demand is higher. For this kind of

purpose where energy storage volumes are low, battery technology is usually sufficient[25]. Seasonal variations, such as higher energy demands in winter for heating which is unnecessary in summer, are better solved by using excess electricity to generate electrolytic hydrogen for LOHC systems, because of the stability and ease of storage of the hydrogen-carrying compounds[26-28]. The LOHCs produced in this fashion could be used to store energy which is later returned to the electricity grid, or could be used to fuel vehicles[29].

2.3.2 LOHCs for Automotive Fuels

There are a number of reasons for choosing a LOHC system for automotive purposes. The typical hydrogen content of cycloalkanes is $14 - 32$ mol H_2/L, higher than many alternatives such as metal hydrides $(2 - 6$ mol H_2/L$)^{[22]}$.

Also prevalent is the safety aspect – a stable liquid fuel system in which the public never come into direct contact with hydrogen gas is preferable to highly pressurised gas or cryogenic liquid.

Finally, the most critical factor is the use of the existing infrastructure - as liquid fuels with similar properties to the existing liquid fossil fuels, LOHCs could exploit the existing fuel infrastructure, which is worth several hundred billion dollars[18], with some additional investment. Existing petrochemical pipelines, tankers, storage tanks *etc* could be used with no or little modification[18, 22, 23, 30, 31]. This may be the critical advantage of the LOHC fuel over other alternatives. In contrast, the existing fuel infrastructure is entirely unsuitable for pure hydrogen transportation, either as liquid or gas, due to the pressures and temperatures involved, as well as the problem of hydrogen embrittlement of metals. An entire new infrastructure would be required to support these pure hydrogen systems, incurring a large capital expenditure.

Beyond the hydrogen carrying capacities of each system, the thermodynamics should also be examined. Pez *et al*.[32] seek a system in which hydrogenation is an "ideally reversible reaction". Figure 2-1 shows the reversible hydrogenation of molecule A with an equilibrium constant K.

$$A + nH_2 \quad \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \quad A\text{-}H_{2n}$$

Figure 2-1: A reversible hydrogenation reaction

With reference to the relationship shown in Figure 2-1, the relationship between K and Gibbs Free Energy of reaction, ΔG_r, is shown in Equation 2-1.

Equation 2-1

$$\Delta G_r = -RTlnK = \Delta H_r - T\Delta S_r$$

Where R is the ideal gas constant, ΔH_r is the enthalpy change of reaction, T is reaction temperature and ΔS_r is the entropy change of reaction. Pez *et al* explain that ΔG_r should be 0 where T is approximately 80 ^{o}C to bring the dehydrogenation reaction temperature in line with the operating temperature of a PEM fuel cell. This would allow useful heat exchange between the fuel cell and the dehydrogenation reactor. This is an advantage because the dehydrogenation reaction is endothermic and requires heat input.

Although aligning the reaction and fuel cell temperatures in this way is a sensible engineering approach which would remove the need to directly burn fuel to maintain reaction temperature, this neglects a view of the overall heat management strategy, *i.e.* an ICE or SOFC may be used in the place of a PEM fuel cell, which would entirely change the balance between the temperatures, and would change the optimum value of ΔG_r.

A more advanced form of heat integration strategy is to use side reactions for heat management. In a report from the same Pez *et al* research group[33], a strategy was outlined to use the heat from an exothermic oxidation reaction of a side chain to balance the endothermic dehydrogenation reaction, therefore making the overall dehydrogenation process autothermal (independent of external heat sources/sinks). Figure 2-2 shows an autothermal dehydrogenation cycle from the Pez group research.
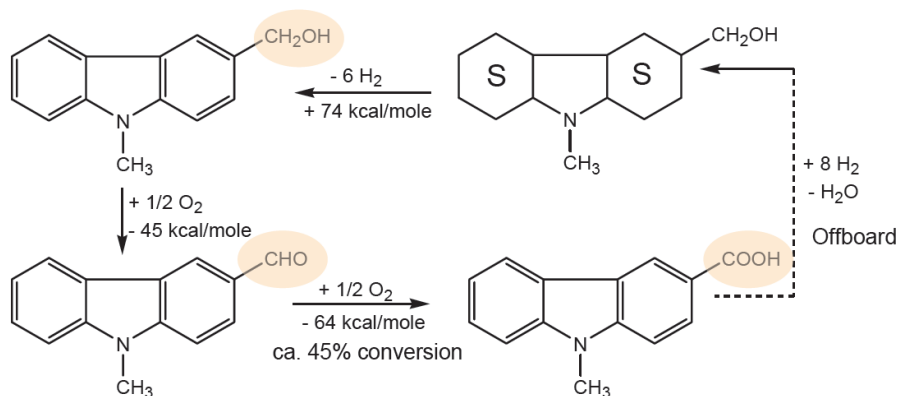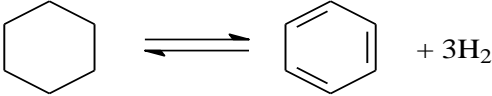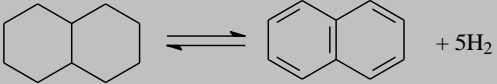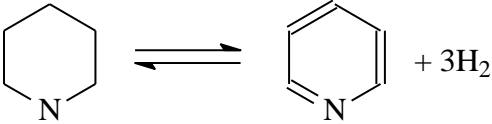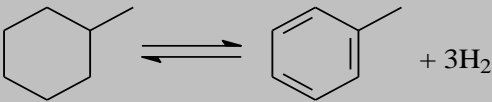
Figure 2-2: An autothermal dehydrogenation system[33]

The net ΔH_r for all reactions is almost exactly zero, meaning no net heat is given out, but more importantly, no external net heat input is required.

Although this is an interesting and perhaps valuable concept, it is still a new concept, and much work would be required to get this technology to the stage of commercialisation, such as, in this case, selective catalyst development for the exothermic oxidation reactions.

Table 2-2 shows a selection of classical LOHC systems which are well studied and ready for commercialisation. This is followed by a description of each system, with the benefits and drawbacks of each.

Table 2-2: Selected LOHCs and their reactions with chosen thermodynamic data. *Methanol is not cracked but rather combusted directly in an ICE or DMFC. **This cannot be accurately converted to heating value of fuel because the entire hydrocarbon is combusted

No.	Carrier	(De)hydrogenation Reaction	Enthalpy of dehydrogenation (kJ/mol H_2)	H_2 content of saturated carrier mol H_2/L (STP)	wt%
1	Benzene	$\rightleftharpoons$ + $3H_2$	+68.6[30]	28.8	7.2
2	Naphthalene	$\rightleftharpoons$ + $5H_2$	+66.4[30]	32.4	7.3
3	Carbon dioxide (to give methanol)*	—OH $\underset{-1/2\,O_2}{\overset{+1/2\,O_2}{\rightleftharpoons}}$ $CO_2 + 2H_2$	N/A*	4.9**	12.6
4	Nitrogen (to give ammonia)	$2NH_3 \rightleftharpoons N_2 + 3H_2$	+30.7[34]	5.2	17.8
5	Pyridine	$\rightleftharpoons$ + $3H_2$	+67.4[35]	34.6	7.1
6	Toluene	$\rightleftharpoons$ + $3H_2$	+68.3[30]	23.5	6.2

1. The Benzene System

Although a technically and economically feasible system[36], benzene is a known carcinogen[37], and so would be unsuitable for automotive application where the public would regularly come into contact with the carrier.

2. The Naphthalene System

The hydrogenated decalin carries a high volumetric proportion of extractable hydrogen, but the endotherm of hydrogen liberation is high. This system also possesses practical difficulties, in that the unsaturated carrier, naphthalene, is a solid at room temperature. It has been suggested[38, 39] that this could be overcome by the addition of a small amount of a different hydrocarbon to put the naphthalene in an "oily state", but this would add another step to the process and the presence of the extra hydrocarbon may affect vapour pressures hence carrier recovery after dehydrogenation.

3. The Methanol System

An exception among LOHC systems, the carrier (CO_2) is charged with hydrogen, but the resultant methanol is not cracked to reclaim hydrogen but is rather directly combusted. Two CO_2 sources are suggested[40]:

- Industrial exhausts containing high concentrations of CO_2

- Atmospheric CO_2

If the CO_2 source is the former, although recycling a by-product with limited applications, the reduction of CO_2 to methanol merely acts as an interim step in releasing the harmful emissions into the atmosphere, as shown in Figure 2-3.
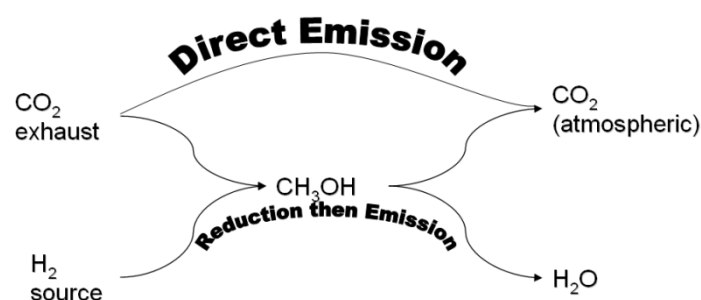
Figure 2-3: Methanol cycle with industrial exhaust gases as the source of CO_2

If the CO_2 source were atmospheric, the net result would be a carbon neutral cycle. Also, atmospheric CO_2 is available to everyone in the world, so companies would not be restricted by feedstock availability in deciding plant location. At the time of writing (January 2014), the atmospheric concentration of CO_2 stood at 397.70 ppm, or 0.040% as recorded at the Mauna Loa observatory[41], so extraction is energy intensive. By necessity, this extraction process would be unending due to the open-cycle nature of the process, as shown in Figure 2-4.
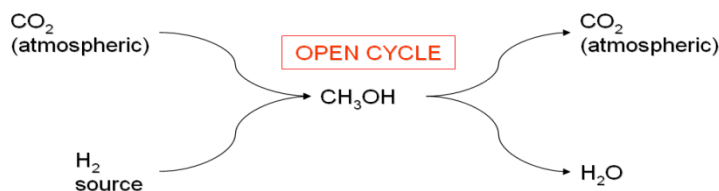
Figure 2-4: Methanol cycle with an atmospheric CO_2 source (open cycle)

4. The Ammonia System

Another open-cycle process, the ammonia system is based on a time-tested procedure, the Haber cycle, and is inherently simpler than the methanol system because the atmospheric concentration of nitrogen is 78% rather than 0.040% in the case of CO_2. Although gaseous at room temperature, ammonia can be liquefied under mild conditions and stored in an inexpensive pressure vessel. If the ammonia is cracked before hydrogen combustion, the only emission is atmospheric nitrogen. Direct combustion of ammonia is also an option, but this releases NO_x so would be environmentally damaging although carbon-free[34].

However, ammonia is highly toxic, and would be dangerous in the event of a storage vessel rupture. Additionally, some fuel cells (*e.g.* PEM fuel cells) can be easily poisoned by traces of ammonia, so if the hydrogen stream is not thoroughly purified, compatibility issues arise. Finally, ammonia cracking is energy intensive, with required temperatures of 923 K – 973 K for high conversion of ammonia to hydrogen and nitrogen. This is therefore not an optimal solution.

5. The Pyridine System

Pyridine is given as an example of a nitrosubstituted ring, a group which have been shown to thermodynamically favour dehydrogenation [18, 35, 42]. Also pointed out is the fact that 5-membered rings also favour dehydrogenation, but the consequence is that the dehydrogenated carrier is very stable, and so recycling of the carrier is thermodynamically more difficult, although this could be carried out under severe conditions on a large industrial scale.

A major limitation to this system and others like it is toxicity, as well as the uncertainty of the thermal stability of the compounds (*i.e.* the potential of undesired spontaneous hydrogen discharge or molecule breakdown) and the manufacturing costs of some of the more novel molecules. It may seem desirable to reduce the endotherm of hydrogen liberation as much as possible (within sensible limits), but the entire system should be considered before taking a view on this. For example, the endotherm does not present an issue if the hydrogen conversion device is a high-temperature fuel cell, for example, because with a good system of heat integration, the system can sustain itself, as was suggested by Taube[43].

After describing some of the classical LOHC systems above, it should now be discussed why the MCH system should be chosen above these, and why it is likely to be superior to its LOHC rivals.

2.4   The Case for the MTH System

As pointed out in the analysis of the other systems, the major barriers to the processes are as follows:

- Toxicity

- Physical properties

- Carbon emissions

- Open-cycled carrier recycling

- Severe cracking conditions

- Manufacturing costs of carriers

The MTH system is an excellent compromise between all of these factors. The components of the system can be described as toxic, but in fact have similar toxicity to petrol and diesel, the dangers of which are widely known and accepted. Toluene is already a substantial component of modern day petrol – the EPA estimates that 37% of global toluene is used for petroleum blending[44].

Some carbon emissions are inevitable at the current level of technology with this system, because the carrier is not entirely recovered after dehydrogenation. Trace toluene and MCH is found in the hydrogen stream on a vehicle[23], but these emissions are minimal in comparison with current petrol emissions and this situation would be the same with almost any other hydrocarbon carrier.

The MTH system is a closed cycle, which makes carrier recovery simple, as shown in Figure 2-5.
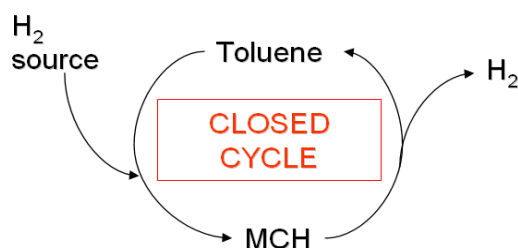
Figure 2-5: The MTH system – a closed cycle

Effective cracking of MCH requires more severe conditions than some other carriers, but these conditions are a compromise. Some carriers require less or similar external heat input and yet carry a higher wt% of hydrogen such as pyridine, ammonia, methanol and benzene (see Table 2-2), but pyridine and ammonia are highly toxic, as explained above methanol does not prevent carbon emissions, and benzene is a known carcinogen. Good hydrogen evolution rates are reported from MCH at a temperature of 571 K, which is achievable with a good system of heat integration. This also means that recharging does not require severe conditions, with reports of 100% toluene conversion to MCH at 423 K[45], and the significant energy input required for dehydrogenation means that spontaneous hydrogen discharge is unlikely.

 Finally, the manufacturing costs of toluene are very reasonable due to the already high demand. Approximately 13 million tonnes per year is consumed as a petrol additive worldwide[44], so toluene already has a very large scale manufacturing sector, and is readily available.

Other advantages for the MTH system include the fact that it is a proven vehicular fuelling system to an extent that no other system to date is.

Taube *et al*[43] published a complete solution for the use of the MTH system as an automotive fuel. This was a limited study, because it was based on using the MTH system to run a 17 tonne lorry for a set amount of time and with a set distance each year. Commercial passenger vehicles are likely to partake in less predictable journeys. It was found that due to the lower energy density of MCH compared to petrol or diesel when MCH is used as part of the MTH system, the fuel storage tank would have to greatly increase in volume (by a factor of six) and therefore weight, growing from 120 L (diesel) to 710 L (MCH). A further increase in system volume and weight would be required for the catalytic MCH dehydrogenation reactor. Overall, the components necessary to operate the MTH system required a 9% increase in weight – this may be manageable in a 17 tonne lorry, but would cause significant difficulties at the consumer level in a standard car. To this point, although the paper

produced a novel idea, and pointed out effectively the gaps in research needed to realise a functioning automotive MTH system, it worked on the basis of powering only 195 vehicles of the aforementioned type and restrictions, which is not relevant to a wider consumer-based goal.

The author later went on to build a prototype tuck based on this system[46], shown in Figure 2-6.

Figure 2-6: A prototype truck running on the MTH system, built by Taube _et al_, 1985[46]

The author states that this prototype was thought of as a "moveable laboratory" and not a practical vehicle, because the apparatus takes too much volume for this truck to be used for actual haulage. However, the white box behind the cab shows the volume of the apparatus functioning in a second prototype proposed at the time, which would be 300 kg (20%) lighter and occupy far less volume while providing a greater feed of hydrogen.

Although this prototype shows that the MTH system is applicable as a real-life possibility, there were some drawbacks. The author commented that the heat of the exhaust gases was not sufficient to sustain the 400 $^{\circ}$C operating temperature of the reaction vessel, which is a very important point, as this implies the need for a separate heating component in the system, or combustion of a small amount of hydrogen/hydrocarbon fuel additional to that in the engine for heating of the reaction vessel.

The efforts to see the MTH system on a vehicle did not stop there. More recently in 2008, Hrein Energy created a hybrid system which uses waste heat from a fossil fuel ICE to dehydrogenate MCH and add 3% hydrogen to the air feed in the engine[47]. This mixing of hydrogen allows the fossil fuels to achieve a lean burn, and therefore fuel efficiency increases by 30%, the vehicle emits 30% less

CO_2, and emissions of NO_x and CO are also reduced. The reactor can be retrofitted to a conventional fossil fuel vehicle, and Hrein have demonstrated this with a 1200cc production car[48]. Although this is not a complete solution, this shows that the technology functions well on-board a vehicle, and this system may be a good temporary solution to begin commercialising the dehydrogenation technology.

To conclude, some ideas mentioned in this and the previous section (ammonia/methanol as carriers, nitrosubstituted rings *etc*) in the current literature are interesting concepts and may prove to be valuable in the future, but at this stage, much research and testing is still required before any type of commercialisation could take place. Other possibilities are theoretically promising but logistically difficult (autothermal carriers), and these difficulties need to be solved before any kind of system for an automotive application could be developed. In contrast, the mechanisms governing the reactions of the MTH system are well known, and the key properties of the constituents are convenient, being similar to the petrol which is used worldwide today. Furthermore, the MTH system could take advantage of current industrial production of its constituents to a greater degree than other alternatives.

The next step is to visualise the design of a vehicular MTH system.

2.5   The MTH System: Process

The MTH system process consists of an MCH feed which is vaporised before entering a catalytic bed where it is cracked to yield toluene and hydrogen. This gaseous feed enters a condenser where the toluene is condensed out of the feed and stored in a tank until it is reclaimed for recycling. Hydrogen remains in the gas phase, and is sent from the condenser to the engine/fuel cell for combustion.

The essential stages of the MTH system are as shown in Figure 2-7.

Figure 2-7 treats each part of the system as a black box, and is a summary of the most important steps. The steps outlined in Figure 2-7 are central to the process and either present potential problems to the system or otherwise warrant possible further study.

This section deals with each major step in turn, and evaluates any barriers or particular areas of interest.
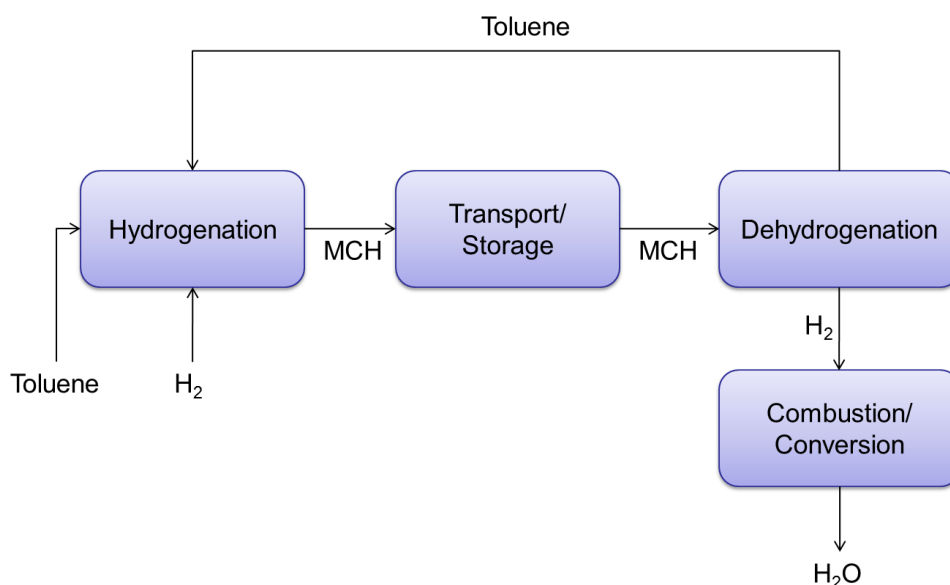
Figure 2-7: Major processing stages in the MTH system

2.5.1 **Hydrogenation**

Although not considered a major barrier to the MTH system, much hydrogenation research has been carried out, occasionally for hydrogen storage purposes[49], but more often as a step in removing heteroatoms in petrochemistry[50] or to reduce the aromatic compounds in diesel[51, 52]. The hydrogenation of toluene is represented by Figure 2-8.
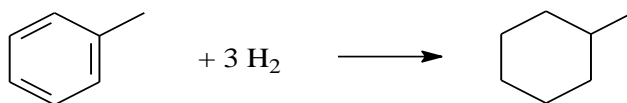
Figure 2-8: Hydrogenation of toluene to give MCH

Studies tend to revolve around the identity of the catalyst(s) used. Catalysis of hydrogenation is somewhat complex with this reaction, because bifunctional catalysis is observed (where the support plays a role as well as the metal[45]). Selected findings from the literature are given in Table 2-3.

These findings suggest that toluene hydrogenation has been achieved under relatively mild conditions, and with high conversions and selectivity. Therefore the hydrogenation process does not present a barrier to the use of the MTH system.

Table 2-3: A selection of catalysts and their success in toluene hydrogenation under variable conditions (data provided as available). HBEA and ZSM-22 are zeolite supports.

Catalyst	Temp/K	Pressure/bar	Conversion/%	Selectivity/%	Ref.
Noble Metal Catalysts					
1% Pt/Al$_2$O$_3$	523	-	34	-	[53]
3% Pt/HBEA	373	0.07 – 0.12	100	100	[45]
3% Pt/HBEA	423	0.07 – 0.12	100	94	[45]
3% Pd/HBEA	473	0.07 – 0.12	58	83	[45]
3% Pt-3% Pd/HBEA	423	0.07 – 0.12	≈100	100	[45]
0.5% Pt/ZSM-22	423 - 498	1.1 – 3.6	5 - 45	-	[51]
Non-noble metal catalysts					
Mo$_2$C (Commercial)	473	27.6	70	100	[50]
Mo$_2$C (Synthesized)	473	27.6	98	100	[50]
1% Ni/MgF$_2$	423	-	≈90	100	[52]

Further study in this part of the system has been carried out in the use of hydrogenation as an inherent hydrogen purification method, for hydrogen from an impure source (such as syngas from biomass gasification or sulphur-containing hydrogen)[54-56]. A hydrogenation process using syngas as the hydrogen source is illustrated by Figure 2-9.

$$H_2 + CO_2 \text{ (Syngas)} + Toluene \xrightarrow[\text{Catalyst}]{\text{Heat}} MCH \text{ (l)} + CO_2 \text{ (g)} \underset{\text{Separation}}{\Huge\langle} \begin{array}{c} CO_2 \text{ (g)} \\ \\ MCH \text{ (l)} \end{array}$$
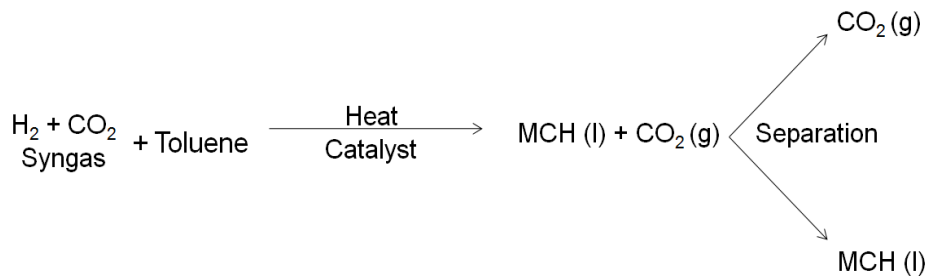
Figure 2-9: Separation of hydrogen and carbon dioxide by toluene hydrogenation

This technique assists separation by selectively transforming hydrogen into the liquid phase (as part of MCH), whilst carbon dioxide remains in the gas phase, making separation simple and easy. Where this has been studied, it has been found that although CO_2 is itself inert, its presence can substantially hinder the hydrogenation reaction. Under hydrogenation conditions, the Reverse Water Gas Shift (RWGS) reaction can occur [55, 57]. This reaction is illustrated in Figure 2-10.

$$H_2 + CO_2 \xrightarrow{\text{Noble Metal Catalyst}} H_2O + CO$$

Figure 2-10: Reverse Water Gas Shift Reaction

The CO species, although usually only present in minute volumes at hydrogenation temperature, binds to noble metals such as Pt more strongly than hydrogen does, and so poisons the catalyst[55]. This binding acts as a CO sink, and stimulates further production of CO until all of the active Pt sites are bound to CO.

It would be valuable to have a hydrogen storage technique which could inherently purify an impure hydrogen feed. The discovery of a CO-tolerant catalyst for MCH hydrogenation is one way in which the MTH system could be improved.

2.5.2 Transport/Storage

It is stated in several LOHC-based papers that an LOHC system could use the existing fuel distribution infrastructure with only minor modifications[18, 22, 31, 33, 35, 58]. However, exactly what these modifications are tends to be unclear. It would be interesting to see a quantitative assessment of exactly what these changes would be, and therefore to carry out an economic analysis of the transition to the new infrastructure, which could be compared to alternatives *e.g.* high-pressure hydrogen pipelines, cryogenic liquid hydrogen tankers, *etc*.

2.5.3 **Dehydrogenation**

The MTH system of automotive fuel proposes that dehydrogenation would take place on-board the vehicle, which limits the dehydrogenation process in the range of conditions it can accommodate and the system weight/volume.

Again, the focus here is the choice of catalyst, but more emphasis is also placed on reactor and environment, perhaps due to the more challenging nature of dehydrogenation over hydrogenation. Also, the overall conversion of reactants is now less important with a higher emphasis placed in hydrogen evolution rate, which must be sufficient to satisfy the energy demands of the driver. Examples of experimentally investigated MCH dehydrogenation reactions from literature sources are given in Table 2-4.

Table 2-4: A selection of catalysts and their success in MCH dehydrogenation under variable conditions (data provided as available). AC is Activated Carbon and CB is carbon material.

Catalyst	Temp (K)	Pressure (bar)	Hydrogen evolution rate $(mmol/g_{metal}/min)$	Reactor system	Ref
10% Pt/AC	298	-	520	Continuous flow	[30]
0.1% K + 0.6% Pt/Al$_2$O$_3$	320	1.01	744 $(mmol/L_{cat}/min)$	Fixed bed	[59]
3% Pt/La$_2$O$_3$	623	1.01	21.1	Continuous Flow	[60]
3% Pt/La$_{0.7}$Y$_{0.3}$NiO$_3$	623	1.01	45	Continuous Flow	[60]
0.4% Pt/CB	573	1.01	342	Fixed bed	[61]

There is a lack of non-noble metal catalysts in the literature, because the dehydrogenation process is more challenging than the hydrogenation step. Dehydrogenation is thermodynamically favoured at higher temperatures, so the chosen catalyst must be thermodynamically and structurally stable at the chosen temperature. Although high temperatures are challenging for an on-board process, these higher temperatures do help to prevent catalyst poisoning by coking to some degree[62-64].

It would be interesting to research catalysis under milder conditions to make a less energy intensive process. The ideal process would be one under which dehydrogenation occurs with the hydrocarbon in the liquid phase, as this would remove the need for MCH evaporators/superheaters before dehydrogenation and subsequent condensation, and would allow for easier hydrogen/toluene separation as well as improving the already high toluene recovery rate.

2.5.4 Fuel Utilisation

Even if a clean, economical method of hydrogen production were immediately available, and a practical, well researched transport and storage network were established, this still leaves the problem of how to utilise the hydrogen at the point of use. In terms of automotive applications, the main argument is whether to use a conventional ICE, or to use a fuel cell, which has distinct advantages over the ICE but is far less widespread and is established to a lesser extent. This is not the only problem. In fact, the entire running system of the vehicle comes under question, because when hydrogen is used in place of liquid fossil fuel, possibilities outside of the well-established and accepted system for a vehicle become available. Due to the volume of possibilities, an entire paper could be written on this topic alone, so this paper will manly focus on the comparison between ICE and fuel cell and the associated factors.

2.5.4.1 Internal Combustion Engine vs. Fuel Cell

In the original study by Taube *et al*[43], the endothermic nature of dehydrogenation was considered. Specifically, it was calculated that the catalytic reactor would need to hold a temperature of 400 $^{\circ}$C to drive the reaction. This could be sustained by a good system of heat exchangers (such as Metcalfe and Cresswell[23]), but only under steady state conditions. During start-up where equipment is at ambient temperature, dehydrogenation is not immediately possible. Taube suggested that this could be addressed by a flexible fuel feed, where toluene is combusted in an ICE for the first few minutes until the dehydrogenation catalyst reaches sufficient temperature. If MCH were combusted instead of toluene, this would release more energy per unit mass with the same amount of carbon emissions per mole. This is demonstrated in Table 2-5.

Table 2-5: Carbon emissions from hydrocarbon combustion at start-up, calculations based on figures from [32]

Hydrocarbon	Heating value (MJ/kg)	Mass combusted for start-up (kg)[43]	Carbon emissions per cold start (kg)	Average emissions (gCO$_2$/km)
Toluene	40.589	0.70	2.34	9.36
MCH	43.380	0.65	2.04	8.16

The burning of MCH over toluene would result in a yearly difference of carbon emissions of 75 kgCO$_2$ per vehicle, which would be significant over many vehicles. However, MCH has a lower octane number than toluene. Octane numbers, both Research Octane Numbers (RONs) and Motor Octane Numbers (MONs) are used to describe the propensity of a fuel to "knock", *i.e.* to prematurely combust under the pressure of the cylinder of the engine[65]. The higher the octane number, the higher resistance the fuel has against premature combustion. Toluene has a high RON of 121, and so is added to petrol to raise the octane number of the fuel blend. MCH, on the other hand, has a RON of 75, and so would be more likely to cause engine knocking if combusted directly. Direct combustion of MCH as suggested could therefore lead to engine problems. The solution may be to combust toluene directly as suggested by Taube *et al,* or to combust a blend of MCH and toluene to reduce the total carbon emissions.

This flexible fuel feed strategy could not be considered if using a fuel cell due to the inability of fuel cells to directly oxidise liquid hydrocarbons, therefore the start-up problem would still be a concern, but a flexible fuel feed *would* be possible with an ICE.

Further advantages of the ICE over the fuel cell are that ICEs are well established, affordable, and easy to maintain. Major facilities already exist to produce and service ICEs, and their use would make social acceptance of the new system easier than in the case of an unrecognisable novel fuel cell system. It is important, however, to carry out further research into ICEs specifically for hydrogen combustion, as most investigations to date have been carried out using conventional petrol/diesel engines, modified to a variable extent[66]. It was announced in 2009 by BMW that they had developed a purpose-built hydrogen engine, capable of delivering a power of 100 kW with a fuel efficiency of 42%, comparable to modern diesel engines[67], with a forecast of 50% efficiency in the near future.

Despite the above advantages, ICEs also have disadvantages, many of which can be solved by replacement with fuel cells. ICEs are inherently limited by the Carnot efficiency, whereas fuel cells suffer from no such restrictions, and can reach a fuel efficiency of 50 − 60%[15, 18]. Higher fuel efficiency means that it becomes necessary to carry a lower volume of fuel, which minimises one of the critical disadvantages of the MTH system, namely the high volume (hence weight) of MTH/toluene required to give a comparable range to a petrol/diesel system. In the study by Taube *et al*[43], it is stated that 120 L of diesel is energetically equivalent to 710 L of MCH under the operating conditions studied in the paper. Had Taube used a fuel cell instead of an ICE, this 710 L could potentially be reduced to *circa* 355 L with the same range.

A further advantage of the fuel cell is the desirable quiet operation, as opposed to ICEs which create noise pollution, particularly in areas of high traffic such as cities, and during rush hours. The use of fuel cells would significantly reduce the disturbance for residents in homes or workers near areas of high traffic. However, it could be speculated that the quiet operation of vehicles has a safety implication in that pedestrians may not hear vehicles approaching, and would need to take more care crossing roads.

Fuel cells with a range of operating temperatures are available, and many papers study the use of the lower temperature examples, often PEM fuel cells[22], and carrier dehydrogenation with a heat input in line with the operating conditions of low-temperature fuel cells are sought *i.e.* endotherms of dehydrogenation should be low enough that heat exchange with the low temperature fuel cell is sufficient to drive the dehydrogenation reaction forward[33]. However, the use of high-temperature fuel cells such as solid oxide fuel cells (SOFCs) offer opportunities for heat integration which their low-temperature counterparts do not, and offer a solution to the problem of energy supply to the catalytic dehydrogenation vessel. In a study by Metcalfe and Cresswell[23], a system is proposed which uses the heat of the SOFC to sustain temperature appropriate to dehydrogenation of MCH. Under these operating conditions, the MTH system was shown to be more efficient, offer a higher range in terms of distance, and produce significantly fewer carbon dioxide emissions than a PEM fuel cell system proposed by Scherer[26] using methanol as the LOHC.

2.5.4.2 Primary Power Source vs. Range Extender

Another factor of the MTH system is how operation can be affected by hydrogen production rates. Before a full system can be established and commercialised, it must be made certain that the demand of the driver can be met by the system, *i.e.* when the accelerator is pushed, the power

supply must be sufficient to meet the requirements, and no breaks in power should be experienced. If rates of dehydrogenation are not kinetically fast enough to meet the power demands, it could be convenient to use the MTH system as a range extender for an electric, battery-operated vehicle rather than a direct source of automotive power. An example of a possible modified MTH system is given in Figure 2-11.
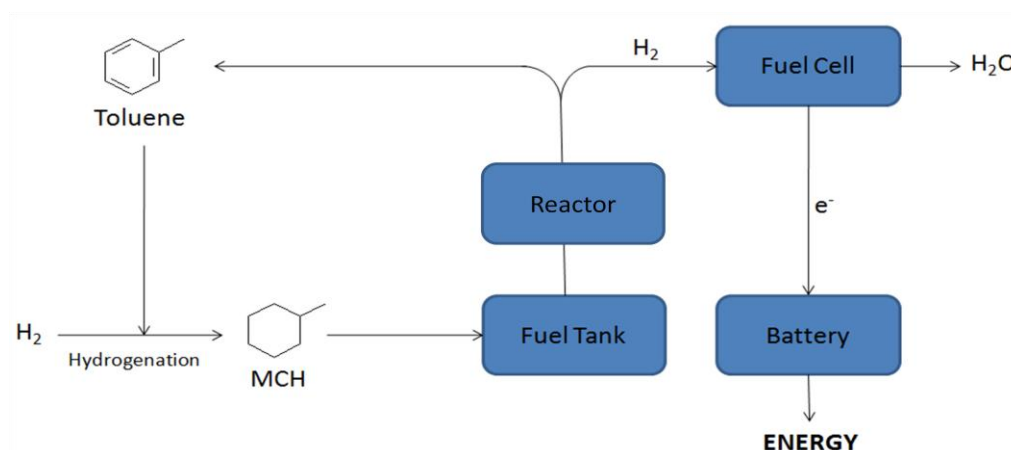
Figure 2-11: The MTH system, modified to act as a range extender rather than a primary power source

In Figure 2-11, the fuel cell provides electrical power through hydrogen combustion, which is then stored in the battery until it is required. The battery provides automotive power directly, and is topped up as required by the fuel cell. This extends the range of the vehicle beyond the capabilities of a battery alone, and removes the need to recharge the battery while the vehicle is not being used. If at any time, hydrogen evolution falls short of the energy demand, the battery acts as an energy buffer by releasing this stored energy as required. The extra energy taken from the battery can then be replaced when the vehicle is decelerating or idle. Also, the battery could be used to provide power to vehicle during start up while the catalytic dehydrogenation vessel is reaching an operative temperature.

This is a good start-up solution and removes the need for hydrogen evolution to directly match power demands, but adds to system volume. In addition, the battery may run flat if the vehicle is used for such short journeys (*e.g.* school runs) that dehydrogenation is never initiated.

2.6 Literature Survey Conclusions

The literature review demonstrates that the MTH system, although it does not solve every problem of hydrogen storage, shows potential above its technological rivals. It has already been tested in a

(limited) vehicular environment[43, 46, 48, 68], and although the system volume and weight as well as the start-up situation present obvious problems to the system, the system is worth further investigation.

Among hydrogen storage strategies, the MTH system is competitive on many levels, and although further refinement is required to bring the technology to the level of commercialisation, both short- and long-term strategies for using this technology can be visualised. These visions are represented by Figure 2-12 and Figure 2-13.
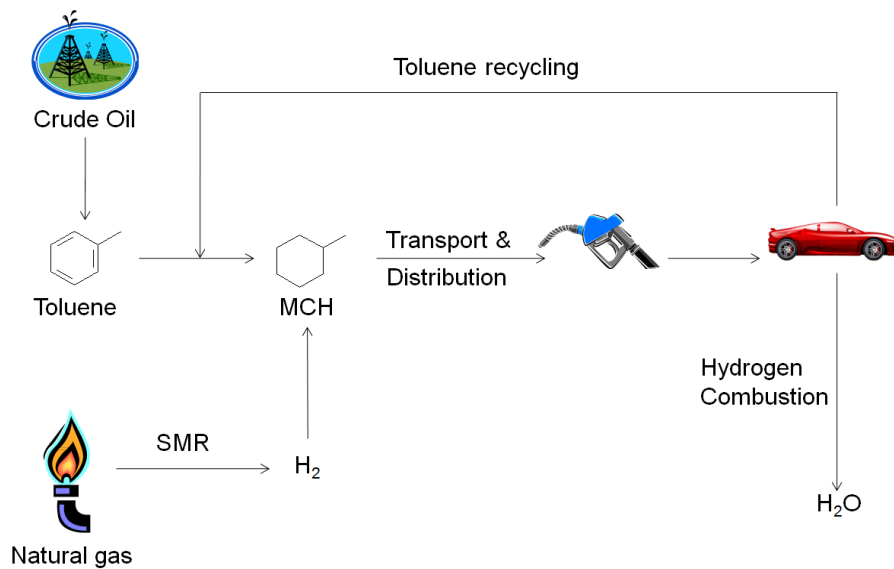
Figure 2-12: Short-term commercialisation of the MTH system, with fossil fuel feedstock sources
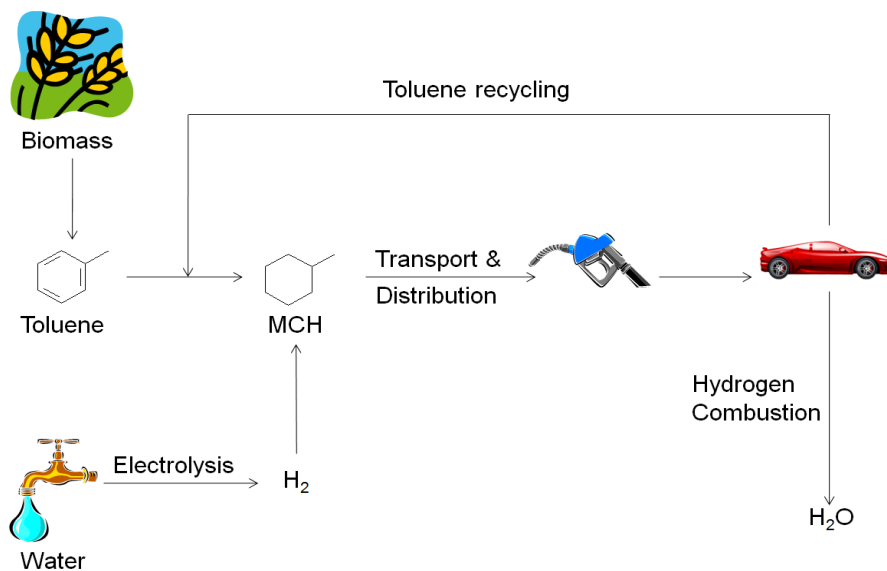
Figure 2-13: Long-term commercialisation of the MTH system, with environmentally friendly feedstock sources

Figure 2-12 illustrates a supply chain strategy for the short-term commercialisation of the MTH system using cheap, readily available fossil fuel derived feedstock. As more environmentally friendly technology matures and becomes economically competitive, this can replace fossil-fuels to give a system that can be used indefinitely as shown in Figure 2-13. It has been shown in a recent publication[69] that it is possible to synthesize commodity chemicals such as toluene from biomass sources, and that the process can be tuned to give a high yield of the desired compound. Although this is a young technology, it could form part of the long-term vision. The recycling of the toluene would mean that crops would be required in relatively low quantities, so this route is essentially a biofuels route but the hydrocarbon recycling prevents excessive land use.

The first step in refining the technology is to evaluate potential fuel distribution infrastructures. The most promising scenario should be chosen to act as a basis for further investigation, and research into the barriers to the process will be considered on this foundation.

Chapter 3   MTH System Direction of Study

3.1 Introduction

The literature review in has shown that there are some gaps in knowledge concerning the MTH system and LOHCs in general. The focus tends to be on the chemistry of the (de)hydrogenation reaction, with investigations often centred on the identity of the catalyst, the reaction conditions or the type of reactor used. If the MTH system is to be used as a viable fuel storage solution, there are other important factors to consider beyond the chemistry.

This chapter aims to outline the entire MCH system, as it would be on a scale large enough to provide automotive fuel. This analysis is intended to identify bottlenecks in the process *i.e.* areas which require further investigation, or parts of the process which need to be changed for the MTH system to become viable. Having a list of bottlenecks will direct the further research of this project.

3.2   Process Steps

The major steps in the MTH system are those listed in Figure 2-7. These are:

- MCH manufacture, *i.e.* toluene hydrogenation
- MCH/toluene transport and storage
- MCH utilisation, *i.e.* dehydrogenation and hydrogen combustion
- Vehicle considerations – Start-up, control and process.

Note that all of these steps are linked by the closed loop nature of the toluene retrieval; therefore they cannot be treated as entirely separate steps.

A factor which will not be considered in any detail is hydrogen production. Existing hydrogen sources will be examined but no effort will be made to improve on existing hydrogen production technologies. Hydrogen production is an important part of the process and the cost of hydrogen can dictate the economic viability of the whole process, but improvement of H_2 production technology is beyond the scope of this hydrogen-storage-based project.

Each of the bullet points above will be examined, and a basis for further investigation will be chosen and justified. Following this, the process bottlenecks will be identified and so points to be researched as part of this project will be selected.

A largely technoeconomic approach will be adopted for this chapter. This is to keep the focus on viability, because a technically perfect system may still be too expensive to be viable. Therefore bottlenecks will be identified using technoeconomic analysis, and these bottlenecks will be examined technically in later chapters.

3.3 MCH Manufacture

This section details the main possibilities for large scale MCH manufacture by hydrogenation of toluene, and evaluates these possibilities in terms of their hydrogen sources, energy integration potentials, economics and other criteria.

Firstly, the scale of MCH manufacturing operations must be chosen. The scale of the units may be important in dictating the economic success of MCH manufacture, therefore this should be chosen carefully. Fundamentally, two broad options for scale exist:

- Local manufacture: Toluene is reclaimed from vehicles at the filling station and processed on-site to yield MCH for redelivery to vehicles
- Central manufacture: Toluene is reclaimed for vehicles at the filling station and transported to a central facility for processing. MCH is then returned to the filling station for redelivery to vehicles.

These possibilities will be investigated and a decision reached.

3.3.1 **MCH Manufacturing Scale: Analysis of Strengths and Weaknesses**

Table 3-1 gives a summary of the strengths and weaknesses of the MCH process when choosing between centralised and local MCH manufacturing.

Table 3-1: Strengths and Weaknesses Analysis between centralised and local MCH manufacture

	CENTRALISED	LOCAL
H_2 Production	Large scale, centralised, various possible sources (CH_4 *etc*)	Small scale, grid/electrolyser only likely option
Capital Cost	Likely to be lower due to economy of scale and	Likely to be greater due to restricted hydrogen source

	CENTRALISED	LOCAL
	freedom of choice regarding hydrogen source	and small scale
Energy Integration	Opportunities for effective use of waste heat are maximised	Limited heat integration opportunities
Toluene Storage	Variable quantity between filling stations due to variable demand, some collections more frequent than others	Hydrogenated within 24 h, each filling station can meet its own goals
Transport	MCH to filling stations nationwide, return of toluene	Toluene replenishment and MCH exchange network – much less transport needed
Security of supply	If nationwide MCH plants are large and few, supply could be disrupted (strike action, protests, foreign threat...)	Very difficult to disrupt thousands of small-scale supply centres

This analysis shows that there is no obvious first choice due to the mix of advantages and disadvantages of each approach. Further analysis is required, so each scenario will be studied on the basis outlined below.

3.3.2 Basis for decision

- Qualitative discussion of hydrogen sources

- Flow diagrams (Mass/volume balances)

- Transport evaluation

- Discussion of energy integration

- Economic analysis (to encompass all of the above)

Each scenario will be systematically investigated and compared on each of the points above.

3.3.3 Assumptions

- 50% of UK vehicles run on MCH (15.5 million)

- Average annual mileage per vehicle is 10000 miles

- 96% of hydrogen-depleted toluene is recovered and recycled[23]

- No hydrocarbons are combusted for start-up

- The UK has 9500 filling stations, all equipped for MCH delivery

- The toluene hydrogenation process is 100% efficient

These assumptions simplify the modelling approach for a first approximation analysis.

3.3.4 Discussion of hydrogen sources

3.3.4.1 Local Processing

Hydrogen sources for local MCH production are limited. The geographical location of a filling station is decided by the need for fuel, and there are more filling stations where the need is greater. Therefore, the flexibility does not exist for the filling station to be situated near to a convenient hydrogen source *e.g.* a source of natural gas where steam methane reforming (SMR) could take place.

It is therefore more sensible to assume that for this scenario, all hydrogen comes from electrosplitting of water – the only feedstock required is distilled water, and energy can be delivered from the grid, which all filling stations have access to. Although this is among the most expensive sources of hydrogen, this is also one of the cleanest (or indeed the cleanest), so from an environmental point of view, this is an excellent option.

3.3.4.2 Central Processing

Hydrogen sources for central MCH production are not limited by geographical location. Much like the existing oil refineries are located on the coast for convenient delivery of crude oil, the MCH processing plants can be fabricated near to a convenient and cheap source of hydrogen, such as methane. Due to the freedom of source and, in addition, the large production scale, hydrogen from this route is likely to be cheaper than that from a small scale electrolyser. However, the carbon emissions from this route are likely to be significantly higher.

3.3.5 Flow Diagrams

This section offers process flow diagrams for the MCH manufacture processes on the different scales of production. For detailed calculations, see Appendix A.

3.3.5.1 Local Processing

By accounting for the relative densities of MCH and toluene, and the recycling efficiency of toluene, the relative tank sizes can be calculated. Then, assuming 6 kg of hydrogen offers a satisfactory range of 186 miles for a vehicle (based on the use of an Internal Combustion Engine (ICE) as opposed to a fuel cell), the vehicle tank size of 126.5 L can be obtained. This 186 mile range is retrocalculated from a paper[15] which claims that 8 kg of hydrogen can satisfy a 400 km range in a passenger vehicle. Finally, with the assumed average annual mileage of 10000 miles, the yearly MCH demand can be calculated.

A complete flow diagram of a filling station can now be represented. The result is shown in Figure 3-1.

The flows given in Figure 3-1 are average flows, and it is recognised that real-life tank sizes would need to be greater than the volumes given to protect against overfilling *etc*. The flow diagram represents the average filling station – some will be larger in high-demand areas (cities *etc*) and some may be smaller (rural communities).
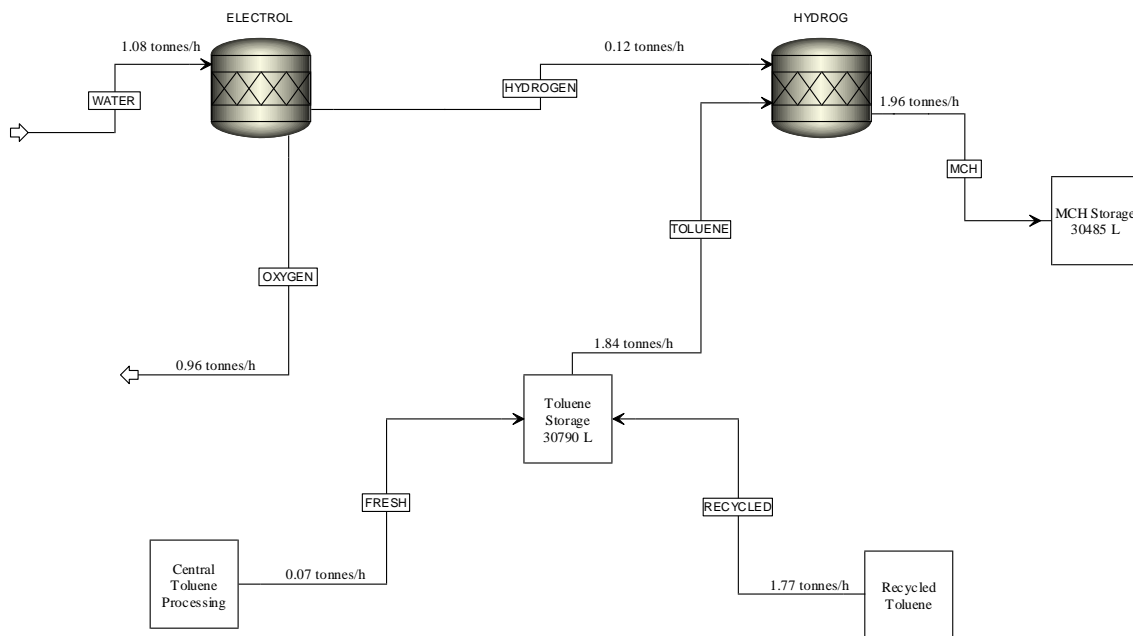
Figure 3-1: Complete flow diagram for an average MCH filling station, functioning for 12 h/day

Normally, hydrogenation will take place overnight to take advantage of cheap electricity tariffs. However, it is recognised that not all filling stations will be operative all the time. Therefore, for the purposes of the rest of this document, it will be assumed that at any one time:

- 80% of stations (7600) function normally, carrying out toluene hydrogenation over 12 hours per 24 hour period.

- 10% of stations (950) are non-operative (maintenance, breakdown *etc*)

- 10% of stations (950) hydrogenate 24 hours a day, and an exchange system is created to fill the gap for the non-operative stations.

Note that a further advantage of this system is flexibility – rather than hydrogen being used for MCH production, the hydrogen could instead be pressurised and delivered as a gas if required by the user. If a market emerges where a combination of MTH vehicles and CHG vehicles are used, MCH could be delivered directly or hydrogenated on-site respectively. This would prevent the investment becoming defunct in the case of the market moving towards CHG rather than MCH, but would increase the station capital cost due to the installation of a compressor, investment in compressed hydrogen cylinders for storage, and a hydrogen pump for vehicle refuelling. Although potentially convenient, this possibility will not be investigated further in this document.

3.3.5.2 Central Processing

Two separate scenarios will be studied within central processing. These will involve:

- **Scenario 1:** Many small plants based upon the plant size and capabilities of similar existing facilities.

- **Scenario 2:** A small number of large plants, based upon the current fossil fuel infrastructure (11 major refineries in the UK).

However, aside from the quantities involved, the flow diagrams will be the same. This can be represented by Figure 3-2.

Note that in this case, the hydrogen source is not discussed in detail. A report from the US Department of Energy[70] states that hydrogen can be produced centrally by SMR from as little as 2008 US \$1.25/kg H_2 "at the well", which is equivalent to £0.79 in 2011. A detailed evaluation of hydrogen production from a number of sources is beyond the scope of this report, and so the price of £0.79/kg H_2 will be used for central processing scenarios. However, if operating on this basis, it should be remembered that SMR has associated carbon emissions, and so should not be considered as environmentally friendly when comparing central MCH production with local MCH production.
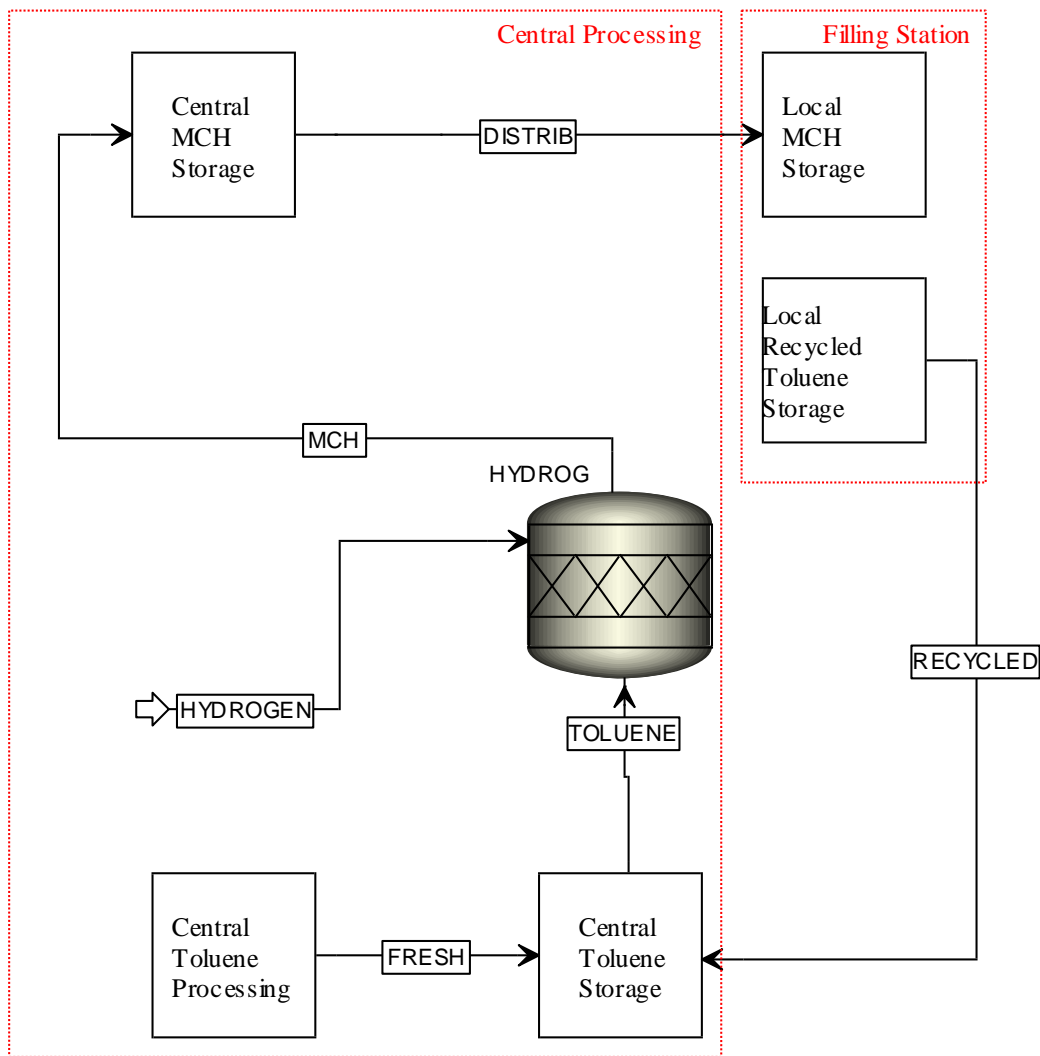
Figure 3-2: General flow diagram for central MCH manufacture

3.3.5.3 Central Scenario 1

For detailed calculations, see Appendix B.

Plants are based on an existing SABIC plant, of which there would be 199 nationwide to fulfil fuel requirements. The flows for each plant are represented in Figure 3-3.
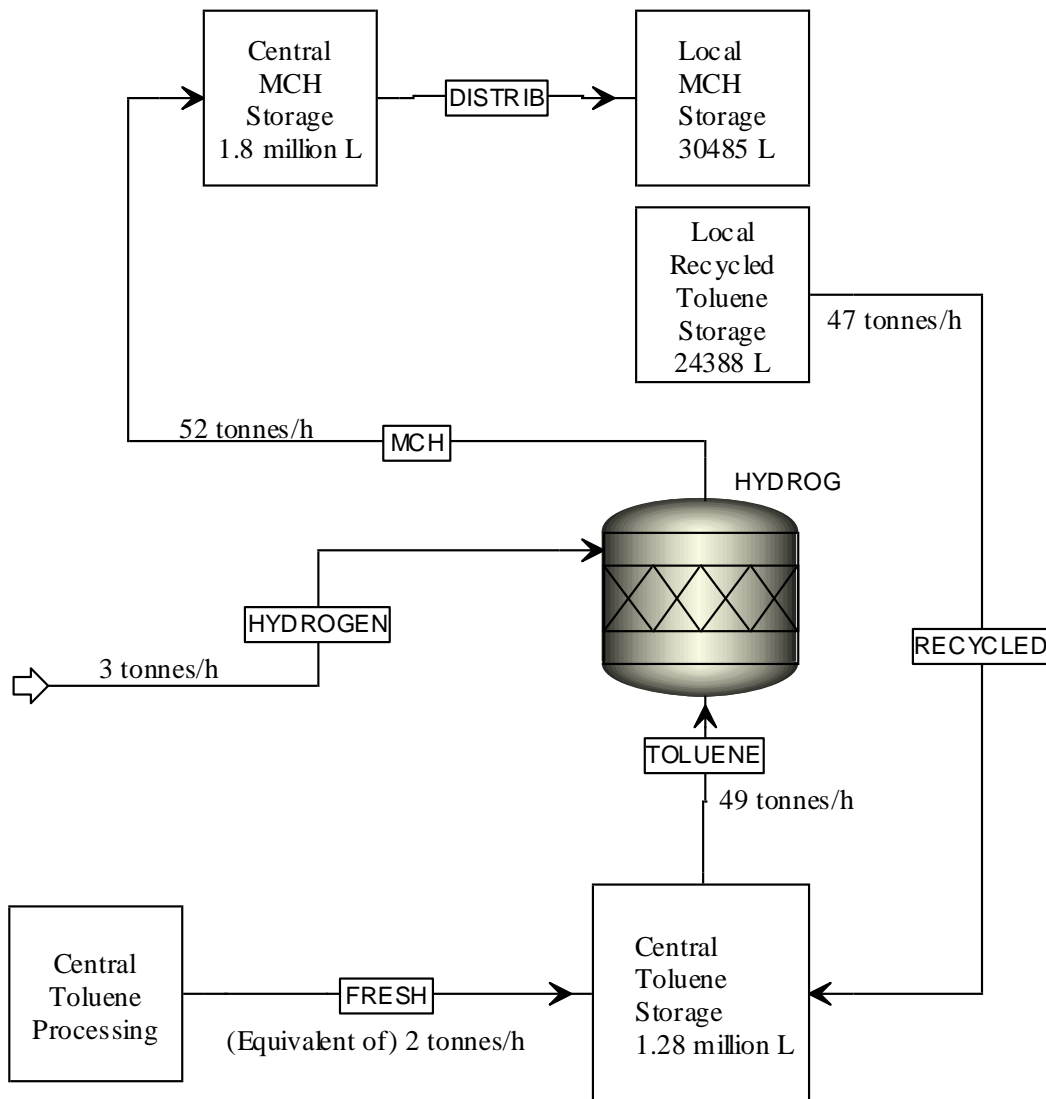
Figure 3-3: Mass balance for an MCH production plant under Central Scenario 1

The storage capacities at the filling station for MCH will be the same as that required for local MCH production, and for toluene will be less, because replenishment of toluene will take place at the central plant, and will not need to be stored at the filling station for a considerable period.

In particular, note that the relatively high central storage volumes for MCH and toluene are to prepare for 24 hours demand or collection respectively in the case of a non-operative hydrogenator, routine maintenance *etc*. In practice, if the plant is in constant operation, only a percentage of the storage space would be used.

3.3.5.4 Central Scenario 2

In the UK today, there are 9 major refineries, as illustrated by Figure 3-4. Although they are shown on Figure 3-4, Coryton and North Tees refineries are no longer in operation.

© Institute of Petroleum

Figure 3-4: Map of UK oil refineries

This shows that the majority of combined UK petrol and diesel for road use and many other products and applications (fuel for sea/air use, plastics *etc*) was at one time produced from only 11 very large scale plants, before the closure of Coryton refinery in 2013 and the North Tees refinery in 2009. Recall that as shown in Figure 1-2, the UK has been a net energy importer since 2004, but before this time, the UK was able to satisfy its own energy needs.

It is likely that MCH could be produced in larger quantities than the largest existing plant, but the current demand does not require this. Therefore, it is assumed that the yearly MCH requirement can be met by 11 large plants, each producing approximately 7.4 million tonnes (9.6 billion litres) of MCH per year, calculated by dividing the speculated MCH demand by 11. (see Appendix C). The flow diagram for such a plant is shown in Figure 3-5.
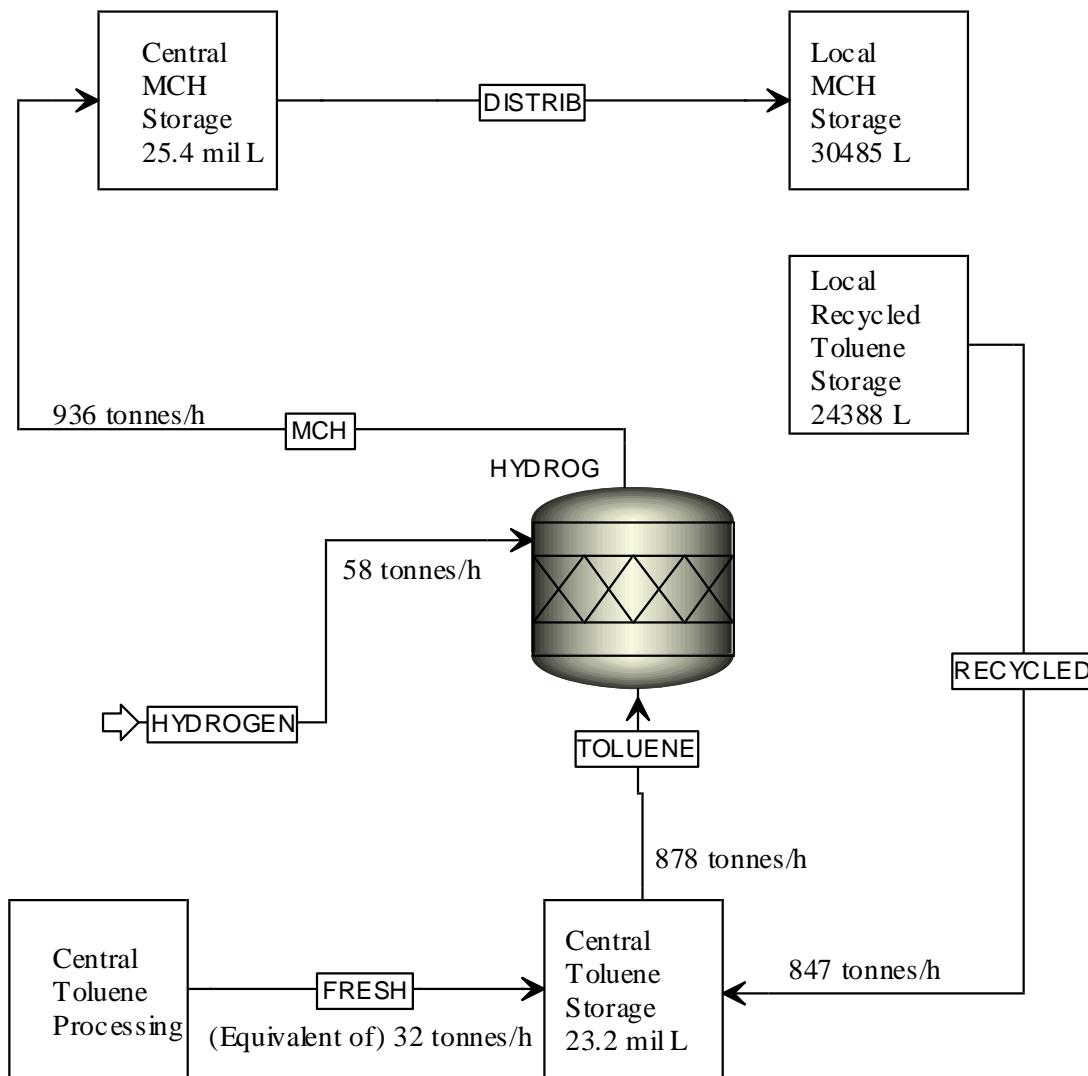
Figure 3-5: Mass balance for an MCH production plant under Central Scenario 2

3.3.6 **Transport evaluation**

3.3.6.1 Local Processing

For detailed calculations, see Appendix D.

The transport of feedstock *etc* is likely to be very scarce in the case of local processing, compared to both the liquid fossil fuel transport that occurs today, and MCH production on a central level.

Water is required for electrolysis to produce hydrogen, and this could be centrally demineralised and transported to each station by pipeline. Perhaps more appealing is the idea that each station could have small-scale demineralisation equipment, and could use ordinary tap water, meaning the

development of any extra water infrastructure would be unnecessary (although the enhancement of the existing one to cope with increased volumes may be needed).

The only other feedstock to be transported to each station would be a replenishment of toluene to replace that which could not be recycled from recovery from vehicles. This would be a minor delivery, considering toluene can be recovered in excess of 96% per cycle.

In order to implement a delivery infrastructure to transport: toluene replenishments to each station once a week; MCH replenishments and toluene removals at non-operative stations, **1293 tankers** would be required nationwide.

In reality, it is likely that some liquid transport would take place by pipeline, sea tanker, or alternative transport. However, for comparative reasons, it is assumed that all transport takes place by road tanker.

3.3.6.2 Central Scenario 1

For detailed calculations, see Appendix E.

Deliveries in this scenario are to simultaneously distribute new MCH and collect depleted toluene. This would require **3483 tankers** nationwide.

3.3.6.3 Central Scenario 2

For detailed calculations, see Appendix F.

Fewer journeys per day between plant and station using a single tanker are possible due to increased distance, and this is reflected in the larger number of tankers required. For this scenario, **10,450 tankers** are required nationwide.

3.3.6.4 Transport Summary

Table 3-2: Summary of transport requirements for each processing scenario

MCH Processing Scenario	Tanker Requirement	Arbitrary Scale
Local	1293	12

MCH Processing Scenario	Tanker Requirement	Arbitrary Scale
Central 1	3483	33
Central 2	10,450	100

3.3.7 Discussion of Energy Integration

3.3.7.1 Local Processing

The opportunities for efficient energy integration in a local process are somewhat limited due to the small scale of local MCH processing. However, significant heat is evolved through the hydrogenation of toluene, and it is important that this heat be put to good use to achieve the optimum efficiency and cost.

One possibility is to use the waste heat in a distillation process, to ensure the purity of the recycled toluene coming back from the vehicles after use. However, the purity of reclaimed toluene is not considered a major barrier to the process – the only major impurity is trace MCH, and although this can form a 10% mol fraction of the incoming toluene (calculated from [23]), this presents no barrier to reaction. Also, the boiling points of toluene and MCH are within 10 K of one another, so separation by distillation would be difficult, practically speaking.

Perhaps a more useful application of the waste heat would be to assist the electrolysis process. At room temperature, liquid phase water electrolysis to give oxygen and hydrogen requires approximately 5 kWh/m^3 hydrogen[71], whereas high temperature steam electrolysis using a Solid Oxide Electrolysis Cell (SOEC) at a temperature of 1273 K requires less electricity, which has a subsequent cost saving. However, such high temperatures are more likely to be technically viable only in conjunction with a nuclear reactor, or purpose designed heater, neither of which is in line with the idea of the filling stations. Assuming the hydrogenation runs at a temperature of 473 K, it can be reasoned that this is the maximum temperature the water can be heated to before electrolysis. This will therefore be assumed to be the temperature of electrolysis. If waste heat can be manipulated to offer a cost saving, while simultaneously increasing the efficiency of electrolysis, this possibility should certainly be investigated. A detailed energy balance was carried out (Appendix G), which calculated that by using waste heat to prepare water for electrolysis, the minimum

required electrical input would be only 2.56 kWh/m^3 H$_2$, a saving of almost 50% on the quoted value. However, this is a theoretical value which assumes 100% of the electrical energy is converted to the chemical energy of hydrogen – assuming a more realistic electrolysis efficiency of 60% (an optimistic estimate), the actual required input would be 4.26 kWh/m^3 H$_2$, a saving of 15%.

3.3.7.2 Central Processing

The opportunities for efficient heat integration are much greater in larger scale plants than in the small scale electrolysis plants. If hydrogen production from SMR were carried out in-house, waste heat from hydrogenation could be used to assist in the process, *e.g.* water heating to give steam. If the hydrogen were supplied by an external company, the waste heat could nonetheless be used for toluene purification by distillation (either if the toluene manufacture takes place in-house or if supplied by an external vendor) or to provide plant heating. However, it is difficult to assess this quantitatively at this time.

3.3.8 Economic Analysis

For detailed calculations, see Appendix H.

The economic analysis can be summarised by looking at the cost of MCH at the pump, as this is ultimately the factor which would decide how widely accepted the technology is likely to be. Pump costs are shown in Figure 3-6.
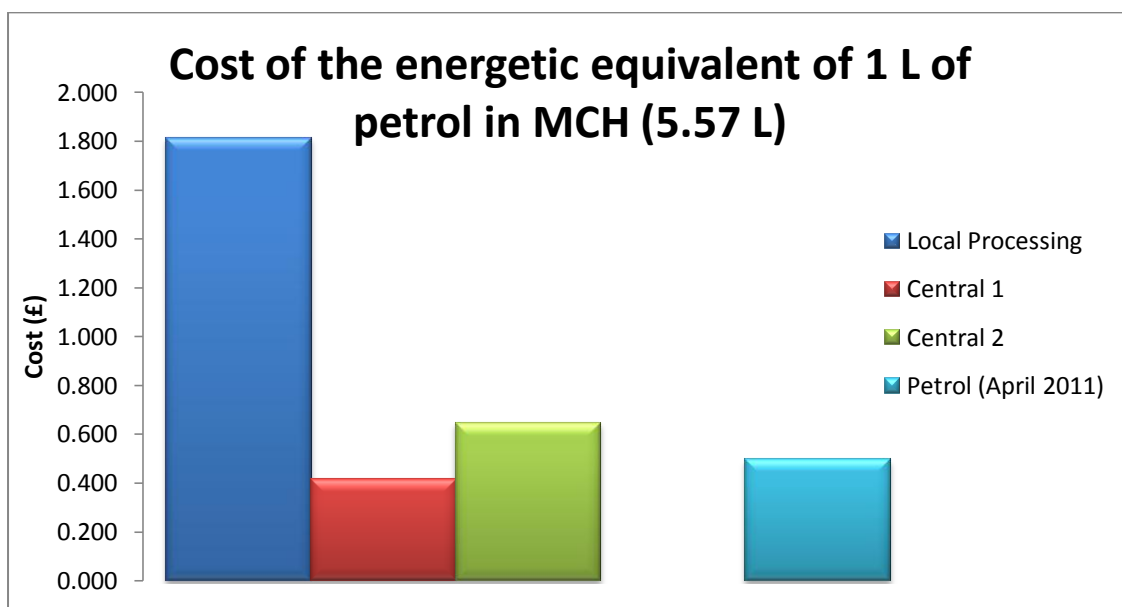
Figure 3-6: Comparison of MCH cost at the pump with different MCH processing scenarios

The cost of petrol has been adjusted to reflect manufacturing costs only and does not include fuel duty and VAT.

It is clear that local MCH processing is not economically viable unless the price of petrol increases by a very large amount. Unsurprisingly, central processing is a far cheaper option leading to a vastly reduced cost at the pump. More surprisingly is that the larger central scale (Central 2) leads to a higher cost that the smaller scale (Central 1). This can be attributed to the higher cost of transport due to the processing plants being far more disperse. This difference in cost is critical, because MCH under the Central 2 scenario is in fact more costly than petrol, leaving the Central 1 scenario as the only economically viable choice (unless the cost of petrol increases).

3.3.9 MCH Manufacture Conclusions

The qualitative investigation of scale shown in Table 3-1 was not sufficient to make an informed decision on the most sensible scale of MCH manufacture. Thanks to the further analysis carried out, the choice is now clearer.

The economic analysis for Section 3.3.8 clearly indicates that the Central 1 scenario, where 199 plants are used across the UK to fulfil the given fuel requirements, is the most attractive. These large scale plants can take advantage of distributed hydrogen sources, and yet can still be strategically placed near to centres of high fuel demand to minimise transport and lead time on fuel. Security of supply would be difficult to disrupt with 199 plants operating in tandem, and there is opportunity to recycle waste heat to increase process efficiency.

The Central 1 scenario will therefore be carried forward and used as a basis for further investigation.

3.4 MCH Utilisation

3.4.1 Scenario Compatibility

It is clear that not every scenario for MCH processing is compatible with every MCH utilisation strategy – this is outlined in Figure 3-7.
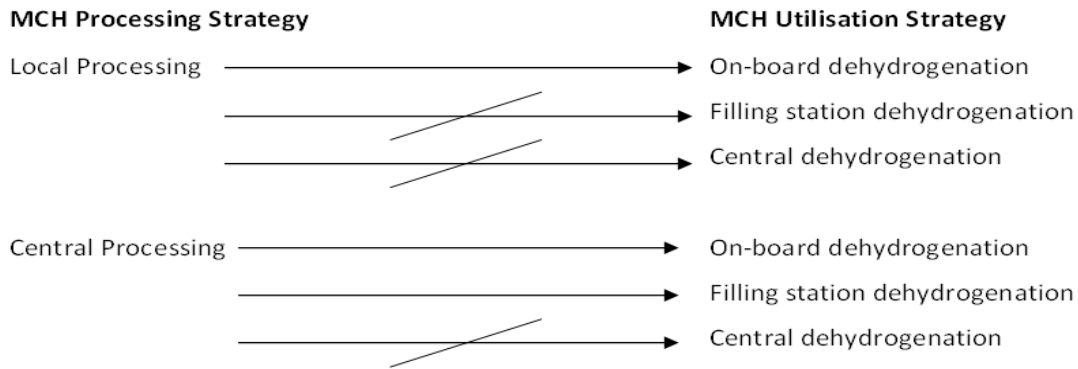
Figure 3-7: MCH processing strategy compatibility with MCH utilisation strategies

In words:

- It would not be sensible to hydrogenate then dehydrogenate at the same site, therefore local and central processing do not match with local and central utilisation respectively. This is particularly true of local processing, because hydrogen gas is produced on-site, so if required, this could simply be compressed and delivered with no carrier involvement

- The advantage of local processing is that hydrogen and hence MCH are produced where they are needed, cutting down on transport. It would therefore be illogical to then centrally dehydrogenate the product.

Central dehydrogenation would only be feasible if MCH were produced for the purposes of seasonal storage. This is where excess energy (*i.e.* not needed for the national grid) from sources such as nuclear, wind, wave power *etc* is stored as hydrogen, which is subsequently stored as MCH (for safety and extended possible storage period). This MCH can then be centrally dehydrogenated as required and the hydrogen can be used for electricity (to the grid) or compressed and delivered to the point of need, if compressed delivery is the direction the hydrogen infrastructure takes.

This represents a possibility where the MTH system is used for a marginal market, and is unlikely to be used directly for vehicles, apart from as a temporary hydrogen storage medium for subsequent compression. Therefore, for the remainder of the document, this will not be considered.

Three scenarios remain, as shown in Figure 3-8.
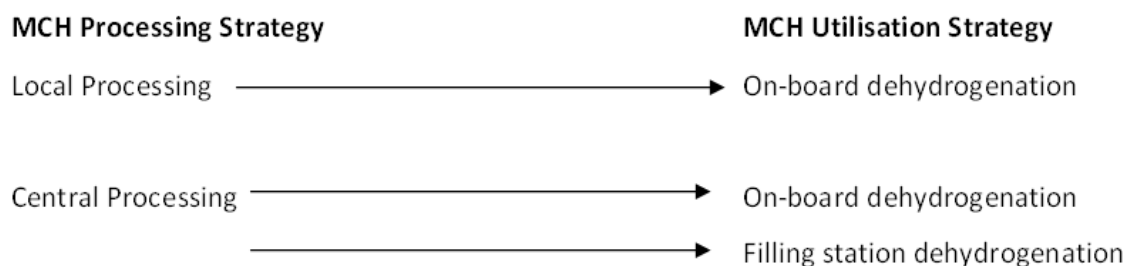
Figure 3-8: Overall strategies to be considered

In this chapter, on-board dehydrogenation and filling station dehydrogenation will be considered separately of MCH processing scenario components.

3.4.2 Analysis of Strengths and Weaknesses

Table 3-3 shows the qualitative strengths and weaknesses of the two MCH utilisation strategies. These are on-board dehydrogenation and filling station dehydrogenation.

Table 3-3: Strengths and Weaknesses analysis between on-board and filling station dehydrogenation

	ON-BOARD DEHYDROGENATION	FILLING STATION DEHYDROGENATION
Energy integration	Good potential system efficiency (use of waste exhaust heat from H_2 combustion)	Limited integration opportunities – no source of waste heat
Energy efficiency	Very efficient – no more processing steps than absolutely necessary	Added dehydrogenation/ compression step reduces energy efficiency
Market compatibility	Limited – customers would need an MCH car specifically	Good – if the markets lean towards compressed H_2, the system would be compatible with that

	ON-BOARD DEHYDROGENATION	FILLING STATION DEHYDROGENATION
Safety	Similar to diesel/petrol, small quantities of H_2 gas present (depending on system design – see Section 3.5)	Tentative – many safety issues with compressed H_2 gas
Fuel distribution	Distributed as MCH – safe and efficient	Distributed as MCH – safe and efficient
Capital Costs	Larger - fabrication/ production of novel MCH car	Smaller – CHG cars already exist and manufactured by select companies
Fuel delivery	Delivered as liquid MCH – safe and can use existing pumps with minor modifications	Delivered as gaseous hydrogen – safety concerns, trained personnel required, production of new expensive delivery pumps
Hydrogen storage	As MCH at every stage	As CHG on-board vehicle, MCH otherwise

At this stage, it would appear that on-board dehydrogenation has a slight advantage, but this is by no means definitive enough to base a decision on. Further analysis will be required.

3.4.3 Basis for decision

- Flow diagrams

- Discussion of energy integration

- Energy efficiency

- Discussion of safety

Each of these points will be discussed in the following sections with respect to each MCH utilisation possibility.

3.4.4 Flow Diagrams

3.4.4.1 On-board dehydrogenation
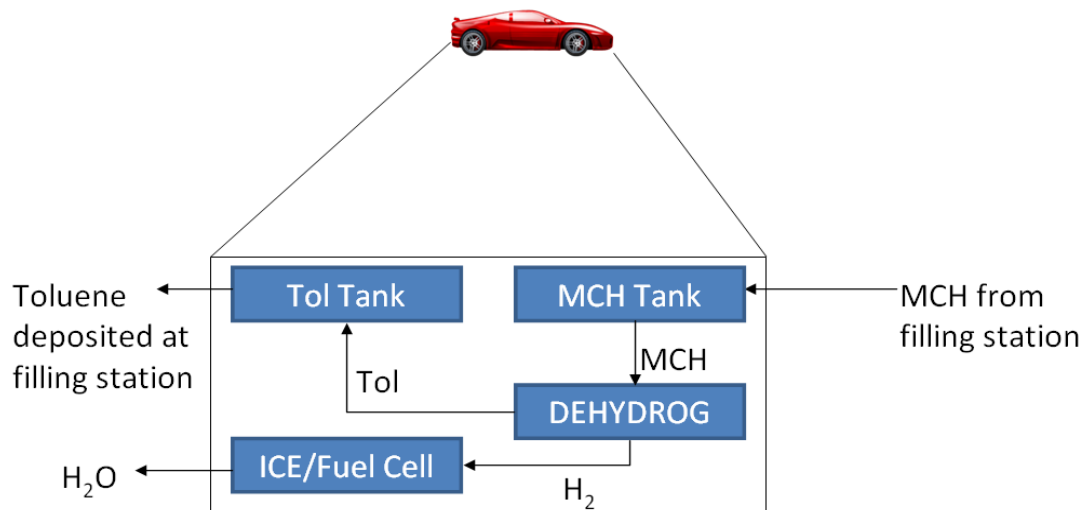
Figure 3-9: Block diagram for an MCH vehicle

Figure 3-9 shows a simplified representation of the on-board dehydrogenation system. This could potentially be modified in several different ways, as discussed in Section 3.5. Specific flows are not calculated at this point, because fuel consumption varies with speed, acceleration, vehicle mass *etc*. System volume is a barrier to this process, and one way in which this could be modified would be to have a single hydrocarbon storage tank with a partition in between the toluene and the MCH. As well as halving the fuel storage volume, this could also have a practical advantage in refuelling – the pressure of replenishing MCH could push the toluene from the tank through a separate pipe back to the filling station storage.

Up to this point, the following assumptions have been made:

- 6kg H2 storage per vehicle

- Vehicle range of 186 miles

This is based on the use of an ICE, but when considering the dynamics of the system, the possible use of a fuel cell would need to be considered as well. The possibilities which become available with consideration of a fuel cell are outlined in Table 3-4.

Table 3-4: Vehicle range and hydrogen storage capacities with fuel cell use

Power Train	H$_2$ storage capacity/kg	Vehicle range/mi
ICE	6	186
Fuel Cell	6	372
Fuel Cell	3	186

Both of the fuel cell possibilities are attractive – increased vehicle range would offer drivers a higher level of convenience, and the lower hydrogen storage capacity would make the system easier to handle from an engineering point of view (reducing fuel storage volume to 63 L). It is likely that the different system configurations would appeal to different markets. The advantages would be offset, at least in the short-term, by the high purchase cost of fuel cells owing to their early development stage, a problem which is not encountered by the technologically mature ICE.

3.4.4.2 Filling Station Dehydrogenation

In this case, the vehicle would be a 'normal' compressed hydrogen car, as developed by several car manufacturing companies.

The flow diagram can be represented as shown by Figure 3-10.

The gaseous hydrogen storage in Figure 3-10 only needs to be as large as demand could call for at any one time. The bulk of the hydrogen could remain stored as MCH for safety purposes and to decrease capital cost of gaseous hydrogen storage. The hydrogen gas tank could be refilled throughout the day as required.

Alternatively, the dehydrogenation process could take place 'on demand'. Although this would be more energy efficient by removing the need to store hydrogen in compressed gaseous form, it could increase refuelling time, and the catalyst bed would need to be held at increased temperature throughout station opening hours, which could negate the energy saving made by omitting

compressor. This alternative is shown in Figure 3-11. Although practically difficult, this process eliminates the need for on-site hydrogen storage, which has positive capital cost and safety implications.
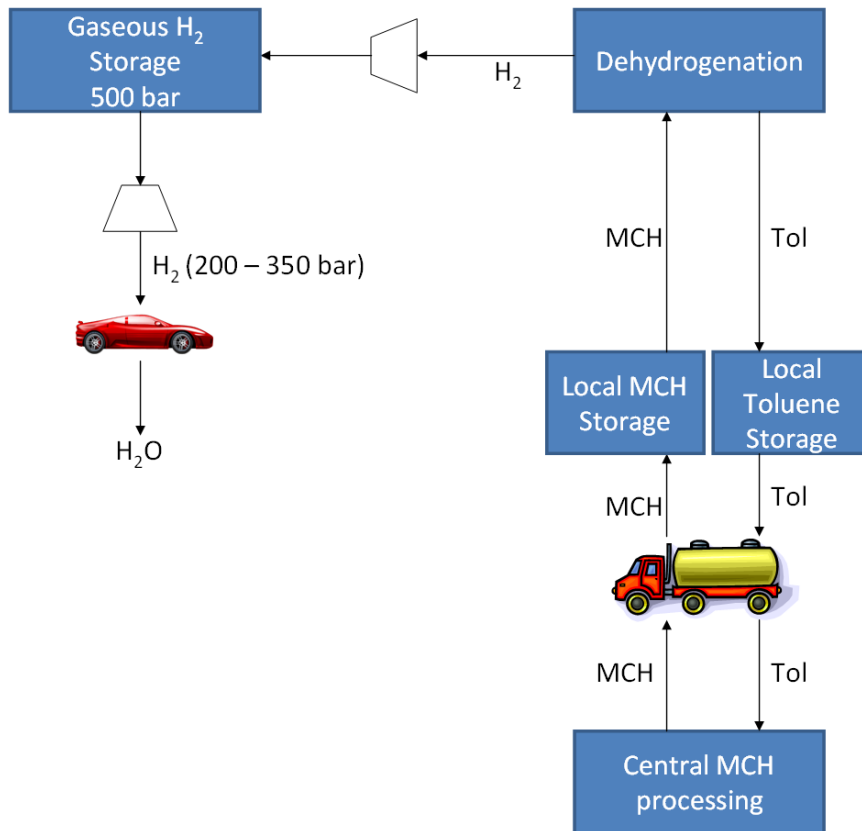
Figure 3-10: Flow diagram for filling station MCH dehydrogenation
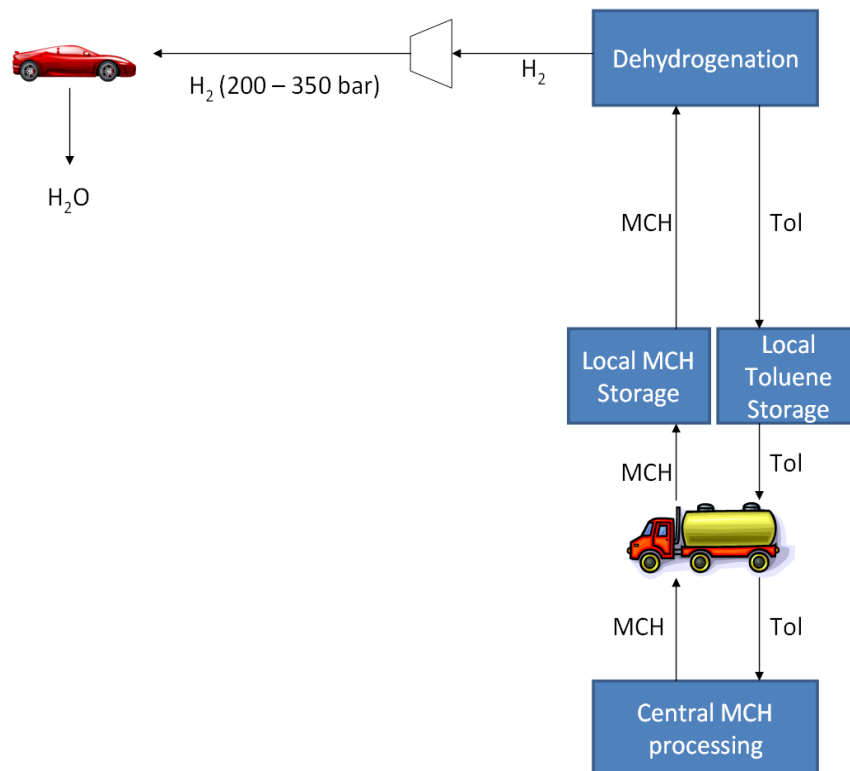
Figure 3-11: Flow diagram for filling station MCH dehydrogenation omitting gaseous hydrogen storage

3.4.5 Discussion of Energy Integration

Energy integration in this case refers to the heating of the dehydrogenation reactor, using waste heat from elsewhere in the process.

3.4.5.1 On-board dehydrogenation

Energy integration can be carried out effectively in this case, and could be an important deciding factor in system feasibility. If waste heat from the fuel cell/ICE were used to heat the dehydrogenation reactor, this would negate the need for the direct use of fuel for heating, which would not only improve fuel consumption, but could also be the difference between an impractical and a feasible system volume/weight (important factors in any system built for a mobile application).

A potential energy integration strategy has been outlined in the literature[23].

3.4.5.2 Filling station dehydrogenation

In this case, the hydrogen combustion takes place in a separate system to the dehydrogenation reaction (at the filling station and on the vehicle respectively), and therefore waste heat from combustion cannot be used to heat the dehydrogenation reaction. This limits energy integration opportunities. This also strongly affects the vehicle system design – if waste heat cannot be used, a high temperature fuel cell (*e.g.* a SOFC) would not be appropriate, and a lower temperature fuel cell would be more suitable (*e.g.* PEM fuel cell), as this would eject lower temperature emissions. Unlike fuel cells, ICEs do not operate at a wide range of temperatures, so a conventional ICE (adjusted for hydrogen combustion) is also an option (discussed further in Section 3.5).

Fuel cost at the pump would also likely be affected by this scenario, because a separate heating unit would be required for dehydrogenation (powered by electricity from the grid or by direct fuel combustion) as well as a compressor to bring the hydrogen to the required pressure for delivery, both of which cost money to run if no waste heat is available to provide energy.

3.4.6 Energy Efficiency

This section does NOT consider energy integration – see Section 3.4.5.

Of the two utilisation scenarios, on-board dehydrogenation represents the most energy efficient route because of the minimised number of steps, therefore minimal energy input. The minimal approach is represented by Figure 3-12.
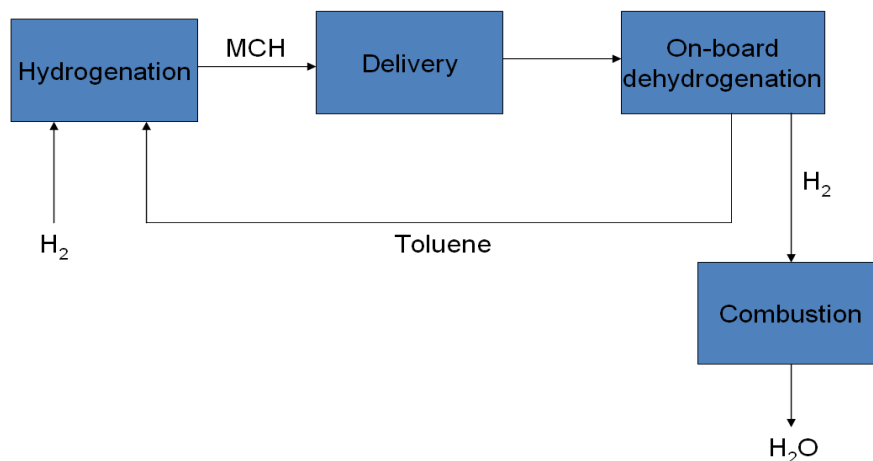
Figure 3-12: Major processing steps for on-board dehydrogenation

Compare this to the filling station dehydrogenation route (shown in Figure 3-13) which features extra steps to adjust the hydrogen pressure.
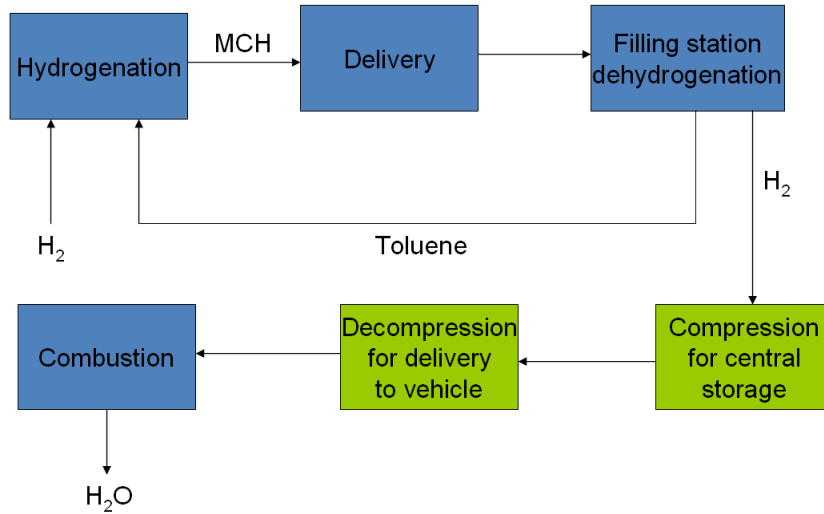
Figure 3-13: Major processing steps for dehydrogenation at the filling station

Alternatively, as mentioned in Section 3.4.4, the process could neglect central gaseous hydrogen storage, in which case the process could be illustrated by Figure 3-14.
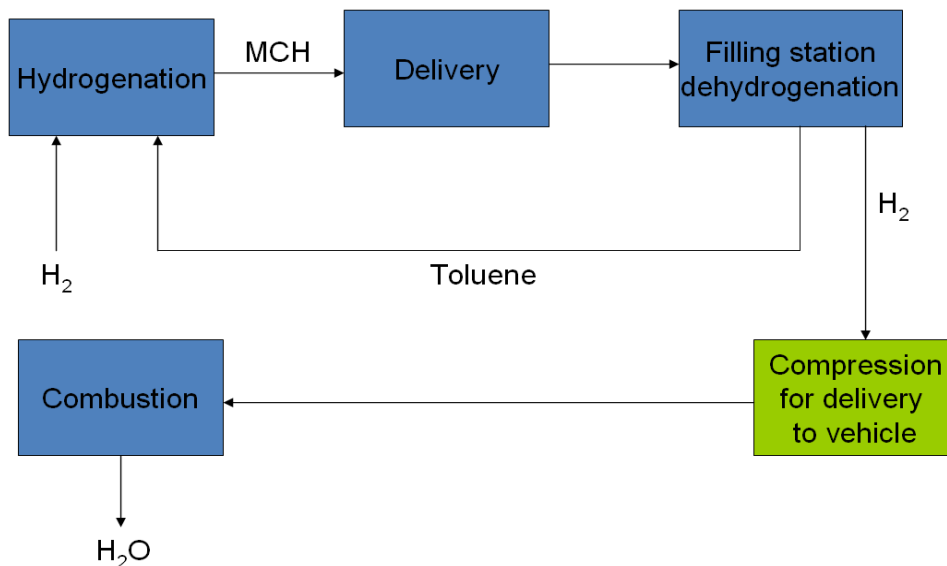
Figure 3-14: Major processing steps for dehydrogenation at the filling station omitting gaseous hydrogen storage

Compression costs approximately 7% of the energy content of the hydrogen, and further losses occur in the subsequent decompression for delivery to the vehicle (if applicable). For instance, the managers of the hydrogen buses running in London (trialled as part of the CUTE project, 2003 – 2007[72]) have their hydrogen delivered in a cryogenic state, after which it is stored at a central depot

as a 500 bar gas, followed by decompression for delivery to the vehicle at 300 bar. It will be assumed that these pressures are required by CHG passenger vehicles also, and a pressure of 15 bar is required for the fuel cell/engine. This yields the pressure profile by process stage shown in Figure 3-15.

Unless the energy of decompression is recovered and used, which would be difficult to achieve efficiently, this energy is lost.
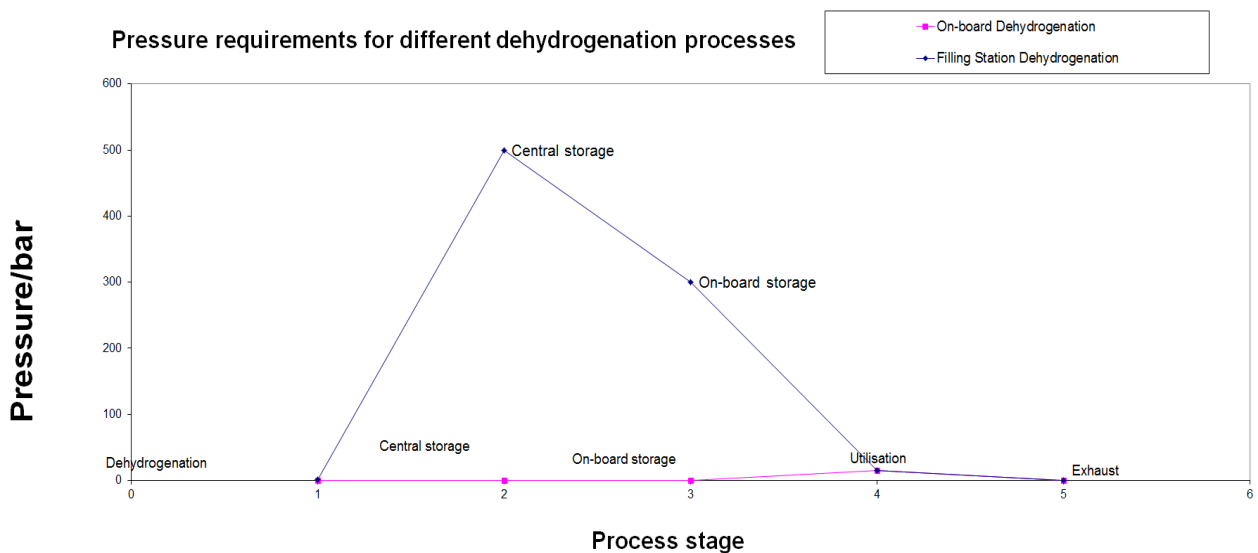
Figure 3-15: Pressure-Process Stage comparison between on-board dehydrogenation and dehydrogenation at the filling station

3.4.7 Discussion of Safety

3.4.7.1 On-board dehydrogenation

In terms of safety, this scenario presents approximately the same risk factors as the current fuel situation.

Firstly, in terms of fuel delivery at the pump, the user would only come into contact with the organic carrier, never gaseous hydrogen. The difference to the current delivery setup is the two-way fuel delivery for toluene reclaiming, but this presents no more risk than petrol delivery if the appropriate control elements are in place *e.g.* no MCH delivery without the pipe being correctly attached for toluene collection. Alternatively, and depending on system design, a co-axial fuel pump could remove toluene then fill up with MCH.

The second major difference is the presence of gaseous hydrogen within the system. This should not present any significant hazard, because at any one time, the bulk of the hydrogen on the vehicle is stored as MCH. Hydrogen is evolved as required (in the majority of cases depending on system design – see Section 3.5), and therefore only small quantities of gaseous hydrogen exist within the system at a given time. Any leak would therefore cause minimal disruption. Also, high pressures of hydrogen (350 – 700 bar) are only required for storage purposes. For utilisation, hydrogen need only be compressed as much as is required by the fuel cell (1.01 – 3.08 bar for a PEM fuel cell, up to *circa* 15 bar for a SOFC).

3.4.7.2 Filling Station Dehydrogenation

Although the delivery of hydrogen to the filling station as MCH would be much safer than delivering as liquid/compressed hydrogen, if dehydrogenation took place at the filling station before gaseous delivery to the car, all of the dangers of compressed hydrogen delivery would apply. This includes the use of untested novel pump designs, the direct contact between untrained customers and compressed hydrogen, the large volumes of a highly flammable compressed gas on-board the vehicle with associated risk of leaks, fires, explosions, over-pressures *etc*, and risk of hydrogen leak in the event of a road traffic accident.

3.4.8 Conclusions

For reasons of energetic efficiency, good energy integration, and safety, on-board MCH dehydrogenation has the major advantage. However, there is scope to believe that car manufacturers and fuel companies could lean towards compressed hydrogen regardless of the disadvantages in engineering, therefore it is important to remember that the MTH system is compatible with this outcome by offering to opportunity to transport hydrogen as MCH for safety and use of the existing infrastructure before on-site dehydrogenation to yield compressed hydrogen gas.

3.5 Start-up, Control and Process

For the design of the vehicle, only on-board MCH storage will be considered. This is because in the case of filling station dehydrogenation, hydrogen is stored on the vehicle as a compressed gas, and so this stage of the process development is not changed by the fact that the hydrogen was once

stored as MCH, and the vehicle is in fact a 'normal' hydrogen car as studied by numerous car manufacturers and research groups. This kind of study is not the focus of this project.

3.5.1 **Problem definition**

Despite the safety and management advantages of on-board storage of hydrogen as MCH, there are some problems with the MTH system for vehicles. These are given below:

- Vehicle start-up

  - o Potentially the most important barrier to the process. Dehydrogenation requires heat, and when the system is running under steady-state conditions, this can potentially be harnessed from the waste heat of the hydrogen conversion unit (fuel cell or ICE). However, at start-up, the entire system is at ambient temperature, and so a secondary source of heating must be provided, or an additional source of fuel must be present before hydrogenation begins.

- Primary vs. secondary power source

  - o To use a fuel cell or ICE to directly provide automotive power, the rate of MCH dehydrogenation must be sufficiently fast that enough hydrogen is evolved to meet the power demands of the user. If this is not the case, a buffer system needs to be in place, such as a hydrogen buffer tank or a range-extender (battery).

- Control systems

  - o Control elements must be in place to prevent unusual or dangerous system behaviours. For example, a system cut-off should be in place in the case of a large proportion of hydrocarbons entering the hydrogen stream, especially if a fuel cell forms part of the system, which could easily be poisoned.

    As an additional example, it could be envisioned that a driver may try to release toluene without return to the filling station, to decrease vehicle weight and increase performance. Although this could potentially be prevented by a monetary reward system (charge a large sum for MCH, and deduct from the cost in exchange for toluene return), it would be desirable to prevent such behaviours by control systems

(*e.g.* a system of constant pressure, where MCH is not pushed through the system without pressure from toluene).

Other similar behaviours should be predicted and prevented.

Each possibility will be studied in turn. Clearly, some system set-ups could solve more than one problem, *e.g.* a pressurised hydrogen buffer tank would solve the problems with start-up and would also act as a primary power source if reaction kinetics of dehydrogenation cannot cope with user demand. Therefore the full situation will be assessed for each possibility, rather than carrying out a problem-based analysis as in previous sections.

3.5.2 **Hydrogen Buffer Tank**

3.5.2.1 **Theory**

This scenario represents a possibility where a pressurised hydrogen buffer tank is in place between the dehydrogenation vessel and the power train. This would lend the advantages of an immediate supply of hydrogen on demand without kinetic delays, and a supply of fuel for the vehicle to run from during start-up, thereby solving two problems. This system is represented by Figure 3-16.
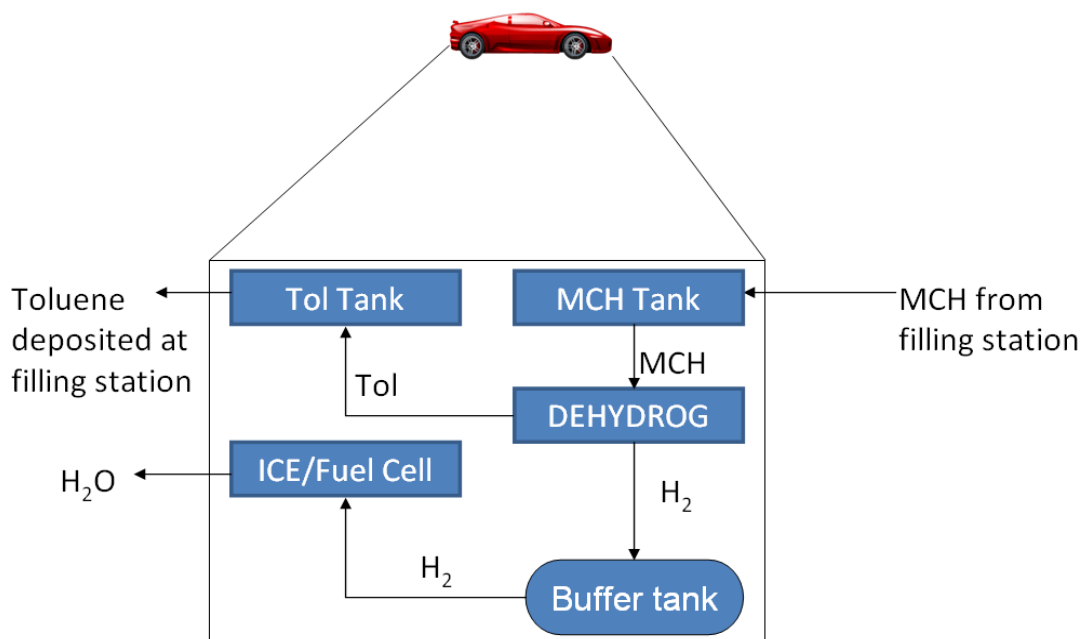
Figure 3-16: Block diagram for an MCH vehicle including pressurised hydrogen buffer tank

3.5.2.2 Advantages

The buffer tank means that when the vehicle is started from ambient temperature, a store of hydrogen is already present to start running on. Combustion of this hydrogen will provide waste heat to start dehydrogenation, so as long as the tank has sufficient volume, dehydrogenation will start before the buffer tank is empty. Dehydrogenation will then refill the tank at times of low demand when the vehicle is idle, decelerating *etc*.

A further advantage is that dehydrogenation does not need to be kinetically fast enough to directly satisfy the energy demands of the driver. If the evolution of hydrogen from MCH is not sufficient to fill demand, the hydrogen already stored in the buffer tank will supply energy until such time as it will be refilled when demands are lower.

3.5.2.3 Problems

Problems with this system setup include the presence of compressed gas on-board the vehicle and the associated safety hazards. Although the pressure need not be as high as conventional hydrogen vehicles (300+ bar), this is still a safety hazard. In addition, the tank of gaseous hydrogen will be present when the vehicle is parked, and may sit in the tank for extended periods of time.

Additionally, the buffer system will only work if the vehicle is used for journeys of a certain length. If the vehicle is used for very short journeys (school run, corner shop) then the dehydrogenation vessel will never attain sufficient heat to function, and so the buffer tank will empty and the vehicle will no longer be able to function. Therefore a backup heating system would need to be in place to heat the dehydrogenation vessel to refill the buffer tank under these circumstances.

Finally, the presence of a buffer tank and associated compressors, piping *etc* adds to system volume, which is an important consideration for vehicles.

3.5.3 Fuel Cell Hybrid System

3.5.3.1 Theory

In this scenario, a fuel cell is used alongside a separate heating system used to provide thermal energy for dehydrogenation. This would mean that the hydrogen from dehydrogenation would be used directly to provide automotive power with no interim storage. The heating system would be

powered by a battery, which would be recharged by the fuel cell when the vehicle is in operation. The system is represented by Figure 3-17.
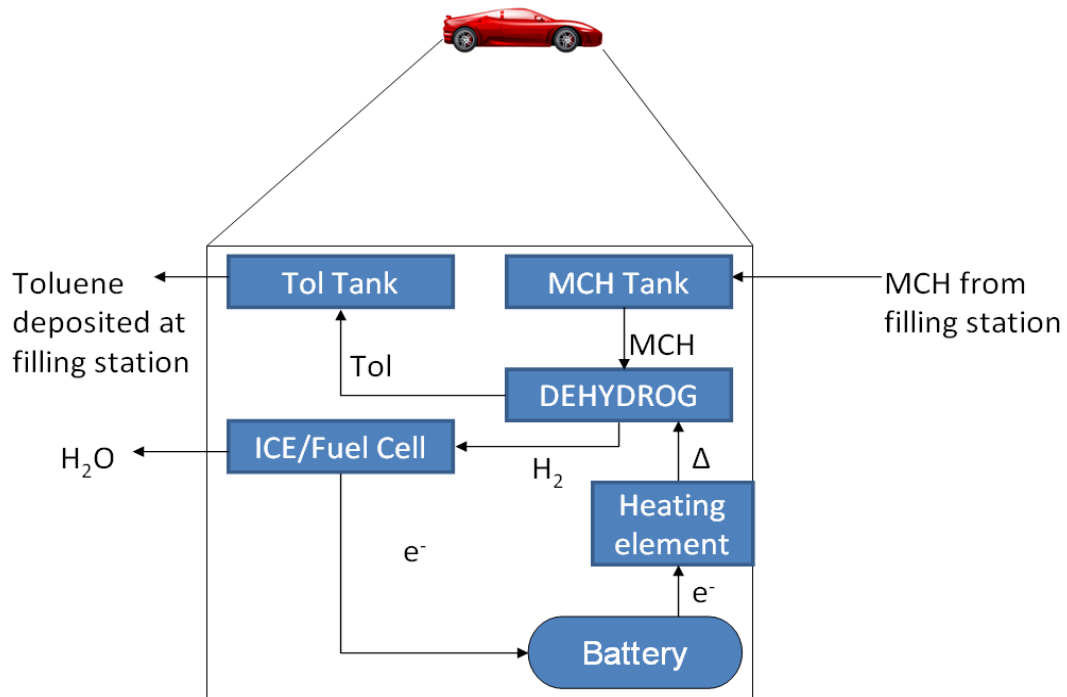
Figure 3-17: Block diagram for an MCH vehicle including a battery powered heating element

3.5.3.2 Advantages

The heating element would only be required for start-up, after which it would disconnect. For the majority of any mid- to long-range journey, the dehydrogenation vessel would be heated by using the waste heat from the fuel cell/ICE.

This system has the advantage of not being dependant on a hydrogen/energy store which could run out on short journeys. The vehicle would only start when the dehydrogenation process has started, and therefore the battery is being recharged from the outset of the journey. When the battery is fully charged, the hydrogen flow can decrease appropriately.

The battery in the system could also be used for other functions in the vehicle, such as electric windows, radios *etc*.

3.5.3.3 Problems

This system would require time to warm up before the vehicle could be used, and this would cause a delay in starting the journey. Due to the fact that fossil fuel vehicles can be driven immediately, this delay may not be accepted by drivers.

Also, the system relies directly on the fuel cell/ICE to provide automotive power, which in turn relies on the rate of dehydrogenation, as discussed above.

3.5.4 Flexible Fuel Feed (ICE)

3.5.4.1 Theory

The flexible fuel feed is a theory devised by Taube (1983)[43] in his paper for a 17 tonne truck powered by the MTH system. He proposed that a starting sequence lasting 6 minutes during which toluene is directly combusted would be required, burning 0.7 kg toluene per cold start. This is based on the use of a 150 kW engine – in the case of passenger vehicles (cars, vans, *etc*) the power requirement would be reduced, and therefore so would the amount of toluene combusted.

An ICE is required to allow flexibility in the fuel feed, and so this scenario is incompatible with fuel cells.

3.5.4.2 Advantages

The major advantage is that the vehicle can be started and immediately driven without delay. Regardless of how many short journeys are taken, the vehicle will still run until eventually the vehicle runs out of hydrocarbon.

To avoid the problem of users simply burning the hydrocarbon as a default to extend the range of the fuel tank, a monetary reward system for toluene return as outlined above should be in place.

Carbon emissions are a concern, and this system would take the vehicle from being nearly zero-carbon to low-carbon. However, it can be retro-calculated from the paper by Taube that a 17-tonne lorry would emit an average of only 9.36 g CO_2/km due to toluene burned for start-up. This is a startling reduction on current carbon emissions, with average emissions in the UK standing at 684 g CO_2/km (calculated from [73]). Clearly, emissions would be fewer in the case of an ordinary passenger vehicle.

A further advantage is in the use of an ICE – this is well-established, mature, cheap, and readily available technology which represents potential minimal losses from an investment point of view.

3.5.4.3 Problems

The clear disadvantage is the combustion of hydrocarbons. Although this is still a low-carbon option, it is not zero-carbon, and therefore is at a disadvantage compared to other systems using only hydrogen.

Also, 96% toluene recovery is possible, but this would be reduced by hydrocarbon combustion. This would affect the cost of fuel at the pump, because a higher proportion of the recharged MCH would come from fresh toluene rather than recycled toluene. With more toluene replenishment, the running costs of the process would increase.

Finally, the use of an ICE may cause problems if not properly handled. When hydrogen is combusted, a lean burn is possible, and if achieved, the only emission is water. However, if a lean burn is not achieved, emissions of NO_x become an issue. Unless the ICE can be adjusted *in situ* each time the vehicle is started from cold, it would be difficult to tune the engine to burn efficiently using two very different fuel feeds, and therefore emissions of NO_x may cause the vehicles to be less environmentally friendly than they potentially could be.

3.5.5 Range Extender (Fuel Cell)

3.5.5.1 Theory

In this scenario, a battery, connected to the fuel cell, provides automotive power to the car. This battery is then recharged by the fuel cell, which is in turn powered by hydrogen from the MTH system. Power for heat for dehydrogenation would also be provided in the start-up stages by the battery. Therefore, the vehicle runs as an electric vehicle, but the range is extended beyond that of a normal battery by the fuel cell system.

The subtle difference between this scenario and the fuel cell hybrid system is that in this scenario, the battery is used to directly power the vehicle, and therefore is used constantly, and would require a large capacity. The battery in the hybrid system scenario is used only in the initial stages, and for most of the journey would not be used.

3.5.5.2 Advantages

This removes the need for any delay in starting the vehicle. During start-up, the vehicle runs exactly as an electric car would, but meanwhile, the dehydrogenation vessel is being heated, and eventually when hydrogen is evolved, this recharges the battery. This system takes advantage of the favourable aspects of an electric vehicle, but extends the range well beyond electric-only capabilities.

The use of the battery also compensates for possible problems with the kinetics of dehydrogenation. If hydrogen demand cannot be directly met by hydrogen evolution, the battery can nonetheless power the car, and the deficit in power will be replaced by hydrogen conversion when the vehicle is idling, slowing *etc*.

3.5.5.3 Problems

The immediate problem is the use of the system for short journeys. If the vehicle is used for journeys so short that hydrogen evolution is never achieved (school runs, supermarket trips *etc*), the battery is never recharged, and will eventually become depleted. However, this need not be a disadvantage. This vehicle could be thought of as an electric vehicle with the added benefit of range for long journeys. That is to say, if the journeys are usually short, the battery can be charged by attachment to the mains electricity supply, as with a normal electric car. If a long journey is required, this is possible (unlike an electric car), and the vehicle can be refuelled remotely in a short time at the filling station. Therefore, if this system is thought of as an electric car with the benefit of range extension if required, this system could appeal to the market.

A further problem is system volume – this system requires a powertrain, dehydrogenation apparatus and all the associated peripheral equipment (fuel tank, heat exchangers…) *and* a battery large enough to provide automotive power to the vehicle. System volume could be problematic.

3.5.6 Qualitative Summary

Summarised by Table 3-5 are the advantages and disadvantages of the vehicular configurations discussed in this section.

Table 3-5: Qualitative summary of start-up and control systems

Solution	Problems/System Factors					
	Instant Start-up?	Kinetic Delays Likely?	Power Source	Delayed Start?	Emissions	Pressurised Gas?
H₂ Buffer Tank	✓		Secondary		Negligible	✓
Fuel Cell Hybrid		✓	Primary	✓	Negligible	
Flexible Fuel Feed	✓		Primary		Some CO₂, possible NOₓ	
Battery Range Extender	✓		Secondary		Negligible	

It is immediately clear from this summary that the fuel cell hybrid system has many more disadvantages than the other scenarios, with a delayed start and the likelihood of kinetic delays.

The other scenarios all have instant start-up capability and suffer from no delayed start. However, the H₂ buffer tank must contain compressed gas, and the range extender technology is still young, so for short-term commercialisation the flexible fuel feed option is the most favourable. Although this does give some emissions, these are minute in comparison to current volumes, and this system has been shown to work by Taube[46].

3.6 Bottleneck Summary

This chapter has examined the major parts of the MTH system for vehicular fuels. Based on this analysis, Table 3-6 shows the variations for each part of the process which have been chosen to take forward for further investigation, or as a basis for investigation.

Table 3-6: Justification for basis of further study

Basis for study	Justification
MCH Production: Carried out centrally with 199 plants in the UK	• The most economically viable system, and the only one which is competitive with petrol • Good security of supply due to relatively disperse nature of plants • Good opportunities for effective energy integration • Relies on a well-known dependable process
MCH Dehydrogenation: Carried out on-board the vehicle	• Presents the best energy efficiency of any possibility • Gives the best opportunities for energy integration • Safe – no volatile gas comes into contact with the public • The possibility with the least necessary changes to the forecourt
On-board system: ICE with flexible fuel feed	• Reduces carbon emissions by >90% • Allows immediate vehicle start-up • Has been demonstrated on a working vehicle[46] • Prevents shortfalls in power

For each of these chosen scenarios, some bottlenecks have become apparent which need to be solved before this technology can become viable. Investigation of these bottlenecks will form the basis of this project.

The bottlenecks identified for each part of the process shown in Table 3-6 are given below.

- **MCH production**
    - No technical bottlenecks, only an economical one - procuring the investment required to build the facilities.

- **MCH Dehydrogenation**
    - The on-board dehydrogenation system requires a functional heat-exchange system in order to use waste heat to the best advantage while supplying heat to the endothermic dehydrogenation reaction.
    - Dehydrogenation kinetics must be sufficient to sustain the engine

- **On-board system**
    - The system weight and volume must be optimised to allow realistic and practical vehicle use
    - As aforementioned, dehydrogenation kinetics must be sufficient to sustain the engine in order to avoid combusting large amounts of hydrocarbon
    - Toluene recovery should be maximised (although the addition of refrigeration equipment *etc* would contradict the desire to reduce system weight and volume)
    - The ICE must be designed to accept both hydrocarbon and hydrogen fuels

- **Infrastructure**
    - The factor which underpins every other point – without an infrastructure to deliver MCH/H_2, no vehicular system can exist

To make the vehicular MTH system a viable success, all of these points must be addressed. The MCH production part should be the final investigation after all other technical bottlenecks have been solved. The Infrastructure should also be a late investigation, because no investor would seek to build an infrastructure without any viable vehicle to use it. Therefore, the two points for immediate investigation are the on-board system and the MCH dehydrogenation parts of the process.

The MTH system is well established and well-known in industry. The dehydrogenation of MCH is a common industrial process which this project seeks to reduce to a small scale with a view to yielding vehicular hydrogen. The dehydrogenation process must be intensified as much as possible without resorting to extreme conditions.

In industry, the dehydrogenation process for many organic molecules can be carried out in either the vapour-phase or the liquid-phase[74]. This work has so far assumed that the reaction would occur in the vapour-phase, as this would not require high pressures and offers favourable reaction kinetics and conversion rates. However, carrying out the reaction with hydrocarbons in the liquid-phase would act as a process intensification strategy, because it would eliminate the need for some pieces of equipment (vaporisers and superheater pre-reaction, condenser post-reaction). If feasible, this would also result in the use of milder conditions, which is advantageous with respect to energy expenditure.

This possibility will be investigated. The dehydrogenation kinetics of liquid-phase MCH should be investigated to find whether they are sufficient to sustain an engine. An on-board heat management strategy should also be devised to use waste heat as efficiently as possible. If the proposal is successful, the system weight and volume would be reduced. Combined, these advantages would solve most of the bottlenecks identified for MCH dehydrogenation and the on-board system.

Chapter 4 Evaluation of Liquid Phase Dehydrogenation of Methylcyclohexane

4.1 Introduction

When attempting to achieve the dehydrogenation of MCH in the liquid phase, reaction conditions (temperature and pressure) are restricted by the boiling points of MCH and toluene. Reaction conditions must be below the boiling points of both of these hydrocarbons so that the liquid-phase condition is retained. The resulting acceptable combinations of reaction temperature and pressure carry with them thermodynamic and kinetic boundaries which impact on thermodynamic equilibrium, reaction rates, and yield, among other factors. The imposed boundaries are even more important if MCH is used to store hydrogen as an automotive fuel. The range of temperatures and pressures which can be used on-board a vehicle are limited by practicalities, such as system volume and weight, safety, expense, *etc*. The aim, therefore, it to arrive at a set of reaction conditions where the hydrogen yield, evolution rate *etc* is sufficient to power a vehicle but the conditions do not compromise the practicality of the vehicle.

The evaluation of liquid-phase dehydrogenation of methylcyclohexane (hereafter referred to as LP-MCHDR) will be carried out first in terms of thermodynamic boundaries, before examining the kinetics of the system aided by experimental data. This is followed by a system design.

4.2 Thermodynamic Evaluation

4.2.1 Equilibrium Constant Derivation

Obtaining the optimum liquid-phase reaction conditions for this system requires an understanding of the thermodynamic equilibrium. Figure 4-1 shows a simplified reaction scheme for MCHDR:

$$A \longrightarrow B + 3\,C$$
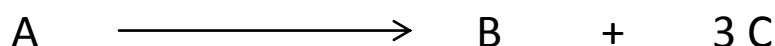
Figure 4-1: Simplified reaction scheme. A =MCH; B = toluene; C = hydrogen

From this reaction scheme, an expression for the vapour-phase equilibrium constant can be derived, as shown in Equation 4-1.

Equation 4-1

$$K_P = \frac{P_B P_C^3}{P_A}$$

However, for LP-MCHDR, this expression is not sufficient, because the partial pressures of toluene and MCH do not describe their entire presence in the reactor, owing to their liquid state. This expression must be modified to reflect this.

The first step in this modification is to carry out a material balance on the reaction represented by Figure 4-1. The general scheme for a material balance, shown in Equation 4-2, will be used. This can further be simplified to the scheme shown in Equation 4-3 on the assumption that the system runs under steady state conditions, *i.e.* the accumulation term is zero.

Equation 4-2

Input = Output + Accumulation + Consumption - Generation

Equation 4-3

Input = Output + Consumption - Generation

To assess the material balance, terms must be derived for the number of moles of each of the reagents and products at thermodynamic equilibrium. The equilibrium moles of each constituent, n_i, can be described in terms of the moles of MCH at time = 0, n_{A0} , and the reactive conversion of MCH, x_A. Following this, the total number of moles at equilibrium, n_T, can also be evaluated. Descriptions of the moles of reagents and products are given in Equation 4-4 to Equation 4-7.

Equation 4-4

$$n_A = n_{A0} - n_{A0}x_A = n_{A0}(1 - x_A)$$

Equation 4-5

$$n_B = n_{A0}x_A$$

Equation 4-6

$$n_C = 3n_{A0}x_A$$

Equation 4-7

$$n_T = n_A + n_B + n_C = n_{A0}(1 + 3x_A)$$

Partial pressures of reaction components can be linked to molarity using the Ideal Gas Equation, given by Equation 4-8. If constant temperature and volume are assumed, the gas equation for each component of the reaction, i, can be divided by the gas equation for the sum of all components, T, to yield Equation 4-9.

Equation 4-8

$$P_i V = n_i R T$$

Equation 4-9

$$P_i = \frac{n_i P_T}{n_T}$$

For each of the component molarities calculated in Equation 4-4 to Equation 4-7, the respective expressions for n_i can be substituted into Equation 4-9. This yields expressions for P_i in terms of molarity, which can be used to construct a modified version of the equilibrium constant equation, Equation 4-1. The separate P_i terms followed by the modified K term are described by Equation 4-10 to Equation 4-13.

Equation 4-10

$$P_A = \frac{(1 - x_A)P_T}{1 + 3x_A}$$

Equation 4-11

$$P_B = \frac{x_A P_T}{1 + 3x_A}$$

Equation 4-12

$$P_C = \frac{3x_A P_T}{1 + 3x_A}$$

Equation 4-13

$$K = \frac{27\, x_A^4\, P_T^3}{(1 + 3x_A)^3(1 - x_A)}$$

It is convenient to calculate the equilibrium constant in terms of conversion, x_A, as shown in Equation 4-13. This eliminates discrepancies between the equilibrium constants in the gas phase and

the liquid phase because x_A is independent of component phase changes. The elimination of discrepancy is demonstrated in Appendix I.

4.2.2 Using the Equilibrium Constant K for Temperature Estimation

With the equilibrium constant defined, the required temperature for a given conversion of MCH, x_A, at a given pressure can be estimated. This can be achieved by using a correlation between ΔG_d and reaction temperature T shown in Figure 4-2.
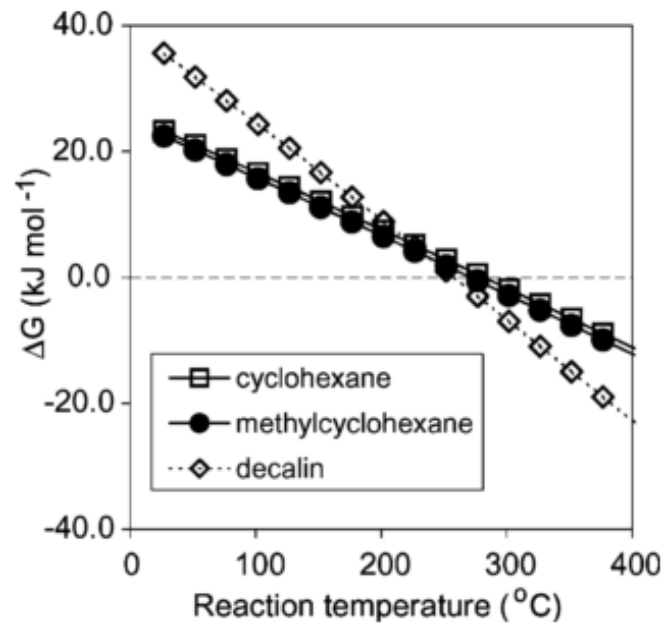
Figure 4-2: Correlation between reaction temperature and ΔG_d [30]

This correlation gives the linear equation corresponding the enthalpy, entropy and Gibbs free energy changes of MCHDR, Equation 4-14. The equation for Gibbs free energy, Equation 4-15, can be rearranged into a $y = mx + c$ form to match Equation 4-14, which yields Equation 4-16.

Equation 4-14

$$\Delta G_d = -0.3657T + 202.26$$

Equation 4-15

$$\Delta G_d = \Delta H_d - T\Delta S_d$$

Equation 4-16

$$\Delta G_d = -\Delta S_d T + \Delta H_d$$

It can therefore be concluded that:

Equation 4-17

$$m = -\Delta S_d = -0.3657 \text{ kJ mol}^{-1} \text{ } K^{-1}$$

Equation 4-18

$$c = \Delta H_d = 202.26 \text{ kJ mol}^{-1}$$

The enthalpy change, ΔH_d, of MCHDR at 298 K is given in the literature[23] as 205 kJ mol^{-1}, so the correlation shows a reasonable degree of accuracy (within 1.3%).

Using Equation 4-13, it is possible to calculate equilibrium constants, K, at a given pressure and x_A. By manipulating these K values alongside the information from the correlation (Equation 4-14), it is now possible to calculate corresponding reaction temperatures for the given conditions.

First, Equation 4-15 can be combined with Equation 4-19 by simultaneous equations to give Equation 4-20:

Equation 4-19

$$\Delta G_d = -RTlnK$$

Equation 4-20

$$\Delta H_d - T\Delta S_d = -RTlnK$$

Equation 4-20 can then be rearranged in terms of *T* to give:

Equation 4-21

$$T = \frac{\Delta H_d}{\Delta S_d - RlnK}$$

Equation 4-21 gives the reaction temperature T required to achieve a given x_A at a given system pressure P_T (if given P_T and x_A have been used to calculate K). In this case it is assumed that ΔH_d and ΔS_d are constant in the range of temperatures studied (the Ellingham approximation).

4.2.3 **Hydrocarbon Boiling Point Estimation**

It is possible to manipulate Equation 4-21 in a way which gives a temperature T required to achieve close to 100% conversion ($x_A \approx 1$), which is desirable. However, in this work, reaction conditions are bound to those under which the hydrocarbon constituents of the system are in the liquid phase.

In this work, reaction pressure P_T is a variable. A change in P_T causes a proportional change in the hydrocarbon boiling points, which hence changes the window of reaction temperatures T which are accessible.

Boiling points under variable P_T were calculated using the Clausius–Clapeyron relation, Equation 4-22. This can be rearranged in terms of the new boiling point T_2 which corresponds to the new pressure P_2 as shown in Equation 4-23:

Equation 4-22

$$ ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) $$

Equation 4-23

$$ T_2 = \left(\frac{1}{T_1} - \frac{Rln\left(P_2/P_1\right)}{\Delta_{vap}H}\right)^{-1} $$

Therefore, the boiling temperature of each reaction component was found in the literature[75] under standard conditions then calculated at new pressures using Equation 4-23.

4.2.4 Definition of Reaction Conditions

4.2.4.1 Reaction Conditions Defined by Conversion

Given values of x_A, ranging from 0.001 (effectively zero conversion) to 0.999 (effectively total conversion) were used to calculate corresponding equilibrium constants K at variable P_T using Equation 4-13. These K values were used in Equation 4-21 to calculate required T corresponding to the given x_A. This yielded the graph shown in Figure 4-3.

This shows that higher T is required for a given x_A at higher P_T. It may therefore be given that atmospheric pressure or even sub-atmospheric pressure would be appropriate to carry out the reaction. However, consideration must be given to:

- System volume – on-board a vehicle, process intensification *i.e.* reducing system volume by dehydrogenating at elevated pressure would be an advantage
- The conditions under which the hydrocarbon components are in the liquid phase.

The latter requires examination of how the boiling point of the hydrocarbons varies with system pressure P_T.
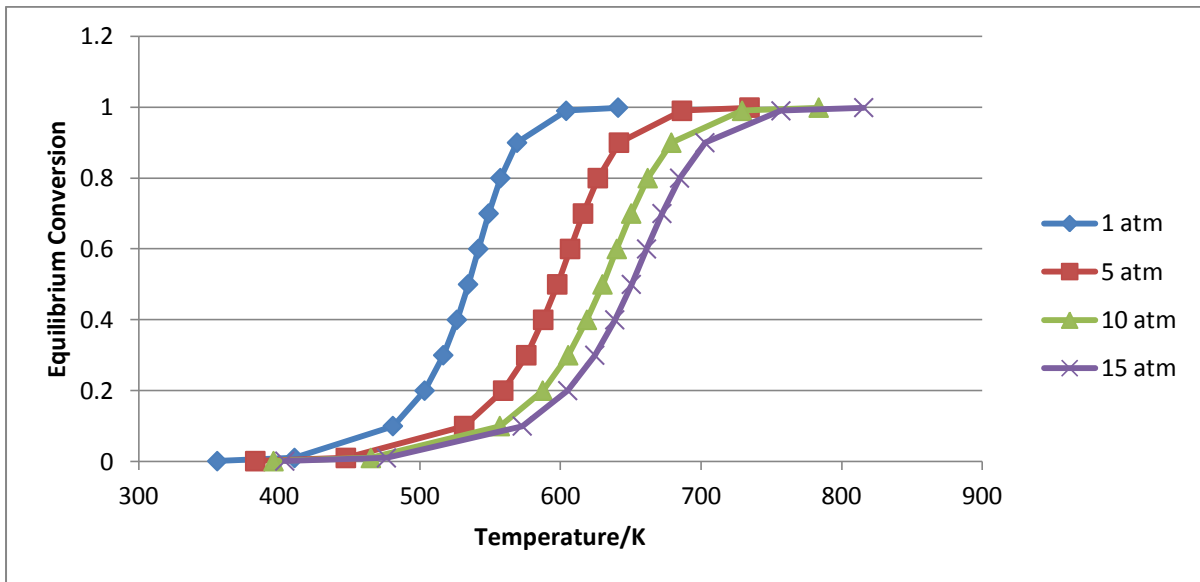
Figure 4-3: Temperatures of reaction to achieve equilibrium conversions at various pressures

4.2.4.2 Reaction Conditions Refined by Hydrocarbon Boiling Points

Using Equation 4-23, a graph was constructed to show how the boiling points of pure toluene and pure MCH vary with pressure. This is shown in Figure 4-4.
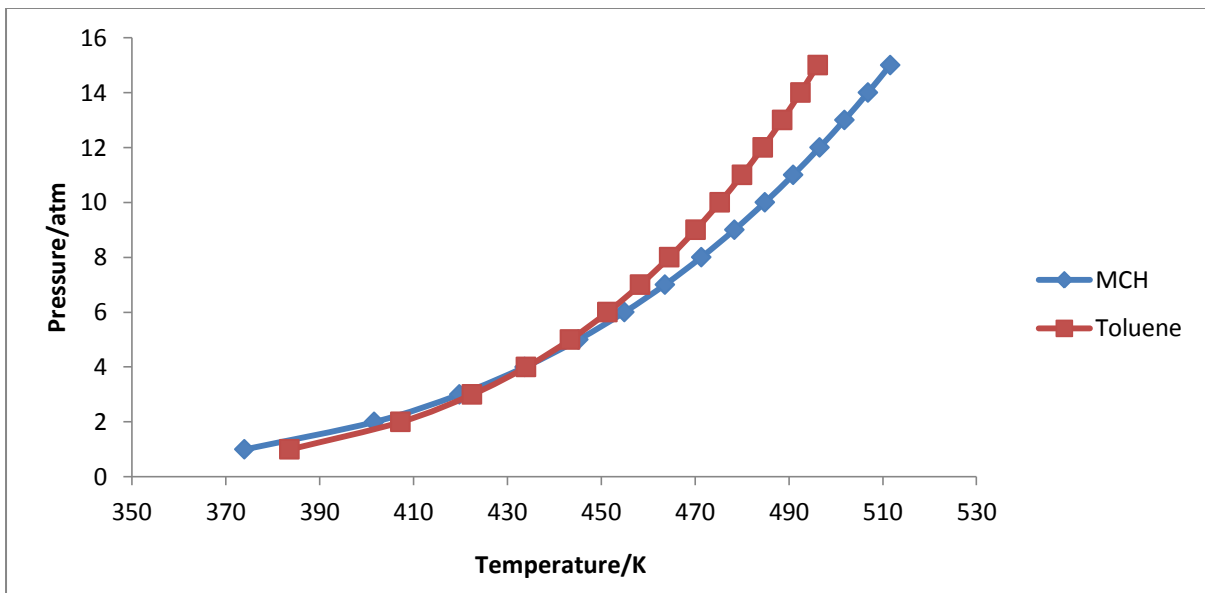
Figure 4-4: Variation of toluene and MCH boiling point with pressure

Manipulation of the data from Figure 4-3 and Figure 4-4 yields Figure 4-5, which shows the conversions x_A achievable in the liquid phase.
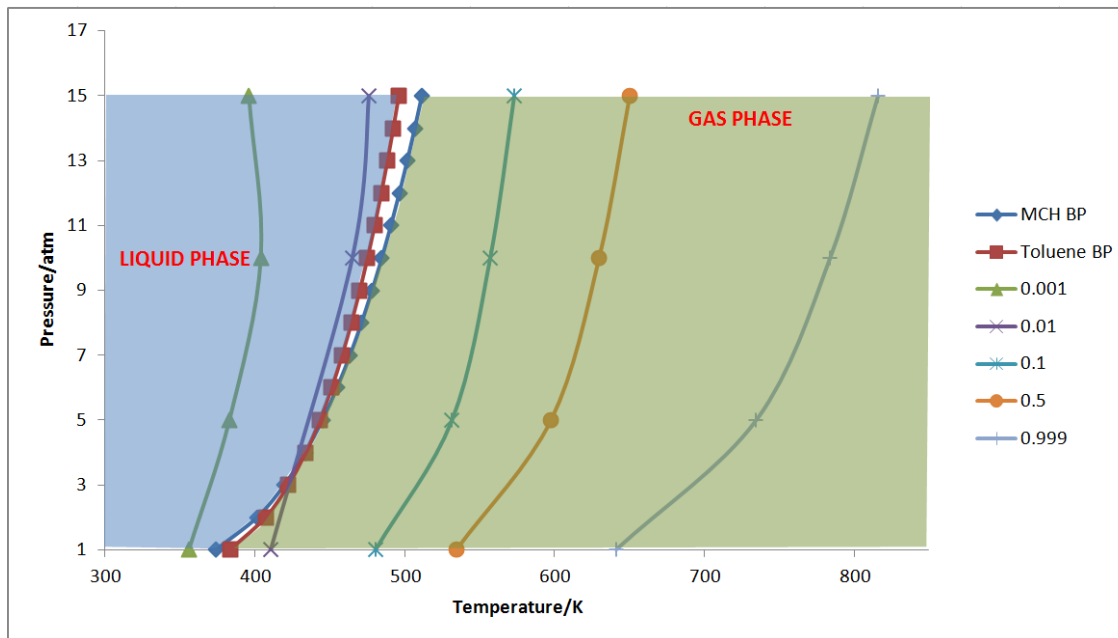
Figure 4-5: Reaction conditions (P_T & T) required for various x_A, with corresponding boiling points of MCH and toluene (numbers in the legend are x_A). Blue region – liquid phase; Green region – vapour phase; White region – intermediate (mixture of vapour and liquid).

As shown in Figure 4-5, reaction conditions must be in the blue (liquid) region. This limits reaction conditions to those of very low x_A. However measures can be taken to exceed x_A, such as the use of a sweep gas to remove product hydrogen.

To proceed, the highest possible x_A in the liquid phase (*i.e.* those at the limit of the blue region) should be calculated to maximise x_A while remaining in the liquid phase.

By rearranging Equation 4-21 in terms of K, x_A can be calculated for a given T (Equation 4-24). The temperature T used for each given pressure P_T is the borderline boiling point for the lowest-boiling hydrocarbon.

Equation 4-24

$$K = e^{\left(\frac{\Delta S_d}{R} - \frac{\Delta H_d}{RT}\right)}$$

This gives us the value of K required to substitute into Equation 4-13. Using Equation 4-13, x_A can be calculated under the most favourable liquid phase conditions by iteration. When x_A is known, this can be used to calculate the partial pressure of hydrogen P_{H_2} available at equilibrium under these conditions, as well as the mole fraction of hydrogen, y_{H_2}. The results are shown in Table 4-1.

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Table 4-1: Maximum LP-MCH equilibrium conversions x_A and resultant equilibrium H$_2$ partial pressures P_{H_2} and mole fractions y_{H_2} at a range of system pressures P_T

P_T/atm	Boiling point/K	BP for:	Calculated K/atm^3	x_A	P_{H_2}/atm	y_{H_2}
1	374	MCH	7.133 x 10^{-10}	2.277 x 10^{-03}	0.007	0.007
2	402	MCH	6.288 x 10^{-08}	4.165 x 10^{-03}	0.025	0.012
5	443	Tol	1.883 x 10^{-05}	8.793 x 10^{-03}	0.129	0.026
10	475	Tol	7.490 x 10^{-04}	1.324 x 10^{-02}	0.382	0.038
15	496	Tol	6.461 x 10^{-03}	1.686 x 10^{-02}	0.722	0.048

This leads to an interesting conclusion. As shown in Figure 4-6, the maximum possible equilibrium x_A achievable in the liquid phase is proportional to P_T *i.e.* a higher P_T allows a higher maximum equilibrium x_A, as long as the temperature is increased to the maximum allowable temperature within liquid phase conditions. The same trend appears to be true for the achievable mole fraction of hydrogen y_{H_2}. It would therefore be advisable to carry out the dehydrogenation process at the highest practical P_T.
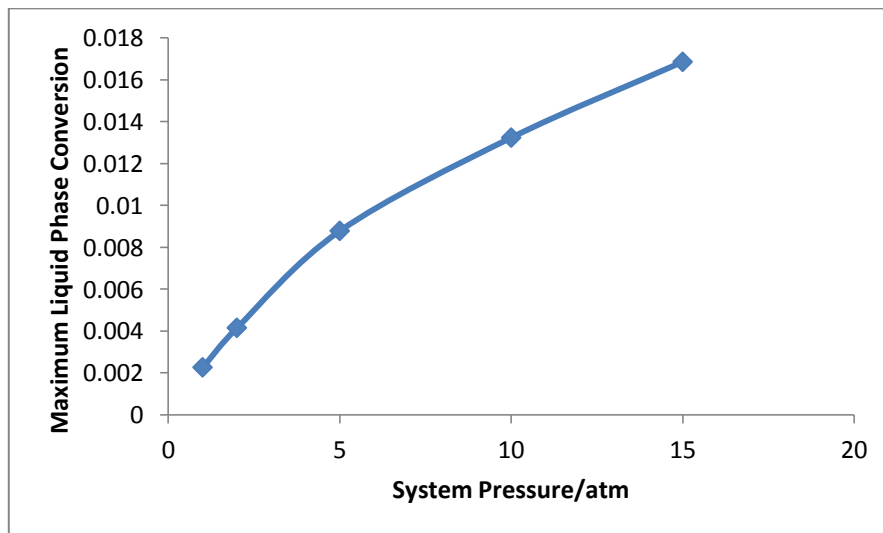
Figure 4-6: Overall system pressure P_T in relation to maximum achievable LP-MCH conversion x_A

There is also a correlation between the equilibrium constant K and the maximum P_{H_2} at equilibrium, shown in Figure 4-7. This relationship indicates that the maximum achievable P_{H_2} converges to a maximum within liquid phase conditions.
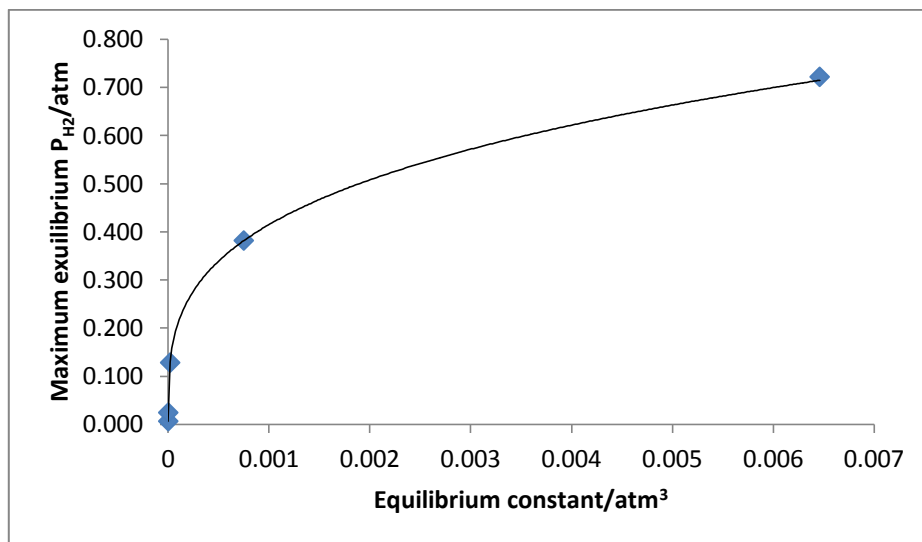
Figure 4-7: Equilibrium constant in relation to maximum achievable partial pressure of hydrogen (at equilibrium)

Although equilibrium x_A is low in all cases, this can theoretically be overcome.
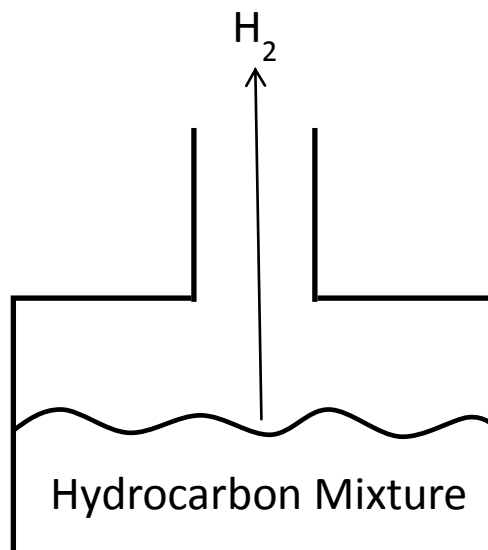
Figure 4-8: A representation of the LP-MCHDR reactor

Figure 4-8 shows a representation of a reactor. This shows that the hydrocarbons are in the liquid phase, and therefore cannot leave the reactor. With respect to the liquids, this reactor is a closed system. However, these liquids are evolving gaseous hydrogen, which is free to leave the reactor, making this an open system with respect to gases. With product hydrogen constantly leaving the system, the equilibrium will shift to the right, meaning that the thermodynamic equilibrium position, hence x_A, can be overcome.

However, the maximum achievable P_{H_2} and y_{H_2} cannot be overcome by evacuating hydrogen from the reactor. As Table 4-1 shows, these values correlate with P_T, which defends the argument that reaction pressure should be as high as practically feasible. It should be noted, however, that this is not a direct correlation. The y_{H_2} actually increases because of the rise in temperature T. This rise in P_T merely acts to make this rise in temperature achievable in the liquid phase by increasing the boiling points of the hydrocarbons.

4.2.5 **Conclusions on Thermodynamic findings**

These findings indicate that dehydrogenation in the liquid phase is thermodynamically possible. Equilibrium x_A is low under the acceptable reaction conditions, but it may be possible to shift the position of equilibrium to the product side by removing hydrogen from the reactor, hence exceeding equilibrium x_A and theoretically allowing the reaction to go to unity.

However, this does not mean that LP-MCHDR is practical. In order to sustain the operation of an engine, hydrogen evolution rates will need to meet a certain value, which is defined in a later section. Although it is possible to exceed equilibrium x_A, it is not possible to exceed partial pressures, P_{H_2}, or mole fractions of hydrogen, y_{H_2}, for a given set of reaction conditions. This has a bearing on whether or not the hydrogen evolution will be sufficient to sustain an engine. As shown by Table 4-1, higher reaction pressure allows a higher temperature to be reached within the bounds of liquid-phase conditions, which in turn leads to a higher attainable P_{H_2} and y_{H_2}. Higher reaction pressure may therefore improve the feasibility of the liquid phase MTH system.

Also important to system feasibility is the hydrogen evolution rate. This means that reaction rates of MCHDR must be measured, and so an experimental investigation of LP-MCHDR kinetics is necessary.

4.3 Kinetic Evaluation

The aim of this series of experiments was to ascertain a rate of MCHDR, r_A, under different pressure/temperature combinations given in Table 4-1. This would offer an indication of how much hydrogen per unit time per unit mass of catalyst it is possible to evolve from LP-MCHDR. Following this, it would be possible to calculate the rate constant, k, under each condition, and hence the activation energy of dehydrogenation, E_A, would be known.

4.3.1 **Experimental**

4.3.1.1 System Setup

The system used to measure the rate of LP-MCHDR, r_A, is shown in Figure 4-9. The chosen reactor is a trickle bed reactor. Liquid MCH is introduced to the reactor bed via a high-pressure pump alongside a nitrogen sweep gas. This liquid-gas mixture passes through a packed bed of catalyst (1 g) and the resultant mixture is passed through a high-pressure condenser. Gases are vented from the system and liquids are collected for subsequent analysis by GC-FID. By analysing the concentration of toluene in the liquid sample, it is possible to obtain the extent of reaction, x_A, in a measured amount of time. This allows calculation of r_A.
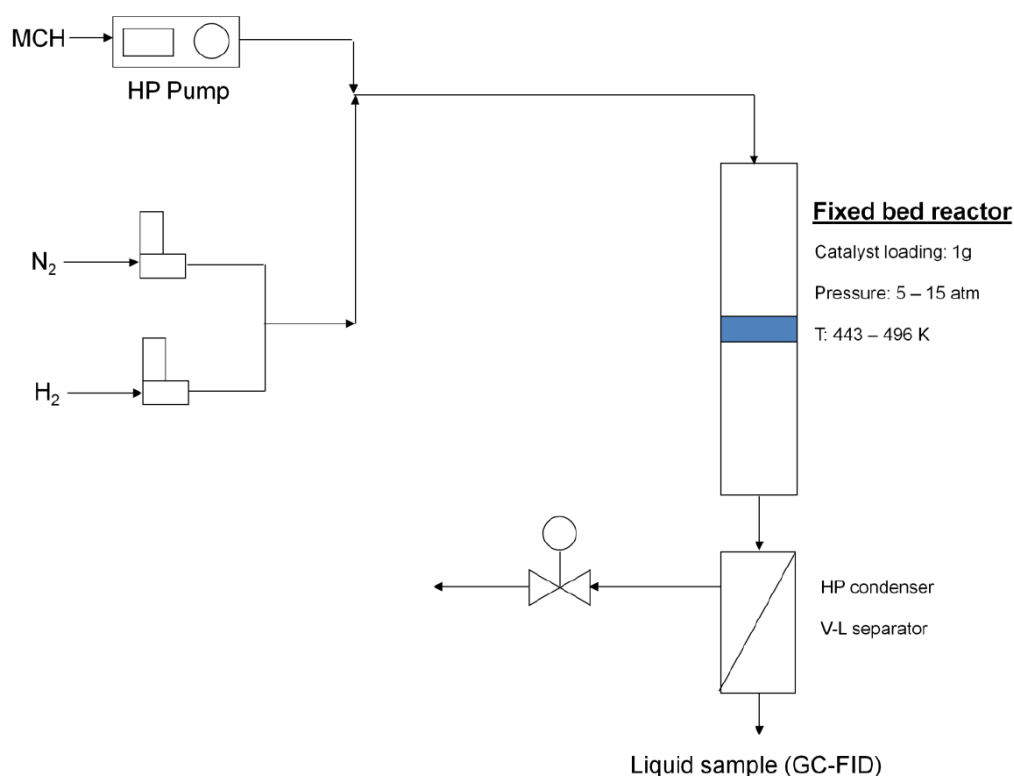
Figure 4-9: Reaction setup for MCHDR

MCH was used as supplied from Sigma-Aldrich, 99% pure.

4.3.1.2 Catalyst choice and preparation

A commercial 0.3 wt% Pt/Al$_2$O$_3$ catalyst was used, as this was readily available, and Pt/Al$_2$O$_3$ is widely employed for dehydrogenation and other reforming reactions[62, 64, 76]. This was provided by the

suppliers as an eggshell type catalyst, which was crushed. The particles were then separated using a sieve, and particles in the size range of 315 – 425 μm diameter were used for reaction. This was to reduce internal diffusional restrictions in the particle and to minimize the wall effects with respect to the axial flow in the reactor, and was based on the heuristic experience of the experts who had used the trickle bed reactor before.

The catalyst was mixed in a 1:1 volumetric ratio with SiC (silicon carbide) to promote a homogeneous heat distribution before being prepared by heating under a mixed H_2/N_2 flow. The temperature was ramped from room temperature to 300 °C at a rate of 5 °C/min, and then held at 300 °C for 1 h. This was to remove any moisture from the catalyst as well as any oxygen which existed in the catalyst due to Pt oxidation in air.

In some cases, the same catalyst was used for more than one experiment (to a maximum of three) in order to streamline gathering of data. This was not thought to be of consequence, because coking is the major route for deactivation of catalysts, and this is unlikely to present a significant influence on the results for the following reasons[62, 63].

- Conversion x_A is expected to be low

- Temperature T is low (<300 °C in all cases)

- Pressure P_T is high

- Hydrocarbons are in the liquid phase

If catalytic deactivation is not measurable, this means that the same catalyst sample can be used for multiple experiments.

Deactivation was tested by repeating the same experiment twice, taking six samples for each, with each sample separated by one hour of MCH flow through the catalyst bed. Although a dip in x_A was observed after the first hour (sample), the subsequent x_A values were consistent (see Figure 4-10), and this indicates that the decrease is caused by the time taken for a fluid dynamic steady state to be reached, or for full contact between the catalyst and the reactant to be established. This trend was observed in other experiments using the same catalyst sample, which ratifies this explanation. Deactivation was therefore deemed too small to be measurable, if indeed any deactivation had occurred.

Due to the fact that catalyst deactivation is insignificant, the same catalyst sample was used for three experiments before being changed. After the first catalyst preparation (as above), the catalyst was prepared for subsequent experiments by the same means, but with only 15 mins suspended at 300 °C. This would be sufficient to remove any trace oxidation, because the catalyst was held under a flow of nitrogen between experiments.

4.3.1.3 GC Calibration

GC-FID was used to analyse liquid samples after reaction. A high polarity polyethylene glycol column was used, 30 m x 0.25 mm x 0.25 μm film thickness.

GC calibration mixtures were made with accurate toluene concentration, designed to have a toluene concentration in the range of the expected concentrations from the planned experiments (based on expected conversions given in Table 4-1). These calibration mixtures were analysed by GC-FID, and the resultant toluene peaks were integrated.
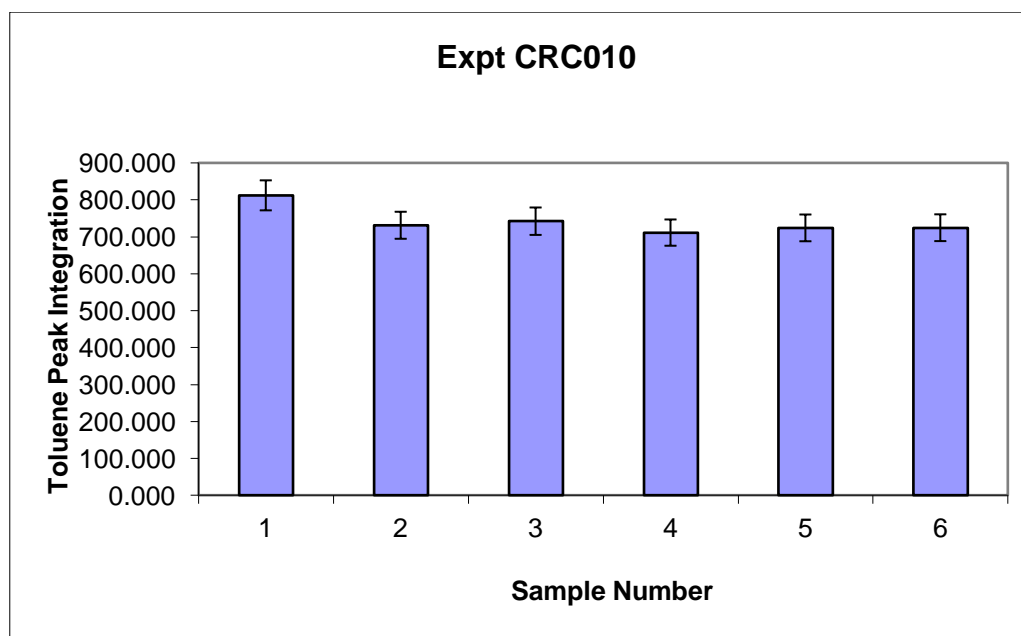
Figure 4-10: Example GC-FID peak integrations of samples. Samples are taken from a single experiment at 1 h intervals. The first peak is an over-estimation of toluene presence, and subsequent sample integrations are within 5% of one another (the manufacturer-quoted error of the GC analytical software). 5% error bars are shown.

By plotting the accurate toluene concentration in the calibration mixtures against the toluene peak integration from the GC spectrum, a correlation could be derived. This plot is shown in Figure 4-11.
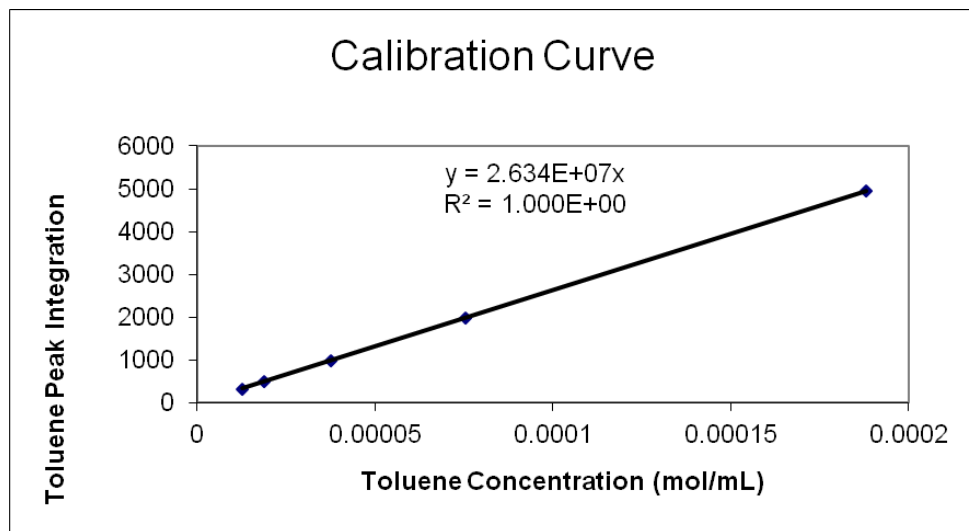
Figure 4-11: Calibration curve relating toluene concentration to peak integration from GC-FID analysis.

By taking the equation of the linear trendline in Figure 4-11, the relationship shown in Equation 4-25 can be obtained.

Equation 4-25

$$[\text{Toluene}]/\text{mol mL}^{-1} = \frac{\text{Toluene Peak Integration}}{2.634 \times 10^7}$$

Therefore, integrations from reaction mixture samples measured by GC-FID can be correlated to a toluene concentration, and thus a reactive conversion x_A.

A blank run was carried out in the reactor without catalyst to check for measurable toluene impurities in the MCH or autocatalytic behaviour in the reactor. No toluene peak was observed by GC-FID.

4.3.1.4 Reaction

After catalyst pretreatment, the system was allowed to cool to reaction temperature T, and in the meantime the system was flushed with nitrogen (100 mL min^{-1}) to remove hydrogen traces (15 mins). Thereafter, the system was pressurised to P_T, and the nitrogen gas flowrate was set to 50 mL min^{-1}.

As an extension to the battery of tests carried out, a further set of experiments was conducted under the most favourable conditions recorded with an altered nitrogen flowrate of 100 mL min^{-1}, in an attempt to further dilute evolved hydrogen and therefore encourage higher conversion x_A.

When reaction conditions were reached, MCH flow was allowed to begin. Experiments were run at the pressure-temperature combinations calculated earlier (shown in Table 4-1), apart from the lower pressure conditions which were omitted because initial testing showed no detectable reactivity at 1 atm and associated temperature. For each of the remaining pressure-temperature combinations (Table 4-2), the flowrate was varied in order to vary the residence time τ of the MCH. These flowrates were 0.10, 0.20 and 0.25 mL min^{-1}.

Table 4-2: Reaction conditions

P_T/atm	T/K
5	443
10	475
15	496

The start time of reaction, t = 0, was estimated by the time taken to observe liquid condensation in the high-pressure (HP) condenser. Figure 4-12 shows a comparison of the volumes of the different parts of the reactor.

Reaction begins (t = 0) when the MCH reaches the catalyst bed. The liquid in V1 is therefore pure MCH and the liquid in V2 has reacted or is reacting. However, the majority of liquid-filled volume exists in V1, with V2 largely filled by solid catalyst or SiC, therefore we make the assumption that V1 + V2 = V1. If this is true, then t = 0 when the first condensate is observed in the condenser. This is taken to be the case. This definition of t = 0 is important to ensure that the start time is the same for every experiment in order to ensure repeatability in testing.

t = 0 when the first condensate is observed, and samples are taken hourly after this time.

Samples are taken by completely evacuating the condenser of liquid, and then allowing it to fill to ≈ 1 mL. This is then taken as the sample and analysed by GC-FID.
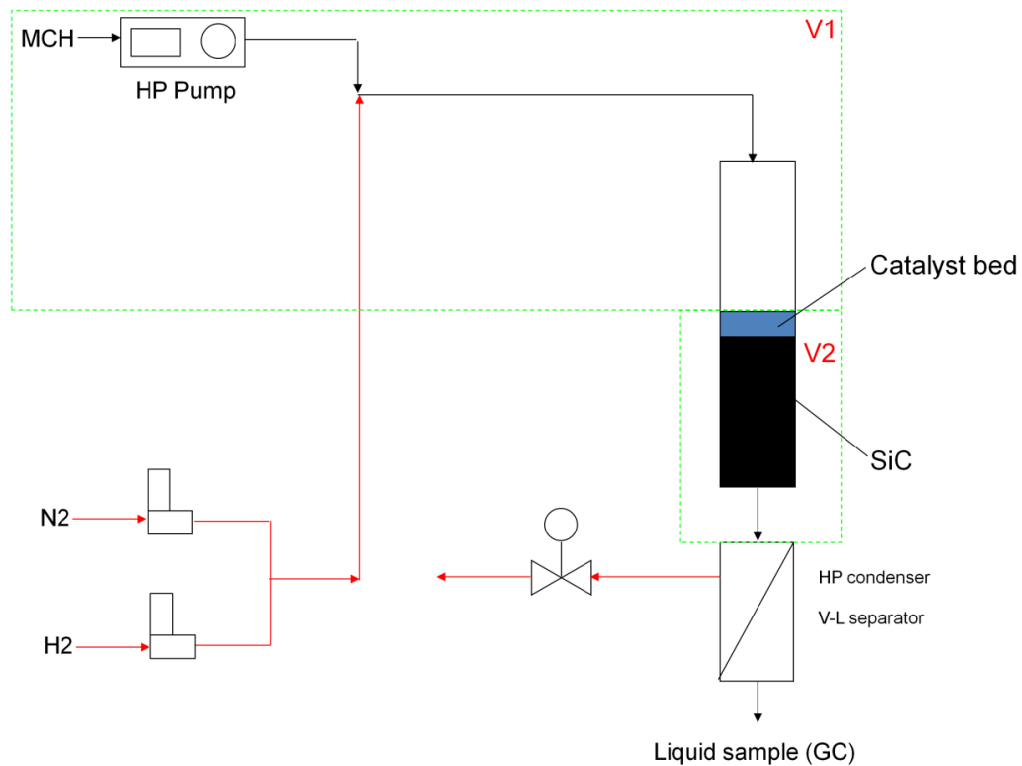
Figure 4-12: Reaction system split into two volumes, V1 (before catalyst bed) and V2 (after catalyst bad). Red arrows - gas flow. Black arrows - hydrocarbon flow.

4.3.2 **Results**

Table 4-3 shows the results of the tests for each temperature/pressure combination:

Table 4-3: Reaction conditions and observed MCH conversions. *These reactions were performed with increased nitrogen gas flow

P_T/atm	T/K	Liquid Flowrate/mL min^{-1}	Residence time, τ/ x 10^4 s.g mol MCH^{-1}	Conversion, x_A/ x 10^{-3}
15	496	0.25	3.08	1.23
15	496	0.20	3.86	1.75
15	496	0.10	7.58	3.51
10	475	0.25	3.02	0.96
10	475	0.20	3.79	1.33
10	475	0.10	7.44	2.59

P_T/atm	T/K	Liquid Flowrate/mL min^{-1}	Residence time, τ/ x 10^4 s.g mol MCH^{-1}	Conversion, x_A/ x 10^{-3}
5	443	0.25	3.08	0.38
5	443	0.20	3.86	0.57
5	443	0.10	7.58	1.15
15*	496	0.25	3.06	1.45
15*	496	0.20	3.84	1.81
15*	496	0.10	7.55	4.21

4.3.3 **Analysis**

4.3.3.1 Calculation of rate constant, k

In analysing the data from Table 4-3, the plug flow approximation was taken for the liquid phase. It was assumed that the reactor operated in a differential mode. This assumption allows the PFR design equation to be used, shown in Equation 4-26.

Equation 4-26

$$\delta F_A = (r_A)\delta W$$

Where $\delta F_A = F_{A_0} - F_A$, and $F_{A_{[0]}}$= molar flowrate [at t = 0] of MCH, δW = differential reactor volume.

As x_A is observed to be <0.1, it can be assumed that r_A is a constant under each P_T/T combination and all points of the reaction. This gives rise to Equation 4-27, which can be rearranged to give Equation 4-28.

Equation 4-27

$$\delta F_A = F_{A0}\delta x_A = r_A\delta W$$

Equation 4-28

$$r_A = \frac{x_A F_{A_0}}{W} = \frac{x_A}{\tau}$$

For each experimental test, the residence time of the liquid ($\frac{W}{F_{A_0}} = \tau$) was known and the conversion x_A was measured by GC-FID. Therefore, for each set of reaction conditions specified in Table 4-2, three residence times were measured (altered by changing F_{A_0}) with three corresponding x_A values. This data for each condition set was plotted on a graph of x_A vs. τ, and if the assumption of a valid PFR design equation and a constant r_A made are correct, the relationship is linear, with the gradient corresponding to r_A for the appropriate experimental conditions. An example plot of this kind is given in Figure 4-13.

The plot shows Conversion (y-axis, from 0.00E+00 to 4.00E-03) vs. Residence time (s.g/mol MCH) (x-axis, from 2.50E+04 to 8.50E+04) with fitted line:

y = 4.5364E-08x
R² = 9.8854E-01
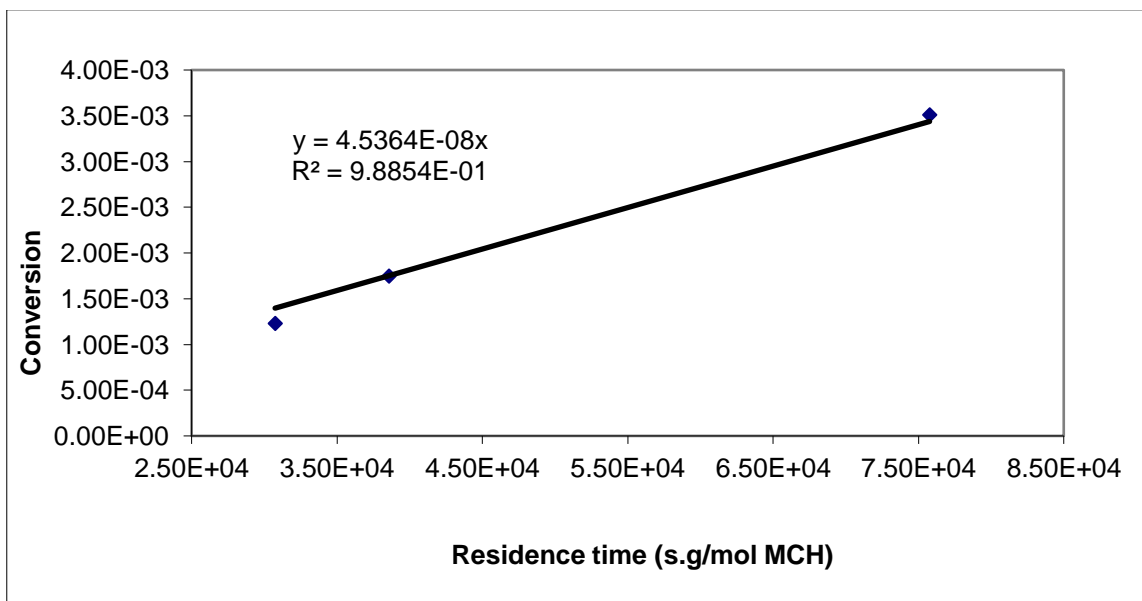
Figure 4-13: Residence time vs. MCH conversion for experiments conducted at 15 atm and 496 K

With r_A values calculated, the next step was to calculate associated rate constants, k. This would allow subsequent calculation of activation energy E_A for the reaction by using the Arrhenius relationship, Equation 4-29.

The results of this analysis are given in Table 4-4.

Figure 4-14 shows how r_A varies with increasing P_T (with appropriate maximum liquid temperature also changed).

Table 4-4: Results of the kinetic interpretation of the conversion data. *This reaction was performed with increased nitrogen gas flow

P_T/atm	T/K	r_A /x 10^{-8} mol MCH g^{-1} s^{-1}	k /x 10^{-9} mol MCH atm^{-1} g^{-1} s^{-1}
15	496	4.536	3.05
15*	496	5.319	3.06
10	475	3.454	3.49
5	443	1.473	2.94
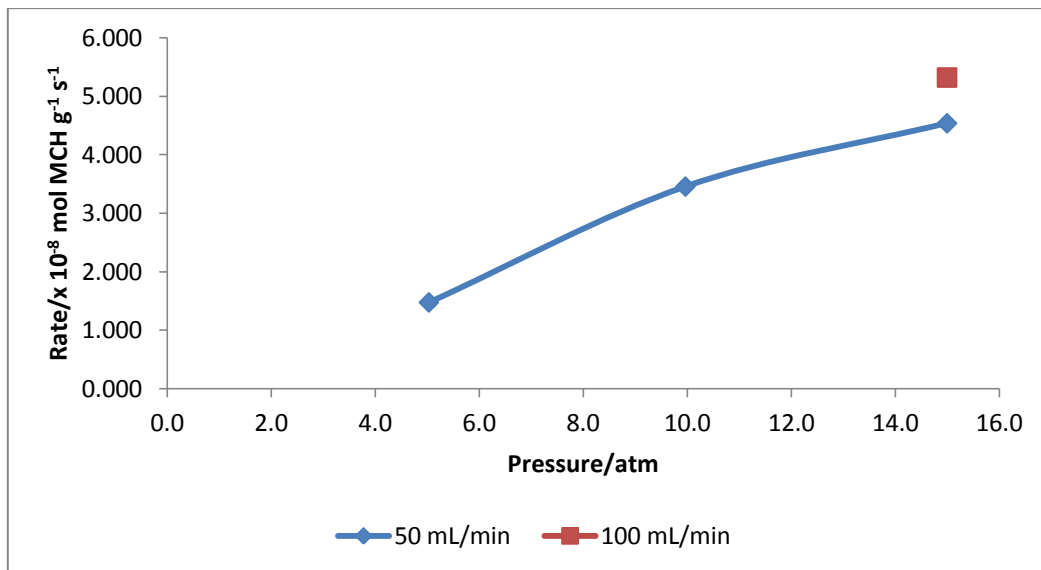
Figure 4-14: Variation of r_A with changing reaction conditions, P_T and T (each P_T on the x-axis is matched with the appropriate T, shown in Table 4-4. Also includes r_A with increased N$_2$ sweep gas volume (referred to in legend)

This shows that the flowrate of sweep gas makes a significant difference to r_A, indicating that the gas-liquid contact in the reactor is reasonable, assuming the observed effect is caused by more effective hydrogen dilution. It is unclear whether the increased gas flow is overcoming a kinetic or thermodynamic limitation. If the limitation is thermodynamic, then the increased dilution of evolved hydrogen is causing equilibrium to shift to the product side according to Le Chatelier's principle. If the limitation is kinetic, it may be that the gas flowrate is not independent of the liquid flowrate, and so the liquid residence time is increased.

Alternatively, the increased gas may be overcoming mass transfer limitations by causing a higher rate of collision between the liquid and the catalyst, resulting in a higher rate due to increased activity.

4.3.3.2 Calculation of activation energy, E_A

Note that the calculation of E_A is only valid if there are no mass transfer limitations in the reactor. This is assumed to be the case.

With values of k calculated, it is now possible to plot E_A and pre-exponential factor A using the Arrhenius relationship, shown in two forms as Equation 4-29 and Equation 4-30.

Equation 4-29

$$k = Ae^{\frac{-E_A}{RT}}$$

Equation 4-30

$$\ln(k) = \frac{-E_A}{R}\left(\frac{1}{T}\right) + \ln(A)$$

Equation 4-30 shows the Arrhenius relationship in the form of $y = mx + c$, therefore $\ln(k)$ can be plotted against $\left(\frac{1}{T}\right)$, yielding a linear plot where the gradient is equal to $(-E_A/R)$ and the y-intercept is equal to $\ln(A)$.

The Arrhenius plot is given as Figure 4-15.
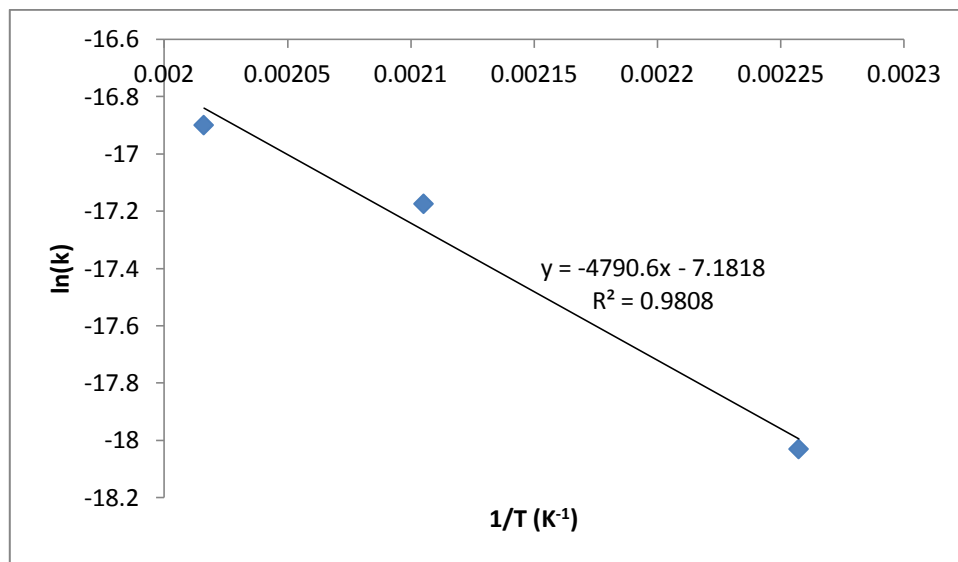
Figure 4-15: Arrhenius plot used to calculate MCH dehydrogenation E_A and the pre-exponential factor A

This shows that:

Equation 4-31

$$\frac{-E_a}{R} = -4790.6 \text{ K}^{-1} \therefore E_a = 40.0 \text{ kJ mol}^{-1}$$

Equation 4-32

$$\ln(A) = -7.1818 \therefore A = 7.60 \times 10^{-4} \text{ mol MCH g}^{-1}\text{s}^{-1}$$

4.3.3.3 Uncertainty

Some uncertainty was unavoidable with these experiments. The GC-FID technique used for sample analysis has a 5% uncertainty associated with it based on the manufacturer's literature, which carries through to all subsequent calculations based on these readings. In fact, uncertainty is greater than this would suggest – each r_A value was based on only 3 data points, and subsequently the Arrhenius plot shown in Figure 4-15 was also based on only 3 data points. The statistical uncertainty of such a low number of points is vast. However, in depth statistical analysis is beyond the scope of this report, and so the following analysis of uncertainty should be taken as a "minimum uncertainty", *i.e.* the uncertainty *if* the data points all lie firmly within the bounds of instrumental error. This uncertainty is quantified in Table 4-5.

Table 4-5: Estimation of data uncertainty based on quoted instrumental error

Pressure/atm	r_A/x 10^{-8} mol MCH g^{-1} s^{-1}		k/x 10^{-9} mol MCH atm^{-1} g^{-1} s^{-1}		E_A/kJ mol^{-1}	
	Max	Min	Max	Min	Max	Min
15	4.766	4.315	3.224	2.890		
10	3.613	3.269	3.664	3.291	42.9	35.6
5	1.548	1.401	3.090	2.787		

Shown by Table 4-5 is the uncertainty that exists within the values reported, including an uncertainty of 7.3 kJ mol^{-1} in the activation energy. Even as a minimum uncertainty, this is significant. The spread of values would be expected to increase further with rigorous statistical analysis.

4.3.3.4 System Application

The question remains as to whether these results reveal a practical, realistic system. As a benchmark, the r_A results will be compared to a target value given by Klvana et al[77]., quoted as a rate of MCH conversion of 16.25 x 10^{-2} mol s^{-1}. This is equivalent to hydrogen evolution of 0.98 g s^{-1}.

The dehydrogenation process could be scaled up to meet the quoted target value.

Table 4-6 gives the amounts of catalyst which would be required to meet the target value.

Table 4-6: Scale up requirements based on calculated rates. "Required Catalyst" assumes overcoming of thermodynamic equilibrium by hydrogen removal. * Increased gas flow

Pressure/atm	Temperature/K	r_A/ x 10^{-8} mol MCH g^{-1} s^{-1}	Required Catalyst/kg
15*	496	5.32	306
15	496	4.54	358
10	475	3.45	470
5	443	1.47	1103

This shows two important factors.

- A change in the volume of sweep gas causes a difference in the rate, and therefore a difference in the mass of catalyst required
- Clearly, this is an unrealistic catalyst requirement for a mobile application.

Therefore, for a practical application, the process must be optimised. Optimisation strategies could include:

- Increasing the metallic weight percentage of the catalyst
- Changing the identity of the catalyst
- Further increasing the pressure, with corresponding maximum liquid temperature
- Further increasing the flow of sweep gas
- A combination of the above.

4.3.3.5 Comparison to Gas Phase Reaction

The literature shows no clear consensus on the kinetic data associated with this reaction.

Table 4-7 shows literature values for the E_A of MCHDR using a Pt/Al$_2$O$_3$ catalyst.

Table 4-7: Literature values for activation energy of gas phase MCH dehydrogenation over a Pt/Al$_2$O$_3$ catalyst

E_a/ kJ mol^{-1}	Reference
17.9	[78]
40.0	This work
50.0	[31]
100.6	[76]
133.3	[79]
220	[80]

It is preferable to compare reaction rates rather than activation energies, because rates are directly relevant to the feasibility of the system to the chosen application *i.e.* fuelling an engine. However, authors do not tend to be forthcoming with this information in their publications, therefore activation energies are compared here.

It is clear that there is a great deal of disparity among results from different researchers. The E_A calculated in this work is at the lower end of the range given in Table 4-7.

x_A at thermodynamic equilibrium is another point of comparison. Conversion x_A and selectivity in MCH dehydrogenation are often very high, as much as 100%[77]. x_A in the liquid phase as studied here is far lower, peaking at only 0.42% (see Table 4-3). However, this thermodynamic equilibrium could be overcome if the reactor was designed to allow the release of hydrogen from the system (as shown in Figure 4-8). Therefore, as aforementioned, the important factors *i.e.* those which cannot be overcome are the mole fraction of hydrogen y_{H_2} and the hydrogen evolution rate, dictated by r_A.

The next point for comparison is hydrogen evolution rate, or MCH conversion rate r_A. Again, gas phase reaction exceeds the results in this work. Klvana et al[77]. show that a rate of 6.19 x 10^{-6} mol MCH s^{-1} g$_{cat}$$^{-1}$ is possible, over two orders of magnitude higher than presented in this work, and equating to the need for 26 kg of catalyst (in this case Pt-Sn/Al$_2$O$_3$) to sustain an engine according to the benchmark figure used in this work. It is clear, therefore, that improvements must be made to the liquid phase system for it to become feasible.

Finally, it would be useful to directly compare values of k between a gas phase and liquid phase dehydrogenation. The k values from Usman[76] were used due to the similarity in experimental procedure and the availability of data. By using Usman's data, the k values were derived as shown in Table 4-8.

Table 4-8: Comparison of rate constants between this work and the work of Usman[76]

Hydrocarbon phase	T/K	k/mol MCH g^{-1} s^{-1}	Reference
Gas	703	3.18 x 10^{-5}	[76]
Gas	653	1.84 x 10^{-5}	[76]
Liquid	496	4.58 x 10^{-8}	This work
Liquid	475	3.48 x 10^{-8}	This work
Liquid	443	1.48 x 10^{-8}	This work

In order to compare these results, the natural logs of the k values, $\ln(k)$, were plotted against the inverse temperatures. This means that, according to the Arrhenius relationship, this should produce

a linear plot if the k values from the two pieces of work are in agreement. This plot is shown in Figure 4-16.
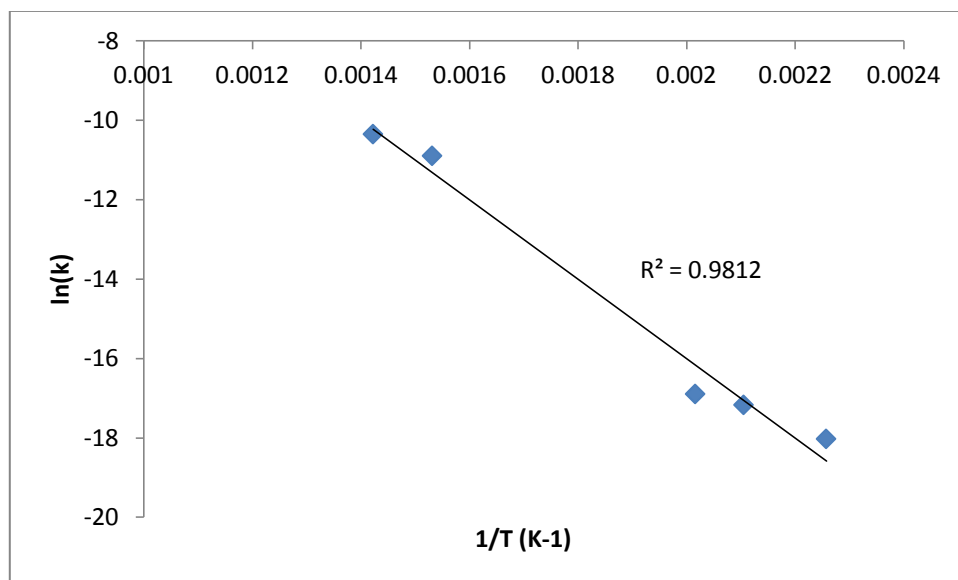
Figure 4-16: Arrhenius plot comparing k values from this work with those of Usman's[76] work

Correlation between these k values is inexact but reasonable, with a correlation factor (R^2) of 98%. If the two data sets are analysed separately, it is observed that they share a similar gradient (therefore similar E_A for MCHDR, see

Table 4-7) but there is a disparity between the values of A (the pre-exponential factor):

Table 4-9: Disparity between A values

Reference	A/mol MCH g^{-1} s^{-1}
This work	7.60×10^{-4}
[76]	4.00×10^{-2}

Table 4-9 shows that the difference between the two A values is approximately two orders of magnitude. This could be accounted for by the difference in state (collision theory indicates that A is higher in the gas phase due to a higher degree of freedom to collide) and due to the difference in temperature (A is temperature dependant).

4.3.4 Kinetic Evaluation: Conclusions

It is clear that a vehicular system based on these experiments would be impractical due to the low conversion of MCH and the low hydrogen evolution rate. However, the next steps in improving the LP-MCHDR system are clear, and are iterated in Section 4.3.3.4. Without making these improvements, it is too early to determine whether or not the LP-MCHDR system is kinetically feasible. Therefore, investigation will continue, starting with analysis of the system design.

4.4 Process Analysis

The next step is to speculate on how an on-board vehicular MCHDR reactor might look, and to use the data that is available to date to calculate system parameters *e.g.* material balances, flowrates and hydrogen partial pressures on entering the engine. Even if the best results obtained so far are not sufficient to run a vehicle, this exercise will help to focus on the areas which require improvement for future work.

A simple representation of the on-board system is given in Figure 4-17. This treats the reactor and the engine as "black boxes" for simplicity at this stage. The hydrocarbon storage tank is assumed to have a moveable diaphragm, which can displace according to how much fuel has been spent, *i.e.* the diaphragm would be to the severe right immediately after filling, and to the severe left when all fuel was depleted. The identity of the sweep gas is at this stage unknown, but is assumed to be inert (the exhaust gases could potentially be used for this purpose, which would be a mixture of nitrogen and steam, alongside some trace inert gases).

An important first step is to quantify the outlet stream from the reactor (Stream 2 in Figure 4-17). This requires knowledge of the hydrogen partial pressure P_{H_2} as well as the hydrocarbon vapour pressure. Discrepancy between the sum of these pressures and the reaction pressure P_T will be filled with sweep gas partial pressure.
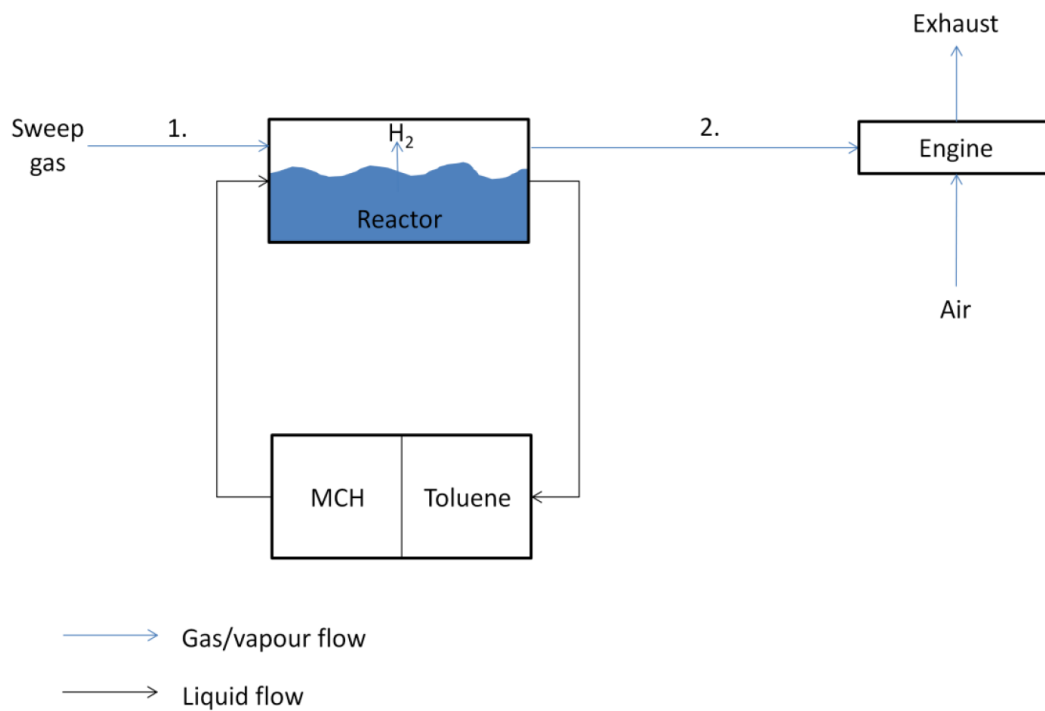
Figure 4-17: Simple representation of an on-board MCHDR system

Table 4-10 identifies the components of each of the numbered streams shown in Figure 4-17.

Table 4-10: Composition of streams according to Figure 4-17

Stream	Composition
1	Pure sweep gas
2	H_2, trace hydrocarbon mix, sweep gas

The molar ratios of the constituents of Stream 2 will vary depending on reaction conditions. Assuming the reaction is able to reach equilibrium conversion x_A, P_{H_2} for each set of reaction conditions is already known. Following this, the vapour pressure of the hydrocarbons should also be known. These values are additive, so if the sum of hydrogen and hydrocarbon partial pressures are subtracted from P_T, this will give the pressure of sweep gas.

Hydrocarbon vapour pressures were estimated under each set of reaction conditions for either pure MCH or pure toluene, relating to approximate conditions near to the start and end of the reaction respectively (assuming reaction is allowed to go to completion).

For calculation of hydrocarbon and hydrogen partial pressures, see Appendix J.

Table 4-11 shows the partial pressures of constituents of Feed 2. It is immediately clear that the lower pressure condition set (≤5 atm) is not feasible, because the sum of the partial pressures of MCH and H_2 near the start of the reaction exceeds P_T. In essence, this makes the reactor into a boiler, and so there is no advantage to liquid-phase reaction. The 5 atm condition will therefore be omitted from further discussion.

Table 4-11: Partial pressures of constituents of Stream 2 (reactor outlet feed). P_{inert} refers to sweep gas

		Reaction Start			Reaction End		
Pressure/atm	Temperature/K	P_{H2}/atm	P_{MCH}/atm	P_{inert}/atm	P_{H2}/atm	$P_{Toluene}$/atm	P_{inert}/atm
5	443	0.129	4.954	N/A	0.129	4.173	N/A
10	475	0.382	8.759	0.859	0.382	7.670	1.948
15	496	0.722	12.238	2.040	0.722	10.930	3.348

From there, the results become no more optimistic. The hydrocarbon partial pressures in Stream 2 are prohibitively high. Without condensation of Stream 2, the feed carried to the engine will carry a very high mole fraction of hydrocarbon (this is given in Table 4-12).

Table 4-12: Mole fractions of hydrocarbon and hydrogen in Stream 2 at the start and end of reaction (with MCH and toluene as the hydrocarbon respectively), omitting sweep gas

		Reaction Start		Reaction End	
P_T/atm	T/K	y_{H_2}	y_{MCH}	y_{H_2}	y_{Tol}
10	475	0.038	0.876	0.038	0.767
15	496	0.048	0.816	0.048	0.729

This indicates that the liquid phase system is not practically feasible under these conditions without the use of a condenser. To illustrate this point, Table 4-13 shows how much energy from the complete combustion of Stream 2 under variable reaction conditions comes directly from hydrogen combustion.

Table 4-13: Proportion of energy from combustion of feed which comes from hydrogen

Pressure/atm	Temperature/K	Reaction Coordinate	Energy per mole of feed/kJ	% from H_2
10	475	Start	3769	0.25
10	475	End	2905	0.32
15	496	Start	3515	0.33
15	496	End	2764	0.42

With no more than 0.42% of the combustion energy of Stream 2 coming from hydrogen, it is clear that this system is not feasible without hydrogen:hydrocarbon separation, *i.e.* the use of a condensor. If we plan to condense the outgoing feed from the reactor, then it would be sensible to carry out the reaction in the gas phase and take advantage of higher yields (up to 100%[77]) and more favourable rates (several orders of magnitude higher[77]).

4.5 Conclusions

It is interesting to find that MCHDR can be carried out under liquid-phase conditions. The range of reaction conditions is restrictive, however. This leads to a restrictive window of thermodynamic equilibrium positions, reaction rates, and hence rate constants.

The following conclusions can be drawn from this work:

- Dehydrogenation of methylcyclohexane is possible in the liquid phase, having been demonstrated experimentally
- Catalyst deactivation is not problematic for the reaction durations used in these experiments (up to 7 hours). However, further research into deactivation is necessary to see whether the time scales for deactivation are compatible with the intended application
- The activation energy of LP-MCHDR, E_A, is within the range of energies seen for gas phase dehydrogenation
- Reaction rates r_A are not comparable to those observed in gas-phase work, and so optimisation is required
- The practicality of this system rests on the assumption that equilibrium can be overcome by easy separation of gaseous hydrogen and liquid hydrocarbons – this must be demonstrated

- All results must be aligned with a realistic system for automobiles (*i.e.* is the mol% H_2 high enough to combust? Is enough sweep gas available?)
- The design is not practically feasible due to the high mole fraction of hydrocarbon in the vapour phase

4.6 Future Direction

At this point, the project comes to a crossroads. The experiments shown in this work have demonstrated that LP-MCHDR is possible, but it is clearly not useful due to the restrictive window of reaction conditions available. These conditions clash with unfavourable VLE behaviour which causes high hydrocarbon vapour pressures, and gives the system no practical value.

4.6.1 **Potential options**

This leaves the project with a choice of future directions:

- Continue to pursue a liquid-phase dehydrogenation system by searching for an alternative carrier with a more favourable combination of properties *i.e.* favourable VLE behaviour under conditions which give a good conversion and rate of dehydrogenation, or;
- Continue to study the MTH system, but discount the liquid-phase conditions and find an application other than the automotive sector. The practicality issues encountered in the project so far have revolved around the mobile nature of the application, so it may be prudent to direct research towards a stationary application.

For the former point, the liquid-phase dehydrogenation idea in isolation has distinct advantages despite the setbacks discovered in this work. It may therefore be useful to examine other possible liquid organic hydrides. If the hydrogen is weakly bonded to the carrier compared to MCH, then it follows that the endothermicity of the dehydrogenation will be less *i.e.* less energy input (heat) will be required. A carrier possessing a lower vapour pressure under reaction conditions which achieve satisfactory yields and rates would be more suitable for liquid phase conditions. Therefore, it would be interesting to examine a wider range of carriers in order to continue down the liquid-phase route.

For the latter point, it would be sensible to carry out the MCHDR in the vapour phase as is standard industrial practice. This is because in a stationary application, system volume is no longer such an important constraint, therefore it would be best to take advantage of the higher reaction rates *etc* observed in the vapour phase reaction, with post-reaction condensation.

The next aspect to consider is a hydrogen source for this proposed stationary MTH system. Recall that hydrogen is an energy vector, *i.e.* energy which is difficult to store for useful periods (like electricity of heat) can be used to produce hydrogen as the product of a chemical reaction. As a chemical, hydrogen can be stored for long periods, unlike the energy that was used to isolate it. If hydrogen is stored as an LOHC, then the storage period is indefinite. This leads to an interesting opportunity which is developing in the UK. It is not a new idea that the MTH system, or a system like it, could be used to store hydrogen made using excess electrical energy generated by wind farms[25-28], as described above. Waste of energy generated from wind has a serious impact on the feasibility of wind power projects. Due to the intermittent nature of energy from wind, it is seldom that supply and demand for electricity match. Therefore, it is proposed that hydrogen could be produced from electrolysis of water using excess electricity at times where supply of electricity exceeds demand. Such a system could make use of energy that would otherwise be wasted, and may improve the viability of wind farm developments. The traditional outcome of this system is that the process is reversed so that electricity from hydrogen can fill the gaps where demand for electricity exceeds supply. However, in present times where electricity for the grid is still largely supported by fossil fuel power sources, a different strategy could be adopted. It could be proposed that excess wind energy is used to produce hydrogen from water, which is subsequently stored as MCH. Rather than being fed back into the grid at a later time, this hydrogen (as MCH) could instead be sold as a product (whether as a reagent for chemical/process industries or a fuel). This could be a very potent opportunity, because existing wind farms in the present day have no mechanism for dealing with excess energy, so this is being wasted. It would therefore be likely that the excess would be sold at an attractive price, and so this could be a source of relatively inexpensive renewable hydrogen.

The next consideration is to compare this hydrogen storage strategy with other possibilities. This would mean a comparison between the MTH system and other, more conventional systems such as compression, whether into a tube trailer for transport or directly into a cylinder. This assessment would have to be made with several factors in mind, including energy efficiency of storage method, simplicity of use (potentially by non-expert wind farm operators), and economical analysis, both in the sense of capital investment and operational costs.

Perhaps the most important aspect in the feasibility of this proposed project is the target market for the sale of hydrogen. The hydrogen could be sold either as:

- a reagent to a chemical industry or small scale user (steelworks, power stations, food manufacturers, universities)

- o purity is important

- o expected sale price would be higher

- o dehydrogenation process may require difficult purification steps, which could impact on costs.

- a fuel for electricity and/or district heating.

  - o Lower hydrogen purity requirement

  - o Lower expected sale price

  - o Higher profile

In making this decision, a decision needs to be made as to which is the easiest market to break into, and which market is the most feasible/lucrative. A business model needs to be constructed for the chosen market, detailing the mechanism for hydrogen delivery. For example, the hydrogen could be sold directly to the customer as MCH. From there, the customer could buy dehydrogenation equipment to have on-site, or could modify their existing process to incorporate this. Alternatively, the customer could rent the apparatus, leaving the MCH supplier with the responsibility of running and maintaining the dehydrogenation step. The other option is to centrally dehydrogenate, compress hydrogen on-site, and deliver to the customer in gaseous form. These options need to be evaluated before a decision can be reached.

Niche markets could be a fertile pasture to supply initially. These are markets where a special circumstance has arisen, so conventional solutions are not an option. Such markets include those which are off-grid (gas-grid or electrical grid), or which have an inconsistent or unreliable power supply. With the advent of Information Technology and international trade, an increasing number of businesses are running for 24 hours a day, and need to guarantee that their computers and servers have a reliable power supply. In these cases, a backup power source can be used where the electrical grid fails[81]. Conventionally, this would be a diesel generator. If the office in question is situated in a remote area, then this solution can work well, but in or near residential areas, for example, air quality and noise pollution concerns can make planning permission for diesel generators difficult to obtain. In this case, a hydrogen fuel cell could offer a convenient alternative – these can be kept indoors with no harmful emissions and a very low level of noise. However, hydrogen storage becomes an issue at this point, with purpose-built bunkers needed to store compressed hydrogen. If storage regulations for liquid hydrocarbons are less strenuous that those for hydrogen gas, this could be a good niche market to exploit.

Alternatively, as aforementioned, another niche market to exploit could be those companies which are off-grid. A good example is a Scottish whisky distillery. By necessity, distilleries are often off the gas-grid due to a need to be close to a particular natural water source. As a result, they typically have an on-site heating arrangement fuelled by oil[82]. As an industry that consumes 1.5% of Scotland's entire annual energy demand, distilleries will likely be the focus of a push for alternative energy supply, as this will be necessary to achieve Scotland's ambitious target of generating the equivalent of 100% renewable energy by 2020[83].

This seems like a lucrative opportunity for the MTH system. If the distilleries are already equipped to deal with quantities of oil, then few or no structural changes would be needed to store the MTH component chemicals. Also, this would make planning permission easier, as the site already has permission to store hydrocarbons. The changes required (therefore the capital investment cost) would be that of installing the dehydrogenation apparatus. The renewable hydrogen generated from wind farms could be collected and stored as MCH, transported and stored on-site at the distilleries, and used as necessary. Toluene could be removed and replaced with fresh MCH on a regular basis. This solves the problem of reliable on-site renewable power while using facilities already available on-site. The hydrogen generated could be converted back to electricity or could be combusted directly to provide process heat.

A simple representation of this system is given in Figure 4-18.
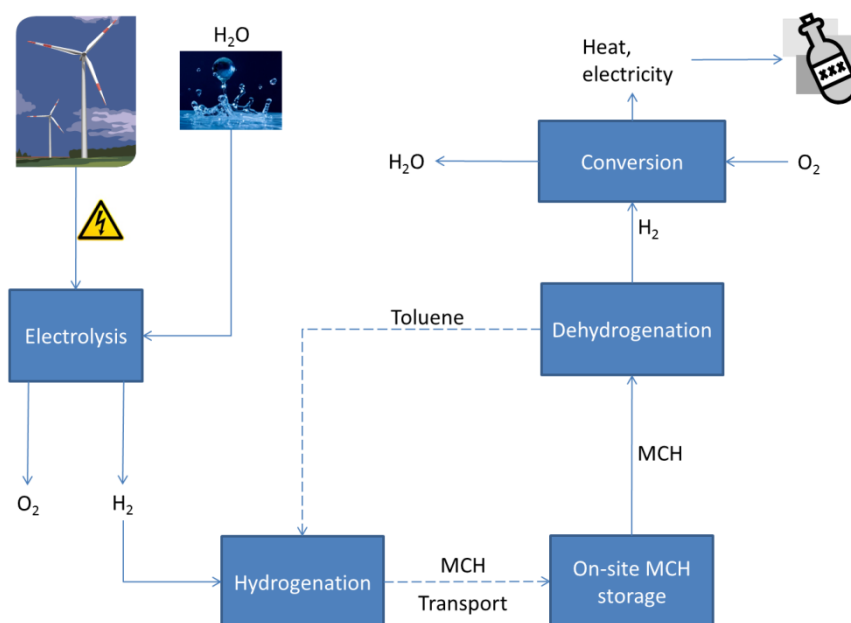
Figure 4-18: A simple diagrammatic representation of a distillery powered by wind electricity, with the MTH system acting as a buffer between supply and demand

To take this idea further would require a business model. Questions need to be answered such as:

- Would the wind farm operators buy the electrolysis and hydrogenation equipment, or would they sell the electricity alone to a third party who would deal with the operational side?

- Would the distillery buy or rent the dehydrogenation apparatus from the company? If the distillery did buy the equipment, what would their return on investment be?

- Who would be responsible for running and maintaining the apparatus?

- What are the tax implications of selling a hydrocarbon? Would this be the same as petrol *i.e.* 60+% tax? Would this be the case if the toluene was rented, not bought?

- Who is responsible for delivering the MTH and removing the toluene?

- Would a greater return on investment be offered by on-site electrolysis and subsequent hydrogen storage at pressure?

- Is the total cost of hydrogen to the distillery less than the cost of heating oil *i.e.* how do operating costs change?

- Are government or other incentives available to help with the capital/operational costs?

Much of the success of this idea depends upon economic feasibility, and this should be a focus alongside the technical aspects of the proposal.

4.6.2 Chosen direction

Through the research carried out in the project so far, a working knowledge of the requirements for a mobile system have been gained, and this could be used wisely in investigating alternative potential hydrogen carriers. However, technical knowledge has also been acquired on the MTH system in particular, and it would be sensible to use this knowledge to find a suitable application for the technology. Therefore, both of these possibilities will be investigated in the following chapters.

Chapter 5   Idealised Carrier Definition

5.1 Introduction

Using the lessons learned from the experiments with the MTH system, it would be useful to define an idealised LOHC for liquid-phase dehydrogenation (LP-DR), and to use this to focus the search for a carrier in reality by defining the carrier's desirable qualities.

In order to do this, several possible automotive dehydrogenation systems could be used. Each system will require a different set of qualities from its idealised carrier, and these should be outlined for each system. The aim of this chapter is therefore to define the different possible approaches with a view to designing an idealised carrier.

For each system, idealised carriers will be defined in terms of:

- Physical properties
    - Melting/boiling points
    - Vapour-liquid equilibrium (VLE) behaviour
- Thermodynamic properties
    - Enthalpy, entropy and Gibbs free energy for dehydrogenation
    - Effect on equilibrium conversion
- Reactor type and reactor conditions for dehydrogenation

One of these systems will be chosen to carry forward, and this choice will dictate the desirable qualities which will be sought in a real carrier. Actual carrier molecules will then be assessed against the desirable criteria.

Note that where liquid-phase conditions are referred to, this implies that the H_2-charged and H_2-depleted carriers are in the liquid phase, but product hydrogen is of course in the form of a gas.

5.2 Dehydrogenation systems

5.2.1 **Reactor systems**

This section outlines the possible dehydrogenation system designs, and shows what each design would require of an ideal carrier. As part of this, the reactor type used for dehydrogenation should be discussed. It is not possible to use standard reactor definitions (CSTR, PFR, batch reactor *etc*)

because the system is dual-phase, with hydrocarbons being in the liquid phase and product hydrogen being in the gas phase. A CSTR reactor, for example, assumes uniform mixing of products and reactants at all times. For the LP-DR system, this is not the case due to the dual-phase situation.

Reactor systems must therefore be defined for LP-dehydrogenation. The critical factor in the design of the reactor is that hydrogen mole fraction in the reactor can be controlled throughout the reaction. The hydrogen mole fraction may need to be reduced during dehydrogenation in order to favourably shift the thermodynamic equilibrium limit of dehydrogenation. This can be done in two ways:

- Include a pressure valve on the gas exit feed to maintain reactor pressure – this will allow gaseous hydrogen feed to exit as pressure builds, reducing the hydrogen pressure and therefore the hydrogen mole fraction
- Use an inert sweep gas to dilute the hydrogen – should be used in conjunction with the pressure valve mentioned above to maintain reactor pressure.

This is possible with a modified version of any of the standard reactors mentioned above. These will be referred to as *pseudo*-reactors *e.g.* a modified CSTR will be referred to as a *pseudo*-CSTR.

The *pseudo*-reactors are illustrated in Figure 5-1 to Figure 5-3.
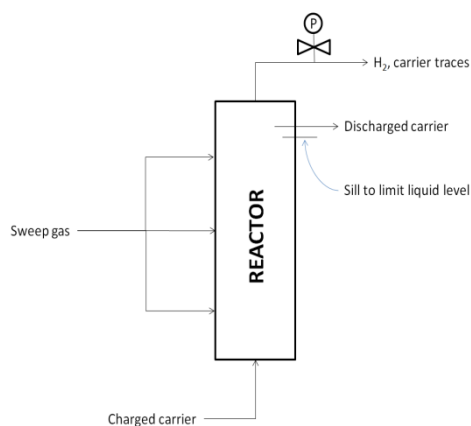
Figure 5-1: *Pseudo*-PFR
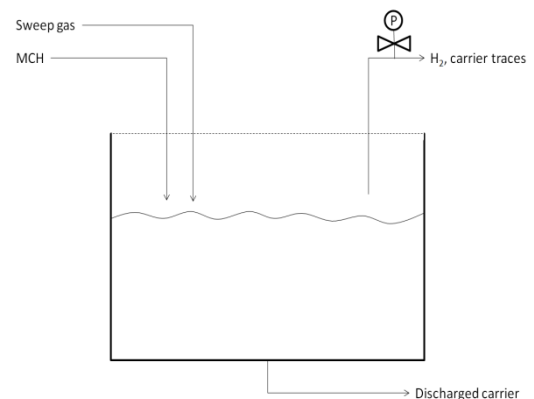
Figure 5-2: *Pseudo*-semi-batch reactor
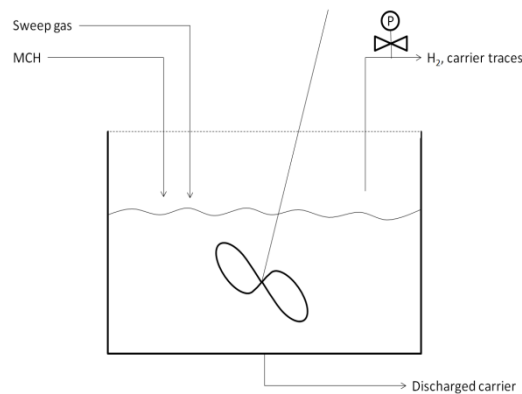
Figure 5-3: *Pseudo*-**CSTR**

In all cases with the exception of the "Spontaneous Decomposition" approach (see Section 5.2.7), the type of reactor used would be a choice between these three.

5.2.2 **Sweep gas identity**

The identity of the sweep gas may also be an important factor in delivering a useful mole fraction of hydrogen to the engine. To avoid adding unnecessary system complication and to keep system weight and volume as low as possible, the sweep gas should be available to the system already, without adding an inert gas cylinder. Two gas streams are available – either air or exhaust gas.

Air would not be considered as a viable option. Although using air as a sweep gas would facilitate direct mixing of hydrogen with oxygen, therefore generating the explosive mixture without diluting the hydrogen in any other inert gas, it would be undesirable to generate such an explosive mixture anywhere in the system except for the engine. Also, it would be unsafe to mix oxygen with hot hydrocarbon liquids/vapours.

This leaves the post-combustion exhaust gas from the engine, which would consist of steam and nitrogen. If a lean burn is assumed, no NO_x substances should be present. The use of this exhaust stream may prove to be advantageous. After the sweep gas has passed though the reactor and collected the hydrogen gas, it would be possible to condense the water from the stream, therefore increasing the mole fraction of hydrogen present in the gas stream. This would also remove trace hydrocarbons from the gaseous stream. The rest of the gas stream would consist of nitrogen, which could not be simply separated from the hydrogen, and which would necessitate the venting of the gas stream to prevent inert nitrogen buildup. This system is illustrated in Figure 5-4.
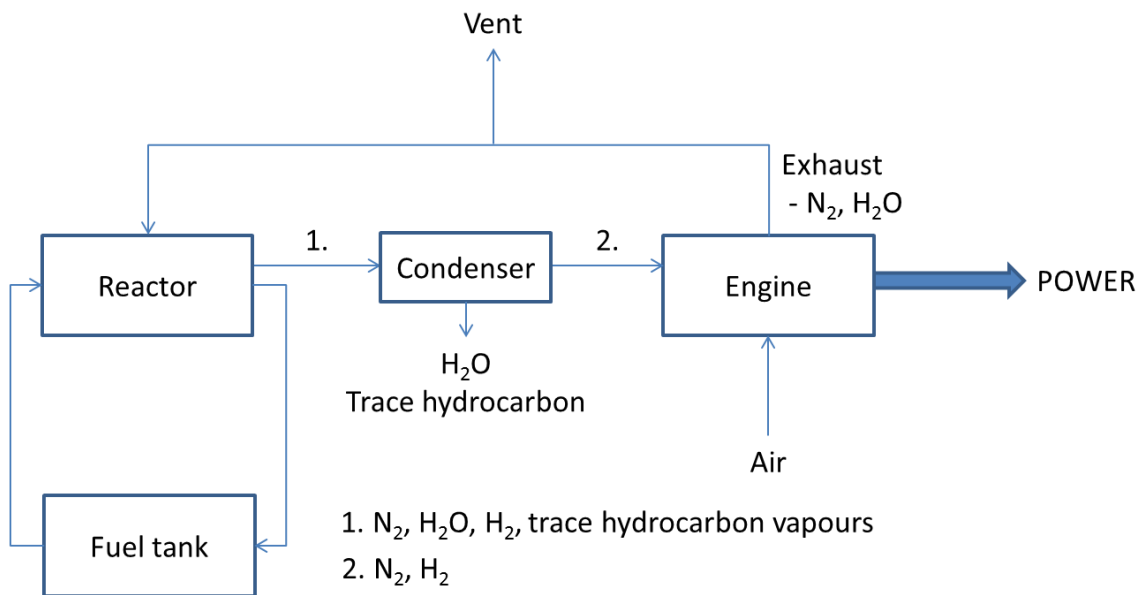
Figure 5-4: Engine exhaust stream as a sweep gas

Although the use of a high temperature fuel cell has been discounted for the purposes of this investigation, an SOFC may prove to have an advantage. The exhaust gas of an SOFC is only steam, because oxygen is separated from nitrogen in the air as the oxide ions pass through the electrolyte before combining with hydrogen. If this pure steam exhaust gas could be used as a sweep gas, then all of the water could be condensed, leaving a pure or near-pure hydrogen stream to enter the fuel cell. This system is illustrated in Figure 5-5.
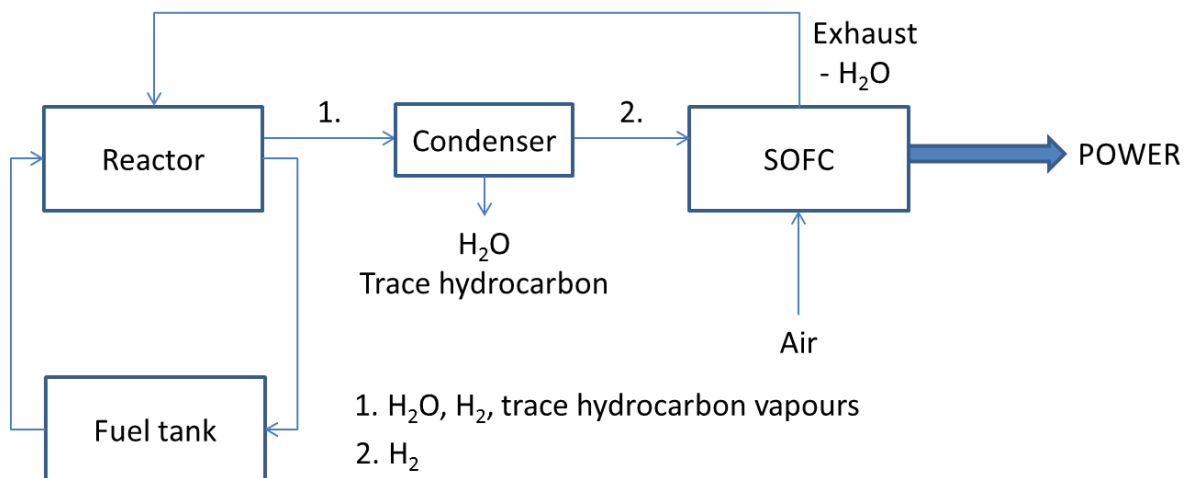
Figure 5-5: SOFC exhaust stream as a sweep gas

The inclusion of a condenser may seem to defeat the object of carrying out the dehydrogenation reaction in the liquid-phase. However, the systems shown in Figure 5-4 and Figure 5-5 still bypass

the need for pre-reaction vaporization and superheating of hydrocarbon. An unfortunate side-effect of this system is to produce waste water which is contaminated with hydrocarbon. This would need to be removed from the vehicle regularly and treated.

5.2.3 **New system approaches**

Carrier requirements are discussed individually for each section throughout the following chapter, but regardless of the approach, all carriers should have boiling/melting points which leave the (dis)charged carriers in the liquid phase at all times, whether stored at ambient conditions or under reaction conditions. In other words, the carriers in (dis)charged form should never become solid at ambient temperature, and should have an acceptably low vapour pressure at reaction temperature/pressure. An "acceptably low vapour pressure" is defined as the vapour pressure where carrier retention after reaction is 96.1 mol%. This is the case throughout this work where "carrier retention" is referred to, a term which is defined as the amount of carrier that is recovered to be recharged and used again after being dehydrogenated. 96.1 mol% carrier retention is considered to be sufficient, based on the carrier retention observed in a vapour-phase dehydrogenation reaction with post-reaction feed condensation[23]. This vapour-phase retention figure sets a sensible benchmark, because the vapour-phase and liquid-phase systems are in direct competition.

With the factors discussed above in mind, the following sections each give one approach to the search for a new, idealised hydrogen carrying hydrocarbon. These approaches are subsequently summarised and discussed, with the outcome of this chapter to be the selection of one approach to carry forward to the rest of the project.

5.2.4 **"Improved MTH" system**

5.2.4.1 Description

This idea involves taking the same general approach as with the MTH system, but using a carrier with physical and reactive properties more suitable to the application.

As in earlier work, this involves a feed of liquid-phase charged carrier into a reactor. The charged carrier is heated to the reaction temperature, which may take place prior to entering the reactor or *in situ*. The carrier is then dehydrogenated over a heterogeneous catalyst while remaining in the liquid phase to yield liquid-phase depleted carrier and gaseous hydrogen. The gaseous hydrogen is

removed from the reactor either using an inert sweep gas or by the buildup of its own pressure, while the liquid-phase dehydrogenation process is allowed to continue.

This approach would involve a detailed examination about why the MTH system was unsuitable for Liquid-Phase Dehydrogenation LP-DR, and therefore what is required of a more appropriate idealised carrier.

5.2.4.2 Carrier Requirements

Examination of what was undesirable or lacking about the MTH system should serve to point towards desirable qualities in a new carrier. According to the experiments described in Chapter 4, issues with the MTH system included:

- A low rate of hydrogen evolution caused by the need to maintain liquid-phase conditions. The best dehydrogenation rate achieved was 5.32×10^{-8} mol MCH g^{-1} s^{-1}.(15 atm, 496 K) compared to a similar experiment[84] which achieved 7.00×10^{-6} mol MCH g^{-1} s^{-1} in the gas phase (1 atm, 703 K), over two orders of magnitude higher. This experiment used the same experimental setup and the same catalyst as presented in this work.

- The use of temperatures near to the carrier boiling points to attain maximum rate resulted in high hydrocarbon vapour pressure in hydrogen exit feed (if feed were combusted, only 0.42% of combustion energy would come from H_2 at best)

The idealised carrier for this approach would have a combination of requirements to solve these problems, given in Table 5-1.

This is a description of an idealised carrier – although it is noted that the factors in Table 5-1 are not always independent of one another (*e.g.* a lower boiling point would only be useful if hydrogen release took place at a similar temperature to MCH, not a higher temperature), each is given on the basis of all other factors being the same as the MTH system. This applies to the Carrier Requirement section for all other approaches also.

Table 5-1: Requirements of an idealised carrier for LP-DR in the "Improved MTH system" approach

Requirement	Reason
Higher boiling point *i.e.* lower volatility	With lower volatility at the dehydrogenation temperature and pressure, less liquid-phase carrier would be vaporised and removed from the reactor with the gaseous hydrogen feed. This would increase carrier retention.

Lower ΔH_d	A lower enthalpy of dehydrogenation would mean a lower energy input. This would also favourably lower the Gibbs free energy of dehydrogenation, ΔG_d.
Higher equilibrium constant, K	A higher equilibrium conversion would permit a higher mole fraction of hydrogen in the sweep gas, ensuring that the gas mixture entering in the engine has a sufficient hydrogen mole fraction to combust.

It is important to note that there are two contrasting goals here. Lower reaction temperature is desirable to lower carrier vapour pressure. However, a higher equilibrium constant is also desirable to increase the attainable mole fraction of hydrogen in the reactor. K is dependent on temperature, and lowering the temperature will also lower the value of K. These factors could therefore be in competition. An optimisation between the two should therefore be performed, where K is high enough that the attainable mole fraction of H_2 is sufficient to create an explosive mixture with oxygen, and yet the temperature is low enough that carrier retention is acceptable.

5.2.5 Thermal Decomposition Approach

5.2.5.1 Description

This thermal decomposition approach could be viewed as a dehydrogenation where the catalytic activity is infinitely small. The approach would involve a hypothetical charged carrier which would not release hydrogen under ambient conditions but would release hydrogen upon heating. At ambient temperature, the rate of dehydrogenation should be sufficiently low to avoid significant hydrogen release. In order to store the (dis)charged carrier as a liquid, and to avoid the high vapour pressure problems encountered with the MTH system, the carrier should be in the liquid state at ambient temperature, and should have a low vapour pressure at reactive temperature.

Pt catalysts are usually chosen due to their high selectivity towards dehydrogenation reaction in preference to other reforming reactions. However, it is unlikely that the absence of catalyst would result in increased by-product production, despite the fact that the decyclisation of MCH to *n*-heptane is exothermic ($\Delta H \approx -34 \ kJ \ mol^{-1}$). It is well known that under the industrially mild conditions used for dehydrogenation (300 − 400 °C), cracking of the MCH to yield an alkane is rare. This is because dehydrogenation of naphthalenes is kinetically fast, whereas cracking is relatively

slow[85]. A larger degree of decyclisation is possible, but only with higher temperatures and a longer reaction time.

5.2.5.2 Carrier Requirements

The idealised carrier would need to have a very specific set of reactive and physical properties. These are given in Table 5-2.

Table 5-2: Requirements of an idealised carrier for LP-DR in the "Thermal Decomposition" approach

Requirement	Reason
High boiling point *i.e.* low volatility	Despite being heated in the reactor, volatility should be low enough as to ensure low vapour-phase (dis)charged carrier presence. This is to increase carrier retention.
Lower E_a	The activation energy would need to be sufficiently low that thermal energy alone could cause dehydrogenation, without a temperature rise high enough to cause a high carrier vapour pressure. However, activation energy should not be so low that spontaneous hydrogen discharge could occur under ambient conditions while in storage.
Higher equilibrium constant, K	A higher equilibrium conversion would permit a higher mole fraction of hydrogen in the sweep gas, ensuring that the gas mixture entering in the engine has a sufficient hydrogen mole fraction to combust.

5.2.6 Ambient Catalytic Decomposition Approach

5.2.6.1 Description

The ambient catalytic decomposition approach would involve a carrier which would release hydrogen in the presence of a catalyst under ambient conditions, but which would not liberate hydrogen in the absence of a catalyst. This would remove the need to heat the carrier and catalyst bed above ambient conditions, although some heating would still be required to maintain the starting temperature, due to the endothermic reaction taking heat from the surroundings. Heat input would be energetically equal to the enthalpy change of the reaction. The catalyst serves to lower the activation energy to levels which can be met at ambient temperatures.

This situation is represented by Figure 5-6.

It should also be remembered that ambient temperature actually describes a range of temperatures, so dehydrogenation would need to be possible under all weather conditions.
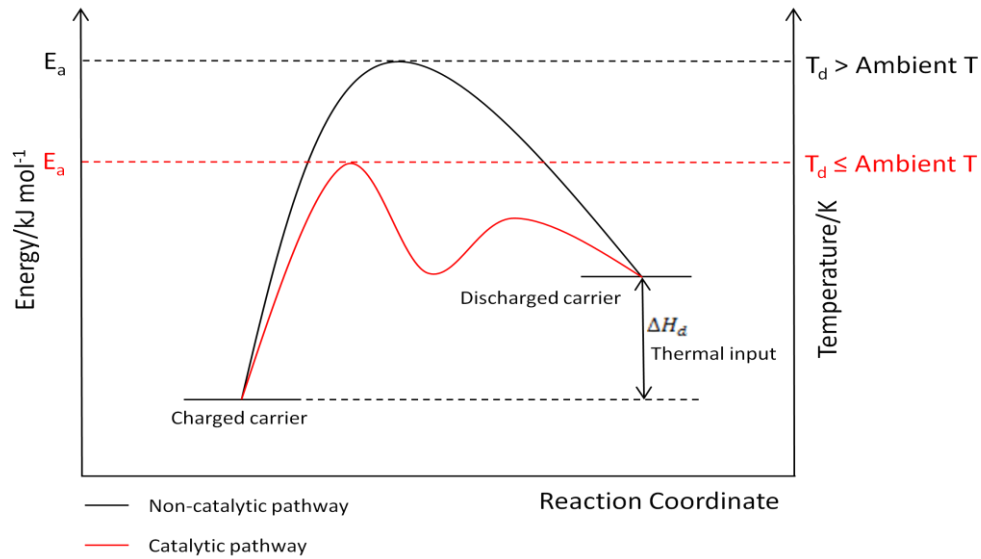
Figure 5-6: Representative energy diagram to compare a catalytic, non-thermal dehydrogenation process with a purely thermal dehydrogenation process

The use of the catalyst means that the product selectivity is not lost with this approach.

5.2.6.2 Carrier Requirements

This approach demands a specific set of characteristics from the carrier:

- The catalytic activation energy must be achievable at ambient temperature
- The thermal activation energy must not be achievable at ambient temperature
- The carrier must have low volatility at atmospheric temperature

These requirements are summarised in Table 5-3.

Table 5-3: Requirements of an idealised carrier for LP-DR in the "Ambient Catalytic Decomposition" approach

Requirement	Reason
High boiling point *i.e.* low volatility	Volatility should be low enough that the presence of vapour-phase (dis)charged carrier is low, and carrier retention is high.
Lower ΔE_a	The activation energy of dehydrogenation would need to be sufficiently high to prevent spontaneous dehydrogenation at ambient temperature, but would need to have sufficiently low activation energy to dehydrogenate at ambient temperature *in*

the presence of a catalyst.

Higher equilibrium constant, K	A higher equilibrium conversion would permit a higher mole fraction of hydrogen in the sweep gas, ensuring that the gas mixture entering in the engine has a sufficient hydrogen mole fraction to combust.

5.2.7 Spontaneous Decomposition Approach

5.2.7.1 Description

This approach could be considered a hybrid storage technique, involving aspects of both compressed hydrogen storage and LOHC storage. A charged LOHC would be stored in a sealed high pressure tank. This carrier would be designed to evolve hydrogen spontaneously under ambient conditions in the absence of a catalyst. The carrier would do so in the pressurized container until the contained release of hydrogen and mounting pressure caused the dehydrogenation to reach thermodynamic equilibrium, arresting the reaction. Free hydrogen would therefore be stored at this pressure until it was released from the high pressure tank for fuel, at which time the hydrogen pressure would drop and the liquid carrier would begin to evolve hydrogen again until thermodynamic equilibrium is once again reached. This would repeat until the hydrogen is depleted.

This could be advantageous over physical pressurized hydrogen storage. For example, pure hydrogen stored at 700 bar has a volumetric energy density of 5.6 MJ L^{-1}. At STP and assuming 100% dehydrogenation, MCH has a volumetric energy density of 5.7 MJ L^{-1} of hydrogen, which is similar to the 700 bar hydrogen. If a carrier can be found with a similar volumetric energy density to MTH from which hydrogen has spontaneous release, it should be possible to contain the energy of 700 bar hydrogen at a fraction of the pressure, with no heat input or catalyst required. Further investigation is required to find at what pressure the dehydrogenation would cease for a given candidate carrier.

As with the Catalytic Decomposition Approach, heating would be required, but only enough to maintain ambient temperature against the drop in temperature caused by the endothermic dehydrogenation reaction.

This would also eliminate the problem of start-up, because some compressed hydrogen will be available at the time of turning on the vehicle.
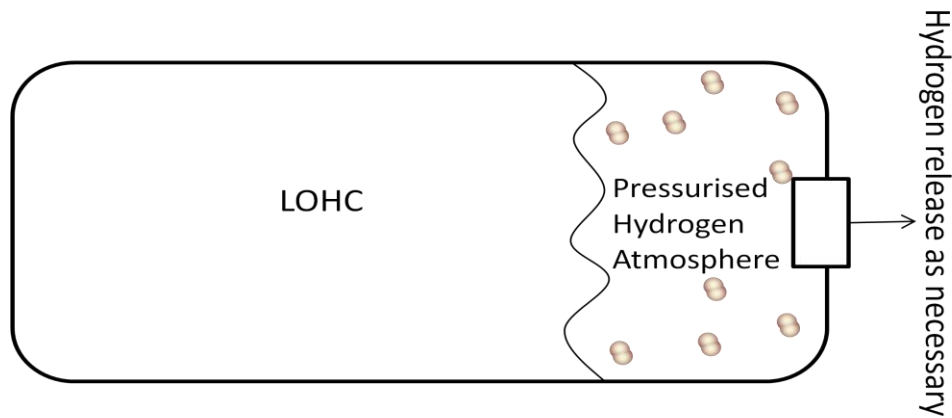
Figure 5-7: A hybrid storage system involving aspects of pressurised and liquid organic hydrogen

Problems with this approach include the constant presence of free hydrogen, which poses a risk to safety in the event of a vessel failure. Also, pressurized hydrogen is quick to disperse in the case of accidental release, whereas the carrier would cause a longer retention of hydrogen, meaning the time for the hazard to pass would be extended.

5.2.7.2 Carrier Requirements

Table 5-4 summarises the requirements for a carrier used in this system.

Table 5-4: Requirements of an idealised carrier for LP-DR in the "Spontaneous Decomposition" approach

Requirement	Reason
Low volatility at ambient temperature	Volatility at ambient temperature would need to be sufficiently low that the great majority of carrier sits in the storage tank in the liquid phase, and so the mole fraction of vapour-phase carrier should be low.
Lower ΔE_a	Activation energy should be sufficiently low that dehydrogenation occurs at ambient temperature.
High equilibrium constant, K	No sweep gas is required for this approach, so the hydrogen purity would automatically be higher than the other approaches, potentially leading to a higher hydrogen mole fraction. However, equilibrium conversion should be sufficiently high that the dehydrogenation is arrested by the thermodynamic limit imposed by mounting pressure to maximise the amount of hydrogen available on demand.

5.3 Choice of Approach for Future Study

The assessment of these possible future directions has been largely qualitative, however, the scope of this project does not allow for detailed analysis of all of the approaches outlined.

- **Spontaneous Decomposition Approach:** This is an attractive concept, because it solves the ever-present start-up issue, and the dehydrogenation reaction benefits from low heat demand. However, the safety problems and the possible refuelling complications make this a challenging approach. The largest disadvantage, however, is that the solid hydride counterpart of this theory has more tuneable dehydrogenation parameters than using a liquid hydride, and could be made to fit detailed specifications more easily. The mechanism for reloading these solid hydrides is unclear at this stage, although potential routes involve charging with gaseous hydrogen on-board the vehicle, or exchanging a depleted hydride cylinder for a charged one at the filling station. However, the distribution network would be unlikely to use liquid hydrides. This approach will therefore be studied no further.

- **Thermal Decomposition Approach:** Although the idea of catalyst-free dehydrogenation is attractive from an economic perspective VLE behaviour has been a major problem, so any system which requires higher temperatures (to compensate for lack of catalyst) would also require a less volatile carrier than the equivalent catalysed process. No further study will be carried out with this approach.

- **Catalytic Decomposition Approach:** The reaction temperature is designed to be low with this approach, which is attractive because carrier volatility could be higher (so this parameter would not be as stringent). However, this approach demands exacting properties from a carrier which are unlikely to exist in a single molecule (low cost, high availability, specific activation energy for dehydrogenation, low volatility). No further study will be carried out with this approach.

- **"Improved MTH System" Approach:** MCH is not an ideal carrier for its VLE behaviour alone, and a new carrier would need to possess different thermodynamic and kinetic properties under dehydrogenation conditions in combination with lower volatility. However, a wealth of information and understanding has been gathered about dehydrogenation processes in general in the study of the MTH system. In the literature, a broad range of research has been carried out on the strengths and weaknesses of several alternative carriers to MCH. These researchers have never performed studies with a view to dehydrogenating in the liquid phase, but nonetheless inspect the same factors which are important to the work presented

here (activation energies of dehydrogenation, hydrogen wt% *etc*). Therefore, information regarding early assessment of carriers may be simple to find. This approach will be carried forward.

5.4 Future Direction

Learning from the experiments carried out with the MTH system and the subsequent analysis above, it is possible to list the factors which are required by a new carrier for LP-DR. The new carrier should compare with MCH in some or all of the following ways:

- Lower ΔH_d
- Same or higher number of H_2 molecules evolved per carrier molecule (to increase the value of ΔS_d)
- Higher boiling point (*i.e.* lower volatility)
- Must be in liquid state under atmospheric *and* reactive conditions
- Similar or greater H_2 wt%, volumetric and gravimetric H_2 density
- Should dehydrogenate at a rate of $\geq 16.25 \times 10^{-2}$ mol s^{-1} [77] and with sufficient hydrogen partial pressure to create an explosive mix in the engine at atmospheric pressure and mild temperature. As noted in Chapter 4, this hydrogen evolution rate would require a minimum of 306 kg of 0.3wt% Pt/Al_2O_3 catalyst under the reaction conditions studied – an unrealistic weight of catalyst for a mobile application.

In addition, an aromatic carrier should still be sought due to the advantage of resonance stabilisation energy which benefits aromatic molecules. This is energy which makes an aromatic structure more stable than if the conjugated pi-bonds existed in isolation with no electron delocalisation. For example, the structure of benzene is 151 kJ mol^{-1} more stable than non-delocalised cyclohexa-1,3,5-triene, as shown by the differing energies of hydrogenation for each bond[86]. Figure 5-8 (adapted from [86]) illustrates this point. The dehydrogenation scheme is the same but in reverse (*i.e.* dehydrogenation of cyclohexane to cyclohex-1-ene has an enthalpy of +120 kJ mol^{-1} *etc*)

The resonance stabilization energy is calculated by taking the difference of the hydrogenation energies of the first and last pi-bonds, and correcting for the stabilization energy of the diene (8 kJ mol^{-1})[86].
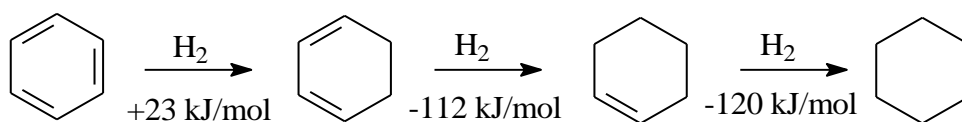
Figure 5-8: Hydrogenation energies of benzene on a bond-by-bond basis

This means that the aromatic nature of the molecule encourages dehydrogenation. That is to say that in non-delocalised cyclohexa-1,3,5-triene, dehydrogenation is approximately 151 kJ mol^{-1} more endothermic than for benzene, meaning ΔH_d would be +366 kJ mol^{-1} instead of +209 kJ mol^{-1}. This is illustrated in Figure 5-9.
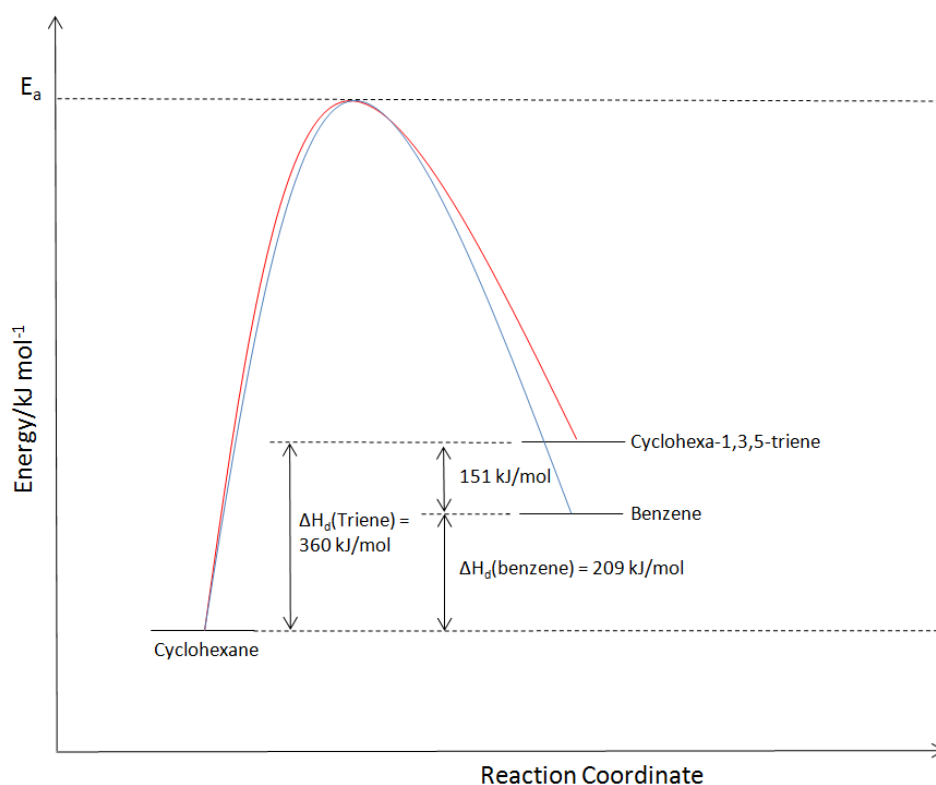
Figure 5-9: Energy diagram to illustrate the difference in dehydrogenation enthalpy caused by resonance stabilisation energy in benzene.

In the interests of lowering the value of ΔH_d, it is therefore recommended that alternative *aromatic* molecules would be a good starting point in the search for a new carrier.

The next step is to compile a list of carriers and test them against the criteria laid out in this chapter.

Chapter 6   Evaluation of Alternative Carriers

6.1 Introduction

Chapter 5 provided a group of possible approaches to Liquid-Phase Dehydrogenation (LP-DR), and showed what each approach would require of an LOHC. One approach has now been selected to take forward, the "Improved MTH Approach". This involves taking the same approach to LP-DR as previously throughout the project, but trying to find an alternative carrier which better fits the specifications of the approach. The aim of this chapter is to devise a comprehensive set of carrier assessment criteria, and then to compile a list of candidate molecules, and to assess each of them for suitability for LP-DR.

In order to assess carriers in this way, it would first be useful to examine the key parameters, and by doing so, define a set of restrictions which would make an appropriate hydrogen carrier for LP-DR. This will be carried out in terms of thermodynamic and kinetic considerations to steer the search for an alternative carrier. Following this, a list of carriers will be compiled to assess.

6.2 Thermodynamic/Kinetic Parameters

6.2.1 **Defining restrictions on Gibbs free energy**

It is desirable to have a sub-zero Gibbs Free Energy of dehydrogenation, ΔG_d, at a temperature which is much lower than the carrier boiling point *i.e.* $\Delta G_d < 0$ when $T \ll T_{boil}$(carrier)*.* The aim of this is for the dehydrogenation reaction to proceed at a temperature where the vapour pressure of the carrier is sufficiently low for overall carrier retention to be high, ≥ 96.1% to match the gas-phase dehydrogenation process[23]. In other words, a minimum of 96.1 mol% of carrier should be available to be recharged with hydrogen and used again, and a maximum of 3.9 mol% leaves the reactor in the gaseous hydrogen stream, and so is not recovered. These are the carrier retention figures calculated from a paper[23] which uses the MTH system in the vapour phase with a condenser employed to remove liquids from the gaseous product stream. It provides a useful benchmark to calculate the temperature at which the liquid-phase system can match the vapour-phase system, because these systems are directly competing.

Although it is clear that ΔG_d should be sub-zero, it is useful to define a value more clearly. This must be carried out for each carrier individually, due to each dehydrogenation reaction possessing different properties (ΔH_d, ΔS_d *etc*).

Firstly, a target equilibrium conversion of carrier, x_A, should be calculated. x_A is dictated by the equilibrium constant, K, and so by defining a target x_A, a target K can also be derived. In turn, K can be related to ΔG_d. Therefore, by deciding on a target x_A, it is possible to derive a target ΔG_d.

x_A is defined as:

Equation 6-1

$$x_A = 1 - \frac{n_A}{n_{A_0}}$$

Where:

n_A moles of charged carrier in reactor n_{A_0} Moles of charged carrier entering the reactor

Equilibrium conditions are assumed for Equation 6-1 to be valid.

For a mobile application such as on-board vehicular dehydrogenation, system volume and weight are of key importance. x_A should be set to a threshold which ensures that weight and volume are practical (*i.e.* if x_A is complete and the system requires A kg and B m^3 of carrier to achieve a given mileage, then an equivalent system where x_A is 0.5 would require 2A kg and 2B m^3 of carrier to achieve the same mileage).

To quantify a "practical" x_A, a comparison is made between an LOHC system and rival technology. In this case, compressed hydrogen is chosen due to its high commercial availability, which makes it the most realistic rival technology. The chosen hydrogen pressure for this comparison is 450 bar (hydrogen is commonly compressed to up to 700 bar, but this is rarely used for mobile applications due to potential safety issues).

The following work is based on a vehicular hydrogen capacity of 8 kg, enough to offer a satisfactory range of 400 km using a H$_2$-ICE in a moderate, modern car[15], built for economic travel rather than status (this is defined as petrol consumption of 0.06 kg petrol/km).

The desired amount of useable hydrogen carried on-board, 8 kg in this case, and the x_A in the reactor dictate the amount of carrier storage requirement on-board the vehicle. The weight and volume of the carrier on-board can be compared to the weight and volume for an equivalent

compressed hydrogen system. The high pressure containers required to contain 450 bar hydrogen would take a volume of 28.3 L $(kg\ H_2)^{-1}$ and would contain, when fully charged, approximately 4 % hydrogen by mass[15].

Mass and volume data for the 450 bar compressed H_2 system containing 8 kg hydrogen is given in Table 6-1.

Table 6-1: Mass and volume of 8 kg hydrogen at 450 bar with appropriate container

Mass/kg	200.0
Volume/L	226.1

To make the weight/volume comparison, the identity of the carrier must be known. As an example, the MTH system will be used. This comparison will be used to choose a target x_A value. The required mass and volume of the MTH fuel at different x_A values is given in Table 6-2.

Table 6-2: Methylcyclohexane fuel mass and volume to carry 8 kg useable hydrogen depending on dehydrogenation efficiency, x_A. Red shaded squares – mass/volume is in excess of that of 450 bar compressed H_2

Conversion, x_A	MTH fuel mass/ kg	MTH fuel volume/ L
0.999	129	168
0.900	143	186
0.800	161	209
0.700	184	239
0.600	215	279
0.500	258	335

For the MTH fuel to take an equivalent weight/volume to the fully charged 450 bar hydrogen cylinder, x_A would need to be 0.65/0.74 respectively. However, the pressurised cylinder contains free hydrogen which is ready to use, whereas the hydrogen stored in MTH must be liberated. This requires peripheral equipment, including a reactor and potentially multiple heat exchangers. These

pieces of equipment, as well as the MCH/toluene container, are not included in the weight/volume estimates given in Table 6-2.

Although a full system design is beyond the scope of this investigation at this point, it is likely that the heaviest and most voluminous piece of equipment besides the filled fuel tank would be the dehydrogenation reactor. The reactor weight is difficult to estimate at this stage, but the volume of this reactor can be estimated.

Assuming the volume of the dehydrogenation system components is negligible except for the fuel tank and the reactor, the MCH fuel volumes in Table 6-2 can be subtracted from the compressed hydrogen container volumes in Table 6-1. This gives a figure for maximum reactor volume *i.e.* the threshold volume which the reactor could take while the dehydrogenation system remains competitive against the compressed hydrogen system. These values are given in Table 6-3. Note that conversions below 0.74 are disregarded, because lower x_A requires more reactor volume than the comparison to the compressed hydrogen system allows.

Table 6-3: Maximum reactor volumes depending on conversion of carrier, x_A

Conversion, x_A	Maximum reactor volume/L
0.999	58
0.9	40
0.8	17
0.74	0

The volume of the reactor can be estimated, but this requires knowledge of a desired reaction rate.

Without any kind of hydrogen gas buffer system in between the dehydrogenation reactor and the engine, the reactor must be capable of producing hydrogen at a sufficient rate to satisfy maximum power demand. Although demand varies in a vehicle depending on speed, acceleration, wind resistance *etc*, engine power figures for personal vehicles are quoted according to the maximum offered by the engine in question.

As an example, take the modern economical hatchback, the Nissan Micra K13. This has a 1.2 L, 59 kW engine[87]. The peak power demand that this engine is capable of delivering is 59 kW, or 0.059 MJ

s^{-1}. Hydrogen fuel has a higher heating value of 141.8 MJ kg^{-1}, therefore the hydrogen requirement for a 100% efficient H$_2$-ICE would be 0.416 g s^{-1}. Efficiency in this case is defined as the percentage of the total energy of fuel combustion which is used to perform useful work, *i.e.* is converted to kinetic energy rather than heat or noise. Engines are not 100% efficient however. BMW forecast that their purpose-build hydrogen engines could reach an efficiency of up to 50% in the coming years, already having achieved an efficiency of 42% in 2009[67]. 50% engine efficiency (*i.e.* 50% fuel combustion energy to kinetic energy) will therefore be assumed, meaning the peak hydrogen demand for the 59 kW engine would be 0.832 g s^{-1}. This number offers the minimum hydrogen evolution rate for the dehydrogenation reactor.

For the example LOHC system, the MTH system, the equivalent rate of MCH conversion is 13.419 g MCH s^{-1}. This is the required reaction rate for MCH conversion, r_A. The reaction is known to be first order.

A *pseudo*-CSTR would be used. This was described in Figure 5-3, part of Section 5.2, and is essentially a reactor which acts as a CSTR with respect to liquids, and a semi-batch reactor with respect to gases/vapours. This means that some assumptions which are valid for a CSTR are no longer applicable. A comparison is given in Table 6-4. Note that for both types of reactor, steady state operation is assumed.

Table 6-4: Differences in assumptions between a CSTR and a *pseudo*-CSTR

CSTR	*Pseudo*-CSTR
Reactor contents are perfectly mixed	Reactor contents are split into two sections, gaseous and liquid. These respective compartments are assumed to be perfectly mixed within themselves
The exit stream is compositionally identical to the reactor contents	Each of the two exit streams are compositionally identical to the part of the CSTR (gas or liquid) to which they connect
Reaction occurs throughout the reactor and is spread uniformly	Reaction occurs only in the liquid section of the reactor

As iterated in Table 6-4, it is assumed that no reaction takes place in the gas phase. The gaseous component of the system is therefore not considered to occupy a volume in the reactor. The volumes of the CSTR and *pseudo*-CSTR reactors would therefore be identical.

To demonstrate this, consider the conventional CSTR design equation. This is derived from a mass balance around the reactor. A CSTR reactor is shown in Figure 6-1, and a *pseudo*-CSTR is shown in Figure 6-2 to illustrate the differences between the two.
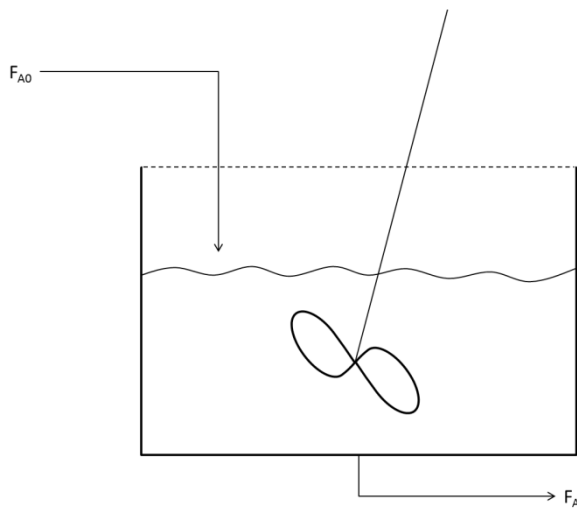
Figure 6-1: CSTR reactor
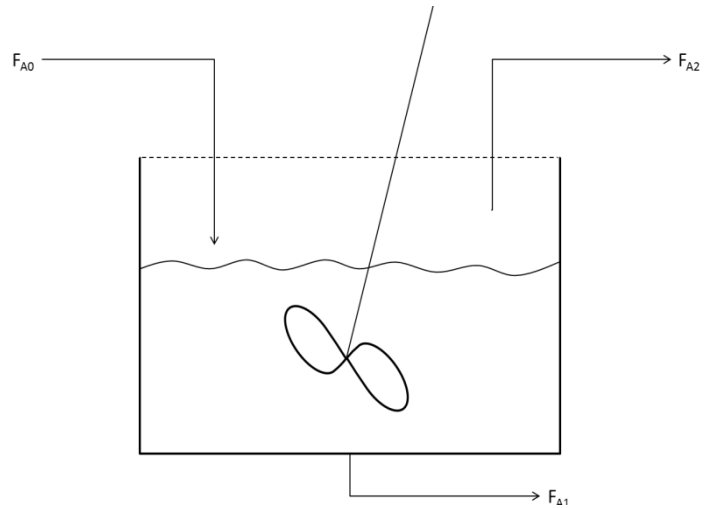
Figure 6-2: pseudo-CSTR reactor

A CSTR design equation is based on a mass balance around the reactor, which is also valid for the *pseudo*-CSTR. This is given in Equation 6-2.

Equation 6-2

Flow of A in - Flow of A out + Generation of A in the reactor = Accumulation of A in the system

Accumulation is assumed to be zero, so with reference to Figure 6-1 and Figure 6-2, Equation 6-3 and Equation 6-4 give mathematical descriptions of the mass balance for the CSTR and *pseudo*-CSTR respectively.

Equation 6-3

$$F_{A_0} - F_A + r_A V = 0$$

Equation 6-4

$$F_{A_0} - (F_{A1} + F_{A2}) + r_A V = 0$$

Where:

F_{A_0}	molar flowrate of charged carrier in/mol s^{-1}	F_A	total molar flowrate of charged carrier out/ mol s^{-1}
r_A	Rate of reaction of A/mol m^{-3} s^{-1}	F_{A1}	molar flowrate of A in the liquid exit stream/mol s^{-1}
F_{A2}	molar flowrate of A in the gaseous exit stream/mol s^{-1}	V	Volume/m^3

Note that $(F_{A1} + F_{A2}) = F_A$, assuming that the reactor is running under steady-state conditions.

If $(F_{A1} + F_{A2}) = F_A$, and the gaseous component of the system is not considered to occupy a volume in the reactor, then the mass balance is the same in the case of both reactors. The differences arise in the way that the flows are measured, and in the assumptions made about the reactor. If the mass balances are equivalent, then the design equation for a CSTR is valid for both reactors.

The volume of the reactor can be estimated using Equation 6-5, derived from the design equation for a CSTR.

Equation 6-5

$$V_{CSTR} = \frac{v_T}{k}\left(\frac{C_{A_0} - C_A}{C_A}\right)$$

Where:

V_{CSTR}	Volume of CSTR reactor/L	v_T	Total exit feed volumetric flowrate/L
k	Rate constant/L s^{-1}	C_{A_0}	Concentration of MCH before reaction/ mol L^{-1}
C_A	Concentration of MCH in exit feed/ mol L^{-1}		

To substitute in the required reaction rate, the first order rate equation given as Equation 6-6 can be used. From Equation 6-5, this yields Equation 6-7.

Equation 6-6

$$r_A = k.C_A$$

Equation 6-7

$$V_{CSTR} = \frac{v_T}{r_A}\left(C_{A_0} - C_A\right)$$

C_{A_0} is the concentration of pure MCH, 7.8 mol L^{-1}.

v_T is equal to the sum of the volumetric flowrates of hydrogen, MCH and toluene. The mass (hence moles, n_{H_2}) of hydrogen in the exit feed is known due to the hydrogen flowrate requirement for a 59 kW engine specified earlier. Therefore, the volumetric flowrates of MCH and toluene can be calculated from this.

Equation 6-8

$$v_{MCH} = \frac{n_{MCH}}{\rho_{MCH}} = \frac{n_{H_2}.(1 - x_A)}{\rho_{MCH}.3x_A}$$

Equation 6-9

$$v_{tol} = \frac{n_{MCH_0}.x_A}{\rho_{tol}} = \frac{n_{H_2}}{3\rho_{tol}}$$

Equation 6-10

$$v_{H_2} = \frac{n_{H_2}}{\rho_{H_2}} = \frac{n_{H_2}.R.T}{P_T}$$

Where:

T	Temperature/K	ρ_i	Density of i, mol L^{-1}
		P_T	Total pressure, atm

Notably, v_{H_2} is the only volumetric flowrate to be affected by pressure. It is assumed that the hydrocarbons are in the liquid state with no vapour pressure and are incompressible (although this assumption is untrue, and is discussed in the following paragraphs). Equation 6-10 shows, as may be anticipated, that pressure is inversely proportional to reactor volume.

One final term in Equation 6-7 must be defined, C_A.

Equation 6-11

$$C_A = \frac{n_{MCH}}{v_T}$$

Equation 6-12 shows the relationship (by mass balance) between n_{MCH} and n_{H_2}, which can be substituted into Equation 6-11 to give Equation 6-13.

Equation 6-12

$$n_{MCH} = \frac{n_{H_2}(1 - x_A)}{3x_A}$$

Equation 6-13

$$C_A = \frac{n_{H_2}(1 - x_A)}{3x_A v_T}$$

Using Equation 6-7, reactor volume can now be calculated based on x_A, which in turn is based on the reaction conditions, P_T and T.

Assuming ΔH_d and ΔS_d are constant, the T required to reach a given x_A can be calculated for any value of P_T. This was calculated for the MTH system in Chapter 4. Necessary conditions to achieve selected values of x_A are given in Table 6-5.

Table 6-5: Temperatures (given in K) required to reach given conversions under variable pressure

P_T/atm x_A	1	5	10	15	30	50
0.999	641.2	734.6	783.9	815.8	877.0	928.3
0.9	569.3	641.8	679.0	702.9	747.8	784.8
0.8	557.4	626.7	662.2	684.9	727.5	762.4
0.74	549.1	616.2	650.5	672.4	713.3	746.9

At this stage, it should be noted that the MTH system is unsuitable for LP-DR no matter what the reactor volumes are. Under the conditions specified in Table 6-5, the hydrocarbons are no longer in the liquid phase. Furthermore, there is no window of appropriate conditions, as demonstrated by Figure 6-3, which shows the boiling points (BP) for MCH and toluene under variable P_T. Also shown is the T required to attain the minimum x_A of 0.74 for the same P_T. Even though P_T is taken as high as 1000 atm, there is never a point where x_A = 0.74 is attained at a T below the boiling point of *both* hydrocarbons. The MTH system is therefore unsuitable for LP-MCHDR as it cannot attain a suitable

x_A while remaining in the liquid phase. However, for the purposes of this example, the analysis shall be completed as if the hydrocarbons were in the liquid phase.
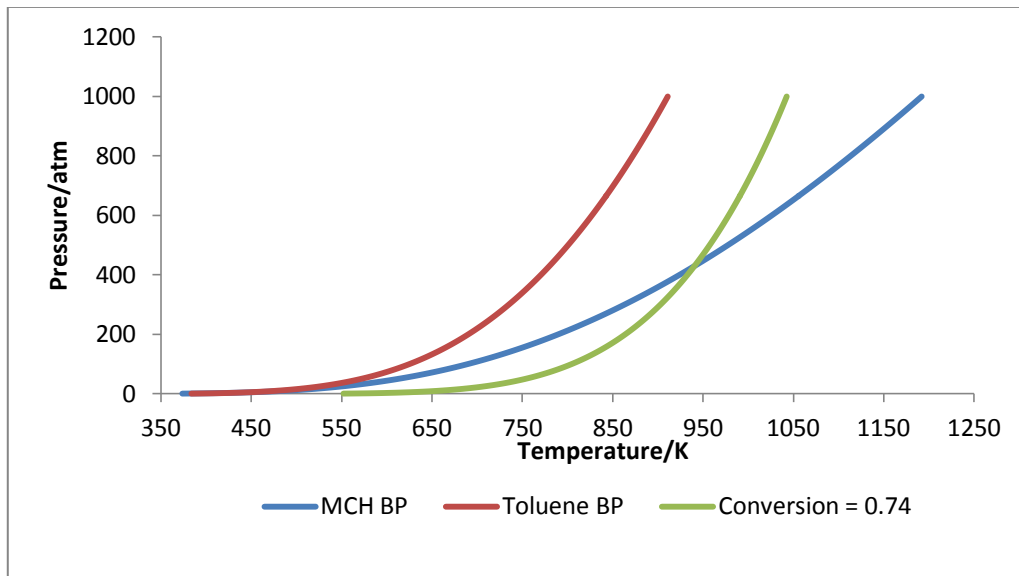
Figure 6-3: Boiling points of MCH and toluene alongside T/P_T combinations required to attain x_A = 0.74

If the hydrocarbons were in the liquid phase under the conditions in Table 6-5, the next step would be to calculate the reactor volume, V_{CSTR}, under various conditions using Equation 6-7, and finding out under which conditions the reactor volumes are equal to or less than the maximum reactor volumes given in Table 6-3. The results are shown in Figure 6-4.
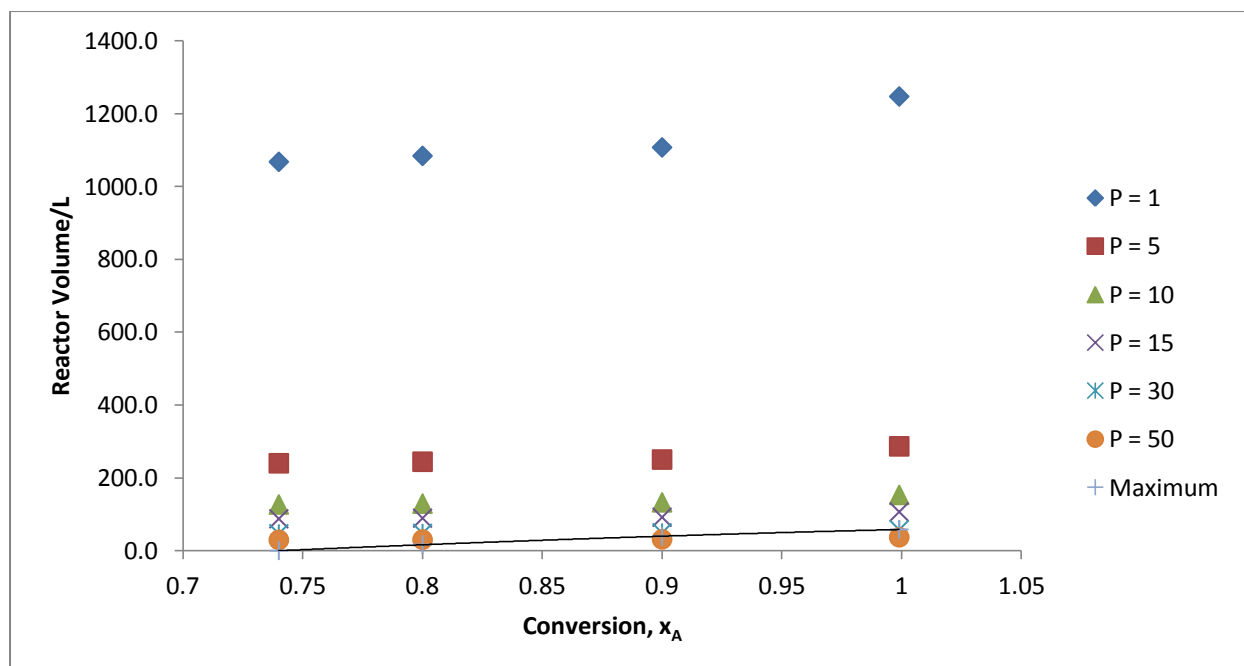
Figure 6-4: Conversion, x_A, vs reactor volume at various reactor pressure, P_T. The trendline represents the maximum feasible reactor volume

Figure 6-4 demonstrates that the reactor pressure has a noticeable effect on the reactor volume, due to the presence of hydrogen gas. Figure 6-4 is shown again as with the P_T = 1 line omitted, in order to better view the remaining results.
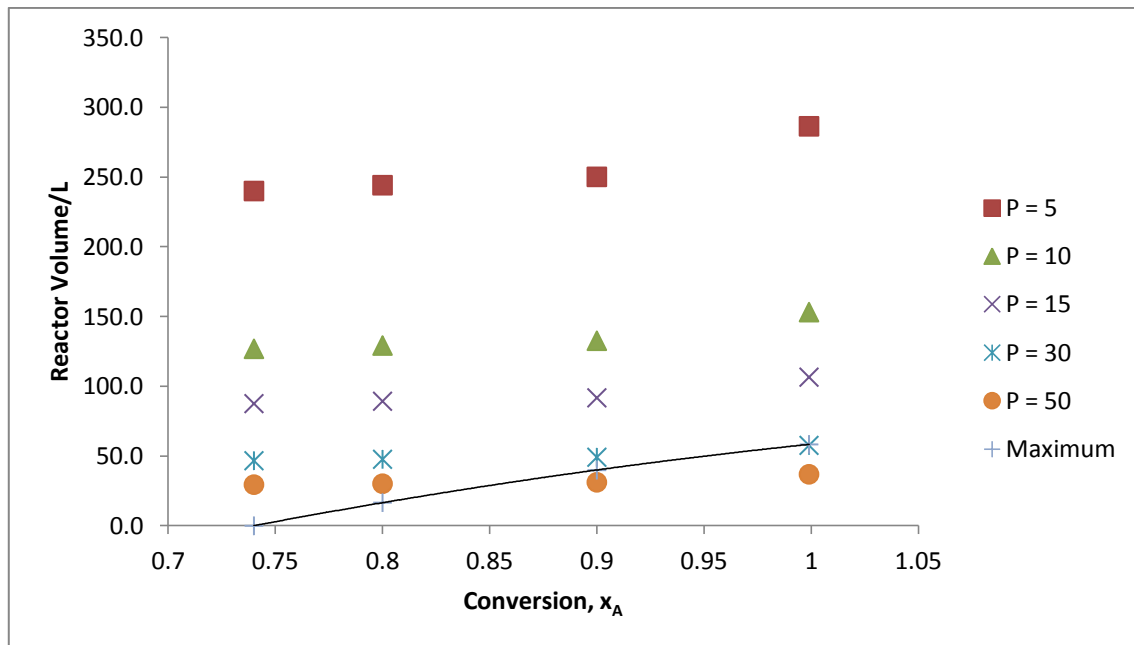
Figure 6-5: Conversion, x_A, vs reactor volume at various reactor pressure, P_T (P_T = 1 omitted). The trendline represents the maximum feasible reactor volume

Figure 6-5 shows that P_T must be a minimum of approximately 30 atm in order to provide a reactor volume which is sufficiently low. This is the case for a high x_A of 0.999. For lower x_A values, the V_{CSTR} must be lower, hence P_T must be higher.

To minimise V_{CSTR} as well as fuel storage volume, it is advantageous to seek the highest x_A possible. However, a higher x_A requires a higher T, which encourages a higher hydrocarbon vapour pressure.

This vapour pressure should be assessed at this point to ensure that there is a window of suitable operating conditions below the Maximum V_{CSTR} line.

The first stage of this is to define the restriction on VLE behaviour of the liquid hydrocarbons in the system. It was stated at the start of this chapter that at least 96.1% carrier should be retained after reaction, ready to recharge with hydrogen and use again.

For a general LP-LOHC system, Equation 6-15 gives the equilibrium partial pressure of hydrocarbon (hydrocarbon being the mixture of charged and discharged hydrogen carrier), P_{HC}.

Equation 6-14

$$P_{HC} = y_{CC}P_{CC}^* + y_{DC}P_{DC}^* = y_{HC_g}P_T$$

Where

y_i	mole fraction of i in reactor	DC	Discharged Carrier
P_i^*	(saturated*) vapour pressure of i	g	gas phase
CC	Charged Carrier	P_T	Total system pressure
HC	Hydrocarbon		

This assumes that all dehydrogenation is occurring in the liquid phase (no gas phase reaction).

Equation 6-14 (Raoult's Law) gives the pressure exerted by vapour-phase hydrocarbons, P_{HC}. This is calculated by multiplying the mole fraction of the hydrocarbon in the reactor, y_i, with the saturated vapour pressure of the pure hydrocarbon at a given temperature, P_i^*, and taking the sum of these values for each hydrocarbon species involved.

This assumes ideal behaviour of liquids and vapour, but the liquid mixtures are not expected to behave ideally. For an ideal mixture, the enthalpy of mixing, ΔH_{mix} = 0. Although data is unavailable for a binary mixture of MCH and toluene, a similar mixture of benzene and cyclohexane at 20 °C invokes an enthalpy of mixing of up to 870 J mol^{-1} when the mole fraction of benzene is 0.535[88]. It would therefore not be expected for an MCH and toluene mixture to behave ideally, but as this calculation is made for indicative purposes only, and will not have a direct impact on any experimental work, it will be assumed that Raoult's Law is valid. It should be noted therefore that the calculated figures should be used only as a suggestion of an appropriate operating temperature for a LP-DR system.

To compete with a gas phase dehydrogenation system, the mole fraction of gaseous hydrocarbon, y_{HC_g}, is restricted to a value of 3.9% of the total hydrocarbon present. Therefore, Equation 6-15 describes the restriction on VLE behaviour of LOHCs for liquid-phase operation.

Equation 6-15

$$y_{HC_g} = \frac{y_{cc}P_{CC}^* + y_{DC}P_{DC}^*}{P_T} \leq 0.039$$

In Equation 6-15, the saturated partial pressures, P_{CC}^* and P_{DC}^* are calculated in the form given in Equation 6-16.

Equation 6-16

$$\ln(P_i^*) = C1 + \frac{C2}{T} + C3\ln T + C4T^{C5}$$

Values of C_i for the calculation of P_i^* in Pa are molecule-specific constants given in data tables[75].

Substituting for the pressure terms in Equation 6-15 using Equation 6-16 gives a definition of y_{HC_g} which contains several temperature terms. This is shown in .

Equation 6-17

$$y_{HC_g} = \frac{y_{cc}e^{C1 + \frac{C2}{T} + C3\ln T + C4T^{C5}} + y_{DC}e^{C1' + \frac{C2'}{T} + C3'\ln T + C4'T^{C5'}}}{P_T}$$

Using Equation 6-17, the P_T and T combinations which give a suitable V_{CSTR} (those under the Maximum line in Figure 6-5) can be scrutinised, and if it exists, a set of conditions can be found which satisfies both criteria.

Equation 6-17 offers a mathematical description of the restrictions on the liquid-phase dehydrogenation system in terms of VLE behaviour. However, this assumes that the constants taken from (C1, C2 *etc*) are available for any carrier under investigation, which is unlikely to be the case.

It may therefore be useful to derive a second mathematical description of the restrictions using and equation for saturated vapour pressure which is more common. One such equation is the Antoine equation (Equation 6-18). In same way that Equation 6-17 was derived, the Antoine equation can be used to derive Equation 6-19. Using Equation 6-19 in place of Equation 6-17 offers no difference to the final answer, but offers a practical benefit by using molecule-specific constants (*A, B, C*) which are more widely available than the constants used in Equation 6-17 (*C1, C2 etc*).

Equation 6-18

$$log_{10}P_i^* = A - \frac{B}{C + T}$$

Where

T temperature/K A, B, C Molecule-specific constants

Equation 6-19

$$y_{HC_g} = \frac{y_{CC}10^{\left(A-\frac{B}{C+T}\right)} + y_{DC}10^{\left(A'-\frac{B'}{C'+T}\right)}}{P_T} \leq 0.039$$

Equation 6-19 is a useful tool in the same way as Equation 6-17, but uses constants which are more widely available for a larger selection of molecules. Care must be taken however, because the Antoine equation often takes a different form, where the log (base 10) is replaced by a natural log (ln), and the constants are altered to reflect this change. In this case, Equation 6-19 can be altered by simply replacing the 10^x term with e^x.

Assuming a suitable P_T and T combination can be found which results in a V_{CSTR} below the maximum V_{CSTR}, under which the hydrocarbon components have a sufficiently low vapour pressure according to Equation 6-17 or Equation 6-19, ΔG_d can now be calculated for these conditions. No such P_T and T combination exists for the MTH system, so ΔG_d will be calculated for x_A = 0.999, P_T = 30 atm and T = 877.0 K.

The equilibrium constant, K, can be calculated using the definition derived in Chapter 4.

$$K = \frac{27\, x_A^4\, P_T^3}{(1+3x_A)^3(1-x_A)}$$

ΔG_d can hence be calculated using the relationship:

$$\Delta G_d = -RTlnK$$

For the MTH system under the specified conditions, this results in a ΔG_d of -17.7 kJ mol^{-1}..

Note that this method assumes equilibrium conditions.

6.2.2 Testing the mathematical restrictions

To test Equation 6-17, it will be used to find the highest x_A where the VLE restriction of $y_{HC_g} \leq 0.039$ is satisfied for the MTH system. The way in which the VLE behaviour affects the hydrocarbon content

of the exit stream depends on the type of reactor used. This is because toluene and MCH have slightly different vapour pressures at a given temperature, and the relative proportions of these two components in the reactor will dictate the exact amounts of vapour-phase hydrocarbon for given conditions and conversions. For example, if a *pseudo*-semi-batch reactor were used, the vapour-phase hydrocarbon content would be variable depending on the reaction time, *i.e.* the proportions of MCH and toluene would vary over time, hence so would the relative amounts of vapour-phase hydrocarbon. If the reactor chosen is a *pseudo*-CSTR instead, a steady-state composition could be expected when the reactor has reached equilibrium *i.e.* the contents of the reactor are compositionally identical to the sum of the exit streams, and would not vary with time after reaching equilibrium. A steady-state system like this is more suitable for this application, because flushing and refilling a batch reactor would take time, and could cause inconsistencies in hydrogen supply, whereas a constant and predictable steady-state hydrogen output would ensure a predictable hydrogen supply.

The model is therefore carried out on the basis of a *pseudo*-CSTR reactor, where x_A is constant, and is not a function of time. It follows therefore that the ratio of MCH:toluene in the reactor, both in the liquid and vapour phases, is constant at equilibrium.

Equation 6-17 will be tested on this basis. Figure 6-6 shows the results of this analysis. Note that to simplify the model, the Ellingham Approximation35 was used, i.e. ΔH_d and ΔS_d were treated as constants, regardless of temperature change. The chosen temperature range, 178.2 − 572.1 K, was used because this is the range in which the constants (C1, C2 etc) in Equation 6-17 are valid.

It was determined earlier that x_A for the MTH system would need to be at least 0.74 in order to be competitive with 450 bar compressed hydrogen on the basis of volume. Clearly the MTH system is not capable of delivering this while satisfying the restriction on vapour pressure, because the maximum x_A within the temperature range studied while y_{HC_g}= 0.039 is 0.004. This maximum corresponds to a reactor pressure, P_T, of 872 atm.

This confirms that the MTH system is not useful within the required thermodynamic and VLE constraints, and shows that the model designed around Equation 6-17 is functional.
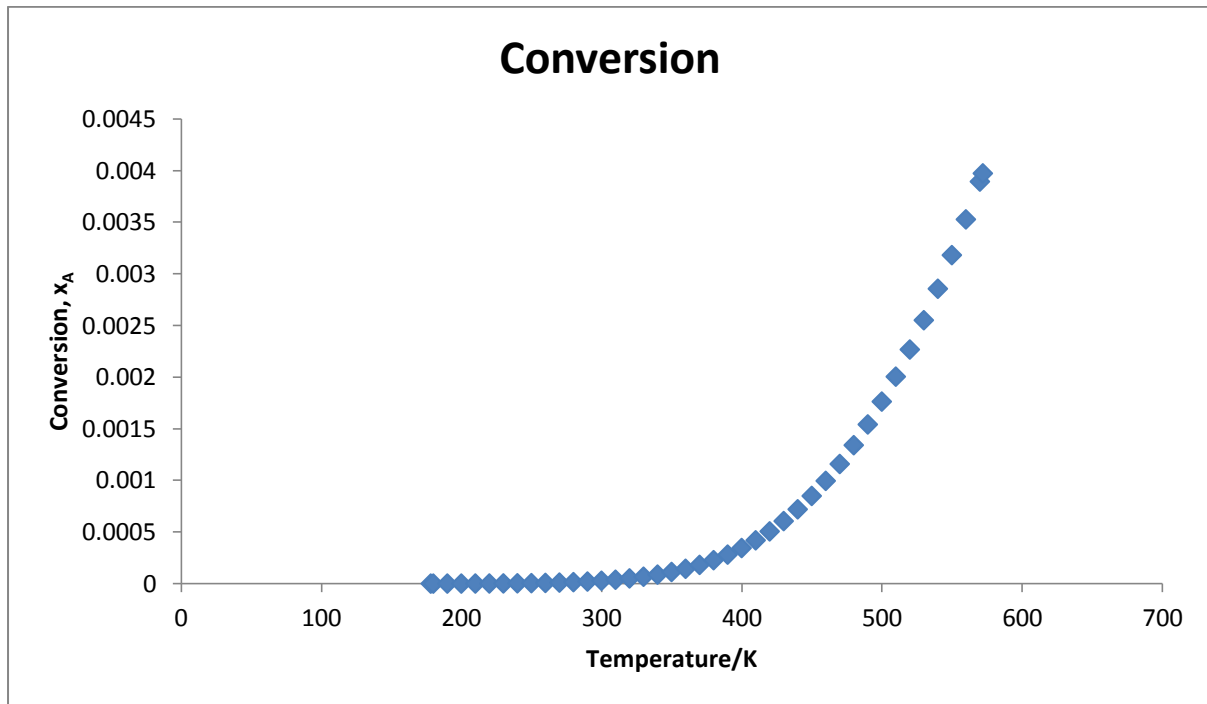
Figure 6-6: Maximum conversion, x_A, for the MTH system while satisfying the maximum restriction on hydrocarbon vapour pressure - y_{HC_g} =0.039

6.2.3 Maximising Conversion

6.2.3.1 Why Maximise Conversion?

As shown in the preceding sections, for the MTH system, conversion, x_A, cannot be high enough to satisfy restrictions on system volume while simultaneously satisfying the restriction on hydrocarbon vapour pressure. However, while assessing other carriers with more favourable VLE behaviour (*i.e.* lower volatility), some thought should be given to maximising x_A. The aim of maximising x_A in this way is to achieve a hydrogen mole fraction sufficient to cause explosion in air. The lower explosive limit (LEL) of hydrogen is 4% by volume in air[86]. Hydrogen is taken from the reactor via sweep gas and transported to the engine where it is mixed with air and exposed to a spark, when it ignites and causes the piston in the engine to move. If less than 4 vol% hydrogen is present after mixing with sweep gas in the reactor and air in the engine, no ignition will be possible. Although equilibrium conversion, x_A, can be overcome by removing hydrogen gas from the reactor, this hydrogen volumetric concentration cannot be overcome. Therefore, x_A should be maximised even though it can be exceeded.

It will be mathematically demonstrated that the volume of hydrogen, V_{H_2}, emitted is proportional to equilibrium conversion, x_A, in the coming pages. An overview of the dehydrogenation system is given in Figure 6-7.
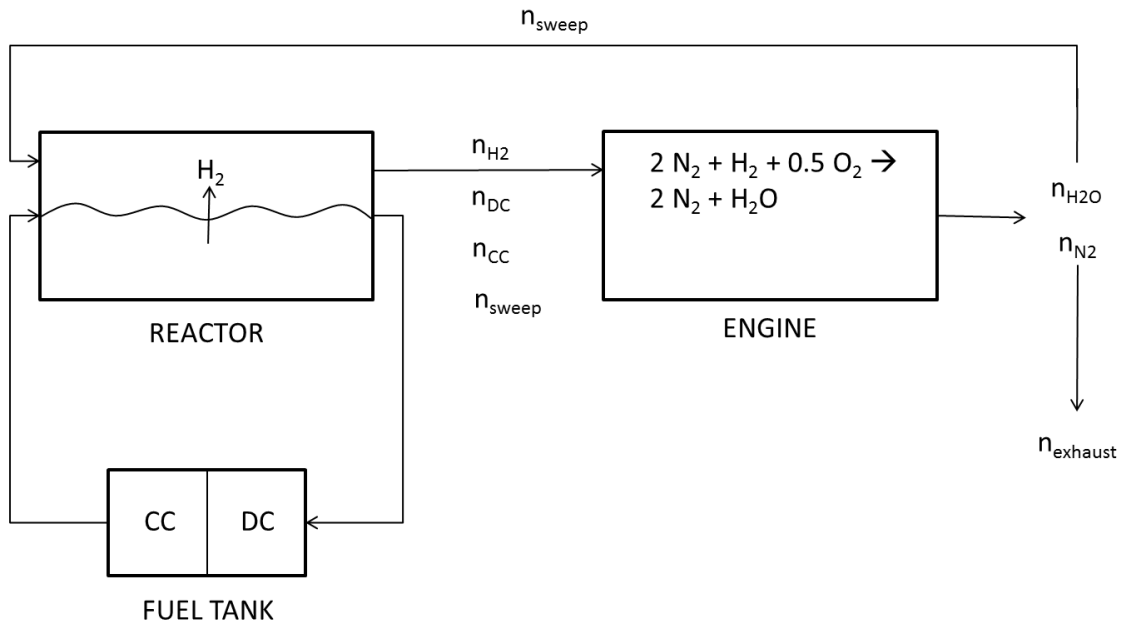
Figure 6-7: Black-box dehydrogenation system, where DC = Discharged Carrier, CC = Charged Carrier

The LEL of hydrogen (4%) is measured at 20 °C and atmospheric pressure. For the purposes of this model, it is assumed that this hydrogen LEL is valid across all temperatures and pressures studied in this work. For combustion to occur, the hydrogen content must be a minimum of 4 vol% in the engine.

The first step in analysing the effect of x_A on the volumetric flowrate of hydrogen sent to the engine, $V_{H_2}{}^E$, is to calculate how x_A affects the volumetric production of hydrogen in the reactor, $V_{H_2}{}^R$. A relationship between $V_{H_2}{}^R$ and x_A is given in Equation 6-20.

Equation 6-20

$$V_{H_2}^R = \frac{y_{H_2}^R n_{H_2}^R R T^R (1 + 3x_A)}{3x_A P_T^R}$$

Where

$V_{H_2}^R$ Volume of hydrogen in reactor/m^3 $n_{H_2}^R$ Moles of hydrogen in reactor

T^R Temperature in reactor/K P_T^R Total pressure in reactor/Pa

$y_{H_2}^R$ mole fraction of hydrogen in reactor

Using the data generated for previous chapters concerning the MTH system, Figure 6-8 was produced to give an indicative relationship between $V_{H_2}^R$ and x_A.
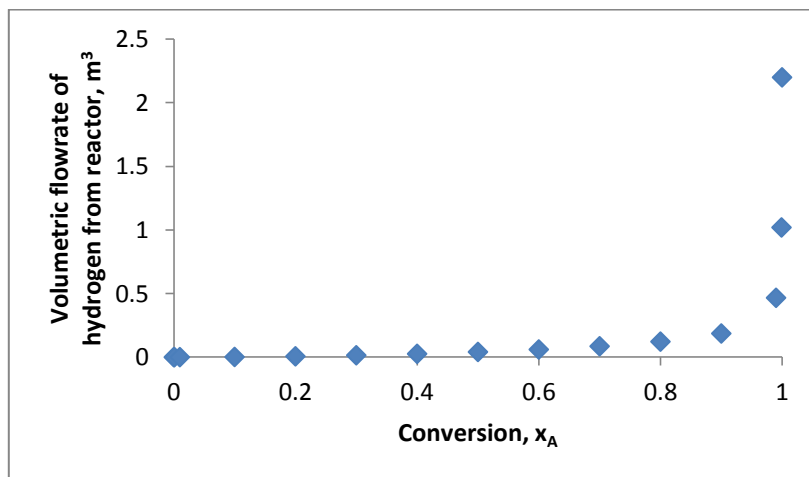
Figure 6-8: The relationship between equilibrium conversion, x$_A$, and volume of hydrogen in the reactor, $V_{H_2}^R$. Based on the MTH system, with an arbitrary incoming flowrate of A, n_{A_0}, of 1 mol/s

Figure 6-8 indicates that high x_A is advantageous if seeking to maximise the hydrogen volume.

Knowledge of $V_{H_2}^R$ is useful, but as aforementioned, the quoted minimum value of hydrogen volume (4%) does not apply to $V_{H_2}^R$, but rather to $V_{H_2}^E$, the volume of hydrogen in the engine. The next step is therefore to define how the partial volume of hydrogen changes between the reactor and the engine. This is given in Equation 6-21.

Equation 6-21

$$V_{H_2}^E = \frac{T^E P_T^R}{3.5 T^R P_{H_2}^E} \cdot V_{H_2}^R$$

Where

$V_{H_2}^E$ Volume of hydrogen in engine/m^3 $P_{H_2}^E$ Hydrogen pressure in engine/Pa

T^E Temperature in engine/K

Equation 6-21 predictably indicates that $V_{H_2}^E$ is dependent on $V_{H_2}^R$, for which it has been established that high x_A is advantageous. Therefore, it is advantageous to maximise x_A in order to promote high $V_{H_2}^E$.

Equation 6-20 can now be substituted into Equation 6-21 and simplified to give a definition of $V_{H_2}^E$ in terms of the moles of hydrogen produced in the reactor. This is given in Equation 6-22.

Equation 6-22

$$V_{H_2}^E = \frac{n_{H_2}^R R T^E}{3.5 P_{H_2}^E} = \frac{3 n_{A_0} R T^E}{3.5 P_{H_2}^E} x_A$$

For a full derivation of Equation 6-22, see Appendix K. Due to the way this equation was derived, it relies on several assumptions, which are as follows:

- The 4% LEL is independent of pressure and temperature
- Gases behave ideally
- System is under equilibrium conditions
- Hydrogen combustion is stoichiometric
- $n_{sweep} = n_A^E = n_B^E = 0$
- For every mole of reacted A, 3 moles of hydrogen are evolved.

As aforementioned, the aim of seeking to maximise $V_{H_2}^E$ is to meet or exceed the LEL of hydrogen and generate an explosive mixture of hydrogen and oxygen in the engine. This derivation indicates that x_A should be maximised to achieve the highest possible $V_{H_2}^E$. This is the reason for maximising x_A.

6.2.3.2 How to Maximise Conversion

The position of thermodynamic equilibrium is the first factor to consider. The overall conversion of charged carrier can exceed equilibrium constraints on conversion by constantly removing product hydrogen from the reactor, therefore causing the system to resist the change and increase

conversion. This is possible due to the dual-phase nature of the system. The gas streams and liquid streams of the system are separate, and so their flow rates are also separate. This is illustrated in Figure 6-9.
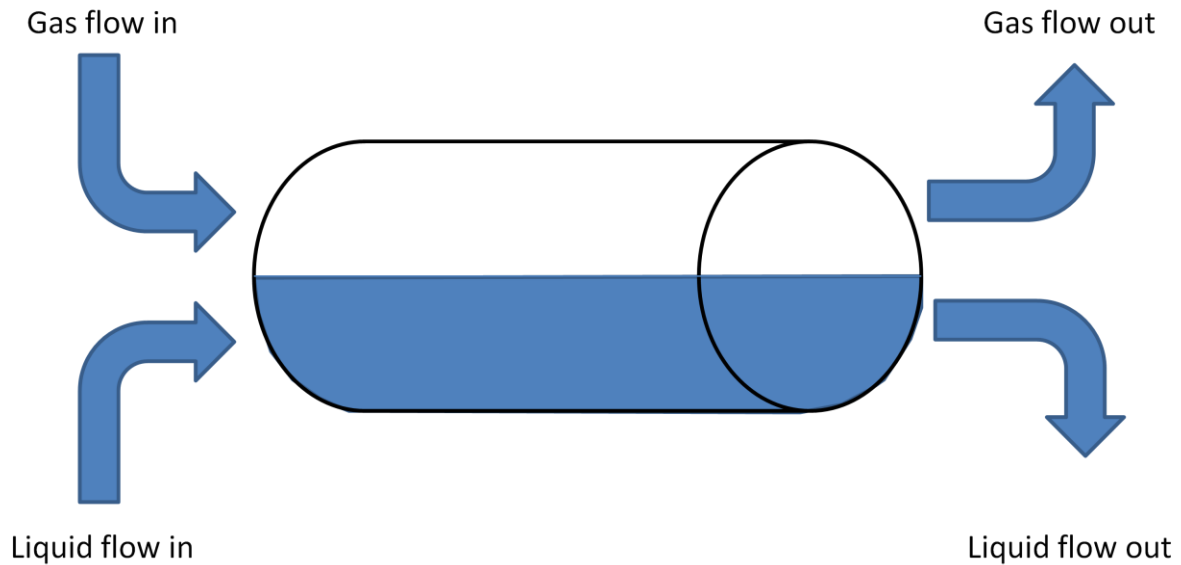
Figure 6-9: Gas and liquid flow rates are separate in this dual-phase system

This can be used to the best advantage possible, *e.g* if it were favourable, it would be possible to have a slow liquid flow rate (to give maximum residence time) but a fast gaseous flow rate (to maximise the rate of hydrogen removal).

Although the conversion at thermodynamic equilibrium can theoretically be overcome by manipulating the relative gas and liquid flow-rates, it is still favourable to maximise the equilibrium conversion as much as possible. As aforementioned, the position of thermodynamic equilibrium dictates the maximum $y_{H_2}^R$ (hence $V_{H_2}^E$) achievable. An equation for the equilibrium constant K for MCH dehydrogenation was derived in Chapter 4. Equation 6-23 gives an equation for K for a general dehydrogenation reaction, where b is the stoichiometric moles of hydrogen produced. Equation 6-24 is the same equation rearranged in terms of total system pressure, P_T.

Equation 6-23

$$K = \frac{b^b x_A^{(b+1)} P_T^b}{(1 + bx_A)^b (1 - x_A)}$$

Equation 6-24

$$P_T = \sqrt[b]{\frac{K.(1 + 3x_A)^b.(1 - x_A)}{b^b x_A^{(b+1)}}}$$

Equation 6-23 shows that P_T affects x_A. Using Equation 6-24, an indicative graphical relationship between P_T and x_A at a constant temperature can be plotted. This is given as Figure 6-10, which is based on the MTH system at equilibrium at a constant temperature of 534 K.
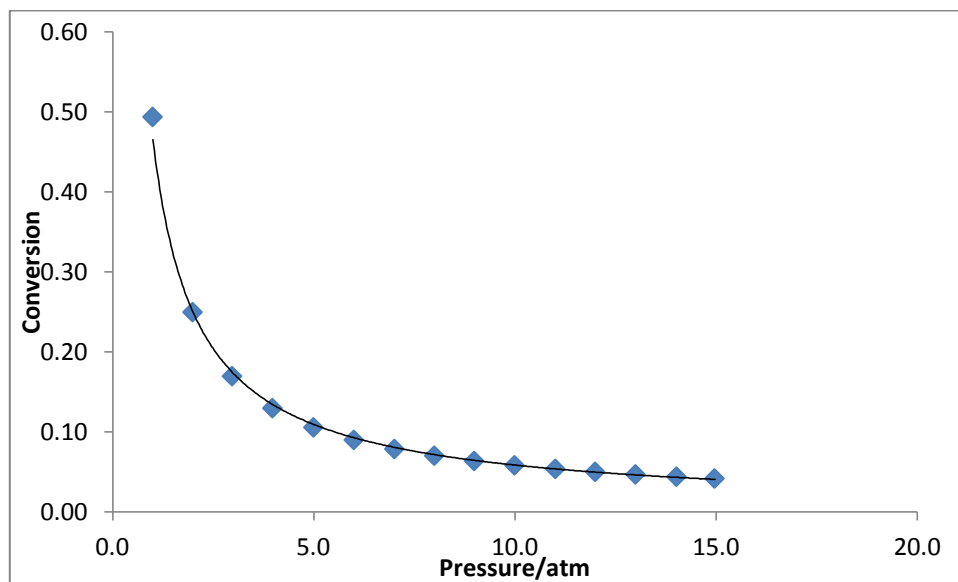
Figure 6-10: The effect of P_T on x_A at a constant temperature of 534 K for the MTH system

Figure 6-10 shows that x_A is inversely proportional to P_T within the pressure range studied experimentally in Chapter 4. Therefore, P_T should be experimentally minimised to maximise x_A.

However, as the studies in the earlier sections of this chapter show, this is an oversimplification. Other factors must be considered. Elevated pressure:

- allows access to higher temperatures while maintaining a low hydrocarbon vapour pressure
- decreases reactor volume.

Although it should be remembered that pressure is inversely proportional to x_A, other system factors should be considered before dropping the pressure.

6.2.4 **Thermodynamic/Kinetic Parameters – Summary**

The difficulty of the LP-DR system lies within the number of competing restrictions which the system depends on. x_A must be high enough that the on-board fuel storage does not exceed practicality or become uncompetitive with rival technologies; hence, ΔG_d must be sufficiently low to result in the given conversion; carrier volatility must be low enough that $y_{HC_g} \leq 0.039$, or otherwise the dehydrogenation must be favourable at a low enough temperature that the vapour pressure restriction is met; $V_{H_2}^E \geq 4\%$ in order to generate an explosive mixture in the engine. Many of these factors involve reaction conditions which compete *e.g.* for a given temperature, lower P_T would stimulate higher x_A (favourable) but would simultaneously increase hydrocarbon volatility, and hence increase y_{HC_g} (not favourable). In analysis of new potential carriers, the task is therefore to find a window of operation which satisfies all criteria.

It has been explicitly shown that the MTH system has no such window. The search for new carriers can now be directed by the failings of the MTH system. The new direction is outlined in Table 6-6.

Table 6-6: Lessons learned from the MTH system

MTH system problem	New carrier solution
No reaction temperature/pressure combination exists where x_A is high enough to offer a satisfactory V_{CSTR}, and simultaneously $y_{HC_g} \leq 0.039$.	Seek a carrier with a combination of lower volatility so that higher temperatures can be employed, *and* ΔG_d is lower than that of the MTH system for a given temperature so that very high temperatures are not required.
V_{CSTR} is restrictive when compared to 450 bar compressed hydrogen.	Employ a carrier with a higher gravimetric and volumetric hydrogen density so that fewer kg/L are required on-board the vehicle.

This approach will be taken in the search for a new carrier.

6.3 Choice of carriers to examine

A list of candidate carriers should now be fabricated and evaluated against the criteria discussed in the preceding section, as well as other important characteristics *i.e.* physical properties.. Outlined

below are three different carrier "types" which define the carriers to be examined. Following this, the list of carriers to be assessed is given in Table 6-8.

6.3.1 Cyclohexane/Benzene Derived Carriers

In order to fit the aforementioned carrier specifications, the initial search will be of substituted benzene rings, *i.e.* benzene rings with substitutions other than the methyl group of methylcyclohexane. This should encourage lower carrier volatility than MCH due to:

- The molecules having higher molecular weight

- Hydrogen bonding between carrier molecules in the case of substituent groups which include heteroatoms.

A list of candidate molecules will be composed, and these will first be assessed for suitability by checking for side reactions which the side-groups may participate in under the necessary redox conditions for (de)hydrogenation.

6.3.2 Heterosubstituted ring carriers

Heterosubstituted rings have been studied for their ability to promote hydrogen release more than their hydrocarbon counterparts. In particular, the introduction of nitrogen atoms into a carbon ring can thermodynamically favour hydrogen release[18, 35, 86, 89, 90]. This is because the nitrogen atom has a strong electron donating effect due to the presence of a lone electron pair on the atom, and this donating effect consequently weakens the adjacent C-H bonds. In addition, the N-H bond is typically weaker than the C-H bond, so hydrogen to be extracted from an N-H bond requires less energy to remove. This effect can be observed by comparing a cyclohexane dehydrogenation with various nitrosubstituted rings, for example, as shown in Table 6-7.

$$\text{Carrier} \longrightarrow \text{Depleted Carrier} + 3\ H_2$$
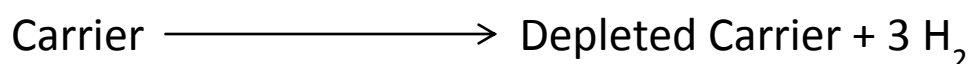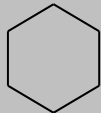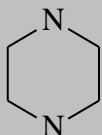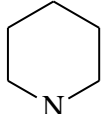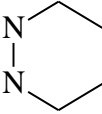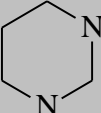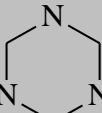
Figure 6-11: Reaction scheme corresponding to Table 6-7.

Table 6-7: Enthalpies of dehydrogenation for different *N*-substituted cyclohexane rings. Information gathered from [35]. Information is calculated except where experimental data is available, given in brackets.

Carrier	ΔH_d/kJ mol (carrier)$^{-1}$	Carrier	ΔH_d/ kJ mol (carrier)$^{-1}$
	221.06 (205.99)		188.41 (170.82)
	202.22 (187.15)		208.50
	179.61		163.29

An estimated difference of 58 kJ mol^{-1} exists between dehydrogenation enthalpies of cyclohexane and 1,3,5-triazine.

Although nitrogen is not the only heteroatom that can be used, it is the most promising and the most extensively surveyed opportunity in the literature. Those papers which have investigated other heteroatom substitutions have not been met with such success, *e.g.* a paper from Moores *et al*[89] shows that a nitrosubstituted benzimidazoline released hydrogen readily, whereas an identical substitution with oxygen in place of nitrogen achieves 0% conversion. Therefore, this study focuses on nitrosubstitutions only.

6.3.3 Low ΔH_d carriers and autothermal dehydrogenation processes

Air Products and Chemicals Inc (APCI) have been an authority on LOHC technology since they collaborated with the US Department of Energy as part of the DOE Hydrogen Programme. During the time of this collaboration, APCI have published several progress reports on LOHC technology[91-95] as well as three US patents[96-98]. Although the researchers involved never state the intention to carry out liquid-phase dehydrogenation, they broadly take the same approach in carrier discovery as concluded in this chapter, stating that their objectives are to seek the "optimal heat of dehydrogenation (10 – 13 kcal/mol H$_2$), [42 – 54 kJ/mol H$_2$] enabling the catalytic dehydrogenation

at unprecedented temperatures (<200 °C)", and furthermore to find a carrier with "Low volatility (boiling point> 300 °C)…"[94].

There has also been some research in the literature concerning molecules which feature hydrogen storage capabilities twinned with a side group which can react with air (O_2) exothermically. This is advantageous because this exothermic oxidation can theoretically counter the endothermic dehydrogenation reaction, giving a low net enthalpy (as low as zero or less). If the exotherm of the oxidation is sufficient, the on-board part of process could be made autothermal, a concept which has the potential to revolutionise hydrogen storage. Energy input would still be required for the off-board hydrogenation, but the dehydrogenation would need no external heat input from hydrogen combustion or waste heat *etc*. An example is the use of fluorene as a carrier – a dehydrogenation and oxidation scheme is given in Figure 6-12 (fluorene is shown as the bottom-left molecule).

These carriers are therefore the final group to be tested for suitability.
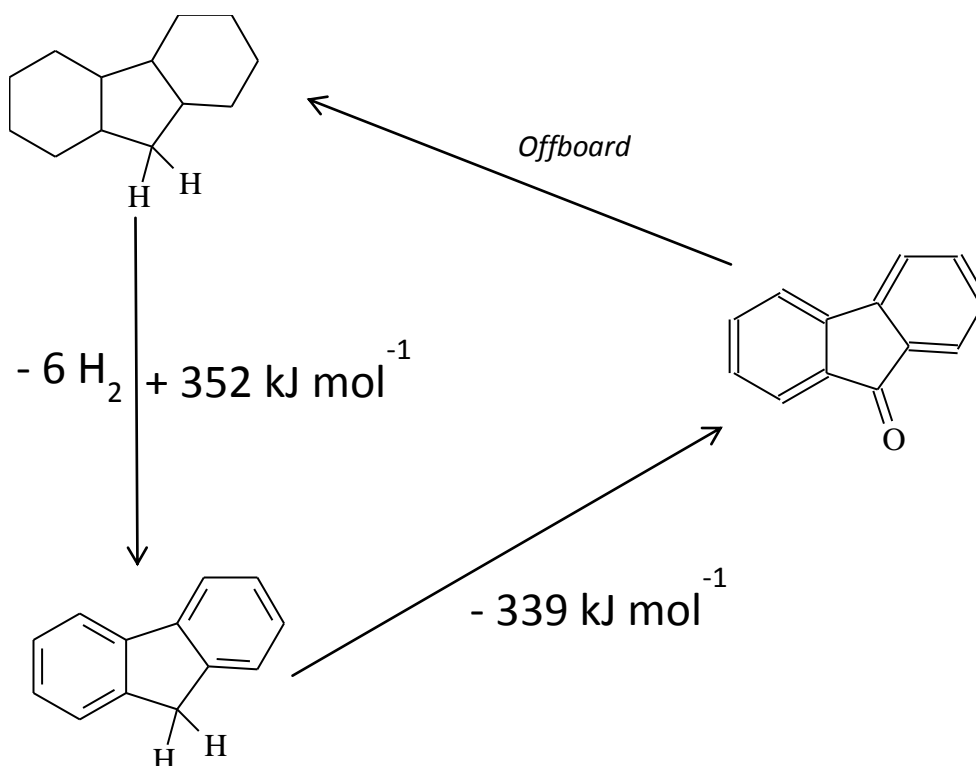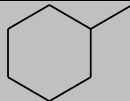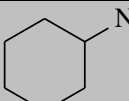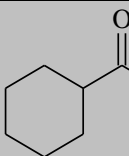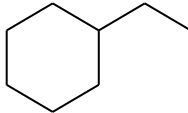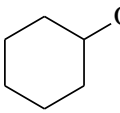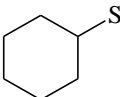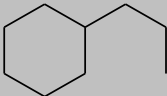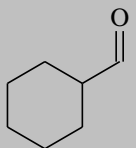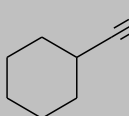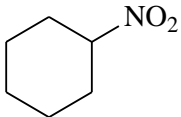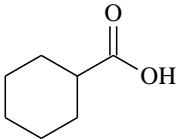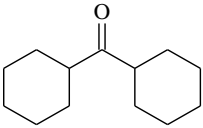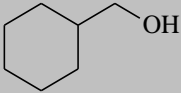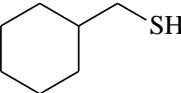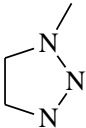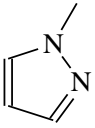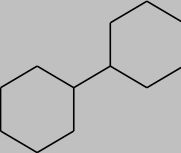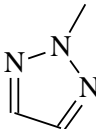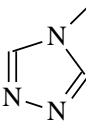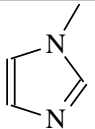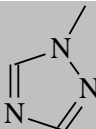
Figure 6-12: A nearly autothermal on-board dehydrogenation process (net enthalpy = + 13 kJ mol^{-1}). The enthalpy for hydrogenation is not specified, but would take place off-board the vehicle and so energy input at this stage is not crucial
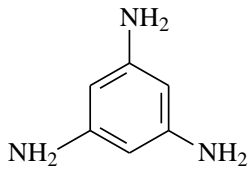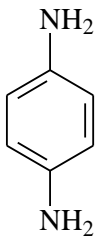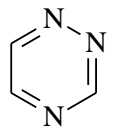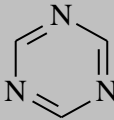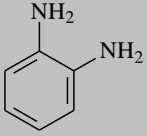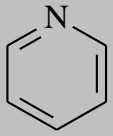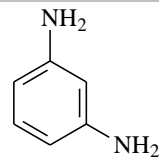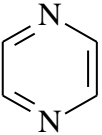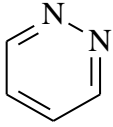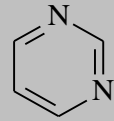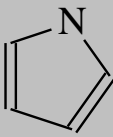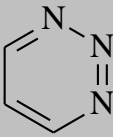
6.4 Candidate carrier molecules

Table 6-8 shows the candidate molecules which have been chosen for examination.

Table 6-8: Cyclohexane/benzene derived (1-15, hydrogenated form), Nitrosubstituted (16-39, dehydrogenated), low ΔH_d (40-42, dehydrogenated), autothermal (43–44, dehydrogenated)

No.	Compound	H$_2$ wt%	No.	Compound	H$_2$ wt%	No.	Compound	H$_2$ wt%
1	Methylcyclohexane	6.2	5	Cyclohexanamine	6.1	9	Cyclohexanecarboxamide	4.7
2	Ethylcyclohexane	5.4	6	Cyclohexanol	6.0	10	Cyclohexanethiol	5.2
3	Propylcyclohexane	4.8	7	Cyclohexanecarboxaldehyde	5.4	11	Cyclohexanecarbonitrile	5.5
4	Nitrocyclohexane	4.7	8	Cyclohexanecarboxylic acid	4.7	12	Dicyclohexylmethanone	6.2

#	Structure	Value	#	Structure	Value	#	Structure	Value
13	Cyclohexanemethanol	5.4	18	1,2,4-triazole	5.6	23	1,3,4-triazole	5.6
14	Cyclohexanemethanethiol	4.6	19	methyl-1,2,3-triazole	4.6	24	1-methyl pyrazole	4.7
15	Bicyclohexane	7.3	20	1,2,5-triazole	5.6	25	Pyrazole	5.7
16	Methyl-1,2,5-triazole	4.6	21	methyl-1,3,4-triazole	4.6	26	1-methyl imidazole	4.7
17	methyl-1,2,4-triazole	4.6	22	1,2,3-triazole	5.6	27	Imidazole	5.7

#	Structure	Value	#	Structure	Value	#	Structure	Value
28	1,3,5-benzenetriamine	4.7	**32**	1,4-benzenediamine	5.3	**36**	1,2,4-triazine	6.9
29	1,3,5-triazine	6.9	**33**	1,2-benzenediamine	5.3	**37**	Pyridine	7.1
30	1,3-benzenediamine	5.3	**34**	1,4-diazine	7.0	**38**	Pyridazine	7.0
31	pyrimidine	7.0	**35**	Pyrrole	5.8	**39**	1,2,3-triazine	6.9

40	*N*-ethylcarbazole	5.8	**42**	1,6-naphthyridine	7.2	**44**	Fluorene	6.8
41	*N*-ethyl-*β*-carboline	5.8	**43**	Perhydro-3-hydroxymethyl-*N*-methylcarbazole	5.4			
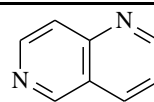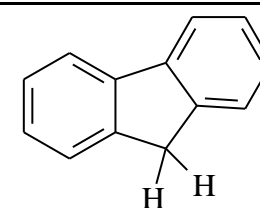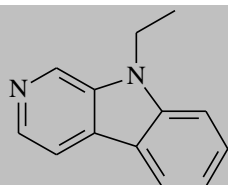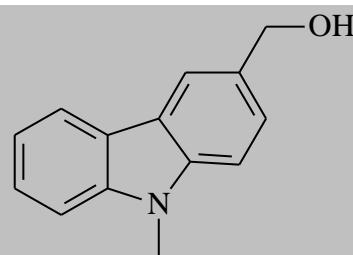
6.5 Side group stability

With reference to Table 6-8, this section aims to test the stability of the side groups of Carriers **2 – 15** under the reaction conditions required, *i.e.* the side groups should not react under redox conditions to give undesirable side products. The other carriers **16** - **43** have been shown by various authors to be suitable for hydrogen storage[18, 35, 58, 89, 92-97, 99, 100], and so are stable under redox conditions.

Table 6-9: Candidate molecules 2 - 15 and the potential for their side groups to react under (de)hydrogenation conditions. Green shading indicates suitability, red shading indicates instability under redox conditions employed for (de)hydrogenation

Compound	Group Reduction	Group oxidation
2	Stable	Stable
3	Stable	Stable
4	In the presence of Pt, reduces to aniline or cyclohexane, depending on reaction conditions.[101, 102]	N/A
5	Stable	Requires strong oxidising agent [O], such as HONO.
6	Stable	Requires strong oxidising agent [O] such as potassium dichromate and acidic conditions to oxidise to ketone.
7	Will reduce to primary alcohol.[103]	N/A
8	Requires a strong reducing agent, [H].	Stable
9	Requires a strong reducing agent, [H], such as LiAlH$_4$.	Stable
10	N/A	Reacts readily with oxygen in air to give a disulphide and water[104].
11	Reduces to amine in the presence of Pt	N/A

Compound	Group Reduction	Group oxidation
	and H$_2$.	
12	Requires a strong [H].	Stable
13	Stable	Requires potassium dichromate and acidic conditions to oxidise to ketone.
14	N/A	Reacts readily with oxygen to give a disulphide and water.
15	Stable	Stable

This leaves a list of nine carriers whose side groups do not react under redox conditions, whose rows are highlighted in green in Table 6-9.

6.6 Remaining Carriers 2 – 15: Physical Properties

These remaining nine candidates in Table 6-9 can also be discounted due to their physical properties or those of their dehydrogenated equivalents, with the exception of **2** and **3**. This arises from the requirement that the carriers are in the liquid state in both their charged and discharged counterparts within the temperature ranges they are likely to encounter. The melting and boiling points of the carriers would change with pressure, but this assessment will be carried out on the basis of atmospheric pressure. The carriers, charged and discharged, will be stored under ambient conditions when not in the reactor, so it is important that they are in the liquid phase under both ambient *and* reactive conditions. If the carrier has a high vapour pressure under reaction conditions, similar problems will be encountered to those of the MTH system. If the carrier solidifies when in storage (in the fuel tank of a car in the winter, for example), the fuel may solidify on-board the vehicle, rendering it unsuitable for operation due to potential pipe blockages.

A practical temperature range is required to assess the suitability of these carriers. For this purpose, figures describing the UK's highest and lowest recorded temperatures were used[105].

As quoted by [105]:

- Highest recorded UK temperature – 311.5 K (2003)

- Lowest recorded UK temperature – 245.8 K (1895, 1982, 1995).

A wider temperature range may be required if the technology is intended for export to foreign countries with different weather systems.

If any of the carriers in their charged or discharged forms are in anything other than the liquid state within this temperature range, they should be considered unsuitable for this application. Table 6-10 gives melting and boiling points of the relevant compounds.

Table 6-10: Chosen carriers in their charged and discharged states, with accompanying melting and boiling points (where available) – red shading shows a melting/boiling point which lies outside of the specified range

Compound Name	Melting Point/K	Ref	Boiling Point/K	Ref
Methylcyclohexane (**1**)	147	106	374	106
Toluene	178	106	384	106
Ethylcyclohexane (**2**)	161	106	405	106
Ethylbenzene	179	106	409	106
Propylcyclohexane (**3**)	178	106	429	106
Propylbenzene	173	106	432	106
Cyclohexanamine (**5**)	255	106	407	106
Aniline	267	106	457	106
Cyclohexanol (**6**)	296	106	433	106
Phenol	314	106	455	106
Cyclohexanecarboxylic acid (**8**)	299	106	506	106
Benzoic acid	395	106	523	106
Cyclohexanecarboxamide (**9**)	461	107	-	
Benzamide	401	106	561	106
Dicyclohexylmethanone (**12**)	-	106	539	108

Compound Name	Melting Point/K	Ref	Boiling Point/K	Ref
Benzophenone	321	[106]	579	[106]
Cyclohexanemethanol (**13**)	-	[106]	454	[106]
Benzyl alcohol	257	[106]	478	[106]
Bicyclohexane (**15**)	277	[106]	508	[106]
Biphenyl	343	[106]	527	[106]

Table 6-10 shows that all of the molecules, except for those which are substituent chain extensions of MCH, have melting points which are too high for this application, and therefore could solidify under cold weather conditions in the UK. This is to be expected. All of these molecules, with the exception of bicyclohexane (**15**), feature heteroatoms, and therefore show hydrogen bonding characteristics. This causes their melting points to be higher than a hydrocarbon, as a side effect to having the desired effect on the boiling point. In the case of bicyclohexane (**15**), the high melting point cannot be attributed to hydrogen bonding, but rather to the high molecular weight of the molecule compared to the other carriers.

This two candidate molecules, ethyl- and propylbenzene. As these were the only candidate molecules which have fit the criteria so far, it would be interesting to extend the selection to include rings with even longer chains.

6.6.1 Extension: Carrier molecules with Formula $C_6H_5C_nH_{(2n+1)}$

As the length of the hydrocarbon chain group increases, the boiling and melting points rise. It is possible to reach n = 7 (heptylbenzene) before the melting points exceed the required melting point (See Appendix L). This gives a list of six candidate molecules, ethyl- to heptylbenzene (n = 2 – 7).

The next step is to evaluate the vapour pressures of all six molecules to indicate a maximum operating temperature while still retaining a competitive amount of carrier (≥96.1%).

A comparison between the candidate carriers is given as Figure 6-13, which compares the % loss of all candidate molecules across a range of temperatures when conversion is equal to 0.5 *i.e.* the molar ratio of charged:discharged carrier in the mixture is 1:1.
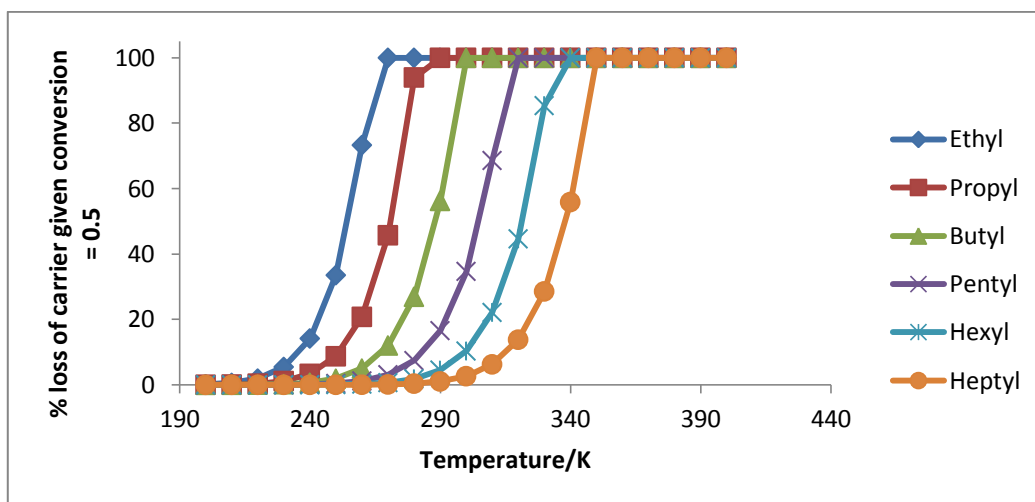
Figure 6-13: A comparison of % carrier loss for all candidate molecules as a factor of temperature with conversion equal to 0.5

As expected, the heptyl-carriers require the highest temperature of all the carriers for a given % loss. However, even the heptyl-carriers suffer from 100% loss at approximately T = 350K (77 °C). To stay below the benchmark 3.9% loss used to evaluate the MTH system earlier, the heptyl system needs T ≤ 304.4 K (31.3 °C), compared to MTH where T ≤ 245.1 K (-28.07 °C). Although this is an improvement, it will prove difficult to achieve useful equilibrium conversions, x_A, at this temperature, considering that thermodynamic equilibrium holds MCH dehydrogenation at a conversion of 0.7% at 374 K. As shown earlier by Equation 6-22, the volume of hydrogen in the engine, $V_{H_2}^E$, depends on x_A, so a sufficient x_A is required to generate an explosive mixture of hydrogen and oxygen in the engine.

Although thermodynamic limits can theoretically be overcome by using an open system with respect to gas-phase products, hydrogen release (diffusion) from the liquid would need to be extremely fast to overcome the low thermodynamic limit on conversion expected at, say, 304.4 K. It is also possible that this thermodynamic limit will not allow a sufficient hydrogen volume in the gas feed for combustion, which cannot be overcome, by fast diffusion or otherwise.

6.6.2 Conclusions: Carriers 2 – 15 & $C_6H_5C_nH_{(2n+1)}$ carriers

As shown above, the stability of various side groups under the conditions required for (de)hydrogenation presents a problem. Of those candidate molecules whose side groups are stable under the necessary conditions, there are few which possess convenient physical properties needed to guarantee liquid state carriers at all times. Finally, the non-MCH $C_6H_5C_nH_{(2n+1)}$ molecules which are

sufficient to satisfy the above criteria do not show favourable VLE behaviour at the tested temperatures.

6.7 Remaining carriers 16 – 44: Enthalpy Change of Dehydrogenation

The next step is to evaluate the remaining carriers. The partial aim of this carrier search is to find a carrier with a low value of ΔH_d, so this parameter should be measured for all candidate molecules.

In some cases ΔH_d can be used as a sole criterion to discount carriers because it is low enough that hydrogen release would be spontaneous under atmospheric conditions. For the "Improved MTH System" approach, this would be undesirable and dangerous (hydrogen should only be evolved on demand so that minimal free hydrogen is present in the system at any time).

6.7.1 Assessment of dehydrogenation enthalpy

A paper from Crabtree *et al*[35] provides a list of nitrosubstituted carriers (shown in Table 6-8 as carriers **16 – 39**), alongside computationally calculated values for dehydrogenation enthalpy, entropy and standard Gibbs free energy, as well as T_d, the temperature at which $\Delta G_d = 0$. Table 6-11 shows the dehydrogenation enthalpies for each of the carriers **16 – 41**, as well as their T_d values.

The remaining carriers, **42 – 44**, are considered separately.

Table 6-11: Candidate carrier molecules 16 - 41 with associated dehydrogenation enthalpies (per mole H$_2$) and temperatures where available. Values are computationally calculated unless experimental data is available, given in brackets.

No.	ΔH_d/kJ mol^{-1}	T_d/K	No.	ΔH_d/kJ mol^{-1}	T_d/K
16	6	46	**30**	57	463
17	6	50	**31**	60	483
18	13	111	**32**	61	490
19	14	114	**33**	64	500
20	14	116	**34**	63	507
21	20	174	**35**	62 (56)	520

No.	ΔH_d/kJ mol^{-1}	T_d/K	No.	ΔH_d/kJ mol^{-1}	T_d/K
22	22	187	**36**	66	527
23	26	218	**37**	67 (62)	546
24	30	230	**1**	67	553
25	35	298	**38**	70	559
26	39	314	**39**	71	569
27	40	333	**40**	47.3	-
28	49	393	**41**	43.4	-
29	54	436			

Immediately, carriers **16 – 25** can be discounted, because they could potentially release hydrogen spontaneously without intention due to their low dehydrogenation temperatures, based on the MET office temperature figures used earlier. These carriers would be useful if investigating the Spontaneous Decomposition Approach.

This leaves a list of 16 potentially useful carriers.

6.7.2 Assessment of physical properties

It was found that boiling points for the remaining 16 candidate molecules were sufficiently high to meet that standard defined earlier by the MET office figures in all cases where data was available. However, the melting points of the molecules were in most cases too high, and would lead to solidified fuels with subsequent associated problems. The melting points of the dehydrogenated carriers (where available) are given in Table 6-12.

Table 6-12: Melting points of dehydrogenated carriers, 12 - 23

Carrier	Melting point/K	Uncertainty/±K	Ref
27	361.9	0.2	[106]

Carrier	Melting point/K	Uncertainty/±K	Ref
28	357.62	0.5	109
29	355.2	1.0	110
30	335.0	0.4	106
31	294	1	110
32	414.2	0.2	106
33	373.9	0.5	106
34	324.0	0.1	106
35	249.7	0.2	106
36	Unavailable	N/A	-
37	232	2	106
38	265	-	110
39	Unavailable	N/A	-
40	340.7	1.5	106
41	Unavailable	N/A	-

Of the candidate molecules for which data is available, only one is not rendered unsuitable by its melting point – this is **37**, pyridine. However, the hydrogenated form of **37**, piperidine, has a melting point which is 31 K higher than its dehydrogenated counterpart, making the pyridine-piperidine system on the whole unsuitable. There is no melting point data available for the remaining three carriers, **36**, **39** and **41**. **36** and **39** are unusual molecules, and **41** was designed in-house by APCI[94] therefore has no literature data.

It is unlikely that any of these carriers would possess suitable melting points – the isomer of **36** and **39** (**29**) has a melting point which is too high by 44 K, and this is unlikely to vary significantly for other isomers. In the case of **41**, this is structurally identical to **40** except for the substitution

of a single carbon atom for a nitrogen atom. This substitution is unlikely to lower the melting point by 29 K. Regardless, these carriers cannot be discounted on these grounds alone. More data should be gathered on these carriers if work is to continue.

Carrier **41** is particularly promising. It is stated that these carriers are designed to have low volatility (BP >300 °C = 573 K) so it could be assumed that the boiling point criteria has been met (BP > 311.5 K). Also, not only is the average enthalpy per mole of H_2 lower for **41** than for MCH (43 kJ mol^{-1} compared to 67 kJ mol^{-1} respectively), but also **41** has a similar gravimetric hydrogen capacity to MCH, standing only slightly lower at 5.8 wt% H_2, compared to MCH with 6.2 wt% H_2.

Finally, the release of six hydrogen molecules as opposed to three from MTH would cause a desirable comparative increase in the entropy of dehydrogenation, ΔS_d.

6.7.3 The Special Cases: Carriers 42 – 44

The last three carriers have not been looked at until now because they require special consideration. Carrier **42** is the 1,6-isomer in a group of naphthyridines, which can dehydrogenate by two different pathways, and carriers **43 – 44** are the "autothermal" carriers, which use the exothermic oxidation reactions of the carrier side-groups to offset the endothermic dehydrogenation enthalpies.

6.7.3.1 Carrier 42 – 1,6-naphthyridine

Carrier **42** has variable energy requirements depending on which dehydrogenation pathway is favoured. The two possible pathways are shown in Figure 6-14.

Pathway One
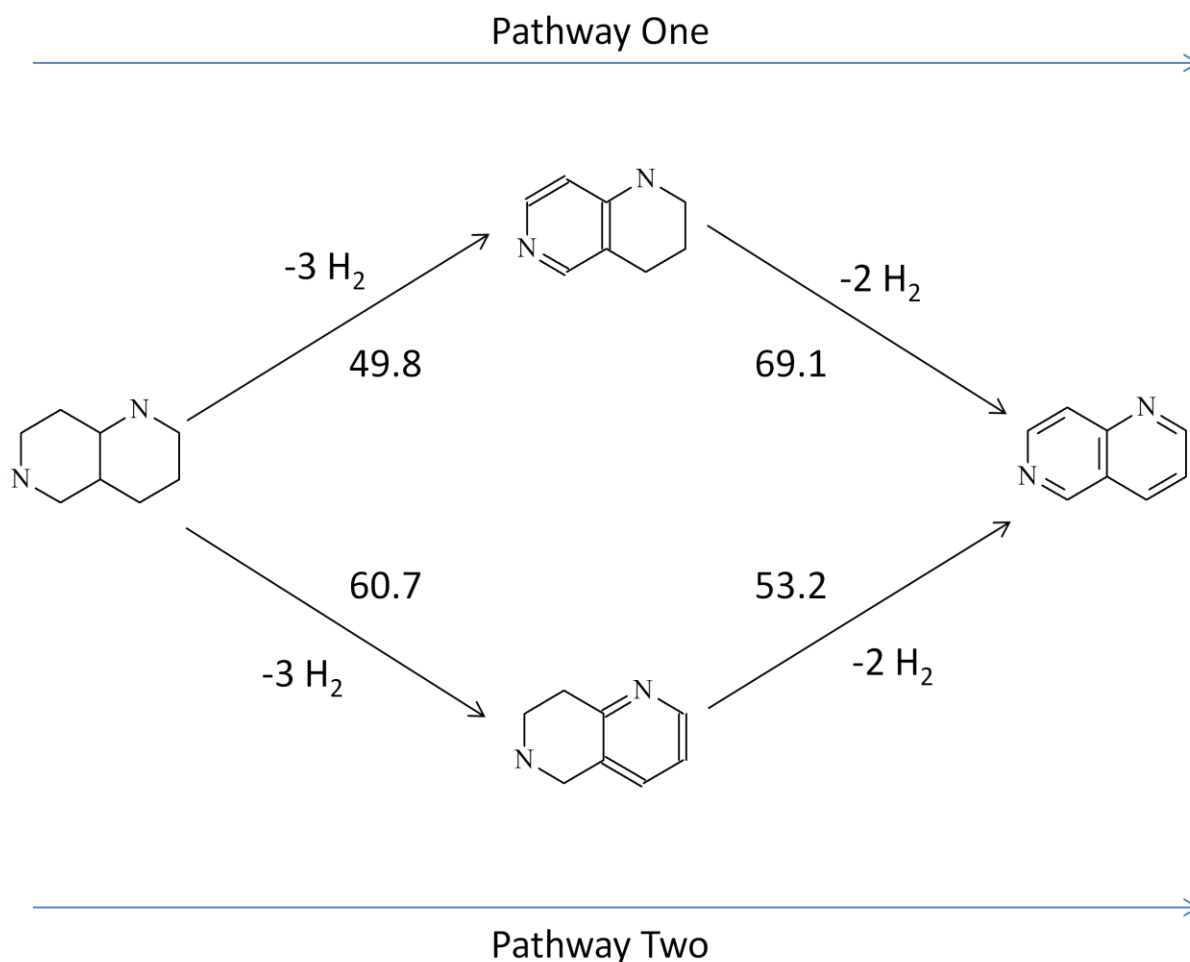
Figure 6-14: Dehydrogenation enthalpies for perhydro-1,6-naphthyridine[94], given in kJ/mol H$_2$

When perhydro-1,6-naphthyridine was tested for dehydrogenation, it was found that the equivalent of 7 wt% hydrogen was evolved from a possible 7.2 wt%. The author then concluded that Pathway One is likely to have been favoured under the conditions used, because a high temperature (approx. 548 K) was required for complete dehydrogenation[94]. It is unclear how the author reached this conclusion, because the required reaction temperature is not related to the enthalpy change of the reaction. This conclusion may have been valid if activation energy was the parameter under scrutiny rather than enthalpy change.

The average enthalpy of Pathway 1 is 57.5 kJ mol (H$_2$)$^{-1}$, which is competitive compared to MCH, but is significantly higher than **41**.

Carriers 43 – 44: The autothermal carriers

The final carriers for consideration, perhydro-3-hydroxymethyl-N-methylcarbazole (**43**) and fluorene (**44**) can theoretically sustain hydrogen evolution with very low or zero net energy input from outside sources. This is achieved by offsetting the endothermic dehydrogenation energy requirement using heat from an exothermic oxidation reaction, which a side-group of the carrier molecule can participate in.

Enthalpy information on the two carriers is given by Table 6-13, and a reaction scheme for each is given by Figure 6-15 and Figure 6-16.

Table 6-13: Dehydrogenation and oxidation enthalpies of carriers 43 - 44, with the resultant net energy input/output

Carrier	H$_2$ wt%	ΔH_d	$\Delta H_{oxidation}$	Net ΔH
43	5.4	+51.6 kJ/mol H$_2$ +309.6 kJ/mol carrier	-456 kJ/mol carrier	-146 kJ/mol carrier
44	6.8	+59 kJ/mol H$_2$ +352 kJ/mol carrier	-339 kJ/mol carrier	+13 kJ/mol carrier
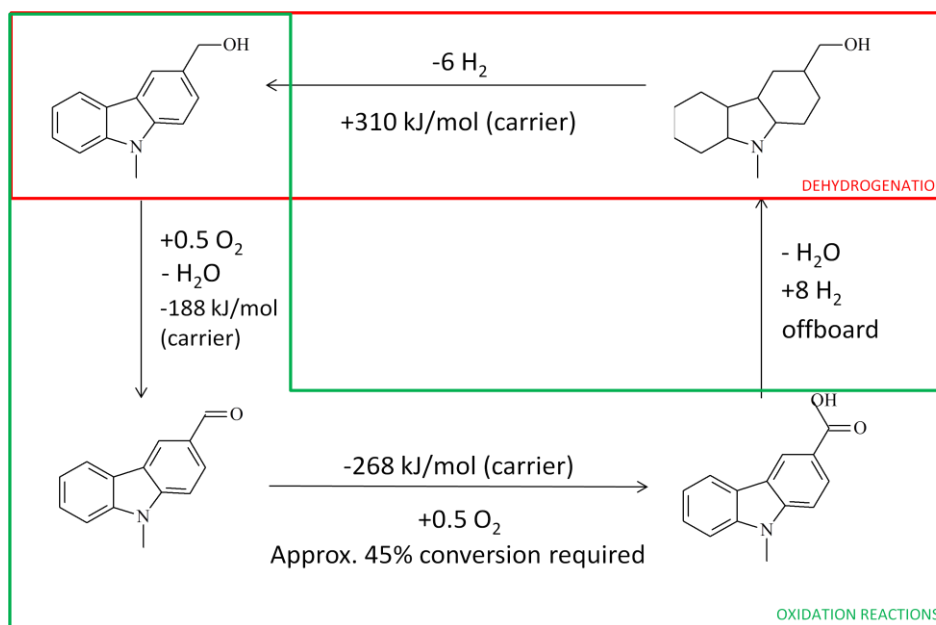
Figure 6-15: Autothermal reaction scheme (for the on-board part of the process only) for Carrier 43
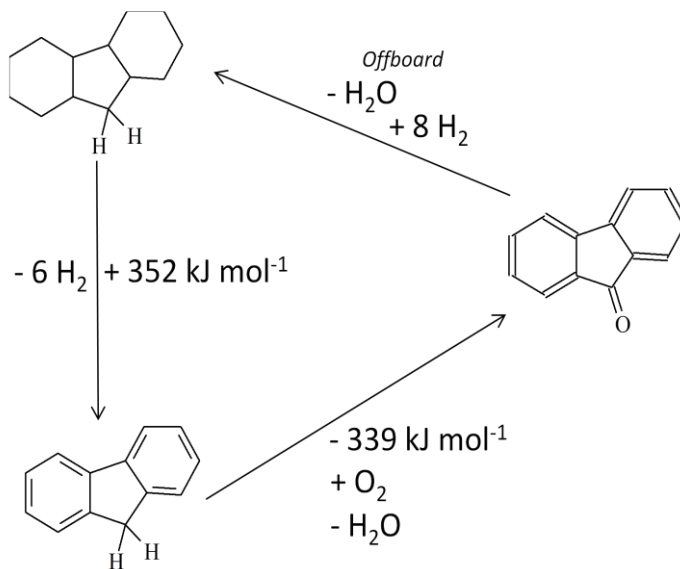
Figure 6-16: Nearly autothermal reaction scheme for Carrier 44

The autothermal approach has the potential to enable a dehydrogenation system where the net enthalpy of dehydrogenation is zero, which is an exciting concept. However, it does not have an impact on the suitability of the carrier for LP-DR. The source of the heat is irrelevant to the dehydrogenation process itself, and the other criteria discussed in this chapter must still be met by the dehydrogenation process in isolation. If high temperatures are required or if volatility is high,

then a large proportion of hydrocarbon will be wasted in the gaseous exit stream regardless of the heat source.

The dehydrogenation enthalpies per mole H_2 are lower than for MCH, similar to carrier **42**, and much higher than carriers **40** - **41**. These carriers could therefore have potential to be competitive candidates for LP-DR, but their suitability would not be related to their autothermal opportunities.

6.8 Conclusions for Alternative Carriers

6.8.1 **Carriers 2 – 15 & $C_6H_5(C_nH_{(2n+1)})$ carriers – variable substituents**

Many of these carriers were unsuitable for not just LP-DR but for any kind of (de)hydrogenation process, due to the instability of their side-groups under redox conditions. Of those candidate molecules which were stable under the necessary conditions, there were few which possessed appropriate physical properties needed to retain the liquid state at all times. The group which passed both of these tests were restricted to molecules with the formula $C_6H_5C_nH_{(2n+1)}$. However, these did not show favourable VLE behaviour at the tested reaction temperatures, and therefore would suffer from the same problems of carrier retention as the MTH system did.

6.8.2 **Carriers 16 – 41 – the nitrosubstituted carriers**

This group of carriers had an advantage over the pure hydrocarbon carrier molecules because the nitrogen atoms in the rings weakened the adjacent C-H bonds as well as being weakly bonded to hydrogen themselves compared to the equivalent carbon atom in an equivalent hydrocarbon structure. This resulted in the nitrosubstituted molecules having a lower dehydrogenation endotherm than their hydrocarbon analogues. However, this was not always advantageous – Carriers **16 – 25** had such low endotherms of dehydrogenation that they would release hydrogen gas spontaneously under ambient conditions. Although these carriers would be worth further consideration for use with the Spontaneous Decomposition approach to LP-DR, unpredictable hydrogen release would be unacceptable for the chosen "Improved MTH System" approach, so these carriers were discounted.

Following this, assessment of the melting and boiling points led to the discounting of yet more carriers. Carriers **27 – 35**, **37** -**38** and **40** all had melting points in either their charged or discharged forms which would lead to solidification under ambient conditions, which would lead to flow problems and potential pipe blockages in the automotive system. These carriers therefore were no

longer considered. The final three carriers, **36**, **39** and **41**, did not have accessible data, so no melting points could be obtained for these. When looking at their isomers or other carriers which closely resemble their structures, it seems unlikely that these carriers would have suitable melting points. However, the carriers were not discounted on these grounds, because further research into this missing data must first be carried out.

It is noted that carrier **41** shows particular promise if its physical properties are appropriate to the criteria. A low dehydrogenation enthalpy of 43 kJ mol^{-1} (compared to 67 kJ mol^{-1} for MCH) makes this carrier appealing .

6.8.3 Carrier 42 – the multiple pathway carrier

This carrier is competitive with MCH in terms of enthalpy of dehydrogenation, but has a higher enthalpy than one of the other feasible carriers considered (**41**), regardless of the dehydrogenation path chosen. However, this carrier is still worth remembering, because it is unclear whether **41** has the necessary physical properties to act as a hydrogen carrier.

6.8.4 Carriers 42 – 43 – the autothermal release carriers

These carriers benefit from having competitive hydrogen release enthalpies. However, despite the fact that the net endotherms are low after taking into account the oxidation reactions, this does not affect the carrier suitability for LP-DR. Although the advantage of autothermal carriers is that this heat can be taken from the carrier itself, this does not mean that dehydrogenation is any less energy intensive than it would be without the oxidation reaction, and has no impact on the vapour pressure of the carrier in the reactor. The dehydrogenation procedure should therefore be assessed for suitability in isolation, and the autothermal opportunities viewed as a bonus if all other criteria are fulfilled.

6.9 Recommendations

Clearly, of the 48 carriers examined in this chapter, the vast majority are unsuitable for LP-DR, largely due to physical properties of the carriers or undesired reactivity. In the effort to decrease the volatility of the carrier by adding hydrogen-bonding side groups or molecular weight compared to MCH, it is impossible to avoid increasing the melting point as well, which would have the undesired effect of causing flow problems in the system. If the carriers are suitable in every other aspect, it may be appropriate to carry out some work on solving this problem. The use of additives to alter

melting points is not unheard of[39], and studying additives to be compatible with the carriers mentioned here may be a worthwhile exercise.

Further information is required about some of the more unusual or proprietary carriers to assess their suitability, and this should be carried out for a final decision to be made. The data required includes physical properties where they are not already available.

Finally, although the carriers with the potential to enable an autothermal system must still possess the same desirable properties as the other carriers to be suitable for LP-DR, it would be very advantageous to carry out the process without heat from an outside source. If one of these carriers, or another like it, could be made to dehydrogenate in the liquid phase and do so while providing its own process heat, this technology would become more viable than ever before.

Although it is recommended to carry out further work with the remaining candidate molecules, no further study will be performed here. After most of the candidate molecules were discounted due to physical properties, the remainder were unusual or proprietary molecules. It is not possible to gather the required information to scrutinise these molecules using the methods proposed at the start of the chapter without experimental data or proprietary knowledge, neither of which are within the reach of this work.

Chapter 7   Alternative Applications for the MTH System – Technical Evaluation

7.1 Introduction

The project so far has focused on a mobile application for LOHC technology. The nature of this vehicular application has implied that system volume and weight are important factors which should be minimised as much as possible. Conditions should be as mild as possible, and energy consumption minimised. The idea of a liquid-phase dehydrogenation was pursued in the interests of minimising equipment weight and volume by making the condenser, vaporiser and superheater redundant. Although this idea is still potentially viable with the discovery/design of a suitable hydrogen carrier, it is clear from the preceding chapters that the MTH system is unsuitable for this application.

However, that is not to say that the MTH system could not be used in a traditional vapour phase process for a different application. As iterated earlier in this work, the MTH system has many advantages, both within the domain of LOHCs and in the wider area of hydrogen storage. These include: competitive weight percentage of hydrogen (6.2 wt%); physical properties similar to petrol; the ability to exploit the existing fossil fuel infrastructure. Through this study, much information and understanding about the MTH system has been gained, so now this insight will be used to pursue an application where the qualities of the MTH system can be exploited to maximum benefit.

As mentioned in Section 4.6.1, an interesting opportunity has arisen in the UK. Much investment has been directed in recent years towards the construction of wind farms. The UK currently has a combined offshore and onshore wind power capacity of over 10 GW, with hundreds of new wind farms at various stages of planning, consent *etc* (see Figure 7-1)[111]. However, wind power is not without its problems. Not only is the load variable on a daily and seasonal scale due to variable wind speed and direction, but user demand is also variable on the same scales[26]. The supply and demand of electricity rarely match, so it would be useful to have a power management system in place, so that surplus electricity can be stored until demand increases, when the stored energy can be released back into the grid. The MTH system has been proposed as a solution to this problem[25-28]. Surplus electricity from wind power which would otherwise be wasted can be used to electrolytically split water, generating hydrogen.
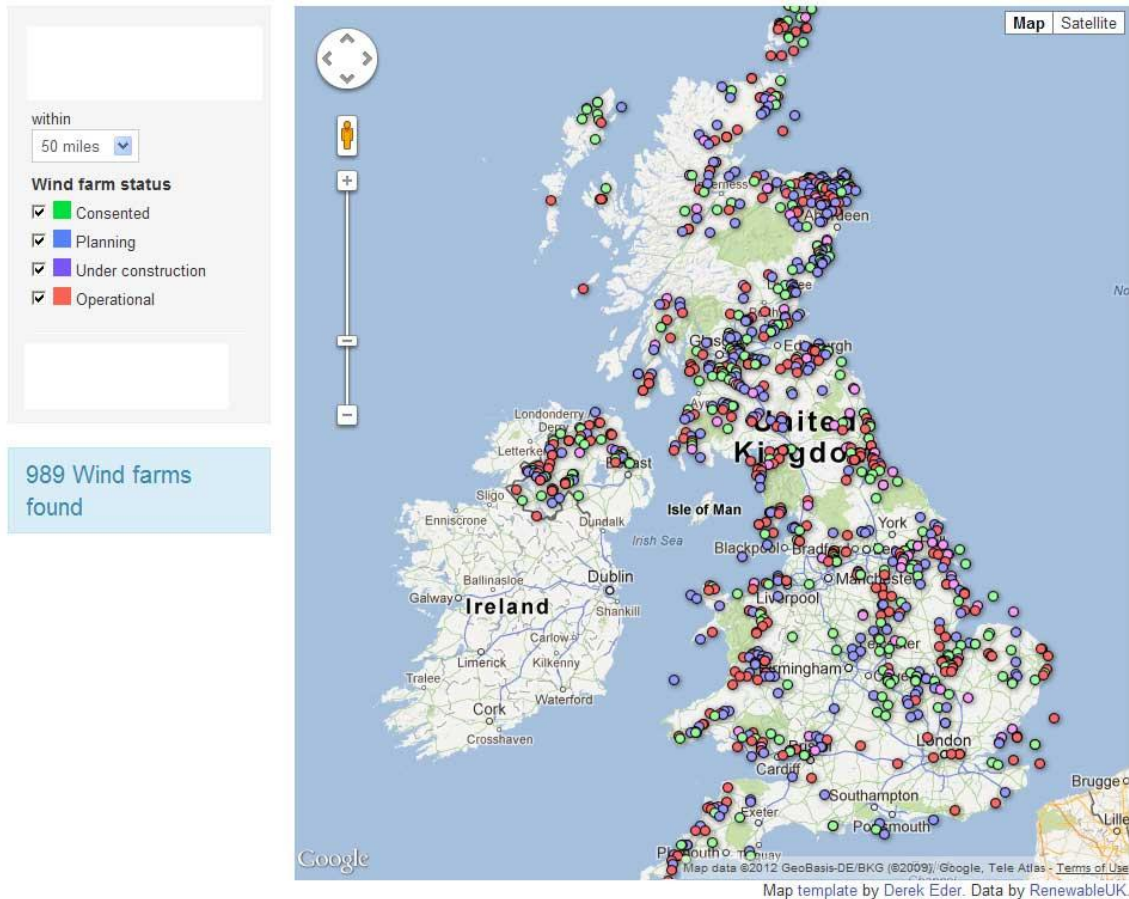
Figure 7-1: Wind farm sites in the UK at various stages of completion

This hydrogen can then hydrogenate toluene and give MCH, which can be stored for an indefinite time until demand is higher. As demand arises, hydrogen is released from its chemical bonds and reconverted into electricity *via* a fuel cell. This system can be used on a daily scale (store hydrogen overnight, use in the day) or on a seasonal scale (store hydrogen in Summer, use in Winter).

However, an alternative system could be proposed. Instead of liberating the LOHC-bound hydrogen on-site, the MCH could be moved elsewhere to fulfil the energy needs of a consumer other than the power grid. For example, the hydrogen could be used to supply industrial power demands, which would decrease the environmental impact of the industry in question by using renewable energy which would otherwise have been wasted.

If using hydrogen to provide heat/electricity, another idea would be to neglect the transport of MCH from the wind farm to the site of use, and instead send the wind-generated electricity *via* the central grid or a private electricity network to a central hydrogenation plant. This hydrogenation plant could be built at or near the site where power is needed. The electricity from the wind farms could then be used directly if required, or stored as hydrogen (and then MCH) until the need for power does arise. This would mean that one large hydrogenation-dehydrogenation plant could be built in place of

several smaller plants at each wind farm, which would likely lead to substantial savings in process capital and operational costs.

In Section 4.6, the possibilities for how to use the hydrogen from wind farm electricity were discussed. To summarise the discussion, the following were identified as important factors in how to decide on a target application for MTH technology:

- H_2 purity – high purity hydrogen would be required to sell as a reagent (food manufacturers, steelworks, universities *etc*), with reagent H_2 likely to attract a higher price. Lower purity hydrogen could be sold as fuel.

- How competitive is MTH with rival energy storage technology? – depending on the application, there may be an alternative energy source or H_2 storage method which would be more appropriate than the MTH system.

- Business model *i.e.* what is the product? – Options include direct sale of liberated hydrogen, sale of MCH for dehydrogenation by the client, or sale of a comprehensive package where MCH is sold to the company as well as dehydrogenation equipment and associated maintenance, operation *etc*.

With any application which is studied in this work, these three points should be examined.

Some potential applications were also discussed in Section 4.6. These included using the MTH system as a fuel for backup power, for businesses which require a guaranteed power supply at all times. Businesses have already started adopting this technology, with companies such as Ballard and Hydrogenics supplying fuel cells and hydrogen fuels for backup power purposes, the former for telecommunications and the latter for telecom and data centres[112, 113].

 Also discussed were off-grid businesses which similarly require power but are unable to access the grid due to geographical constraints. Scottish whisky distilleries are a perfect example of this. Many distilleries are positioned in isolation due to the need to be near to a particular water source, therefore the grid connections (both gas grid and electric grid) are either antiquated and unreliable or non-existent. Many of these distilleries therefore use off-grid power, such as diesel burners[82].

Scotland aims to produce the equivalent of 100% renewable energy by the year 2020[83]. The Scottish whisky industry demands 1.5% of Scotland's entire energy demand, so if this industry could be powered with renewable hydrogen, a considerable step towards Scotland's 2020 energy target could

be made. A preliminary investigation of this opportunity will therefore be made before a more detailed investigation if appropriate.

7.2   MTH and Whisky Production

The aim of revolutionising the whisky industry is not original. On Islay, the Bruichladdich distillery uses an anaerobic digester to break down yeasty waste product from whisky production, which yields methane. Using the methane for process energy saves the distillery £150,000 in electricity bills every year, which offsets the £275,000 capital investment[114]. A group at Strathclyde University also performed a similar study on the idea of using waste products for energy at distilleries, drawing the conclusion that liquid co-products of whisky distillation could be anaerobically digested to produce methane, with a boiler and an electrical generator using the methane to supply 100% of the distillery's power demand.

For the MTH system to be applicable to this industry, it must be competitive not only with current methods of satisfying power demand (*e.g.* use of heating oil/diesel) but also with promising alternatives, such as anaerobic digestion of waste streams.

To investigate the viability of using the MTH system to power a whisky distillery, the MTH process must be designed. A simple illustration of the process is given in Figure 7-2.

Each of the steps shown in Figure 7-2 can be considered a major process step. These are:

- Water electrolysis
- Hydrogenation of toluene to yield MCH
- MCH transport and storage
- MCH dehydrogenation
- Hydrogen conversion to energy.

The first step in analysing this process is to perform a simple feasibility study. This will account for the required amount of hydrogen to support a distillery, and whether this matches the amount of hydrogen which can be produced by electrolysis.
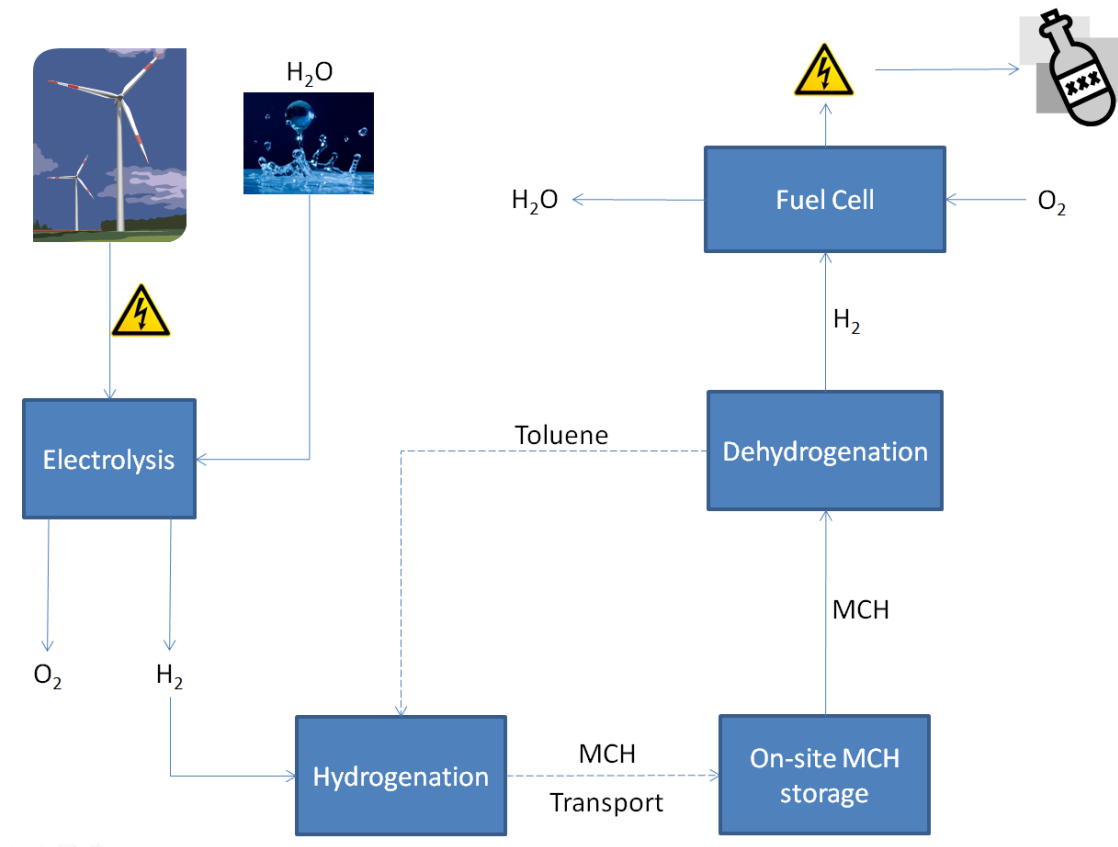
Figure 7-2: Simple illustration of how power would be supplied to a distillery using the MTH system

7.3 Feasibility Study

7.3.1 Preface

A land investor has recently estimated that there may be potential for *circa* 250 small wind turbine sites (200 − 500 kW) in Scotland's highlands and islands, which translates to an output of 5 − 15 tonnes of hydrogen per year per site[115]. This amounts to a minimum of 1250 tonnes of annual hydrogen production, and a maximum of 3750 tonnes.

To determine whether the demand of a distillery lies within this range, power requirements should be assessed. The aforementioned study performed by Strathclyde University[82], hereafter referred to as the Strathclyde Study, used the Balmenach distillery as a case study for their study of anaerobic digestion of distillery by-products. It would be useful to base this MTH system study on the same distillery, because this will allow a direct comparison between the suitability of anaerobic digestion technology *versus* the MTH system, as well as the use of standard heating oil. The MTH system will therefore be analysed with this distillery in mind.

Balmenach whisky distillery generates an output of between 1.8 and 2.3 million litres of whisky annually[82, 116]. In 2010, electricity from the main grid was used to supply lighting, space heating, refrigeration for yeast, and power for electric pumps. The distillery was not attached to the gas grid, so other heating requirements *i.e.* raising process steam were met by one 6400 kW rated oil fired boiler.

Energy requirements for each of these purposes and associated costs are given in Table 7-1.

Table 7-1: Energy requirements for Balmenach Distillery in 2010

Annual factor		Annual Cost
Energy requirement (electricity)	479 091 kWh	£50 304.56 @ 10.5p per kWh
Energy requirement (heating oil)	19 294 870 kWh	£782 002 @ 47.5p/L oil
Energy requirement (total)	19 773 961 kWh	£832 306.60

As shown in Table 7-1, the power requirements for the distillery can be split into two groups – electrical power and thermal power. A key decision to make is the desired outcome of using hydrogen in place of fossil fuels. Hydrogen could be used to replace heating oil, grid electricity, or both. As the heating oil accounts for 94% of the distillery's total energy consumption, this study will focus on replacing fuel oil, with comments on the replacement of grid electricity given.

The Strathclyde Study worked on the basis of directly replacing fossil fuels with biomethane, including heating oil. This methane was combusted in the same boiler used for heating oil, so for the sake of comparability between the two studies, this work will assume that hydrogen directly replaces fuel oil, and is directly combusted to provide boiler heat.

The next step is to calculate the hydrogen requirement to replace heating oil.

7.3.2 Early feasibility analysis

Process stream is raised for the distillery using a 6.4 MW rated boiler, which has a thermal efficiency of 80%[82]. Using the gross heating value of hydrogen, the energy requirement of 19 294 870 kWh/yr could be met with 490 tonnes H_2/annum. Taking into account the efficiency of the boiler, this figure rises to 612 tonnes H_2/annum.

As aforementioned, the wind farm development in question has the potential to provide 1250 – 3750 tonnes H_2/annum. With further analysis, the overall hydrogen demand of the distillery will rise with process inefficiencies leading to losses. However, the initial estimate of 612 tonnes H_2/annum can be comfortably satisfied by the wind farms, with plenty of margin for rising demand with losses. Therefore, this feasibility study finds that this application for the MTH system is viable, and warrants further investigation.

7.4 Process development

7.4.1 Aims

The final aim of this study of the MTH system to provide distillery power is to perform an investment appraisal, which will include estimates of:

- System capital cost
- Annual operating costs

This will be followed by a sensitivity analysis, which aims to identify the key factors in the economic viability of the system by measuring how dramatically the cost outcomes change with variation of these key factors.

This order-of-magnitude economic assessment will also be compared with the current operation of the distillery (use of heat oil) and the alternative Anaerobic Digestion (AD) process proposed in the Strathclyde Study.

This economic analysis will require a thorough mass and energy balance for the system, followed by equipment sizing and costing.

This analysis will be carried out on the basis that this process plant would be owned and operated by the distillery, who buy electricity from wind farm operators and store it as hydrogen with a view to saving money and reducing environmental impact.

7.4.2 **Methods**

7.4.2.1 Timescales

As the system develops, it will be convenient to represent mass and energy movements as flows (in units of mol s^{-1} or kW respectively). This requires a unit time to work with. In a real process, the network would be split into two parts working on two different time frames. The dehydrogenation part would work alongside the operating hours of the distillery, providing hydrogen as required to raise process steam. The hydrogenation part would operate 24 h/day, and would correlate not with the demands of the distillery but rather with the availability of electricity from wind farms. These parts should be viewed as two different processes: average **dehydrogenation flows** should be calculated as average flows during **operating time**, derived from the operating hours of the distillery; **Hydrogenation flows** should be calculated as average flows in **real time**, operating 24 h/day as electricity becomes available. Table 7-2 outlines the difference between the two timescales.

Table 7-2: Timescales for different parts of the process

	Operating time	Real time
Days/year	275	365
Seconds/year	23,760,000	31,536,000

However, when shown as one process, the flows of the two process parts become confusing and appear to be unmatched. For ease of reading and understanding, all flows in this work will be shown with respect to **operating time**, with the understanding that the average hydrogenation process flows shown are slight overestimates. This does not affect the conclusions drawn from this work, and serves only to facilitate easier understanding.

7.4.2.2 Mass Balancing

A mass balance is to be carried out for each part of the process (dehydrogenation and hydrogenation) according to basic principles of chemical engineering. For reactions, appropriate reactive conversions and reaction rates are sourced from relevant literature or based on experience. Flowrates are designed to satisfy the power needs of the distillery, and will be given as average flowrates based on operating time as explained above.

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Hydrogenation and dehydrogenation are considered to be separate processes, although one feeds into the other. The system boundaries between the two parts of the process are buffered by storage tanks, therefore within a finite time period the two processes can run independently of one another.

7.4.2.3 Energy Balancing

Following the mass balance, an energy balance will be carried out. The required energy inputs and outputs for each part of the process will be determined using detailed thermodynamic calculations. This will include energy penalties of heating, cooling and in some cases compression. Following this, the two parts of the system (hydrogenation and dehydrogenation) will be analysed using Pinch Analysis to determine the optimum level of heat exchange between hot and cold streams, as well as the optimum use of outside cooling/heating utilities. No stream matching will take place between the dehydrogenation and hydrogenation parts of the process, because it cannot be guaranteed that both will operate at the same time. However, in practice, it is likely that a dynamic heat exchange system would reduce utility use and cost. The results presented here should therefore be considered a maximum cost for fulfilment of energy requirements.

Pinch analysis seeks to balance the annual cost of cooling/heating utilities with the capital investment of a heat exchange network, with the aim of finding an optimum combination of the two, where as little annual cost as possible is incurred[117, 118]. This is achieved by altering DTmin (in Kelvin), the minimum temperature difference of any two exchanging streams. In other words, the temperature difference between any two exchanging streams will always be equal to or more than DTmin. A smaller DTmin leads to more heat exchange between streams hence a higher capital cost of heat exchangers, but also lower cost of heating/cooling utilities. The optimum value of DTmin is where the sum of the two costs is the lowest. This is illustrated by Figure 7-3[118].
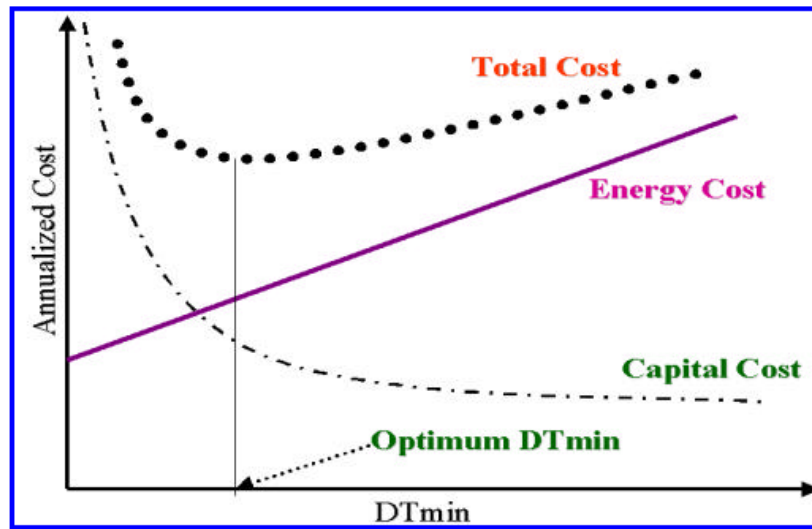
Figure 7-3: How to optimise DTmin

7.4.2.4 Investment Appraisal

Cost estimation for equipment and utilities are sourced from a variety of resources or estimated by various techniques as appropriate. Specific methods and resources are given throughout the analysis.

Total process capital cost is estimated using the FACT (First Approximation Costing Technique) Method of Cost Estimation from Olin Engineering[119]. This method generates an early estimation of the total installed cost of the process as a factor of the cost of major equipment.

Annual operating costs are determined by reference to the mass and energy balances carried out for the systems. Annual material and energy inputs are calculated, and the annual cost of these inputs are estimated. Process maintenance is taken as 5% of total capital cost, as assumed by the Strathclyde Study.

This cost estimation will be followed by a sensitivity analysis. The cost estimations carried out so far act as a base case. The base case is then altered by changing variables on at a time by an arbitrary 20%, and seeing how these changes impact on the capital and operating costs. This will indicate which variables will cause the most impact in the case of departure from the base case estimate. It is usual when carrying out a sensitivity analysis to use profit as the metric to measure impact of variable change. However, in this case the aim is not to make profit, but rather to reduce cost. The metric the sensitivity analysis will therefore be change in capital and operational costs as a subject of the 20% change.

Finally, this economic analysis will be compared to other cases, which are as follows: Business as usual (continue running on heat oil); Anaerobic digestion of distillery waste products for methane production (as suggested by the Strathclyde Study).

7.5 Mass balance

This process consists of 5 major operations. In order to carry out a mass balance of the process, some of the factors surrounding these operations must be determined, such as operation efficiency, reaction conditions *etc*. This section details each of these operations in turn and describes the key factors within each, alongside an explanation of how the factors were determined. The five major operations are:

- Dehydrogenation
- Hydrogenation
- Hydrogen combustion (boiler)
- Electrolysis of water
- Distillation of water to supply electrolysis

7.5.1 **Dehydrogenation**

Factors to be determined for MCH dehydrogenation are: reaction temperature and pressure; thermodynamic factors (enthalpy, entropy, Gibbs energy change of reaction, leading to equilibrium constant); reaction efficiency.

Extensive thermodynamic modelling has been carried out for MCH dehydrogenation in earlier chapters. Taking the learning from this earlier work alongside literature values[23, 31, 76, 77, 84, 120], reaction conditions were chosen as shown in Table 7-3.

Table 7-3: Reaction conditions of dehydrogenation

Dehydrogenation	
Temperature (K)	673.15
Pressure (bar)	3.5

The previous thermodynamic work mentioned, although useful for it's purpose, was indicative and made assumptions which are not appropriate to make at this point *e.g.* the Ellingham approximation, where ΔH_r and ΔS_r are constant. For more specific data, fundamental thermodynamic calculations are necessary. A Hess cycle was used to calculate specific ΔH_r and ΔS_r values under the reaction conditions in Table 7-3. Following this, ΔG_r was calculated leading to derivation of the equilibrium constant K and the equilibrium conversion, x_A. Details of these calculations can be found in Appendix M.

7.5.2 **Hydrogenation**

Factors to be calculated for hydrogenation are the same as those previously calculated for dehydrogenation: reaction temperature and pressure; thermodynamic factors (enthalpy, entropy, Gibbs energy change of reaction, leading to equilibrium constant); reaction efficiency.

Again, reaction conditions based on industry literature[74] and previous experience were chosen.

Table 7-4: Reaction conditions of hydrogenation

Hydrogenation	
Temperature (K)	493.15
Pressure (bar)	24.1

Following this, all other factors listed above were calculated using fundamental thermodynamic formulae and following the same methods outlined in Appendix M.

7.5.3 **Hydrogen combustion (boiler)**

The important factors concerning the boiler are thermal efficiency and maximum capacity. Both pieces of information were freely available[82]. Equation 7-1 defines the former.

Equation 7-1

$$\text{Thermal efficiency (boiler)} = \frac{\text{Thermal energy sent to distillery (kW)}}{\text{Total thermal energy of combustion (kW)}}$$

7.5.4 **Electrolysis of water**

The electrolyser unit chosen to model in this process is the NEL A Atmospheric Electrolyser from Norsk Hydro. This was chosen due to a flexible operating range (20 − 100% of output capacity) which suits the variability of the electricital input from the wind farms. A wealth of technical information was also freely available on this model[121], including the maximum capacity range, power consumption data, operating conditions and feed water consumption.

Norsk Hydro boast a quick start-up and shut-down which allows hydrogen to be produced on demand. The operational hydrogen output adjusts automatically without manual input, and a custom hydrogen capacity can be reached owing to the modular design of the units.

7.5.5 **Distillation of feed water**

Most of the feed water for electrolysis is recycled from the boiler exhaust stream. However, some additional water supply will be required to fill the shortfall due to expected losses of hydrogen in the process. This will require a water distillation unit. This investigation is based on the use of the Norland VC6000 Commercial Distillation System, chosen due to low power consumption and a high distilled water/waste water ratio[122]. Again, technical data on this type of unit was freely available, including the maximum product water capacity and power consumption data.

7.5.6 **Major operations summary**

This section has detailed the factors to be defined for the five major operations in the process. With thermodynamic data calculated where appropriate, and efficiency/power consumption data sourced, the mass balance for the process can now be fabricated.

7.5.7 **Mass balance results**

Figure 7-4 shows the process setup and gives the results for the mass balance of the MTH system applied to the distillery application.

Some points to note concerning Figure 7-4 are as follows:

- The red dashed line separates the hydrogenation (left) and dehydrogenation (right) processes, which are buffered by material storage tanks. These processes can, if necessary, run independently of one another. As aforementioned, the average flows for each side

should be different, because hydrogenation runs on "real time" and dehydrogenation runs on "operating time". However, all flows in Figure 7-4 are based on operating time for clarity.

- Flows are based on average power requirements for the distillery. Actual dehydrogenation flows may vary according to distillery demand, and hydrogenation flows may vary depending on availability of power from the wind farms.

- The yellow dashed line intersects all of the flows entering and leaving the system. The line acts as a boundary line which envelopes the MTH system and shows the inputs required and outputs achieved.

- This diagram assumes that 100% of hydrogen for the boiler (Stream 19) comes from MCH. It would be more efficient in a real working situation to have a dynamic system, where H_2 is sent directly to the boiler from the electrolyser at all times when hydrogen production and demand coincide. However, for the purposes of this investigation, it is difficult to give a useful estimate how often this situation would arise. Therefore, the real system is likely to be less costly and more efficient than shown in this work.
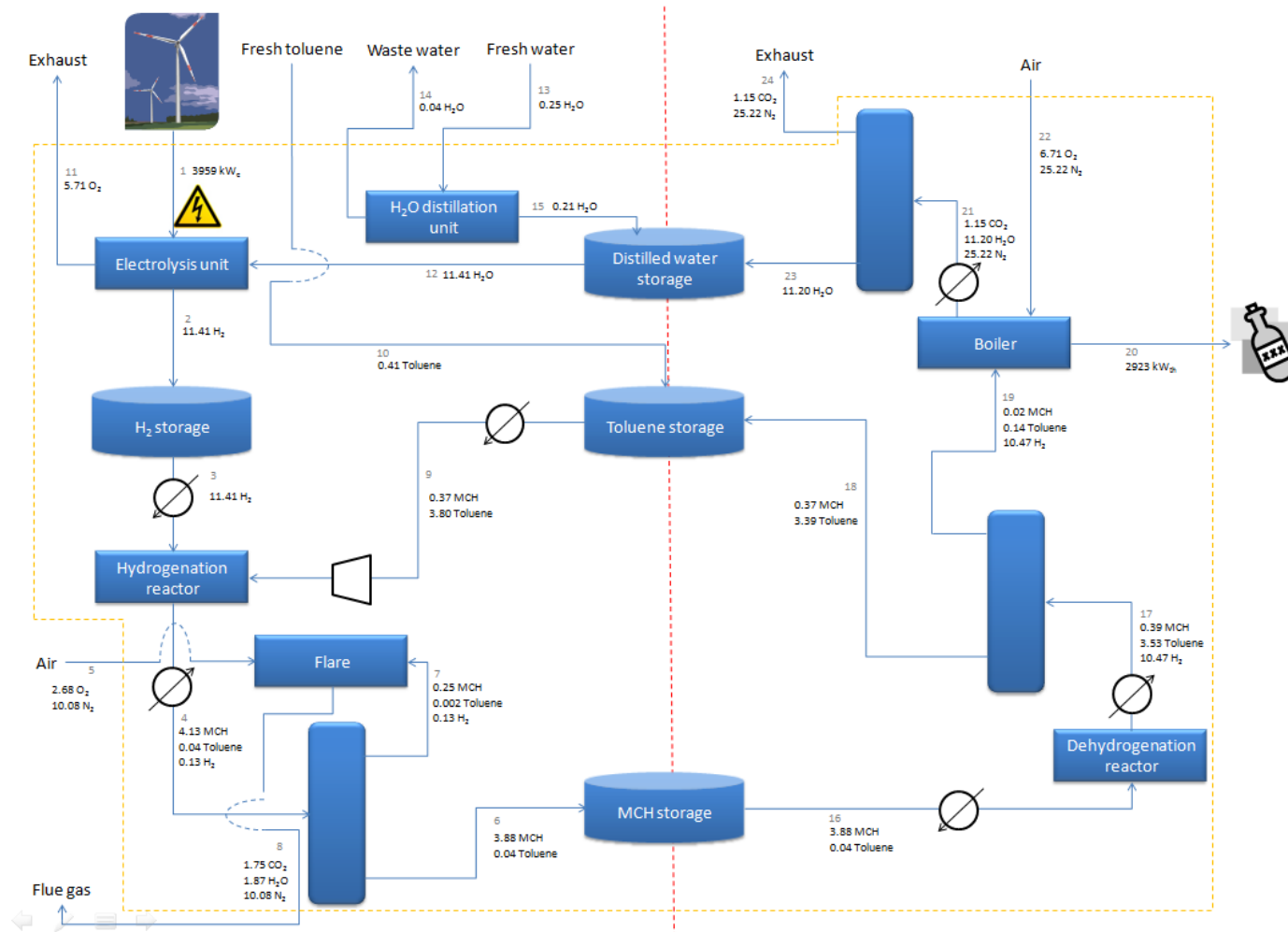
Figure 7-4: Mass balance for the MTH system to provide thermal power to Balmenach distillery. Units in mol/s unless otherwise stated. Grey numbers are stream labels. Red dashed line separates the hydrogenation/dehydrogenation processes, which can run independently of one another. Yellow dashed line is the outside boundary line, which intersects the process input/output streams.

The results of the thermodynamic investigation which made this mass balance possible are given in Table 7-5.

Table 7-5: Factors which were important in calculating the mass balance shown in Figure 7-4

Operation	Factor	Result
Dehydrogenation	ΔH_d (kJ/mol)	196.8
	K(atm^3)	2392.4
	x_A	0.899
Hydrogenation	ΔH_d (kJ/mol)	-210.4
	K	276.2
	x_B	0.989
Electrolysis	Power consumption (kWh/Nm^3 H$_2$)	4.4
	Representing an energetic efficiency of	0.806
H$_2$ combustion (boiler)	Efficiency (Equation 7-1)	0.8
Water distillation	Distilled water:waste water ratio (vol)	6.01

Some points to note on the data given in Table 7-5 are as follows:

- Equilibrium conversion of MCH, x_A, was calculated as 0.993, but this is kinetically difficult to achieve[74], therefore a more realistic value of 0.9 was chosen from the literature[23]. This was adjusted to reflect the effect of the impure MCH on the position of equilibrium (Stream 16 also contains toluene).

- Equilibrium conversion of toluene, x_B, was calculated as 0.990, which is a theoretically achievable figure, and is often surpassed in industry, where conversion of benzene to cyclohexane is generally >99%[74]. This equilibrium conversion was adjusted to reflect the presence of MCH in the toluene feed, Stream 9.

- For this first iteration of the mass balance, the power consumption of electrolysis[121] only was used to determine the draw on power from the wind farms. In reality, and in the final

iteration later in this chapter, power is also required for running water distillation and compression of Stream 9.

- Boiler efficiency from Strathclyde Study[82].
- Water distillation figures from manufacturer literature[122].

The next stage in this analysis is to carry out an energy balance.

7.6 Energy Balance

Both thermal and electrical energy demands feature in this process. All electrical demands sit on the hydrogenation side of the process, and so can be satisfied by incoming electricity from the wind farms. Thermal demand features throughout the process. The thermal energy demand will be assessed and then evaluated by pinch analysis to optimise the balance between energy exchange between streams and heating/cooling provided by utilities. These two factors will be optimised to find the lowest cost combination.

As mentioned earlier, the hydrogenation and dehydrogenation processes are considered to be independent processes, so it will be assumed that no energy exchange occurs between the two sides. However, efficiency could be greatly increased in a real system by using a dynamic heat exchange network to fully utilise all waste heat possible. Therefore, the energy exchange network presented here should be considered to offer minimum energy efficiency, with considerable opportunity to improve.

7.6.1 Energy demands

For compatibility with the process flow diagram shown in Figure 7-4, average energy flows presented here are based on operational time.

In one case, exergy is also used as part of the energy balance. As detailed in a recent paper[123], it is possible to use pressure based exergy to achieve subambient cooling. Stream 4 is under significant pressure upon leaving the hydrogenation reactor, therefore it is proposed to extend the cooling available for exchange by cooling the stream to ambient temperature and then releasing the pressure, bringing the stream to ambient pressure and causing the stream to cool to subambient temperature (illustrated by Figure 7-5). This cold stream can then be used to exchange with a hot stream, reducing the amount of utility cooling required.

P > 1 atm
T = ambient

W

P = 1 atm
T < ambient
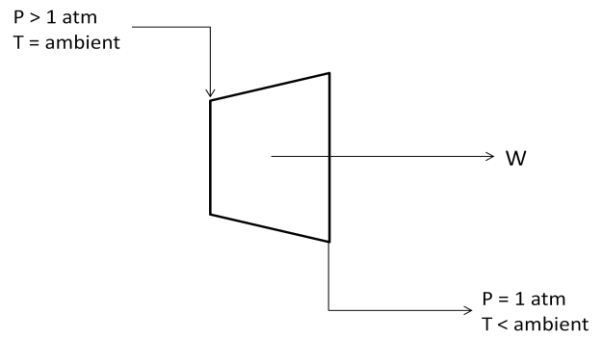
Figure 7-5: Illustration of how decompression exerts work and reduces material temperature

The energy demands of the MTH process are given in Table 7-6.

Table 7-6: Thermal energy demands for the MTH system shown in Figure 7-4, based on operational time

Stream	Process	Hot/Cold	Duty, Q (kW)	T_{start} (K)	T_{end} (K)
4	Hydrog	Hot	255.9	493.15	298.15
Hydrog reactor	Hydrog	Hot	792.9	493.15	493.15
3	Hydrog	Cold	85.9	298.15	493.15
9	Hydrog	Cold	251.8	298.15	493.15
4	Hydrog	Cold	41.4	256.12	298.15
17	Dehydrog	Hot	437.8	673.15	298.15
16	Dehydrog	Cold	462.7	298.15	673.15
Dehydrog reactor	Dehydrog	Cold	688.2	673.15	673.15

This information will be used to evaluate the optimum thermal heat exchange for this system using the principles of pinch analysis. As described in Section 7.4.2, the cost of cooling/heating utilities and the capital cost of a heat exchanger network will be compared for several values of DTmin in order to find an optimum value.

7.6.2 **Pinch Analysis**

In the following analysis, duties (Q) for the hydrogenation process may vary from those described in Table 7-6. This is because these duties were calculated according to real time rather than process time.

7.6.2.1 Composite Curves

The first stage in pinch analysis is to use the data in Table 7-6 to construct hot and cold composite curves (HCC and CCC respectively) to show the stream temperature changes *vs* the enthalpy change of heating/cooling (H). All hot streams are combined in one line to show a cumulative temperature change and enthalpy change, with the cold streams being treated the same way.

Note that the enthalpy of heating/cooling (H) is found by adding the energy input/output (Q) and the work performed (W) (Equation 7-2).

Equation 7-2

$$H = Q + W$$

In pinch analysis, no work is taken into account, therefore $W = 0$. Equation 7-2 now becomes $H = Q$, and the two terms become interchangeable.

The HCCs and CCCs for the two parts of the process based on the data in Table 7-6 are given in Figure 7-6 and Figure 7-7.
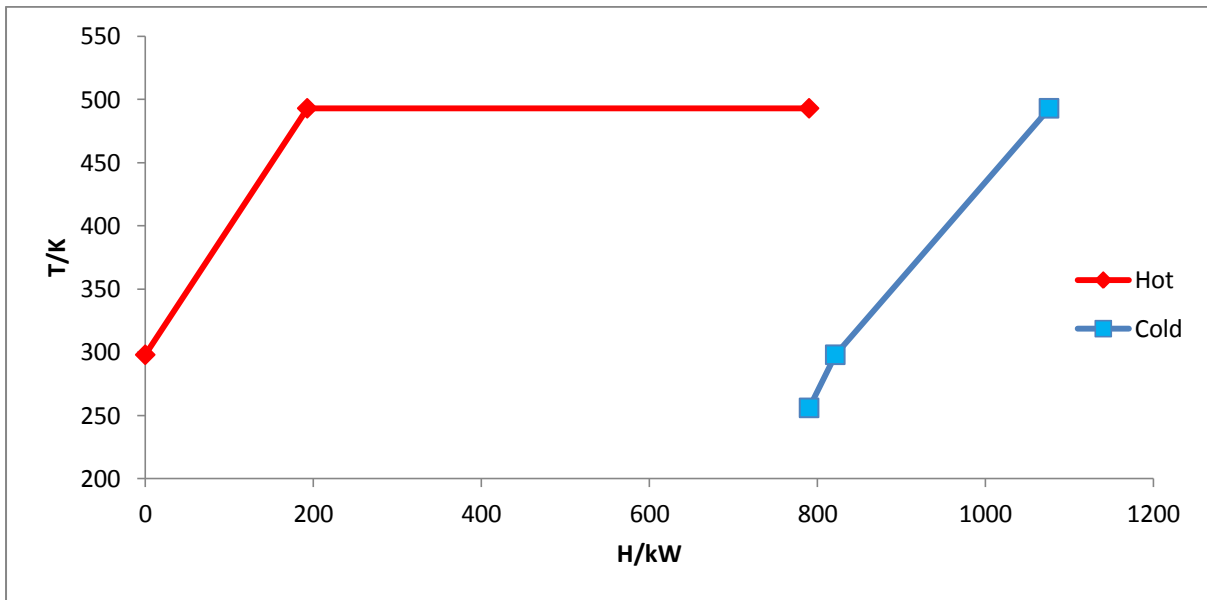
Figure 7-6: HCC and CCC for hydrogenation streams
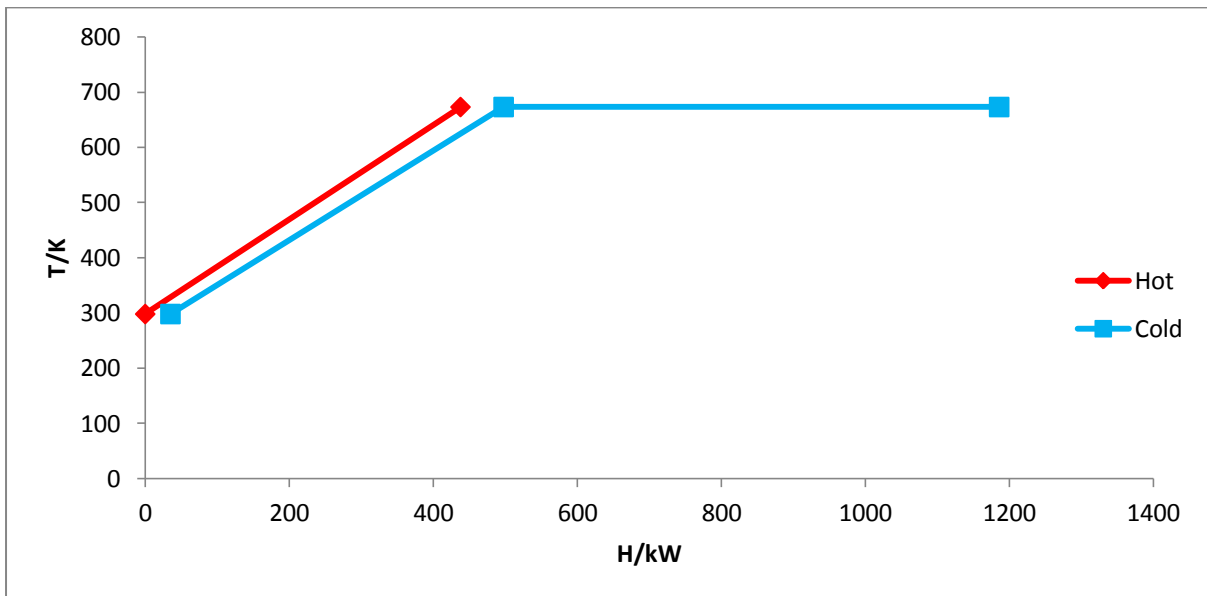
Figure 7-7: HCC and CCC for dehydrogenation streams

The CCCs are now shifted along the x-axis (enthalpy, H) towards the HCC until any part of the two lines are at a distance of DTmin on the y-axis (temperature, T). This leads to calculation of the minimum heating utility required (QH_{min}), the minimum cooling utility required (QC_{min}) and the maximum heat exchange between streams possible (QE_{max}). Determination of these three variables were carried out across a range of DTmin values. For a chemical or petrochemical process, a typical range of DTmin values would be $10 - 20$ K[118], so the range of DTmin values to be studied was set to $0 - 30$ K.

A representative example of a shifted composite curve for hydrogenation (DTmin = 30 K) is given in Figure 7-8.
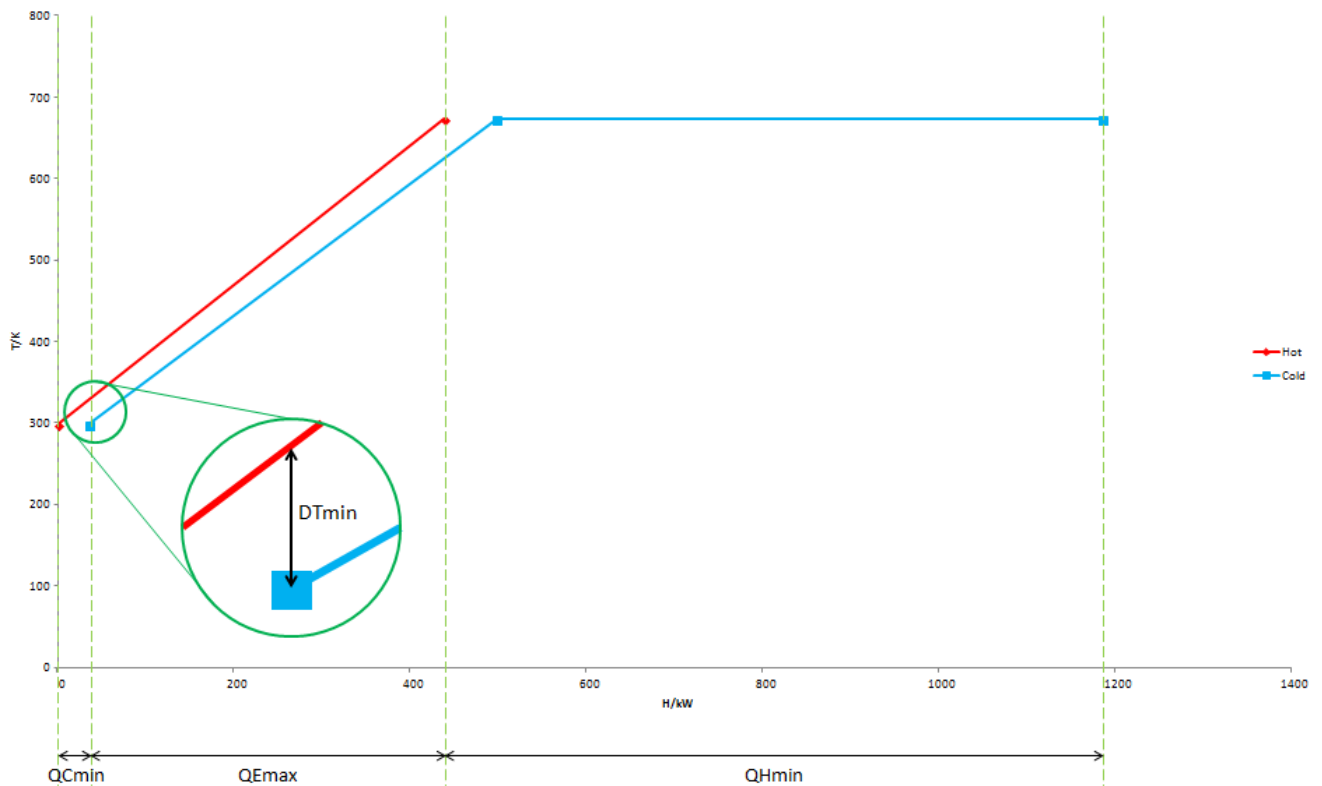
Figure 7-8: Representative shifted composite curves where DTmin = 30 K

The overlapping of the composite curves in this fashion is useful for determining minimum duties of utility cooling, but it does not offer any information about the grade of heating/cooling required. This is satisfied by the Grand Composite Curve (GCC).

7.6.2.2 Grand Composite Curve

The GCC is constructed by shifting the CCC up along the y-axis by taking each point in the curve and adding (0.5 x DTmin). Each point on the HCC has (0.5 x DTmin) subtracted from it. The result is a situation where the HCC and CCC meet at the pinch point (the closest point of contact where DTmin is measured).

The GCC can now be constructed by plotting the distances between the HCC and GCC on this shifted plot. A shifted version of Figure 7-8 is shown with the corresponding GCC in Figure 7-9.
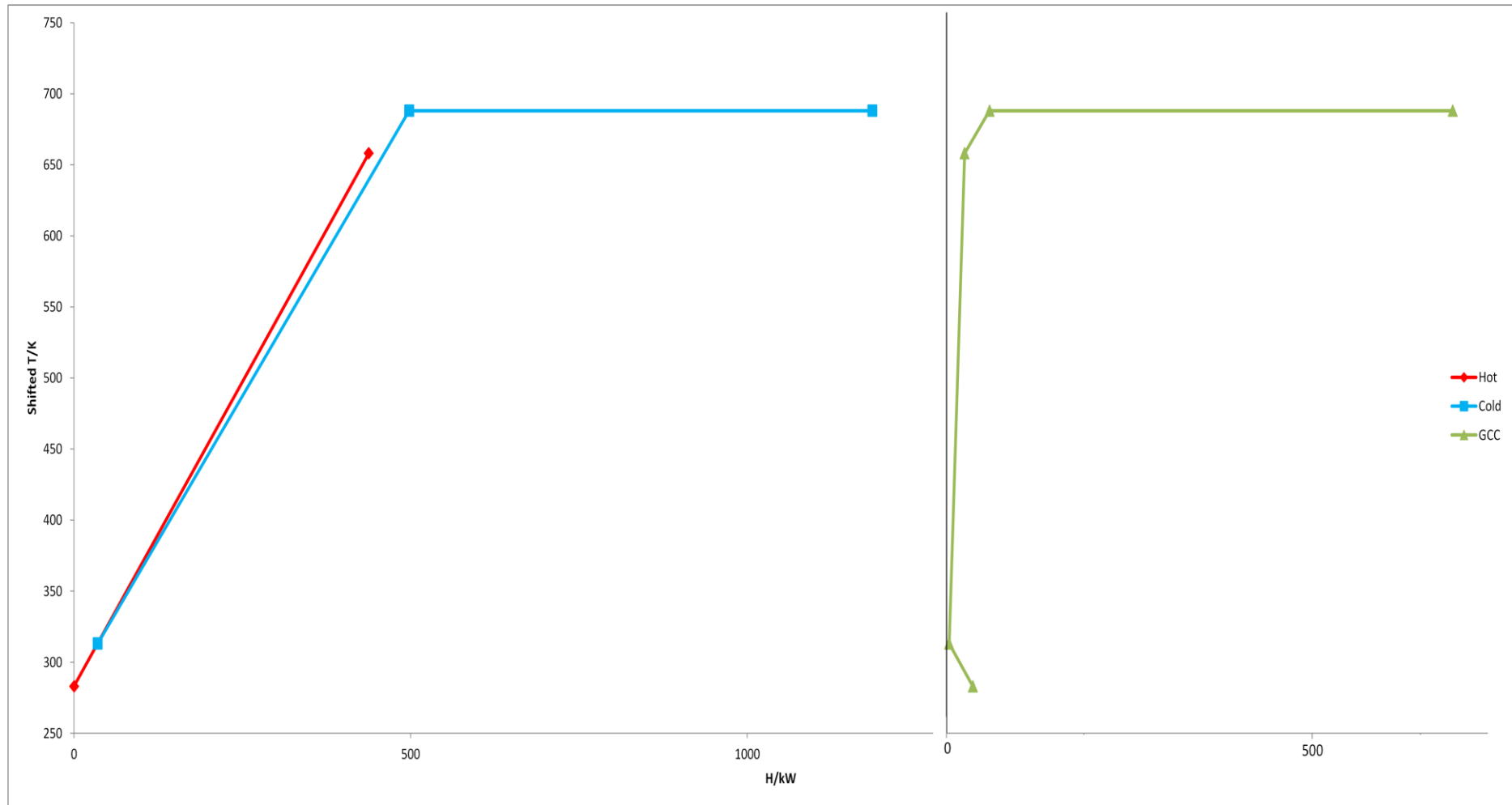
Figure 7-9: Example GCC for dehydrogenation with shifted HCC and CCC, DTmin = 30 K

The GCC can be used to give an indication of the kind of utilities necessary to provide cooling/heating, and can indicate where utility mixing can be carried out. Utility mixing is the use of utilities at different temperatures to provide heating or cooling. This can lend an economic advantage by minimizing the use of expensive utilities (*e.g.* refrigeration) and maximizing the use of cheaper utilities (*e.g.* cooling water). By placing a line from any point on the Temperature axis and drawing across to the GCC line, and by measuring this line along the Enthalpy axis, it is possible to measure the duty (H) which can be satisfied by a utility provided at the $T_{shifted}$ where the line starts. An illustration of this practice from the literature[124] is given in Figure 7-10, which shows how the same cooling demand can be satisfied with either refrigeration or with three levels of warmer, less expensive cooling utilities.
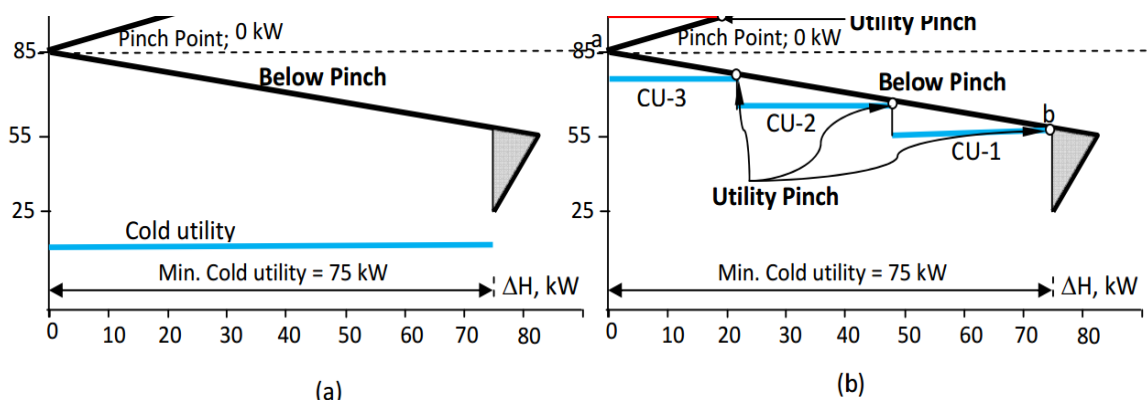
Figure 7-10: Example of how utility mixing can reduce expensive utilities such as refrigeration or high-pressure steam

In Figure 7-9, the highest shifted temperature on the GCC is 688.15 K, indicating that it is necessary to provide at least some of the heating at T = 688.15 K. In the case of Figure 7-9, at least 92% of the enthalpy requirement must be satisfied by a high-temperature utility, so there is likely to be little gain achieved by combining this with a lower temperature utility. For cooling utility, Figure 7-9 shows that the minimum temperature of the utility required is 283.15 K. This also could be combined with higher temperature, less expensive utilities if there were an economic gain in doing so.

7.6.2.3 Optimisation of DTmin

The final stage of this pinch analysis is to calculate the annualised costs of heat exchangers and utilities for each value of DTmin, and adding them to find a minimum cost at an optimum value of DTmin, as shown in Figure 7-3.

7.6.2.4 Utilities

Outside utilities are assumed to be supplied from an outside source where applicable. Where possible, air cooling is used to avoid cost and energetic penalties (the only cost for air cooling is assumed to be the capital cost of purchasing the bare tube air cooled heat exchanger). Where air cooling is insufficient, cooling water and/or refrigeration is employed. No outside heating utilities are required, because they are sourced from within the process. On the hydrogenation side, a very minor amount of heating is required due to the availability of the heat of hydrogenation. Stream 8 (flue gas) carries a duty sufficient to satisfy the remaining heating requirements of the hydrogenation process. On the dehydrogenation side, significant heating is required due to the endothermic dehydrogenation reaction. At a temperature of 673.15 K, the heating utility must also be high grade. It is impractical to use high pressure steam above a temperature of around 493 K, and hot oil or other high-grade heat transfer fluids are only specified for use up to *circa* 548 K. For higher temperature requirements, it is usual to employ a direct fired heater, which is used where the required fluid temperature is up to *circa* 800 K.

Ideally, this direct fired heater would be fuelled by the hydrogen/hydrocarbon waste stream from the hydrogenation process, Stream 7. However, it was a pre-requisite of this study that no energy exchange should occur between the hydrogenation/dehydrogenation processes. The use of a heat oil as fuel would defeat the object of the study, because hydrogen is being used here to directly replace fuel oil. Therefore the fired heater will be fuelled parasitically, using product hydrogen from the dehydrogenation of MCH. This will require modification of the mass balance shown in Figure 7-4, because the amount of hydrogen required per unit energy to the distillery will increase.

7.6.2.5 Limitations of the pinch analysis approach

Pinch analysis does not offer a perfect approach to heat management. In situations where DTmin is a small number, for example, it is common practice to increase DTmin to a manageable number if the monetary penalty of doing so is low[118]. This is because the increase in DTmin may offer a greater process flexibility, making the heat management system easier to control if operating conditions are not ideal, or not precisely those used in the pinch analysis. No such alteration will be made for this study, as the aim is only to come to an order-of-magnitude estimation of system cost. The optimum DTmin value offered by pinch analysis is enough to satisfy requirements.

This leads to the next issue with the pinch analysis approach – there is no allowance for variation in the system. The MTH system in this context in inherently variable, because not only is the influx of power from the wind farms changeable, but the power demands for the distillery is likely to be unpredictable also.

Finally, there is no allowance in pinch analysis for parasitic operation. For this MTH system, the heat of dehydrogenation will be provided by combusting some product hydrogen directly. The necessary calculations to accommodate this must be done by hand separately from the pinch analysis.

This type of analysis is nonetheless a useful tool within its limitations. The MTH process is variable, but a maximum capacity can be calculated, so although it is impossible to predict the patterns of power consumption and demand, a maximum limit of both can be ascertained. For the hydrogenation side, the limit will be set by the maximum capacity of the wind farms. For the dehydrogenation side, distillery process steam is raised using the existing distillery boiler, rated at 6,400 kW – this sets a maximum power demand for the distillery.

Pinch analysis will therefore be executed assuming maximum operation on both sides, and the optimum DTmin determined under these circumstances. This means that the heat exchange areas recommended by the pinch analysis method will be sufficient for the maximum process flows, and excessive for smaller flows but still sufficient. In the later economic analysis, equipment will be sized based on maximum capacity operation also.

For the dehydrogenation side, pinch analysis cannot account for the parasitic heating of the dehydrogenation reactor. Therefore, the analysis will be used to determine the optimum DTmin for cooling only, and the heating requirement will be calculated separately.

7.6.2.6 Pinch Analysis Results

The cost plots which led to the calculation of the optimum DTmin values are given in Figure 7-11 and Figure 7-12.

In the case of hydrogenation, the utility cost is a great deal higher than the capital cost of heat exchangers. This is because a large amount of cooling water is required due to the exothermic nature of the hydrogenation reaction. Nonetheless, a clear minimum cost is apparent when the costs are added together, and an optimum DTmin value of 3.05 K is found.
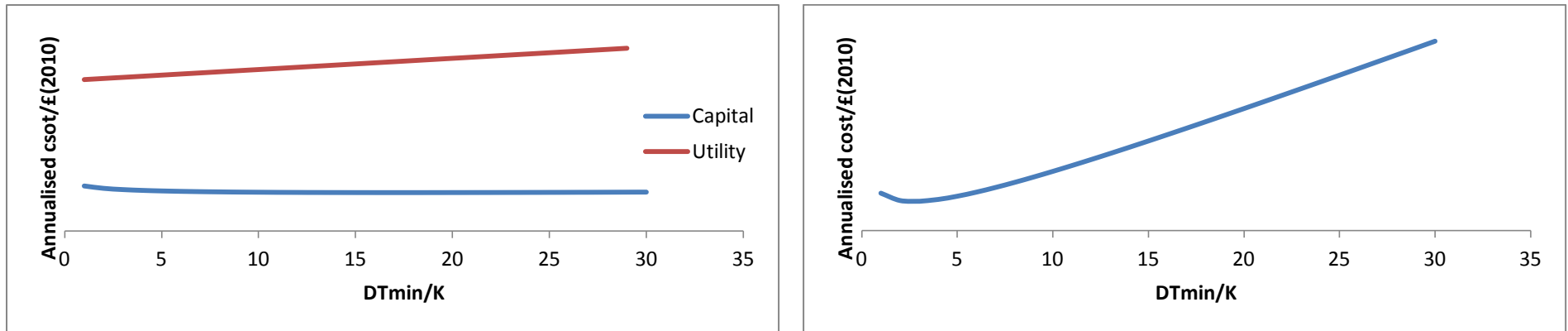
Figure 7-11: Hydrogenation process. Left - Separate annualised utility and capital costs as a factor of DTmin. Right - Total cost of utilities and capital cost as a factor of DTmin
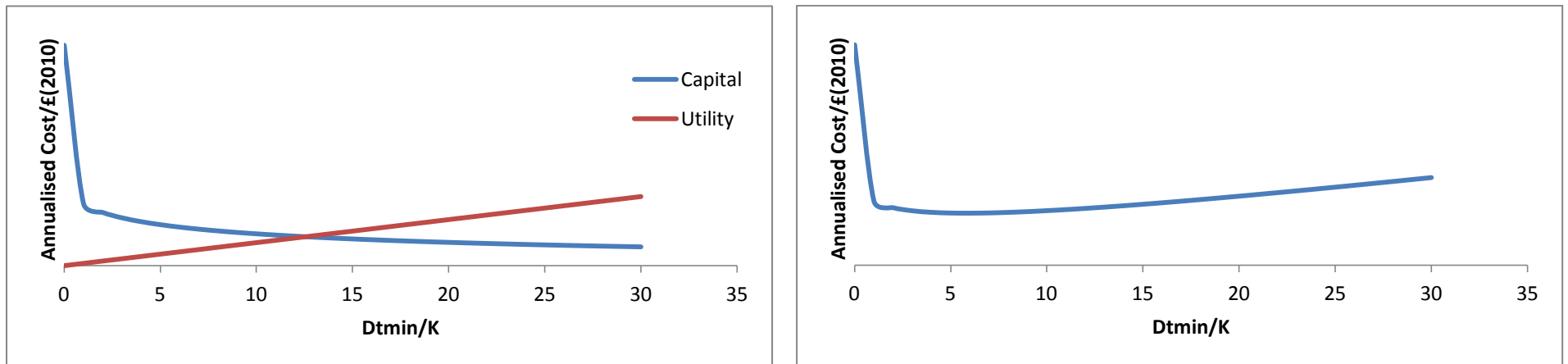
Figure 7-12: Dehydrogenation process. Left - Separate annualised utility and capital costs and a factor of DTmin. Right - Total cost of utilities and capital cost as a factor of DTmin

In the case of dehydrogenation, all heating utility is covered by parasitic combustion of hydrogen, and so is not included as part of this pinch analysis. No facility is offered by pinch analysis for parasitic heat supply, so the analysis for dehydrogenation covers heat exchange between streams and cooling utility only. Again, when the utility and exchange cost curves are combined, a clear minimum cost is visible corresponding to an optimum DTmin value of 5.73 K.

As mentioned earlier, although these are the optimum DTmin values as defined by pinch analysis, they may not be a practically viable solution as the values are low. However, the aim of this work is to estimate a minimum cost of establishing this process, so the conditions set by these DTmin values will be used.

7.6.3 **Final mass balance**

With the introduction of parasitic supply of heat for the dehydrogenation process, an altered mass balance is called for to reflect the increased average hydrogen demand. The increased demand for hydrogen will affect the mass and energy balance for the entire process. However, although the volumes of streams will increase, the relative proportions of streams throughout the process will remain the same. It is therefore the case that the DTmin values identified through pinch analysis are still valid, although the overall enthalpy changes will be larger.

The thermal energy demand to the distillery remains the same, but now for every kWth sent to the distillery *via* the boiler, 0.66 kWth is required to heat the dehydrogenation reactor and partly heat the incoming stream (Stream 16), assuming a DTmin value of 5.73 K. The new thermal power demands are summarized in Table 7-7.

Table 7-7: Process average thermal power demands, taking fired heater operation into account

Power requirement for	Average thermal demand, operational time (kWth)
Distillery	2923
Fired heater	1943
Total	4867

In the same way that the original mass balance in Figure 7-4 was designed by working backwards from the final energy demand, a new mass balance can now be designed for this heightened energy

demand required to include the fired heater. The process flow diagram shown in Figure 7-13 gives the new mass balance.

As part of this redesigned mass balance, the total electrical demand shown as Stream 1 includes the power required to run the water distillation unit and the compressor for Stream 9. No other compressors are required because all other elevated pressures required by the process can be attained by heating alone.

By taking the sum of all streams intersected by the yellow boundary line in Figure 7-13, it is possible to assess the net inputs and outputs of the system. The overall system inputs and outputs are summarized in Table 7-8 (flows in operational time).

Table 7-8: Overall system inputs and outputs (not including utility inputs/outputs). Flows in operational time

Overall inputs	Overall outputs
5303 kW_e	2923 kW_{th}
4.92 mol/s O_2	2.21 mol/s H_2O
0.55 mol/s toluene	3.86 mol/s CO_2

7.7 Conclusions

Simple energetic process efficiency can be calculated according to Equation 7-3.

Equation 7-3

$$\text{Energetic efficiency} = \frac{\text{Energy input (kW}_e)}{\text{Energy output (kW}_{th})}$$

Using the data in Table 7-8, Equation 7-3 yields an energetic efficiency of 0.55, *i.e.* just over half of the electrical energy input from the wind farms contributes to the thermal energy input for the distillery. As aforementioned, this efficiency could be improved by combusting hydrogen directly after electrolysis without intermediate storage wherever possible. The scope for direct use is difficult to accurately forecast, therefore will not be considered as part of this analysis.
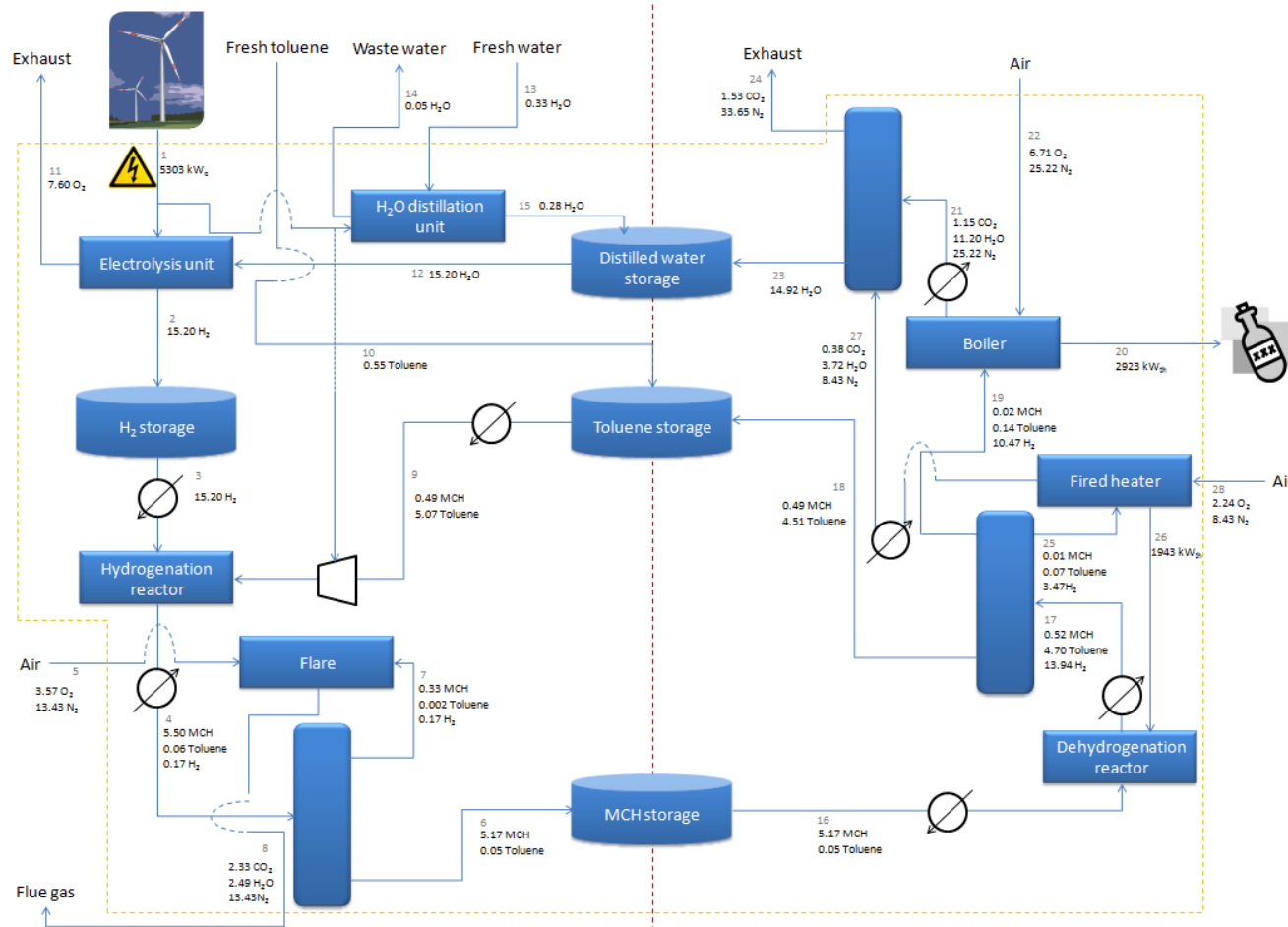
Figure 7-13: The final mass balance for the MTH system as applied to a distillery thermal power application, designed to include parasitic consumption of hydrogen to provide thermal energy for dehydrogenation. Units in mol/s (operational time) unless otherwise stated

This efficiency alone is not sufficient information to validate the use of the MTH system. The acceptability of the process for this application is not measured in efficiency, but rather by comparing the cost of the MTH system with the alternatives, particularly the annual operating costs. Therefore, the final stages in this system analysis are: calculation of capital and operation costs for the process; sensitivity analysis to give an indication of the most important process factors with regard to cost savings and environmental impact.

Chapter 8   Alternative Applications for the MTH System – Investment Appraisal

8.1 Introduction

Following the technical evaluation, which includes a detailed mass and energy balance, the aim of the investment appraisal is to offer an estimate of the capital costs of the MTH system applied to this application as well as the operating costs. This estimate will provide a starting point from which to carry out a sensitivity analysis, where the factors with the most impact on cost and environmental benignity will be identified.

Note that the cost estimates presented here are likely to be higher than in a real system. As aforementioned, a real system would need to be dynamic, whereby heat exchange can occur where possible between the two systems, saving on utility costs and capital investment for heat exchange networks. Also, if the hydrogenation and dehydrogenation systems were running simultaneously, efficiency would be improved by delivering the hydrogen from electrolysis (Stream 2) directly to the boiler (Stream 19) with no intermittent storage or release. This estimate assumes that all hydrogen delivered to the boiler arrives *via* storage as MCH, therefore is likely to be higher than the real situation would dictate.

8.2 Equipment sizing

The variable nature of this process means that the process equipment (reactors, heat exchangers *etc*) cannot be sized according to the average flows shown in Figure 7-13, but must be sized according to the maximum flows anticipated. Maximum flows for hydrogenation and dehydrogenation are set by the maximum wind farm electrical capacity and the boiler rating respectively.

The capacity of a wind farm is no indication of how much power it actually delivers. For this purpose, the capacity factor can be measured, which is defined by Equation 8-1.

Equation 8-1

$$\text{Capacity factor} = \frac{\text{Annual power production}}{\text{Maximum annual rated capacity}} \times 100\%$$

As technology moves forward, the capacity factors of new wind farms are improving. Capacity factors for modern turbines are in the range of $40 - 50\%$[125], so a conservative capacity factor of 40% will be assumed.

If 40% is the average capacity factor for the wind farms as a whole, then it is assumed that this corresponds to the average electricity requirement for the MTH process. This would lead to an overall rated wind farm capacity requirement of 9988 kW (real time). This figure gives the maximum capacity for the hydrogenation process, and leads to maximum flows for all streams on the hydrogenation side.

For the dehydrogenation process, the limiting factor is the rated capacity of the boiler, rated at 6,400 kW. It follows that this is the maximum rate of energy delivery to the distillery, so the maximum flow of hydrogen (plus trace hydrocarbons) to the boiler corresponds to an energetic value of 6,400 kW, accounting for boiler efficiency (so the flow into the boiler has a maximum energetic value of $\frac{6400\ kW}{0.8} = 8000\ kW$, see Table 7-5 for efficiency data).

From these pieces of information, maximum flowrates for any stream can be calculated. Equipment will be sized assuming these maximum flowrates. The installed equipment will be capable of dealing with the maximum duties possible, and will be surplus to requirement when flow is lower but nonetheless sufficient to deliver the required energy to the distillery.

Methods for equipment sizing varied depending on the piece of equipment. Methods for reactor sizing, heat exchanger sizing and the sizing of all other equipment included here are given in Appendix N.

The results of the equipment sizing are shown in Table 8-1.

Table 8-1: Equipment sizing results

Equipment	Metric	Size
Hydrogenation reactor	Volume (m^3)	4.77 (10 × 0.48)
Dehydrogenation reactor	Volume (m^3)	43.12
Electrolyser	Electrical rating (kW)	9932 (5 × 1986)
Water distiller	Production capacity (L/day)	827.0

Equipment	Metric	Size
Shell and tube heat exchangers	Total surface area (m^2)	52.6
Copper coils	Total copper mass (kg)	666.2
Fired heater	Maximum duty (kW)	2124
Air coolers	Total surface area (m^2)	287.8
Compressor	Maximum duty (kW)	54.6
Flare	Max. flue gas vol. Flow (m^3/s)	8.09
MCH storage vessel	Vessel volume (m^3)	125.8
Toluene storage vessel	Vessel volume (m^3)	97.5
Dist. Water storage vessel	Vessel volume (m^3)	44.6
H$_2$ storage vessel	Vessel volume (m^3)	562.3

8.3 Project capital cost

Table 8-1 gives all the information required to estimate the capital costs of the major equipment. The methods of costing are examined first, then the results are presented.

8.3.1 Equipment costing methods

- Atmospheric storage tanks were taken to cost $132/$m^3$ capacity, or £83.02/m^3 [119]
- The pressurised hydrogen storage vessel was priced by calculating the required vessel thickness, and hence calculating the weight of steel required. The resultant cost was then adjusted to reflect the material of construction as Hastelloy to prevent hydrogen corrosion. The method of calculation is outlined in the FACT method of cost estimation[119].
- The cost of Cu coils was taken to be 75% material costs and 25% fabrication cost. Material cost was calculated according to the most recent copper cost data from the London Metal Exchange[126], and hence total cost was calculated.

- The hydrogenation reactor, shell and tube heat exchangers, and the water distillation unit were all calculated using a base cost and recosting for a different size/capacity. This was carried out using the six-tenths rule[75], as shown in Equation 8-2

Equation 8-2

$$C2 = C1\left(\frac{S2}{S1}\right)^n$$

Where: $C1$ = base cost; $C2$ = new cost; $S1$ = base capacity; $S2$ = new capacity; n = exponent. Data for Equation 8-2 was gathered[127], and where appropriate, prices were altered to reflect inflation and bring prices to £ Sterling(2010).

- Air cooled exchangers, the compressor and the fired heater were estimated using a capital estimation website, matche.com[128]. This website estimates capital cost based on historical cost and capacity, and gives estimates in $(2007). These prices were altered to reflect currency conversion and inflation.

- Electrolyser cost was taken as €500/kW installed, or £420/kW installed. This is a projected cost estimated by the European Commission as part of their HYSTRUC research programme[129]. As electrolyser technology is a young technology, the price was adjusted using a Boston experience curve[130] to reflect the probable reduction in cost for ordering 5 units instead of just one.

- Flare cost was taken as $50000/m^3 flue gas.s,[131] or £31,447/m^3.s.

8.3.2 Equipment and project costing results

An order-of-magnitude estimate of the capital costs for the major equipment are shown in Table 8-2, as calculated by the methods iterated above.

Table 8-2: Major equipment costs, rounded to the nearest thousand

Equipment	Cost/£k(2010)
Hydrogenation reactors	67
Dehydrogenation reactor	73
Electrolysers	1,432
Water distillation unit	8

Equipment	Cost/£k(2010)
Shell & tube heat exchangers	9
Air-cooled exchangers	105
Cu coils	4
Compressor	36
Flare	254
Fired heater	162
Storage vessels	349
Total major equipment cost	2,499

Upon inspection of Table 8-2, it is immediately clear that the major expense is the cost of the electrolyser units, accounting for over half of the total equipment cost. Clearly if this cost could be reduced, the saving implications for the project cost would be significant.

The total cost of the project can now be estimated by processing the total major equipment cost according to the algorithm presented in the FACT method of cost estimation, shown in Table 8-3. Note that the cost of the storage vessels are not included in the major equipment costs, as these are counted at the end of the algorithm according to the FACT method. The algorithm and results are given in Table 8-3.

Table 8-3: FACT method of cost estimation[119] applied to the MTH system. *Owners costs assumed to be 0 as the distillery owns the site

	Description	Factor	Running cost/£(2010)
A	Major equipment cost	-	2,100
B	Instrumentation and control systems	15% of A	322,605
C	Major equipment incl. I&C	A + B	2,473,301

	Description	Factor	Running cost/£(2010)
D	Minor material	60% of C	1,483,981
E	Total equipment cost	C + D	3,957,282
F	Freight, insurance and handling	15% of E	593,592
G	Engineering	20% of E	791,456
H	Construction labour	60% of E	2,374,369
I	Construction equipment	10% of E	395,728
J	Construction supervision	10% of E	395,728
K	Total installation cost	SUM(F:J)	4,550,875
L	Total capital cost	E + K	8,508,157
M	Owners costs	8% of L	0*
N	Total installed cost of ISBL	L + M	8,508,157
O	Storage tanks	-	348,717
P	OSBL	30% of N	2,552,447
Q	Cost of facility	P + N	11,060,604
R	Contingency allowance	40% of Q	4,424,242
S	Material setup costs (toluene *etc*)	-	40,981
T	**Project cost**	**O + Q + R + S**	**15,874,545**

Again, the vast majority of this cost can be attributed to the electrolyser units - cost of the electrolysers as part of the Major Equipment Cost is responsible for £10,312,000 of the project cost, almost two-thirds of the entire cost.

Note that the high capital cost quoted here is attributable to the inclusion of installation capital. Many scientific analyses fail to take this into account, instead quoting only the sum of the equipment costs.

8.4 Operational costs

The operational costs fit broadly into three categories:

- **Material costs:** The cost of incoming electricity from the wind farms, toluene replenishment and water for distillation
- **Utility costs:** The cost of cooling as an outside utility
- **Maintenance costs:** The cost of equipment upkeep.

8.4.1 **Material costs**

The major material cost is likely to be electricity from the wind farm. This is the major incoming feed from outside the process. The other feeds are merely replenishment of materials which are largely recycled internally (toluene and water).

The cost of the incoming electricity is difficult to measure. Generally, cost of wind farm electricity in coastal positions such as the UK sits within the range of 4 − 5 c€/kWh[132]. However, this system was designed on the preface that this wind energy was already available and being wasted, therefore the supplier may be willing to offer the electricity at a reduced cost. This is impossible to estimate, so the cost will be taken as the lower estimate in the range, 4 c€/kWh or 3.33 p/kWh.

Toluene cost in 2006 was in the range of $2.25 − 2.38/US gal[133], equivalent to £0.41 − 0.43/L in 2010. The price will be taken as £0.42/L.

The cost of water for distillation is taken as £0.63/tonne[134]

8.4.2 **Utility costs**

Utilities from outside of the process are limited to refrigeration and cooling water due to heat being sourced internally. Refrigeration is priced at £0.038/kWh, and cooling water at £0.032/tonne[134], in £(2010).

8.4.3 **Maintenance costs**

Based on the Strathclyde Study[82], maintenance costs are simply priced at 5% of capital cost annually.

8.4.4 **Operational cost results**

Table 8-4 gives a cost breakdown of the annual operating costs for the process.

Table 8-4: Annual operational cost breakdown

Cost type	Cost element	Annual demand	Cost/£(2010)
Material	Electricity	34,997 MWh	1,165,408
	Toluene	1,208 tonnes	583,123
	Water	141 tonnes	89
Utility	Cooling water	147,213 tonnes	4,669
	Refrigeration	37,582 kWh	1,430
Maintenance	-	-	793,727
Total	-	-	2,548,448

The operational costs in Table 8-4 form the final part of the base case cost analysis. This is an order-of-magnitude cost estimate, and is subject to variation. The potential variability in the cost analysis is discussed in the following section, which is followed by the economic sensitivity analysis.

8.5 Cost analysis variability

The costs of the distillery-based MTH system given here are estimates, and are subject to variation. The likely impact of these variations will be indicated in the following sensitivity analysis. However, variability within the costs already presented is not the only source of uncertainty. There are other potential factors which have not been discussed to this point, such as potential grants

(governmental or otherwise), income from waste heat and cost of borrowing capital for investment. These factors are commented on in this section.

8.5.1 Generating extra income

Due to the stipulation that energy cannot be exchanged between the hydrogenation and dehydrogenation operations in the MTH process, a great deal of waste heat is available from the hydrogenation side due to the large exotherm of hydrogenation. There is also waste heat available from the burning of waste product on the hydrogenation side, and waste heat on the dehydrogenation side from exhaust gases which are too cool to provide useful heat to the process, but could still be sold for a space heating application. Cooling water could be used to provide cooling to these streams and subsequently sold for domestic heating or otherwise space heating. The sources of waste heat from the process are summarised in . These include only waste heat sources where cooling water can reasonably be used to achieve the desired temperature, not those which have been identified by pinch analysis to require refrigeration (the hot streams on the dehydrogenation side).

Table 8-5: Annual saleable waste heat generated by the MTH process

Stream	Material	Temperature/K	Waste heat/GWh yr^{-1}
4	Organics, trace H_2	493	1.69
8	Flue gas	2619	10.32
21	Flue gas	509	6.42
27	Flue gas	509	
Hydrog reactor	Organics, H_2	493	2.77
Total	-	-	**21.02**

Due to the remote location of the distillery, it is unlikely that all of this heat can be sold on and used. In Scotland the average household heating demand is 20 MWh/year[83], so there is sufficient waste heat here to provide heating for over 1000 homes all year.

 Some waste heat can be used to provide space heating for the distillery buildings, lowering the grid electricity consumption for the distillery. As much of the remainder as possible could be supplied to the nearest local population centre, Cromdale (*circa* 0.8 miles). Cromdale contains *circa* 95 households only. Assuming that all of these households are heated directly *via* the distillery, this would amount to an annual sale of 1.9 GWh/year.

The Renewable Heat Incentive is a government-established programme which offers rates for the supply of renewable heat energy[82]. The waste heat from this system would not be eligible to receive these rates (rates are only offered for heat generated from biomethane, biomass, solar thermal or ground sources). However, assuming a private sale agreement could be reached offering a similar rate to the RHI programme, the waste heat could be sold for 6.5 p/kWth, leading to an annual added income of £123.5k

8.5.2 Cost of borrowing

The cost of borrowing money for investment has not been taken into account thus far. At the time of writing (November 2013), interest rates are at a historic low, with some banks lending at a rate of 0.5%[135]. The gross cost of borrowing would depend on the period of borrowing (years). The longer the payback period, the larger the overall amount of interest paid but the lower the annual repayments on the loan. To borrow the full capital cost at rate of 0.5%, the annual repayments would vary as illustrated in Figure 8-1.

The actual cost of borrowing is influenced strongly by the state of the economy and the mood of the banks, and so a detailed analysis of this cost would quickly be out of date.
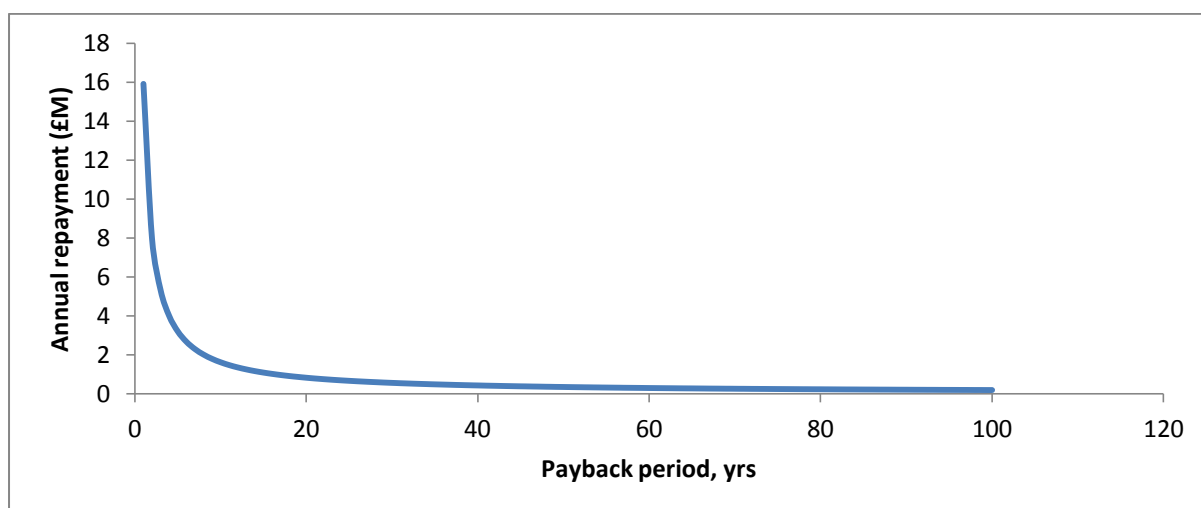
Figure 8-1: Variation of annual repayments on borrowed capital with chosen payback period

8.6 *Process comparison*

With an estimate of capital and economical costs for the Balmenach MTH system, these figures can now be compared to the alternative options. A comparison will be made in terms of cost and environmental impact. The alternative options are: no change (heat provided by fuel oil); anaerobic digestion of distillery waste (Strathclyde Study). The operational costs below include the cost of grid electricity if applicable, and it is assumed that the MTH system results in a 50% saving on grid electricity through direct supply of space heating and wind farm electricity. Also included are any additional income generated by the sale of heat and/or electricity, where applicable.

Table 8-6: Economic and carbon comparison of the three power options for Balmenach distillery

	No change	Anaerobic Digestion	MTH system
Capital cost/£(2010)	0	770,000	15,874,545
Operational cost/£(2010)	787,032	38,500	2,427,463
Annual CO_2 emission/t yr^{-1}	5632	5493	4204

It is immediately clear that the MTH system does not offer an economic driver. The anaerobic digestion approach is clearly more attractive in cost terms due to the use of waste products to provide energy rather than outside resources. It is also economically more sensible to make no change, as the existing operational costs are *circa* a third of those required by the MTH system.

There are several reasons for the high level of capital investment.

- Electrolyser cost – These electrolyser units for hydrogen production are relatively young technologies and hence demand a high price, in this case 57% of the entire major equipment cost

- Equipment sizing – This process has variable flowrates, and equipment must be sized according to the maximum possible flowrate. If the process flows were predictable and constant, then the equipment sizes given in this work would be large overestimates of the required size, hence cost

- Heat exchange & non-flexible process – This model assumes zero heat exchange between the hydrogenation and dehydrogenation parts of the process, and also that 100% of energy delivered to the distillery comes *via* the MTH process. In reality, a dynamic system would be a better design where electricity can be used directly from the wind farms and heat can be delivered by direct combustion of electrolyser hydrogen where supply meets demand, in whole or in part. This would reduce the equipment size needed, and would reduce the required replenishment of combusted hydrocarbon.

It is also likely that the capital cost of the anaerobic digestion plant is underestimated. The average energy requirement of the distillery is approximately 3 MW. To give some illustrative cost examples, a 2.8 MW AD plant build in Doncaster in 2011 came with a cost of £12M[136]. A 3.2 MW AD plant build in Wisconsin, USA in 2013 cost $28.5M to build, which converts to approximately £17.3M[136]. Taking these costs into account, it is a highly unlikely claim that an AD plant could be built to power Balmenach distillery for £0.77M. A more realistic capital cost would also incur a higher operating cost. If the plant cost a conservative £12M to match the example from Doncaster given above, then the operating costs (maintenance only) would become £600k/year. Although this is still significantly less than the cost of the MTH system, it is not as competitive as the authors claim.

Despite the poor economic standpoint, the MTH system has a considerable advantage in carbon savings, with a saving of a 25% carbon emissions based on the existing system and 23% based on the Strathclyde Study system. The choice therefore comes down to the value of a tonne of carbon dioxide.

8.7 Sensitivity analysis

As aforementioned, the final costs presented in Table 8-6 for the MTH system are subject to variability, but the extent of that variability has not been measured. For this sensitivity analysis, factors which are likely to be subject to variation will be altered by a uniform and arbitrary 20%. The impact of these changes on the cost and environmental outcomes will be measured.

It is assumed that when varying process efficiencies, the optimum DTmin values calculated as part of pinch analysis remain unchanged.

A sensitivity analysis is usually performed to indicate how changes can affect the profitability of a process. In this case there are no profits to be made, neither are there savings to be made on expenditure. Therefore, this sensitivity analysis aims to investigate which factors are most important to reduce in price in order to make the MTH system economically viable.

The factors to be varied as part of the sensitivity analysis are as follows:

- Capital cost
- Feedstock cost
- Maintenance cost
- All of the above.

Each of these factors is reduced by an arbitrary 20%, and the effect of the reduction on capital cost and annual operational cost is observed and compared to the base case (no change). This comparison is shown in Figure 8-2 and Figure 8-3.

As shown my Figure 8-2, reduction of maintenance cost has no effect on capital, and a reduction in feedstock costs has an almost indiscernible effect on capital (a 0.05% reduction) due to a small part of the capital cost being incurred by purchasing start-up toluene. Obviously, the only variation which causes a visible difference to capital is capital.

Annual costs are reduced to some degree by every change. The largest reduction comes as a consequence of reducing feedstock costs (the major annual outgoing is the cost of electricity). Reduction of capital cost causes a reduction in maintenance cost, which has almost the same effect as reducing maintenance cost directly. The combination of all these changes results in an annual cost reduction of 24.9%.
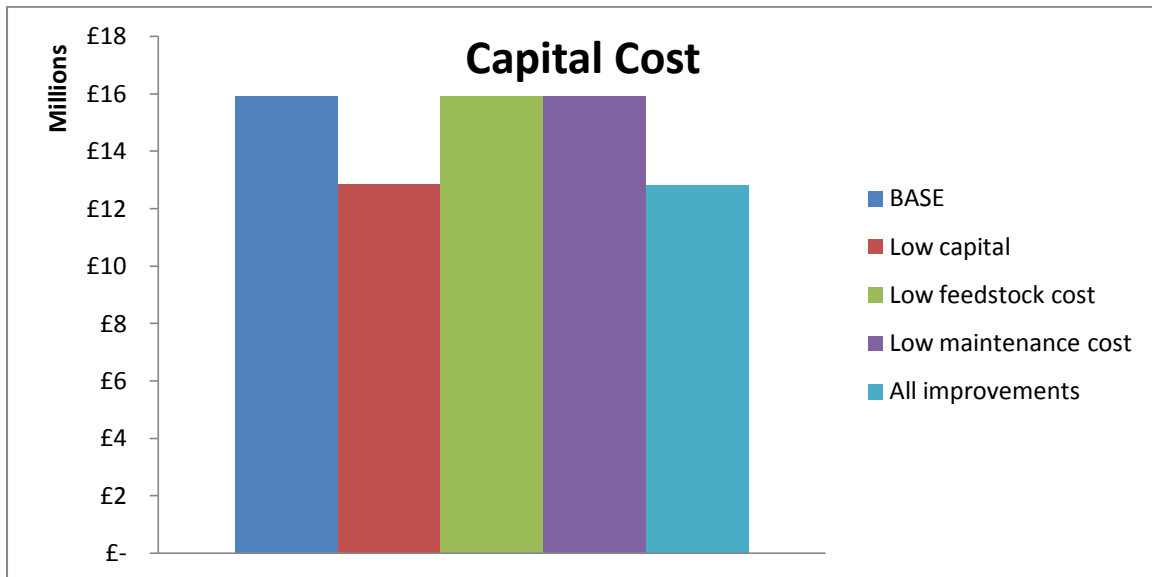
Figure 8-2: The effect of reducing given costs on overall capital costs
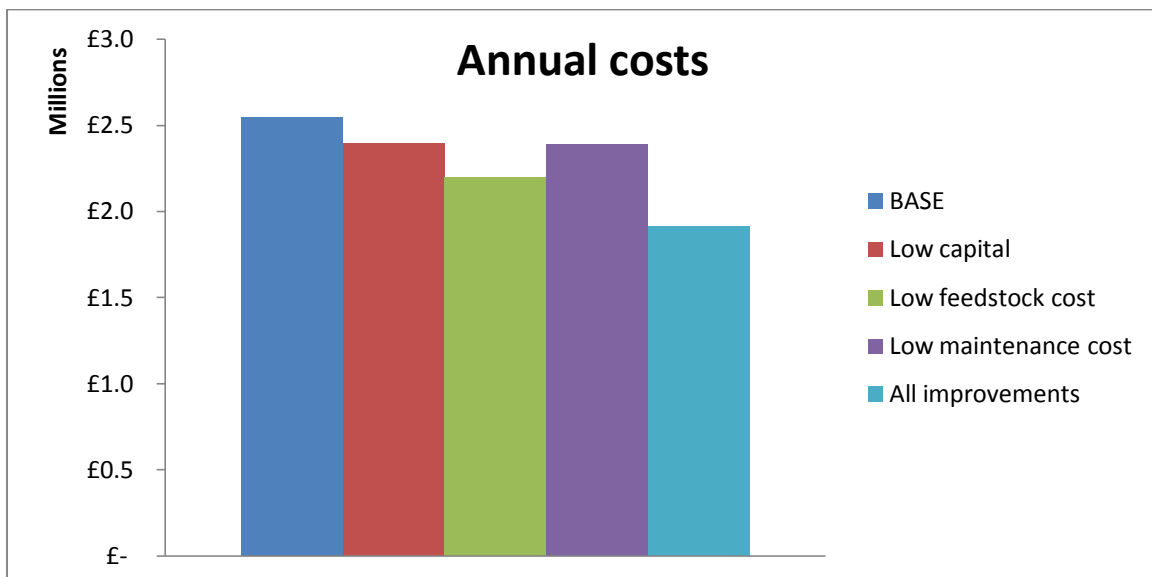
Figure 8-3: The effect of reducing given costs on overall annual costs

8.8 Investment appraisal conclusions

The base case for the MTH-whiskey system, the costs of which are given in Table 8-6, is based on a list of assumptions. These are as follows:

- No heat exchange between the hydrogenation and dehydrogenation processes
- No sale of waste heat to outside consumers
- No grants to reduce capital cost
- All H_2 delivered to the boiler goes through the MTH system

- Equipment sized to handle maximum possible flows

- Wind electricity is bought at a standard price for that technology

- Steady-state operation at all times

- No cost of borrowing is accounted for.

All of these assumptions apart from the latter two are likely to result in a high cost estimate. Heat exchange between processes would result in less utility cost. Sale of waste heat could generate extra income. A grant could make the capital cost more feasible. If a portion of H_2 could be delivered directly from the electrolyser, this would reduce operational costs of running the MTH system and capital cost, as the equipment could be smaller and less expensive. Wind farms are a relatively young technology, and electricity generated by wind is more expensive than fossil fuel derived, however, the premise of this study is that the electricity used is surplus to the wind farm operators requirements, so could likely be bought at a discounted price.

In contrast, not accounting for system start-up and shut-down (*i.e.* assuming steady-state operation) is likely to result in a lower than realistic cost estimate, and the cost of borrowing capital would incur a higher annual repayment.

The impact of changing these assumptions to reflect a more realistic situation cannot be measured without significantly more information than is available, and is beyond the scope of this study. However, it should be noted that the real capital and operational costs for this process could be more attractive than presented here.

If further study were to be carried out, the sensitivity analysis shown here indicates that the most important factors to accurately obtain are feedstock costs and capital cost. Of the assumptions above, the first and most important to investigate would be those which affect these factors. Particularly, accurate equipment costs should be calculated, as capital costs are based on these.

When comparing the MTH system to the logical alternative, anaerobic digestion of waste products, it should be noted that the Strathclyde Study[82] gives costs to set up such a process, but it is unclear how the capital costs are calculated. The capital costs presented in the Strathclyde Study are likely to be underestimated, as shown by comparison to similar facilities built elsewhere[136]. Despite this disparity, this work shows that the AD option is likely to be more cost-competitive than the MTH system.

The MTH system does have an advantage, however, in environmental impact. Use of the MTH system instead of the existing system or the AD system results in a carbon saving of 25% or 23% respectively. Expressed in tonnes, the MTH system saves the emission of 1428 tonnes or 1289 tonnes annually, compared to the existing system and the AD system respectively.

If a more realistic capital and process cost for the AD system were presented, it is likely that it would still be less costly than the MTH system. However, if the reduction in carbon emissions is also taken into account, and a monetary cost is associated with each tonne of carbon emitted (carbon taxes, green incentives *etc*), the AD and MTH systems may not be as disparate as this work suggests.

8.9 Future work

The study presented in this chapter is a first approximation. In order to discover whether the MTH system is truly viable for this application, further work should be carried out:

- Equipment should be more accurately sized and costed by taking into account the potential to deliver H_2 directly to the distillery from the electrolyser, and the potential to exchange heat between the dehydrogenation and hydrogenation processes
- The impact of these factors on operational cost should also be accounted for
- The opportunities to sell waste heat for local space heating or other local application should be investigated
- Opportunities for grants or other monetary incentives to use renewable energy should be explored
- The cost of wind electricity should be accurately estimated by opening a dialogue with wind farm operators
- Implications of process start-up and shut-down periods should be described
- The cost of borrowing capital should be added to the economic analysis.

By carrying out this work, a more accurate interpretation of the system could be made, and a true indication of the viability of the MTH system for this application could be developed.

The most prominent economic barrier is the prohibitively high capital cost. To make this system economically viable, there is a need for lower cost, higher yield technology. This is an important topic for future research.

Chapter 9   Final Conclusions and Future Work

9.1 Conclusions

9.1.1 **Vehicular MTH System Bottlenecks**

Chapter 3 was dedicated to investigating the MTH system bottlenecks with regards to visualising the MTH system as a real alternative to automotive fossil fuels. It would have been impossible to address all of these bottlenecks within the scope of a single project, but the identification of the technoeconomic blocks is a useful task in itself, and this approach to LOHCs is original and unique to this project at the time of writing (January 2014) to the best knowledge of the author.

The bottleneck which took priority in this project was the on-board dehydrogenation system, which was identified as being technically insufficiently defined. A functional heat exchange system was identified as one need, and the need for dehydrogenation kinetics sufficient to match the demands of the engine was also required. The approach taken to solve these problems was to intensify the dehydrogenation system by carrying out the dehydrogenation in the liquid phase in order to reduce energy input requirements. This would also serve to reduce the weight and volume of the system, another issue with the on-board dehydrogenation system. Finally, maximising of toluene recovery was also identified as a key goal, which would theoretically be achieved by carrying out LP-MCHDR as opposed to the traditional vapour-phase system. The start-up problem identified would be solved by using a flexible fuel feed, which would initially combust toluene, switching to 100% hydrogen when enough process heat was available to support dehydrogenation.

9.1.2 **MTH as an Automotive Fuel System**

The attempt to achieve LP-MCHDR was designed to solve the technical dehydrogenation bottlenecks described in the preceding section. The experimental findings from Chapter 4 show that LP-MCHDR is achievable, which is an original contribution of this work to the field. It was also noted that catalyst deactivation would not be problematic due to the mild conditions used for dehydrogenation, although further catalyst testing would be required to make any firm conclusions about deactivation.

The activation energy of dehydrogenation was found to be within the wide range of activation energies taken from the literature at 40.0 kJ/mol. However, there was large error associated with this figure due to equipment uncertainty and the relatively low number of experiments carried out.

Due to equipment error alone, the activation energy lies in the range of 35.6 – 42.9 kJ/mol. Rigorous statistical analysis would reveal the potential error to be higher than the estimation given in this work.

The reaction rates of dehydrogenation were not comparable to the reaction rates observed in a vapour-phase reaction, sitting two orders of magnitude below a given vapour-phase literature figure[77]. To meet a benchmark hydrogen evolution figure sufficient to sustain an engine, a minimum of 306 kg of catalyst would be required – clearly not a realistic figure. This hypothesis assumes that removal of hydrogen gas from the reactor will allow the overcoming of thermodynamic equilibrium, which has yet to be demonstrated.

Finally, system design reveals that the system is not technically feasible due to the high mole fraction of hydrocarbon in the vapour phase, which contaminates the hydrogen stream running to the engine. For the hydrocarbons to remain in the liquid phase, the possible reaction conditions are restrictive, and no feasible compromise between reaction rate and hydrocarbon mole fraction in the vapour phase can be reached.

With competing hydrogen storage technologies in the field such as tuneable MOFs and commercially available compressed hydrogen, it is unlikely that a liquid-phase MTH system has a future in an automotive application. Perhaps with refinement, a vapour-phase MTH system could find a place in an automotive environment. The MTH system as an automotive fuelling solution has been demonstrated[29, 43, 46, 48], and with further technological advancement and a new approach to solve the bottlenecks identified in Chapter 3, the MTH system may yet find itself providing power for vehicles.

9.1.3 **LOHCs as an Automotive Fuel System**

LP-MCHDR may not be a technically feasible solution to provide power to vehicles. However, the possibility of a different LOHC with different physical and reactive properties led the investigation towards the screening of alternative molecules. Four different "approaches" to the search for a new carrier were heuristically devised based on the experience of LOHCs gained in the project so far. Of these, the "Improved MTH system approach" was chosen, which is short was a search for a new carrier based on the identification of the weaknesses of the MTH system. A new carrier would be chosen based on how strong it was against these weaknesses.

The problems with the MTH system were first investigated in an attempt to define the desirable qualities to be sought in a new carrier. This led to an understanding that a great deal of restrictions are present when attempting to dehydrogenate in the liquid phase, and some cases these factors competed with one another, for example a high K is desirable to maximise conversion, but raising the temperature to achieve this encourages a higher mole fraction of hydrocarbon in the vapour phase. The aim was therefore to identify a carrier which possessed properties allowing dehydrogenation to occur in a window of conditions which would satisfy all the criteria of LP-DR. This meant a search for a carrier with a combination of low volatility and a ΔG_d lower than MCH for a given temperature. This would allow lower temperatures to be used for dehydrogenation. Also sought was a carrier with higher gravimetric and volumetric hydrogen density than MCH so that a lower liquid fuel volume and weight would be needed on the vehicle to achieve a given range.

A list of candidate carriers was fabricated, which fell into the following categories: Cyclohexane/benzene derives carriers; Heterosubstituted ring carriers; Low ΔH_d carriers and specialist autothermal carriers. Each was assessed according to their reactivity (if they were not known to be stable under dehydrogenation conditions), physical properties (to ensure that the liquid phase was retained at all times), and enthalpy change of dehydrogenation, with candidate molecules being eliminated as appropriate with each stage of assessment. Where data was available, it was found that no carrier satisfied every requirement, and for those (mostly specialist) carriers which may be able to satisfy the criteria, the relevant data was not obtainable. It was concluded therefore that it is unlikely for a "standard" molecule to be able to satisfy all criteria for LP-DR. If LP-DR were to have a future in the automotive sector, more research would be required into these specialist molecules. It is noted that this notion counteracts the aforementioned idea of using a molecule (like toluene) which is made in large global quantities today, and is therefore an inexpensive product of a mature industry.

9.1.4 The MTH System for Process Power

The preceding investigations led to the idea that although the MTH system is not ideally suited to the automotive industry, it may have qualities to offer which would be useful for other industries. A Scottish whiskey distillery was chosen due to the off-grid nature of his industry, and Scotland's political drive to provide the equivalent of 100% renewable energy by 2020. Whiskey distilleries are energy intensive and account for a large proportion of Scotland's energy needs (*circa* 1.5%). This industry was also chosen due to the substantial presence of wind-based energy in Scotland, much of which is wasted due to the inability of the grid to handle the surplus electricity or the discrepancies

between power supply and demand. This otherwise wasted electricity could be used to split water and produce hydrogen for storage by the MTH system.

The MTH-Whiskey process was first examined technically. The system was shown to be technically feasible, with a first approximation efficiency of 0.55 (that is to say that 55% of the electrical energy from wind farms manifests itself as thermal process energy for the distillery). The efficiency suffers due to the need of the process to parasitically consume some hydrogen to drive the dehydrogenation reaction. However, the efficiency also suffers because of the assumptions that:

- No thermal exchange takes place between the hydrogenation and dehydrogenation processes
- All hydrogen consumed by the distillery comes *via* the MTH system *i.e.* no hydrogen is supplied directly from electrolysis.

It is very unlikely that these assumptions would hold true in a real process. There would be times when the hydrogenation and dehydrogenation processes were running in parallel, so useful heat could be exchanged between the two. There would also be times when hydrogen production matched the demand of the distillery at the same time, hence there would be no need for a storage step. However, these features were not added to the system modelled because it would be difficult to assign meaningful periods of time to these occurrences. The results given here are hence viewed as a "worst case scenario". Despite this, the system was shown to be technically feasible. However, thermal exchange between the two processes and hydrogen storage only when necessary would strengthen the economic case for this system.

The next step was to find whether the system was economically feasible by carrying out an investment appraisal. An order-of-magnitude capital cost of almost £16M was calculated, accompanied by an annual operating cost of £2.5M. These figures are wholly uncompetitive with alternatives such as the anaerobic digestion of distillery wastes, or even with a business-as-usual model (no change). The major part of the capital cost was the cost of the electrolyser.

The MTH system did have an environmental advantage, producing a saving of up to 25% carbon emission every year by mass. The economic feasibility of the system is therefore dependent on the notional cost of a tonne of carbon emitted to the atmosphere.

It is noted that this work only gives an approximation of the cost of a real system. With further work, it is still possible that the MTH system, or an LOHC system like it, could stand as a viable alternative to diesel for off-grid application like this whiskey distillery.

9.1.5 Do LOHCs have a future?

There is no easy way to answer this question. Many competing alternative energy technologies are being researched, and whether one will emerge dominant or a blend of technologies will cover the energy landscape is unclear. The advantages of LOHCs cannot easily be ignored – no other system of energy storage offers the opportunity to use the existing fossil fuel network, and the advantages in public health and safety are compelling. Whether LOHCs have a future can only be answered by the passage of time. However, the question of whether LOHCs *could* have a future is clear, and although the ideal application for LOHCs was not uncovered by this work, the answer is nonetheless *yes*.

9.2 Future Work

If a hydrogen economy is to be realised, then a simple and economically viable route to store and distribute hydrogen must be employed. Gaseous and cryogenic hydrogen storage technologies are commercially available today, but the capital cost associated with building an infrastructure to support the distribution of these materials is likely to be prohibitively high. LOHCs offer a relatively low cost, controllable alternative which allows hydrogen to be stored indefinitely, and distributed using existing channels. However, there are challenges in aspects of the science and technology of LOHCs which need attention before an LOHC-hydrogen economy could become viable.

There is still a need to invest some time carrying out useful work on LOHC systems. For the MTH system in particular, the bottlenecks iterated in Chapter 3 should be investigated, as this project was unable to provide solutions to all of the challenges alone.

The speculative LOHC infrastructure should be studied, with the outcome being a technical and economical summary of any changes which would need to be made to the existing fossil fuel system.

It is obvious that a LP-MCHDR system for vehicles is not feasible, but there is still work to be done on a vapour phase MTH system for vehicles. As aforementioned, a prototype MTH truck was piloted as early as 1985[46]. With 29 years of technological advancement since then, the MTH vehicle idea should be more viable now than it was then, and this is worth investigating. It may be that the MTH system is suitable not to provide hydrogen as a primary fuel source to the drive train, but rather as a

secondary source (see Section 3.5.5). Alternatively, hydrogen could act as a co-fuel with diesel/petrol, as shown by the prototype vehicle developed by Hrein Energy[48], allowing a cleaner burn despite the fact that fossil fuels are still used as the primary fuel source. This would at least serve to commercialise LOHC technology, with the potential for a LOHC system to take over from fossil fuels entirely in the future.

For non-vehicular applications of LOHCs, the range of industries which could use this technology effectively should be examined more broadly than this work has managed. A wider survey of LOHC applications would reveal whether or not the advantages of LOHCs could be used effectively in industries or processes which have not yet been investigated with LOHCs in mind.

Dissemination and Training

For the purposes of dissemination, it is planned to extract a **draft paper** from the thesis. In particular, the content of Chapter 6 would make an interesting paper, as this details thermodynamic and kinetic barriers to liquid-phase dehydrogenation. The experimental LP-MCHDR results presented in Chapter 4 could also be included. This paper could be provisionally submitted for publication in "Chemical Engineering Research and Design".

In addition, a number of conferences and events were attended throughout the project where I presented my work. These are listed in the table below.

Event	Location	Start date	Type of dissemination
International Short Course and Advanced Research Workshop	Jordanstown Campus, University of Ulster	24/01/2011	Oral presentation
International Conference of Sustainable Energy Storage 2011	Hotel Europa, Belfast (University of Ulster)	21/02/2011	Proceedings Paper and Oral Presentation
Generating the Hydrogen Fuel Society	NEC, Birmingham (University of Birmingham)	30/03/2011	Poster Defense
Faraday Discussion 151: Hydrogen Storage Materials	STFC Rutherford Laboratory, Didcot	18/04/2011	Poster Defense
UK-SHEC Researchers' Workshop	University of Bath	09/09/2011	Oral Presentation
CASE Associates Event	Lancaster University	03/03/2012	Poster Defense
Postgraduate Conference	Newcastle University	20/03/2012	Oral Presentation (won First Prize for Best 2nd Year Presentation)
Smart Hydrogen and Fuel Cell Power	NEC, Birmingham (University of Birmingham)	29/03/2012	Poster Defense
European Technical School on Hydrogen and Fuel Cells 2012	Aquis Arina Sands Resort, Heraklion, Crete (University of Ulster)	23/09/2012	Oral Presentation

Event	Location	Start date	Type of dissemination
Postgraduate Conference	Newcastle University	20/03/2013	Oral Presentation (won Second Prize for Best 3rd Year Presentation)
ChemEngDayUK2013	Imperial College, London	25/03/2013	Poster Defense

I also attended a number of formal training events throughout the project, which informed my advancement through the PhD. These are listed in the table below.

Event	Location	Start Date	Duration
Your eThesis: what you need to know	Newcastle University	17/11/2010	1 day
Scientific Writing	Newcastle University	10/12/2010	1 day
Writing a Literature Review	Newcastle University	13/12/2010	1 day
Business Enterprise in Science and Engineering	Newcastle University	10/01/2011	6 months part-time
Introduction to AspenTech modeling software	Centre for Process Innovation, Wilton, Redcar	20/05/2011	1 day
Features of Academic Writing	Newcastle University	11/10/2011	1 day
How to Protect Your Results and your Interests	Newcastle University	04/11/2011	1 day
CVs and Applications	Newcastle University	07/12/2011	1 day
Data Handling and Spreadsheet Skills	Newcastle University	06/02/2012	1 day
Managing Long Documents	Newcastle University	21/02/2012	1 day
Sustainability at the Chemistry and Chemical Engineering Interface	The Nottingham Belfry Hotel, Nottingham (facilitated by EPSRC)	25/06/2012	4 days

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Nomenclature

A	Pre-exponential factor *(not to be confused with subscript-A)*
APCI	Air Products and Chemicals Inc
C_i	Concentration of species i
cal	calorie
cc	Cubic Centimetre
CCC	Cold Composite Curve
CHG	Compressed hydrogen gas
CSTR	Continuous Stirred Tank Reactor
ΔG	Change in Gibbs Free Energy
ΔG_d	Change in Gibbs free energy of dehydrogenation
ΔG_r	Change in Gibbs free energy of reaction
$\Delta_{vap}H$	Enthalpy change of vaporisation
ΔH_d	Enthalpy change of dehydrogenation
ΔH_r	Enthalpy change of reaction
$\Delta H_{oxidation}$	Enthalpy change of oxidation
ΔS_d	Entropy change of dehydrogenation
ΔS_r	Entropy change of reaction
Deg C/°C	Degree celcius
DTmin	Minimum temperature of approach
E_A	Activation energy
F_A	Liquid flowrate leaving the reactor
F_{A0}	Liquid flowrate entering the reactor
FACT	First Approximation Costing Technique
G	gram
Gal	Gallon
GC	Gas chromatography
GC-FID	Gas chromatography with an in-line Flame Ionisation Detector
GCC	Grand Composite Curve
H	hour
HCC	Hot Composite Curve

HP	High pressure
ICE	Internal Combustion Engine
IPCC	Intergovernmental Panel on Climate Change
J	Joule
k	Rate constant
K	Kelvin
K	Equilibrium constant
K_p	Equilibrium constant based on partial pressures
L	Litre
LHG	Liquid hydrogen (cryogenic)
LOHC	Liquid Organic Hydrogen Carrier
LP-MCHDR	Liquid-phase methylcyclohexane dehydrogenation
LP-DR	Liquid-phase dehydrogenation
m^3	Cubic metre
MCH	Methylcyclohexane
MCHDR	Methylcyclohexane dehydrogenation
MOF	Metallic Organic Framework
mol	Mole
mol%	Molar percentage
MON	Motor Octane Number
MTH	Methylcyclohexane-Toluene-Hydrogen
n_i	Moles of species i
n_{i0}	Moles of species i at start of reaction
n_T	Total moles of all substances
P_1	A known pressure corresponding to T_1
P_2	New pressure after pressure change
PEM fuel cell	Proton Exchange Membrane fuel cell
PFR	Plug Flow Reactor
P_i	Partial pressure of species i
ppm	Parts per million
P_T	Total reaction pressure
P_{HC}	Pressure of system hydrocarbons
PV	Photovoltaic

redox	reductive-oxidative
r_i	Rate of reaction of species i
R	Universal gas constant, 8.314 $J\,K^{-1}\,mol^{-1}$
RON	Research Octane Number
RWGS reaction	Reverse Water Gas Shift reaction
SiC	Silicon carbide (carborundum)
SMR	Steam Methane Reforming
SOEC	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell
STP	Standard Temperature and Pressure
Syngas	Synthesis Gas
T	Temperature
T_1	A known boiling temperature corresponding to P_1
T_2	A new boiling temperature corresponding to P_2
T_d	Temperature of dehydrogenation
Tol	Toluene
TSB	Technology Strategy Board
TWh	Terawatt-hour
UK	United Kingdom
V	System volume
V-L	Vapour-liquid
VAT	Value Added Tax
VLE	Vapour-liquid equilibrium
W	Mass of catalyst used
W	Watt
WGS reaction	Water-Gas Shift reaction
Wh	Watt-hour
wt%	Percentage by weight
x_i	Reactive conversion of species i
y_i	Mole fraction of species i

Appendix A

First, consider the relative sizes of the storage tanks at each station:

Assume a storage tank can contain x litres of MCH at STP.

Figure A-1: Relative sizing of MCH and Toluene storage tanks for filling stations

Performing the same calculation but omitting the recycling efficiency, the final answer is 0.83x L toluene, therefore the following conclusions can be drawn:

- At the filling station, the toluene tank must be 0.83 times the volume of the MCH tank.

- 0.03 times the volume of MCH distributed must be replenished in toluene

Therefore:
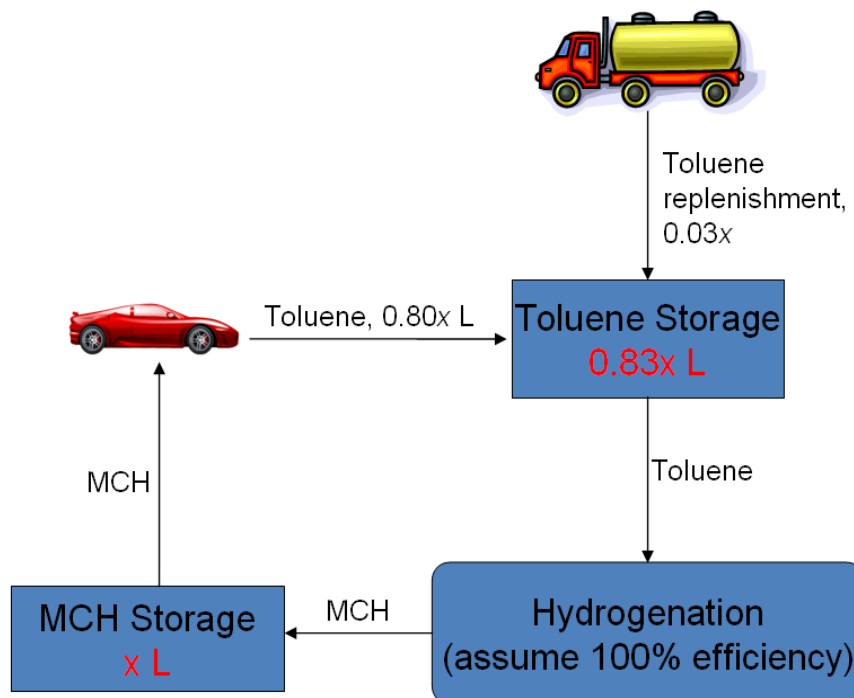
Figure A-2: simplified cycle for an MCH-producing filling station

What is *x*?

4 – 8 kg of hydrogen is required on-board a vehicle to allow a satisfactory range[15, 18], and it can be calculated that 6 kg hydrogen would offer a range of 186 miles[15]. This could be considered an acceptable range, and with the large volume of MCH compared to petrol, this is a good compromise.

According to the equation:
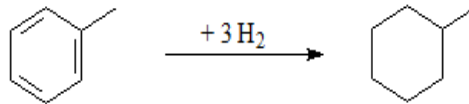
Figure A-3: Hydrogenation of toluene to give MCH

…every 3 moles of hydrogen produces 1 mole of MCH. Therefore (assuming STP):

Figure A-4: Calculation of on-board fuel tank size for MCH vehicles

126.5 L will therefore be the tank size of an MCH vehicle.

Table A-1: Calculation of MCH and toluene demand

Vehicle hydrogen capacity	6 kg
Equivalent as MCH	126.5 L
Vehicle range	186 miles per tank
Average annual mileage	10,000 miles
Tanks (cycles) per year	$\dfrac{10000\ miles}{186\ miles\ per\ tank} = 53.76\ cycles\ per\ year$
Number of MCH vehicles in UK	15.5 million
Annual MCH demand	$126.5L \times 53.76\ tanks\ per\ year$ $\times\ 15.5\ million\ vehicles$ $= 1.05 \times 10^{11}L\ per\ year$

	This is 81.2 million tonnes per year
MCH storage tank size at filling station	30485 L
Toluene minimum storage tank size at filling station	25302 L
Daily delivery amount to each filling station	915 L

Therefore, the MCH storage tank should carry 30485 L MCH on average to allow supply for a day, with hydrogenation occurring overnight to take advantage of cheaper electricity.

The toluene storage capacity represents a minimum volume to:

- collect the depleted toluene and

- receive toluene replenishment deliveries.

However, the tanks size could be bigger to account for the shortfall in reclaimed toluene, and remove the necessity of daily toluene deliveries. This would increase the efficiency of tanker use, and this will lead to an economic benefit.

Table A-2: Calculation of necessary fuel storage volumes with varying gaps between toluene deliveries

Days between toluene deliveries	MCH storage for 1 week (L)	Toluene storage (L)	Total (L)	Delivery volume (L)
1	30484	25302	55787	915
2	30484	26216	56702	1829
3	30484	27131	57616	2744
4	30484	28046	58531	3658
5	30484	28961	59445	4573
6	30484	29875	60360	5487
7	30484	30790	61275	6402

A total storage capacity of 61275 L is not unreasonable. According to publications from the Health and Safety Executive (HSE)[137], the storage volume of hydrocarbons at filling stations is not limited to any set amount. Each vendor of fuels must individually apply for a license to distribute fuel, and individual circumstances are accounted for in each case. It is therefore reasonable to assume that if MCH were a widespread fuel, a storage volume of 61275 L would be acceptable.

The flow chart can now take the following form:
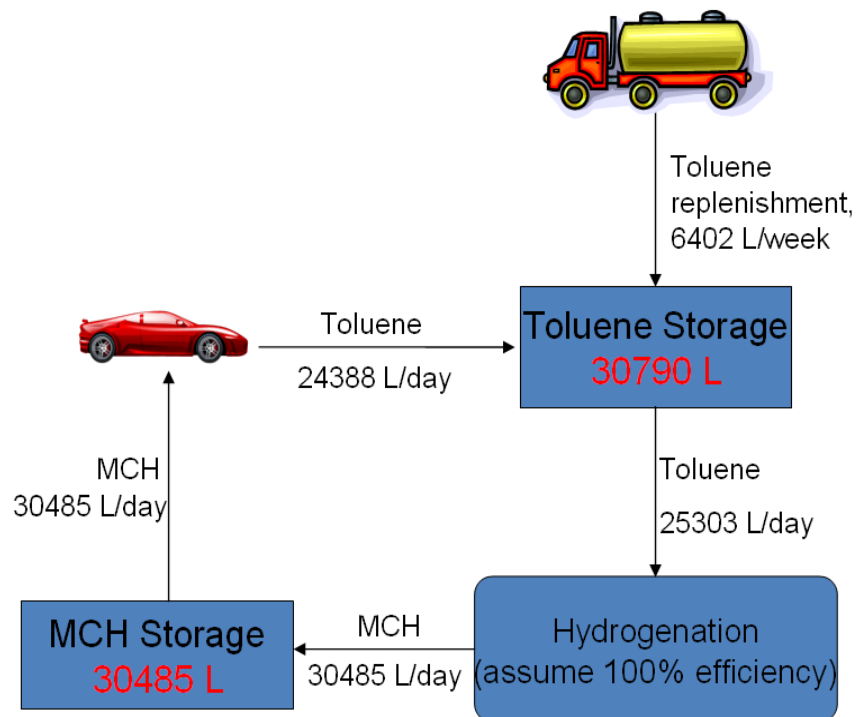
Figure A-5: Specific storage and flows for a simplified average MCH filling station

Appendix B

A single plant, owned by SABIC, has the potential to hydrogenate benzene to manufacture 350,000 tonnes/year of cyclohexane[138]. Therefore, it can be reasoned that the molar equivalent of MCH could be manufactured in a similar process.

Table B-1: Projected MCH production based on an existing cyclohexane plant

Cyclohexane production	350,000 tonnes per year
Cyclohexane molar mass	84.162 kg/kmol
Cyclohexane production in kilomoles	$\dfrac{(350,000 \ tonnes \ \times 1000)kg}{84.162}$ $= 4,158,646 \ kmol/year$
MCH molar mass	98.189 kg/kmol
Expected MCH production per plant	$\left(4,158,646\dfrac{kmol}{yr} \times 98.189\dfrac{kg}{kmol}\right) \times \dfrac{1000kg}{tonne}$ $= 408333 \ tonnes \ per \ year$
Nationwide annual MCH demand	81.2 million tonnes
Therefore number of MCH plants required nationwide	$\dfrac{81.2 \ million \ tonnes}{408333 \ tonnes} = \mathbf{199 \ plants}$

199 MCH plants are required nationwide, each producing 408,333 tonnes MCH/year.

Therefore, flows can be calculated for each of the 199 MCH plants:

Table B-2: Flow calculations for plants under Central Scenario 1

Annual MCH requirement	81.1 million tonnes
Hours per annum	8760 hours
Plant availability	90 %
Operational hours	7884 hours
Number of plants	199 plants

MCH output per plant	$\dfrac{81 \ million \ tonnes}{7884 \ hours} \div 199 \ plants$ $= 51.8 \ tonnes \ per \ hour$
Assumed hydrogenation efficiency	100%
Toluene molar mass	92.141 g/mol
MCH molar mass	98.189 g/mol
Toluene input	$51.8 \dfrac{tonnes}{hr} \times \dfrac{92.141 \frac{g}{mol}}{98.189 \frac{g}{mol}} = 48.6 \ tonnes/hr$
Hydrogen molar mass	2.016 g/mol
Hydrogen input	$(51.8 - 48.6)\dfrac{tonnes}{hr} = 3.2 \dfrac{tonnes}{hr}$
Fresh toluene input equivalent	$48.6 \dfrac{tonnes}{hr} \times \dfrac{0.03}{0.83} = 1.76 \ tonnes/hr$
Recycled toluene input equivalent	$(48.6 - 1.76)\dfrac{tonnes}{hr} = 46.8 \ tonnes/hr$
Number of filling stations	9500 stations
Stations per plant to service	$\dfrac{9500 \ stations}{199 \ plants} = 48 \ stations \ per \ plant$
Central MCH storage	1243 tonnes
Density of MCH	0.77 kg/L
Therefore central MCH volumetric storage capacity	$\dfrac{1243 \ tonnes \times 1000 \ kg/tonne}{0.77 \ kg/L} = 1.6 \ million \ L$
Add 10% volumetric capacity for uneven deliveries	**1.8 million L**
24 hours of incoming toluene	1010 tonnes
Toluene density	0.87 kg/L
Volumetric central toluene storage capacity	$\dfrac{1010 \ tonnes \times 1000 \ kg/tonne}{0.87 \ kg/L} = 1.2 \ million \ L$

| Add 10% volumetric capacity for uneven deliveries | 1.3 million L

This includes overflow in case of 24 hour process shutdown |
| --- | --- |

Appendix C

Table C-1: Flow calculations for plants under Central Scenario 2

Annual MCH requirement	81.1 million tonnes
Hours per annum	8760 hours
Plant availability	90 %
Operational hours	7884 hours
Number of plants	11 plants
MCH output per plant	$\dfrac{81\ million\ tonnes}{7884\ hours} \div 11\ plants$ $= 936\ tonnes\ per\ hour$
Assumed hydrogenation efficiency	100%
Toluene molar mass	92.141 g/mol
MCH molar mass	98.189 g/mol
Toluene input	$936\dfrac{tonnes}{hr} \times \dfrac{92.141\frac{g}{mol}}{98.189\frac{g}{mol}} = 878\ tonnes/hr$
Hydrogen molar mass	2.016 g/mol
Hydrogen input	$(936 - 878)\dfrac{tonnes}{hr} = 58\dfrac{tonnes}{hr}$
Fresh toluene input equivalent	$878\dfrac{tonnes}{hr} \times \dfrac{0.03}{0.83} = 32\ tonnes/hr$
Recycled toluene input equivalent	$(878 - 32)\dfrac{tonnes}{hr} = 846\ tonnes/hr$
Number of filling stations	9500 stations
Stations per plant to service	$\dfrac{9500\ stations}{11\ plants} = 864\ stations\ per\ plant$
Central MCH storage	22463 tonnes
Density of MCH	0.77 kg/L
Therefore central MCH volumetric storage capacity	$\dfrac{22463\ tonnes \times 1000\ kg/tonne}{0.77\ kg/L} = 29.2\ million\ L$
Add 10% volumetric capacity for uneven deliveries	**32.1 million L**
24 hours of incoming toluene	18259 tonnes
Toluene density	0.87 kg/L
Volumetric central toluene storage capacity	$\dfrac{18259\ tonnes \times 1000\ kg/tonne}{0.87\ kg/L} = 21.1\ million\ L$
Add 10% volumetric capacity for uneven	**23.2 million L**

deliveries	This includes overflow in case of 24 hour process shutdown

Appendix D

On average, 916 L of toluene must be delivered to 9500 stations daily, leading to a weekly total of 60.8 million litres. In practice, it may be more practical to carry out less frequent deliveries to ensure efficient use of tankers. Large tankers have a volume of 21k – 34k L so it would be prudent to service a single station every 30 days (27480 L) or 4 stations every 7 days (25648 L) etc, but bear in mind that the longer a station needs to wait without replenishment, the larger the toluene storage capacity at the station must be. This is to ensure that the shortfall of toluene does not cause a shortfall of MCH.

Table D-1: Filling station storage volumes for varying delivery intervals

Days between toluene deliveries	MCH storage for 1 week (L)	Toluene storage (L)	Total (L)
1	30377	24302	54679
2	30377	25218	55595
3	30377	26134	56511
4	30377	27050	57427
5	30377	27966	58343
6	30377	28882	59259
7	30377	29798	60175

NB. 30377 L is the daily demand for MCH on average from each station. It is assumed that all toluene recovered from vehicles as they replenish their fuel supply is hydrogenated and used again.

For practicality, it should be aimed for that the station can supply MCH without toluene replenishment for 7 days. Calculation of tanker requirement based on toluene delivery volumes is shown below:

Table D-2: UK tanker requirement for toluene replenishment

Delivery Volume	6402 L/station/week 3.16 x 10^9 L/yr
Number of stations	9500
UK toluene delivery volume per week	$6402 \ (L/station)/week \times 9500 stations$ $= 61 million \ L/week$
Assumed tanker servicing capability	5 stations/day
Assumed tanker capacity	32009 L
Tanker requirement for replenishment	271 tankers

Therefore, tankers required for toluene replenishment = 271

Also to consider is the extra transport for the exchange network required to deliver MCH to non-operative stations, and to return toluene from these stations to the stations operating 24 hours a day.

Table D-3: Tanker requirement for exchange network, and total UK tanker requirement

MCH transport for exchange network	30485 L/station/day
Total MCH transport per day	$(9500 \; plants \; \times 10\%) \times (30485 \; L/station)/day$ $= 29.0 \; million \; L/day$
Toluene reclaim from non-operative stations	24388 L/station/day
Total toluene transport per day	$(9500 \; plants \; \times 10\%) \times (24388 \; L/station)/day$ $= 23.2 \; million \; L/day$
Tanker capacity	32009 L
Tanker requirement for exchange network	$\dfrac{29.0 \; million \; L}{32009 \; L} = 905 \; tankers$
Total UK tanker requirement	905 tankers + 271 tankers = 1175 tankers
Add 10% for routine maintenance, breakdowns etc	1293 tankers

Therefore, total UK taker requirement for local MCH production = 1293 tankers.

Appendix E

With 199 MCH plants across the UK, MCH supply sources would be disperse, with each plant servicing only 48 filling stations on average. Therefore, transport requirements will be relatively low, because average distances between the MCH processing plant and the filling station will be low compared to the conditions of Central Scenario 2 (11 UK MCH plants), and therefore more deliveries will be achievable by a lower number of tankers within a day/week/month. To reflect this, it will be assumed that a single tanker can make 3 return journeys over 24 hours, whereas in the case of Central Scenario 2, only 1 journey will be achievable. This is fairly arbitrary, but at this stage, detailed evaluation is beyond the scope of the investigation.

Table E-1: Calculation of UK tanker requirement for Central Scenario 1

Assumed tanker capacity	32009 L
Return journeys per day	3 journeys
Time between collections/drop offs	8 hours
Number of stations	9500 stations
Number of plants	199 plants
Stations per plant	48 stations
Tankers required per day per plant	16 tankers
Tankers required nationwide	3167 tankers
Add 10% for routine maintenance, breakdown etc	3483 tankers

Therefore, UK tanker requirement for Central Scenario 1 = **3483** tankers.

Appendix F

The calculation in this case is exactly the same as shown in Appendix E, the only difference being the assumed average number of return journeys possible per day.

Table F-1: Calculation of UK tanker requirement for Central Scenario 2

Assumed tanker capacity	32009 L
Return journeys per day	1 journeys
Time between collections/drop offs	24 hours
Number of stations	9500 stations
Number of plants	11 plants
Stations per plant	864 stations
Tankers required per day per plant	864 tankers
Tankers required nationwide	9500 tankers
Add 10% for routine maintenance, breakdown etc	10450 tankers

Therefore, UK tanker requirement for Central Scenario 1 = **10,450** tankers.

Appendix G

The reasoning for the converse relationship between thermal energy and electrical energy can be explained by the following chart:
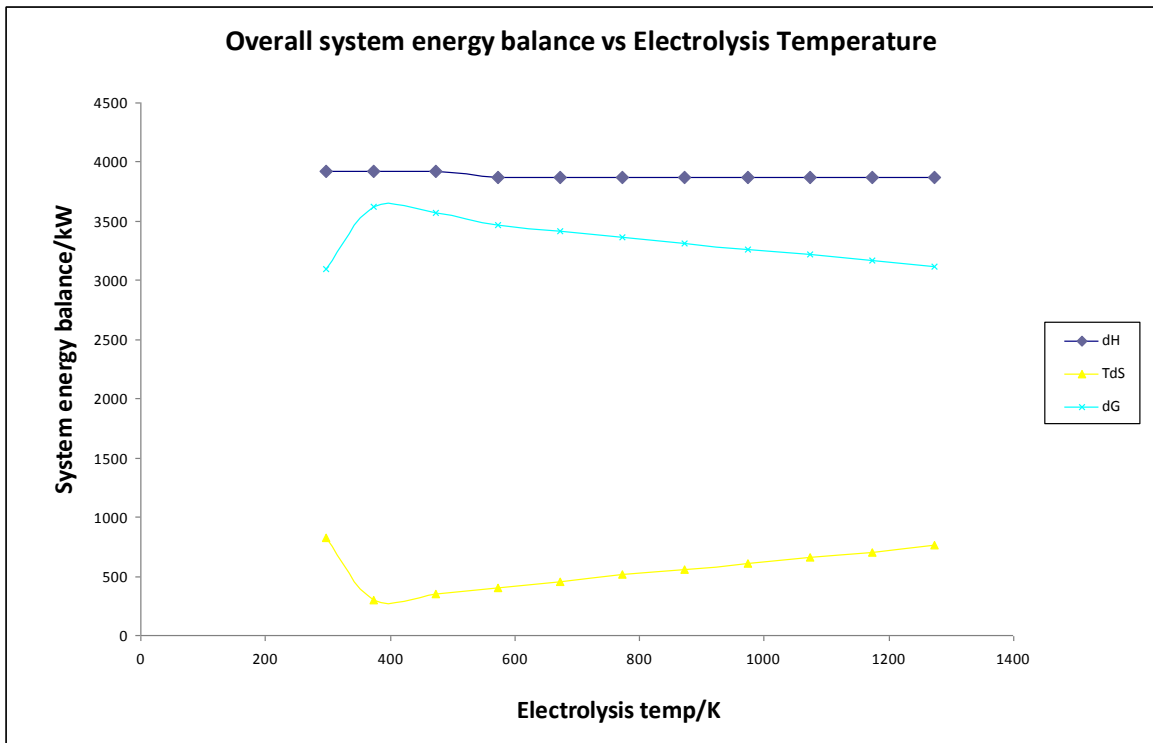
Figure G-1: Enthalpy of electrolysis split into component parts (thermal and electrical energy)

On this chart, dH (or ΔH_d) is the enthalpy of electrolysis. This can be calculated from the following equation:

$$\Delta G_d = \Delta H_d - T\Delta S_d$$

Where ΔG_d (dG) represents the electrical demand, and $T\Delta S_d$ (TdS) represents the thermal demand.

It can be seen that when more thermal energy is available, less electrical energy is required[139].

At the assumed heat of 473 K, the electrical energy, ΔG_d = 3572 kW. On conversion, this becomes:

Table G-1: Conversion of electrical input from kW to kWh/m³ H2

Assumed T_{hydrog}	473 K
dG	3572 kW
	108253 kJ/kg H_2
	9202 kJ/L H_2
	2.56 kWh/L H_2

...2.56 kWh/m^3 H$_2$.

However, this is a theoretical value assuming 100% of the electrical energy is converted to the chemical energy of hydrogen. An optimistic estimate of efficiency would be $50 - 70\%$[140], so assuming 60% efficiency, the actual dG value would become 4.26 kWh/m^3 H$_2$.

Appendix H

The fixed capital was estimated according to the FACT method of cost estimation. The working capital is simply the cost of startup toluene, and the invested capital is the sum of the two.

It was then assumed that the %ROI (% Return On Investment) was set at 20%, and according to the following equation, the annual return could be calculated:

$$\%ROI = (Annual\ Return)/(Invested\ Capital) \times 100\%$$

The annual return on investment was then added to the annual costs (toluene replenishment, hydrogen/water costs, electricity costs etc as applicable) to calculate the total annual income.

The total annual income is the total amount of money required each year to cover costs and achieve a 20% ROI. This amount was then divided between to total projected annual MCH demand (calculated from 15.5 million cars carrying out a yearly average mileage of 10000 miles) to give the cost per litre. 1.00 L of petrol is energetically equivalent to the amount of hydrogen liberated by 5.57 L of MCH, therefore the cost of 1 L MCH was multiplied by 5.57 to give to cost of the equivalent of 1 l of petrol.

The petrol price was adjusted to remove fuel duty (£0.5895/L) and VAT (20%).

Appendix I

The expression for the equilibrium constant would theoretically change if toluene and MCH were in the liquid phase, because these constituents could no longer be expressed in terms of partial pressures. However, hydrogen can still be expressed this way because it is still in the gas phase.

In terms of activities, the equilibrium constant K can be expressed as shown in Equation I-1.

Equation I-1

$$K = \frac{a_B a_C^3}{a_A}$$

Where a_i = activity of i.

Activities can be described by the relationship shown in Equation I-2.

Equation I-2

$$a_i = \gamma_i y_i$$

Where γ_i = activity coefficient of i and y_i = mole fraction of i.

Substituting Equation I-2 into Equation I-1, and describing hydrogen in terms of partial pressures, the equilibrium constant can now be described as shown in Equation I-3.

Equation I-3

$$K = \frac{P_C^3 \gamma_B y_B}{\gamma_A y_A}$$

Activity coefficients describe deviation from ideal conditions, therefore if it is assumed that toluene and MCH act ideally, we can assume that γ_i = 1. This is particularly likely to be accurate in the case of MCH (A) where the mole fraction is high given the low conversions possible in the liquid phase (see Section 4.3). Substituting Equation 4-12 into Equation I-3 and assuming that activity coefficients of the liquids are equal to 1 gives the equilibrium expression for MCHDR in the liquid phase, shown in Equation I-4.

Equation I-4

$$K = \left(\frac{3x_A}{1 + 3x_A} P_T \right)^3 \left(\frac{y_B}{y_A} \right)$$

The mole fractions y_A and y_B can be expressed in terms of conversion as well. Equation I-5 shows a general equation for mole fractions.

Equation I-5

$$y_i = \frac{n_i}{n_T}$$

We have already derived expressions for the number of moles of each component, n_i, and for the total number of moles, n_T, in terms of conversions (see Equation 4-4 to Equation 4-7). By substituting in and simplifying, the expressions for y_A and y_B can be described by Equation I-6 and Equation I-7.

Equation I-6

$$y_A = \frac{1 - x_A}{1 + 3x_A}$$

Equation I-7

$$y_B = \frac{x_A}{1 + 3x_A}$$

Substituting these expressions into Equation I-4 gives Equation I-8.

Equation I-8

$$K = \left(\frac{3x_A}{1 + 3x_A}P_T\right)^3 \left(\frac{x_A}{1 + 3x_A}\right)\left(\frac{1 + 3x_A}{1 - x_A}\right)$$

Simplification of Equation I-8 demonstrates that this is identical to Equation 4-13 – this shows that the equilibrium constant is independent of phase when calculated in terms of conversions.

Appendix J

Hydrocarbon vapour pressures were calculated under the respective reaction conditions using a calculation sourced from Perry's Chemical Engineers' Handbook[75], which gives the vapour pressure of a pure substance in terms of temperature. This formula is given in Equation J-1.

Equation J-1

$$\ln(P_i) = C1 + \frac{C2}{T} + C3\ln T + C4T^{C5}$$

Where:

P_i Pressure of i/Pa Ci Substance-specific constant

T Temperature/K

Hydrocarbon vapour pressure was calculated using Equation J-1 with the relevant reaction temperature, assuming equilibrium conditions.

Hydrogen partial pressure, P_{H_2}, was calculated using data from Table 4-3, which gives the conversion of MCH, x_A, for each set of conditions. Using this, it was possible to calculate the moles of hydrogen present in the reactor at equilibrium using Equation 4-6, which is repeated below:

$$n_{H_2} = 3.n_{A_0}.x_A$$

This could then be used to calculate the mole fraction of hydrogen present in the reactor at equilibrium using Equation J-2.

Equation J-2

$$y_{H_2} = \frac{n_{H_2}}{n_T}$$

Finally, the partial pressure of hydrogen can be calculated by multiplying y_{H_2} by the total reactor pressure, P_{H_2}.

Appendix K
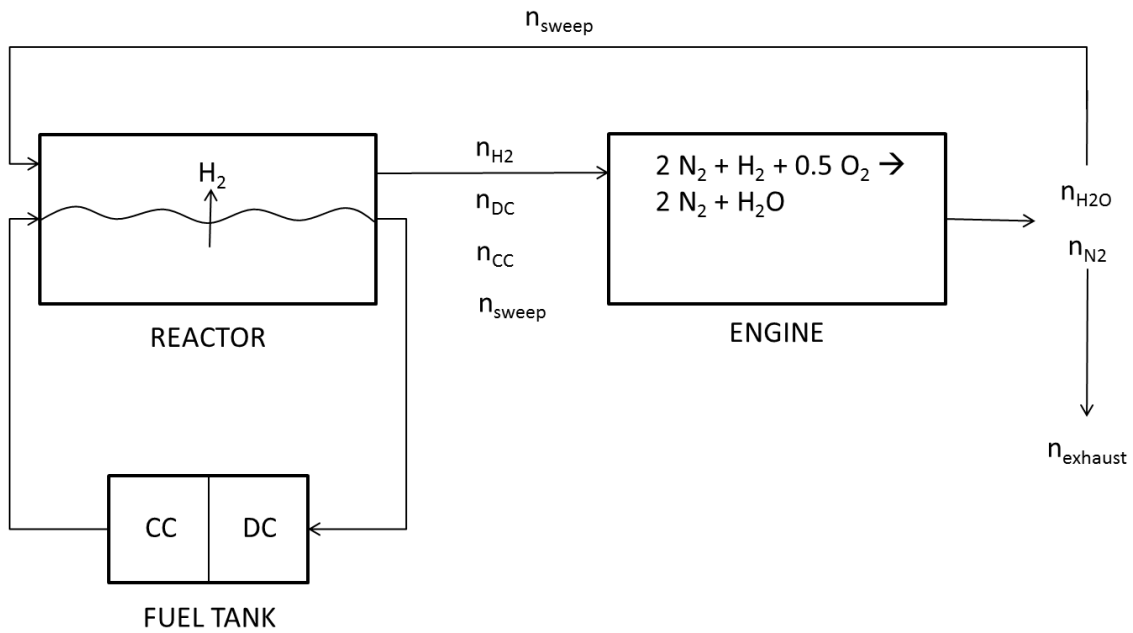
For a system where A →B + 3 H$_2$:

Equation K-1

$$V_{H_2}^{R} = y_{H_2}^{R} V_T^{R}$$

Where

z^R	parameter z in the reactor	V_{H_2}	Volume of hydrogen/m^3
y_{H_2}	mole fraction of hydrogen	V_T	Total volume/m^3

According to the perfect gas equation:

Equation K-2

$$V_T^R = \frac{n_{H_2}^R R T^R}{P_{H_2}^R}$$

n_{H_2}	moles of hydrogen	R	Universal gas constant/J K^{-1} mol^{-1}
T	Temperature/K	P_{H_2}	Partial pressure of hydrogen/Pa

Substituting Equation K-2 into Equation K-1:

Equation K-3

$$V_{H_2}^{\mathrm{R}} = \frac{y_{H_2}^{R} n_{H_2}^{R} R T^{R}}{P_{H_2}^{R}}$$

To redefine $y_{H_2}^{R}$:

Equation K-4

$$y_{H_2}^{R} = \frac{n_{H_2}^{R}}{n_T^{R}}$$

And its terms from a reactor mass balance:

Equation K-5

$$n_{H_2}^{R} = 3 n_{A_0} x_A; \; n_T^{R} = n_{A_0}(1 + 3x_A)$$

Therefore:

Equation K-6

$$y_{H_2}^{R} = \frac{3x_A}{1 + 3x_A}$$

Where

n_T Total moles $\qquad\qquad\qquad\qquad$ x_A Equilibrium conversion of A

n_{A_0} Moles of A at time = 0

Substituting Equation K-6 into Equation K-3:

Equation K-7

$$V_{H_2}^{\mathrm{R}} = \frac{n_{H_2}^{R} R T^{R}}{P_{H_2}^{R}} \cdot \frac{3x_A}{1 + 3x_A}$$

Equation K-7 assumes that gases behave ideally.

At constant temperature:

$$V_i . P_T = V_T . P_i$$

Therefore:

Equation K-8

$$V_{H_2}^{\mathrm{E}} = \frac{V_{\mathrm{T}}^{\mathrm{E}} P_{H_2}^{E}}{P_{\mathrm{T}}^{\mathrm{E}}} = \frac{V_{\mathrm{T}}^{\mathrm{E}} n_{H_2}^{E}}{n_{\mathrm{T}}^{\mathrm{E}}} = \frac{V_{\mathrm{T}}^{\mathrm{E}} n_{H_2}^{R}}{n_{\mathrm{T}}^{\mathrm{E}}}$$

Because:

Equation K-9

$$n_{H_2}^{E} = n_{H_2}^{R}$$

Therefore:

Equation K-10

$$n_{H_2}^{R} = \frac{V_{H_2}^{\mathrm{E}} n_{\mathrm{T}}^{\mathrm{E}}}{V_{\mathrm{T}}^{\mathrm{E}}}$$

Where

z^E Parameter z in the engine

Substituting Equation K-10 into Equation K-7:

Equation K-11

$$V_{H_2}^{\mathrm{R}} = \frac{RT^R}{P_{\mathrm{T}}^{R}} . \frac{V_{H_2}^{\mathrm{E}} n_{\mathrm{T}}^{\mathrm{E}}}{V_{\mathrm{T}}^{\mathrm{E}}}$$

Rearranging Equation K-11 in terms of $V_{H_2}^{\mathrm{E}}$:

Equation K-12

$$V_{H_2}^{\mathrm{E}} = \frac{P_{\mathrm{T}}^{R} V_{\mathrm{T}}^{\mathrm{E}}}{RT^R n_{\mathrm{T}}^{\mathrm{E}}} V_{H_2}^{\mathrm{R}}$$

In the engine, the reaction taking place is combustion of hydrogen: 2 N_2 + H_2 + 0.5 O_2 → 2 N_2 + H_2O.

To simplify Equation K-12, assuming that $n_A^E = n_B^E = 0$:

Equation K-13

$$n_T^E = n_{H_2}^R + n_{O_2} + n_{N_2} + n_{sweep}$$

Assuming stoichiometric combustion:

Equation K-14

$$n_{O_2} = 0.5 n_{H_2}^R; \; n_{N_2} = 2 n_{H_2}^R$$

Therefore:

Equation K-15

$$n_T^E = 3.5 n_{H_2}^R + n_{sweep}$$

Assume that n_{sweep} = 0 and system pressure is achieved by hydrogen gas alone.

Substitute Equation K-15 into Equation K-12 with n_{sweep} = 0:

Equation K-16

$$V_{H_2}^E = \frac{P_T^R V_T^E}{3.5 R T^R n_{H_2}^R} V_{H_2}^R$$

According to the perfect gas equation:

Equation K-17

$$V_T^E = \frac{n_{H_2}^R R T^E}{P_{H_2}^E}$$

Substitute Equation K-17 into Equation K-16 and cancel like terms:

Equation K-18

$$V_{H_2}^E = \frac{T^E P_T^R}{3.5 T^R P_{H_2}^E} V_{H_2}^R$$

This relationship shows how $V_{H_2}^E$ is related to $V_{H_2}^R$.

Equation K-18 can now be combined with Equation K-7 to give a definition of $V_{H_2}^E$ which is not dependent on $V_{H_2}^R$:

Equation K-19

$$V_{H_2}^{\text{E}} = \frac{n_{\text{H}_2}^{\text{R}} R T^E}{3.5 P_{\text{H}_2}^{\text{E}}}$$

Equation K-19 describes how the moles of hydrogen evolved in the reactor, $n_{\text{H}_2}^{\text{R}}$, must be sufficient to give a volume of hydrogen in the engine, $V_{H_2}^{\text{E}}$, of $\geq 4\%$ *i.e.* $\frac{V_{H_2}^{\text{E}}}{V_{\text{T}}^{\text{E}}} \times 100\% \geq 4\%$ in order to create an explosive atmosphere.

Equation K-19 relies on the following assumptions being true:

- The 4% LEL is independent of pressure and temperature
- Gases behave ideally
- System is under equilibrium conditions
- Hydrogen combustion is stoichiometric
- $n_{sweep} = n_A^E = n_B^E = 0$
- For every mole of reacted A, 3 moles of hydrogen are evolved.

Appendix L

Table L-1 shows the relevant data for ethyl- to decylcyclohexane with dehydrogenated analogues.

Table L-1: Chosen carriers in their charged and discharged states, with accompanying wt% hydrogen, melting and boiling points. * - data unavailable, estimated by correlation with other carriers

Compound Name	wt% H$_2$	Melting Point/K	Ref	Boiling Point/K	Ref
Ethylcyclohexane	5.39	161	[106]	405	[106]
Ethylbenzene	-	179	[106]	409	[106]
Propylcyclohexane	4.79	178	[106]	429	[106]
Propylbenzene	-	173	[106]	432	[106]
Butylcyclohexane	4.31	198	[106]	453	[106]
Butylbenzene	-	185	[106]	456	[106]
Pentylcyclohexane	3.92	206	[*]	477	[106]
Pentylbenzene	-	195	[106]	479	[106]
Hexylcyclohexane	3.59	226	[106]	498	[106]
Hexylbenzene	-	210	[106]	499	[106]
Heptylcyclohexane	3.32	232	[106]	510	[106]
Heptylbenzene	-	222	[*]	506	[106]
Octylcyclohexane	3.08	253	[106]	528	[106]
Octylbenzene	-	233.9	[106]	534	[106]
Nonylcyclohexane	2.87	263	[*]	555	[106]
Nonylbenzene	-	246	[*]	552	[106]
Decylcyclohexane	2.69	271	[106]	560	[106]
Decylbenzene	-	259	[106]	566	[106]

This shows that the octyl- to decyl-substituted carriers are unsuitable due to high melting points.

This leaves a selection of six candidate molecules, ethyl- to heptyl-substituted carriers.

Appendix M

Enthalpy and entropy of reaction, ΔH_r and ΔS_r, were calculated at under the conditions given in Table 7-3 by adjusting values at STP using a Hess cycle. An illustrative Hess cycle for calculation of ΔH_r is given in Figure M-1.
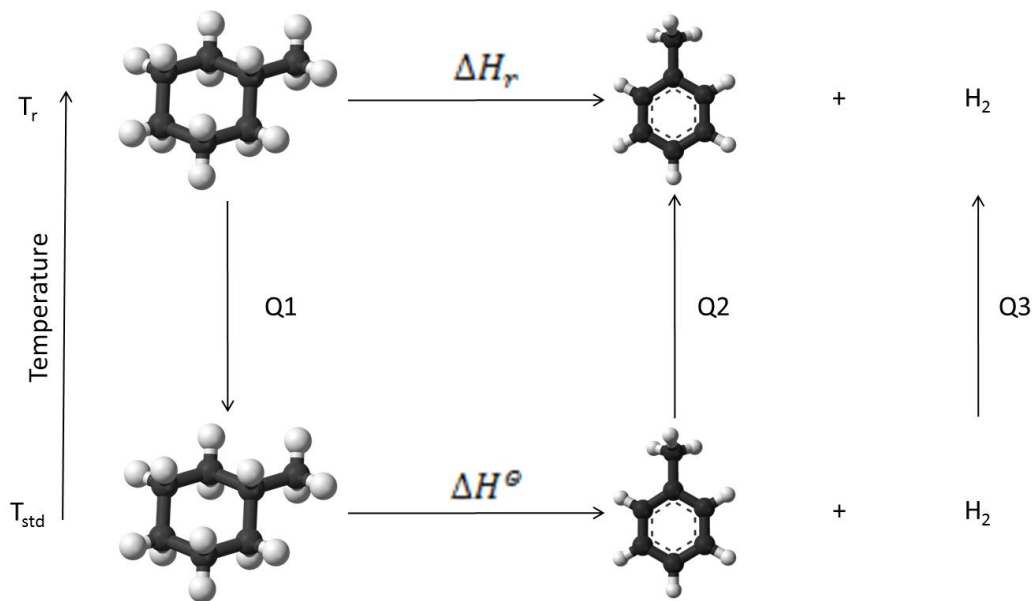

Figure M-1: Illustrative Hess cycle, where T_{std} is the standard temperature at which standard enthalpy change, ΔH^{Θ}, is taken, T_r is reaction temperature, Q_i is the energy change of cooling/heating component i.

With reference to Figure M-1, Equation M-1 and Equation M-2 show how to calculate ΔH_r.

Equation M-1

$$\Delta H_r = Q1 + Q2 + Q3 + \Delta H^{\Theta}$$

Equation M-2

$$Q_i = n_i . Cp_i . dT$$

ΔH^{Θ} is a literature value[23] at a temperature of 25 °C or 298.15 K. Q_i is calculated by integrating the heat capacity of i across the appropriate temperature range and multiplying this with the molar content of the stream. In this case the molar content was set to 1 mol of MCH with other molarities calculated accordingly. In the case of the hydrocarbons, it is necessary to calculate Q_i in three stages. These are: energy of heating/cooling liquid i; energy of heating/cooling vapour of i; latent energy of i. An example is given in Figure M-2, which shows the calculations needed to define Q1.
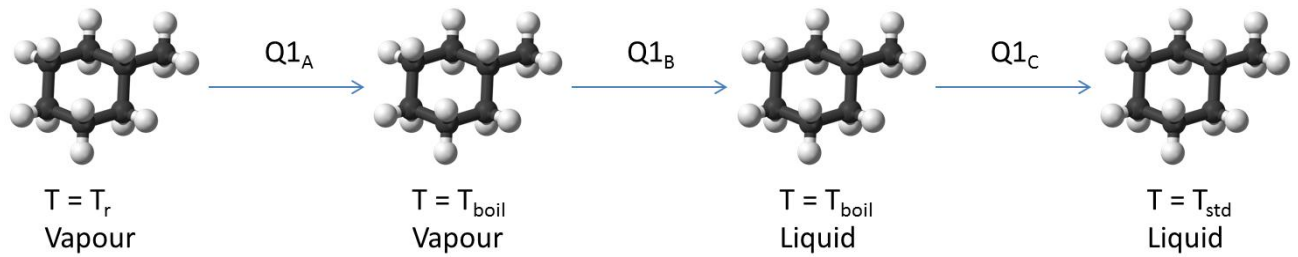
| T = T$_r$ | T = T$_{boil}$ | T = T$_{boil}$ | T = T$_{std}$ |
| Vapour | Vapour | Liquid | Liquid |

Figure M-2: Steps for calculation of Q1

Where $Q1 = Q1_A + Q1_B + Q1_C$; $Q1_B =$ latent heat; $Q1_{A/C} = n_{MCH} \int_{T1}^{T2} Cp \, dT$.

Formulae for Cp in terms of T were sourced from literature[75].

Entropy change of reaction, ΔS_r, was calculated using the same technique. For each individual stage illustrated by Figure M-1, the formula for entropy change is equal to $n_i \int_{T1}^{T2} \left(\frac{Cp}{T}\right) dT$.

With ΔS_r and ΔH_r calculated, it is now possible to calculate the Gibbs free energy change of reaction, ΔG_r, using Equation M-3, which in turn allows calculation of the equilibrium constant, K, Equation M-4.

Equation M-3

$$\Delta G_r = \Delta H_r - T_r \Delta S_r$$

Equation M-4

$$\Delta G_r = -RT_r lnK; K = e^{\left(\frac{\Delta G_r}{-RT_r}\right)}$$

Finally, using the equation derived in Section 4.2.1, identified as Equation 4-13, which gives K in terms of equilibrium conversion, x_A, the equilibrium conversion can be iteratively determined.

Appendix N

Equipment was sized according to several different methods as appropriate to the equipment in question. A brief guide to the methods used is given in this appendix.

Reactors: Reactors were assumed to be *pseudo*-CSTRs as described in previous chapters. The design equation for a CSTR was therefore employed, given as Equation N-1.

Equation N-1

$$V = \frac{F_{A0} x_A}{-r_A}$$

Where: V = reactor volume (m^3); F_{A0} = maximum flowrate in (mol/s) – toluene for hydrogenation, MCH for dehydrogenation; x_A = equilibrium conversion of A; $-r_A$ = reaction rate (mol/m^3.s).

The only factor from the above which is uncertain is $-r_A$. For the dehydrogenation reaction, $-r_A$ was taken to be 0.236 mol/m^3.s, corresponding to an LHSV of 1.10 mol/m^3.s. These figures were calculated from literature values of an experiment which used similar reaction conditions to those specified in this work[76]. This led to a total reactor volume of 43.12 m^3.

For hydrogenation, a reliable rate figure was more difficult to find, and throughout this work less experience has been gathered with the hydrogenation reaction than with the reverse. An indicative LHSV range was found for cyclohexane production by benzene hydrogenation[141]. This was given as LHSV = 0.75 – 2 mol/m^3.s.

Minimum and maximum reactant flows (maximum set by wind farm capacity, minimum set by electrolyser flexibility) into the hydrogenation reactor were calculated, and it was found that the LHSV range was far greater than the recommended range from the literature. It was therefore decided to design a bank of smaller reactors, extending the compatible reactant flowrate range. Total reactor volume was calculated as 4.77 m^3 (much smaller than the dehydrogenation reactor due to higher pressure). In order to ensure that every possible reactant flowrate has a LHSV within the required range, a minimum of 10 reactors is required, therefore a bank of reactors each with a volume of 0.48 m^3 will be used.

These reactors are jacketed for heat exchange – details given in the following heat exchanger section.

Reactor dimensions, surface area and mass were then calculated using the method outlined by Olin Engineering in their FACT method of cost estimation[119], which accounts for internal pressure.

Electrolysers: According to the manufacturer specifications[121], the electrolyser units have an automatically adjusted hydrogen output range of $10 - 485$ Nm^3/h, or $0.1 - 6.0$ mol/s. The maximum hydrogen output (28.6 mol/s) was determined by the maximum wind farm capacity, and this led to a requirement for a minimum of 5 electrolyser units, each with a hydrogen output capacity of 462 Nm^3/h, or 5.73 mol/s. The electrolysers are automatically adjustable to $20 - 100\%$ of their capacity. The minimum hydrogen production possible is therefore 20 % of one of the five electrolysers, or 1.15 mol/s hydrogen. This equates to a minimum electrical supply of 397 kW from the wind farms, or 4% of their total capacity (not including peripheral equipment powered by the wind farms).

Water Distillation Unit: The water distillation unit, based on the Norsk VC6000 unit, was sized simply according to the maximum possible outward flowrate of distilled water.

Heat Exchangers: Several types of heat exchanger were used depending on the needs of the particular exchange. **Shell and tube** exchangers were used to exchange heat between two process fluids. A **jacketed vessel** was used to exchange heat between cooling water and the hydrogenation reactor. **Copper coils** were used to exchange between process streams and the hydrogenation reactor. **Bare tube air coolers** were used to cool process streams to room temperature wherever possible to minimise utility costs. Finally, a **direct fired heater** was used to warm the dehydrogenation reactor, and to partially warm the incoming reactants for dehydrogenation.

For shell and tube, copper coil and air exchangers, the required heat exchange area was calculated using Equation N-2.

Equation N-2

$$A = \frac{Q}{U \times T_{LM}}$$

Where: A = maximum exchanger area required (m^2); Q = maximum exchanger duty (kW); U = heat transfer coefficient (kW/m^2.K); T_{LM} = log mean temperature difference (K).

Q and T_{LM} were calculated as part of pinch analysis, and U was estimated using a variety of sources[75, 142-144].

Dimensions for copper coils are shown in Figure N-1. The inner and outer diameters of the coils were modelled on specifications of coil supplied to industry by company SP Coils, made of C106 grade copper[145].
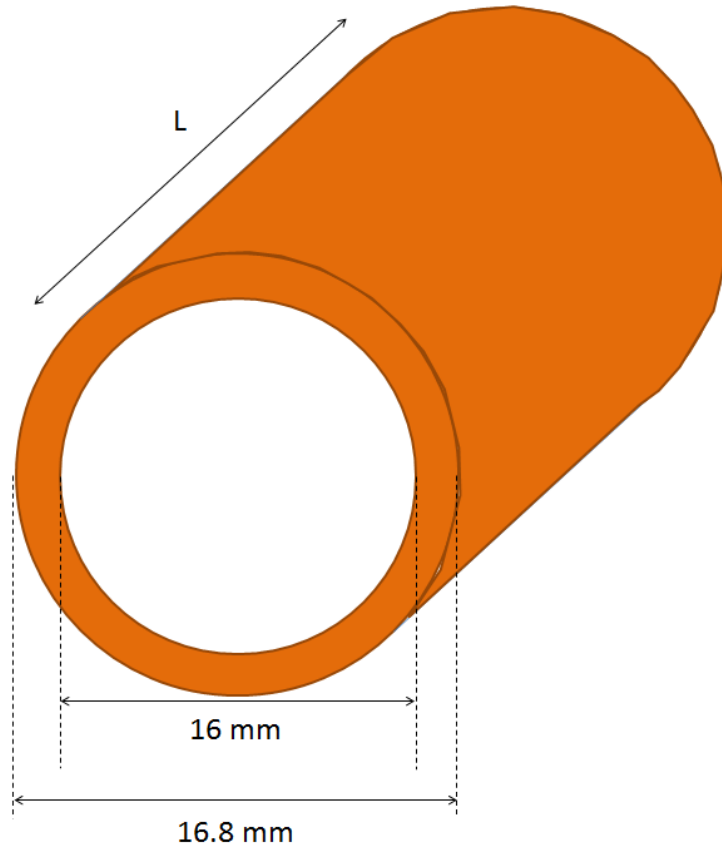
Figure N-1: Copper coil dimensions[145]

With reference to Figure N-1, the length L of copper coil required was calculated by taking the inner surface area SA as the heat exchange area required, and calculating L according to Equation N-3.

Equation N-3

$$SA = 2\pi r L \ \therefore L = \frac{SA}{2\pi r}$$

With length determined, the total copper volume required was calculated.

For shell and tube exchangers and air coolers, the surface area alone was enough to estimate cost, so no further analysis was attempted.

For the jacketed vessels, the volume V was the primary concern. V was calculated first, and the dimensions (radius and length) were calculated by simultaneous equations to satisfy the restrictions on V and SA.

The direct fired heater could be costed with knowledge of the duty alone. Maximum duty for the fired heater (*i.e.* the heating required for flows corresponding to maximum hydrogen production) was calculated as 2124 kW.

Compressor, Stream 9: The compressor was sized by calculating the maximum compression duty required, taking into account compression efficiency (taken as 0.8 electrical efficiency[23]). This was calculated as 54.6 kW.

Flare: The flare stack for combustion of waste products, Stream 7, can be costed by correlation with the maximum volume of flue gas passing through. By calculating the volume of CO_2, water vapour and nitrogen passing through the stack with hydrogen storage at maximum capacity, the maximum volumetric flow was calculated. This was taken as 8.09 m^3/s.

Storage Vessels: Storage vessels (for toluene, MCH, hydrogen and distilled water) were calculated as the required amount of storage space to supply the relevant process for 24 hours without input, based on maximum capacity flows. The exception to his basis was hydrogen storage, because hydrogenation is always carried out upon the production of hydrogen from electrolysis, therefore the hydrogen storage vessel is designed to hold hydrogen corresponding to 1 h of maximum capacity production.