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CARBON-NEUTRAL HYDROCARBON-FUELLED VEHICLE TRANSPORTATION WITH FUEL RE-SYNTHESIS FROM ON-BOARD SEQUESTRATED CO_2

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ABSTRACT

A combination of the Zero Emission Petrol Vehicle (ZEPV) concept, catalytic hydrogenation of CO_2 and the methanol to gasoline process has been analysed to examine gasoline re-synthesis from recycled CO_2. CO_2 from closed-cycle gasoline combustion in a modified conventional IC engine can be readily liquefied and stored on-board. This liquid CO_2 is available to be converted back to gasoline via methanol. Three possible chemical pathways for this re-synthesis are direct CO_2 hydrogenation, the Camere process and the H_2O-CO_2 electrolysis. According to the magnitude of the "ideal" and "practical" energy recycle penalty (η), which are obtained from material and energy balances for around 30 million vehicles in UK, direct CO_2 hydrogenation and the Camere process should be considered. Carrying out this recycling in a set of geographically distributed "re-syn fuel" refineries using offshore wind energy has no further cost for exploration and production of crude oil, no limitation of raw material and furthermore no cost penalty for the emitted carbon value. By predicting that the wind energy cost will be reduced as low at 2.5 p per kWh in the future (2020), it is estimated that the total production costs for this futuristic sustainable re-synthesis refinery would be decreased to 16 p per litre of gasoline. This cost is cheaper than for current conventional oil refineries (18.3 p per litre) and still less than the total cost for a "re-syn fuel" refinery powered by indigenous non-sustainable coal (21.8 p per litre). Based on the initial economic analysis, gasoline re-synthesis from recycled CO_2 (to produce re-syn fuel) using offshore wind energy, is both perfectly sustainable and almost competitive for today and will be cheaper than petrol from crude oil in the future. Although this analysis is based on gasoline, the concept is straight forwardly extended to diesel. In this way, the present 25% of total UK CO_2 emissions from road transport could be reduced to virtually zero.

Keywords: CO_2 hydrogenation, re-syn fuel refinery, offshore wind energy

1 INTRODUCTION

CO_2 emission is the main cause of the greenhouse effect. This particular emission is mostly generated from fossil fuel combustion especially in the industry and transportation sectors. The Zero Emission Petrol Vehicle (ZEPV) is one of the possibilities to eliminate CO_2 emissions from the transportation sector. The CO_2 produced by ZEPV is to be off-loaded at specially adapted service stations during re-fuelling. Gasoline would be re-synthesized from recycled CO_2 and water (as H_2 source) in a new kind of "refinery". There are two main chemical processes in this refinery, methanol synthesis (catalytic hydrogenation of CO_2) and the methanol to gasoline process (MTG) process.

A combination of the ZEPV concept and these chemical processes is called gasoline re-synthesis from recycled CO_2 (to produce "re-syn fuel"). Based on methanol synthesis, there are three possible chemical pathways in this re-synthesis, direct CO_2 hydrogenation, the Camere process and the H_2O-CO_2 electrolysis. The calculation of material and energy balances and the consequent energy recycle penalty (η) were investigated in more detail to analyse and compare these possible chemical pathways. The energy required could be supplied by renewable wind energy. Offshore wind energy possibly represents the nearest term cost-competitive renewable source. According to the initial economic analysis, gasoline re-synthesis from recycled CO_2 using offshore wind energy is almost competitive today and should become cheaper than gasoline from crude oil in the future.

2 ZERO EMISSION VEHICLES

Recently, several researches have looked at zero emission vehicles, such as battery driven cars (Electric Vehicles, EVs), hydrogen fuelled cars, Zero Emissions Membrane Piston Engine System (ZEMPES) and Zero Emission Petrol Vehicle (ZEPV). EVs California is pioneering a zero emission constraint for motor vehicles. They promise major improvements in air-quality. But the limited range and long charge times have created uncertainty about consumer demands (Turrentine et al., 1992). Like EVs, hydrogen fuelled cars are clean on the street because the burning of hydrogen in the engine produces only water. There is no emission of CO, CO_2, NOx, SOx, particulates or unburned hydrocarbon. BMW has developed hydrogen as an alternative to petrol/diesel (Braess et al., 2001), but this solution requires the whole re-fuelling infrastructure to be expensively replaced.

Unlike the other systems (EVs and hydrogen cars), the ZEPV uses conventional petrol (which retains existing infra-structure) and a conventional internal combustion engine (ICE), but by closed cycle combustion (CCC), it is possible to store / sequester liquefied carbon dioxide on board. This carbon dioxide will be traded in at the filling station, returned to a "refinery" and catalytically converted back to petrol via methanol using the methanol to gasoline (MTG) process. As well as being perfectly clean at the street level, this approach presents the possibility of sustainable transport using renewable sources of energy (Brewer, 2000). Both ZEPV and ZEMPES used a highly pure O_2 "locally" separated for fuel combustion in the engine (Dutton, 2003; Yantovski et al., 2004) with temperature control via admixed CO_2 to provide the same moderating effect as N_2.

Dale, Brewer, Carpenter and Dutton have each researched the practicalities and feasibility of the ZEPV, each investigating the various components required to see if they could deliver the desired results.(Dale, 1997; Brewer, 2000; Carpenter, 2002; Dutton, 2003) Figure 1 shows the proposed closed cycle combustion system. The key components of the engine, which are additional to the conventional ICE, are the air separation unit (ASU) and the CO_2 compression unit (Dutton, 2003).

The ASU compresses the air and through the use of the different boiling points yields highly pure liquid N_2, waste gases and highly pure liquid O_2. This liquid O_2 is mixed with fuel and CO_2 and then injected into the conventional engine. As the N_2 has been eliminated, the side effect that nitrogen is converted to NOx will no longer be an issue. With the consequence that the exhaust stream with lean burn contains only CO_2 and H_2O (Dutton, 2003).

The CO_2 can be separated from the water using a cooler/condenser and then liquefied using a combined compressor/cooler, which can be stored on-board in a pressurized container. When CO_2 is liquefied, this reduces both the volume and potentially the compression energy requirements (Dutton, 2003). The CO_2 liquefaction is efficiently energy integrated with the O_2 separation.

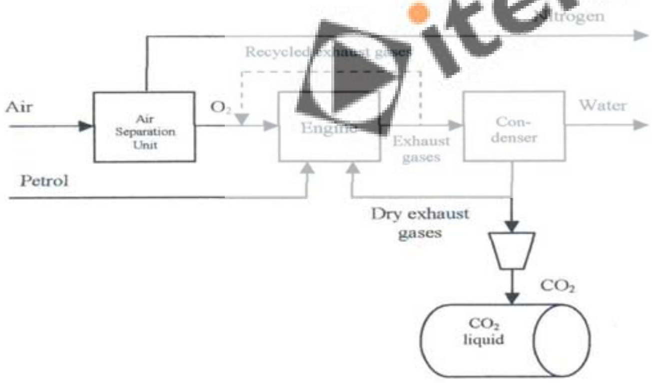


Fig. 1. Schematic of Closed Cycle Combustion for an ICE (after Mann and Dutton, 2005)

3 THE POSSIBLE CHEMICAL PATHWAYS

The CO_2 produced by the ZEPV could be re-processed back into gasoline via three possible chemical pathways, direct CO_2 hydrogenation, the Camere process and the H_2O-CO_2 electrolysis. The overall principle of these chemical pathways is depicted in figure 2. The difference between the chemical pathways lies in the configuration of the "re-syn fuel" refinery, especially the methanol synthesis.

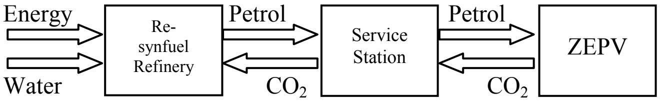


Fig. 2. The principle of recycle chemical pathways for gasoline re-synthesis from CO_2 in the transportation sector (Mann and Dutton, 2005)

The direct CO_2 hydrogenation is the simplest pathway for gasoline re-synthesis from recycled CO_2. In the re-synfuel refinery stage, this chemical pathway involves water electrolysis, the subsequent hydrogenation of CO_2 and the final methanol to gasoline conversion.

The Camere process chemical pathway is a combination of hydrogenation of CO_2 and reverse water gas shift reaction, RWGS reaction, (Joo et al., 1999). Therefore, this pathway involves more processes than reactions in the direct CO_2 hydrogenation. In the "re-syn fuel" refinery stage, the involved processes are water electrolysis, the RWSG reaction, the hydrogenation of CO_2 and the methanol to gasoline process.

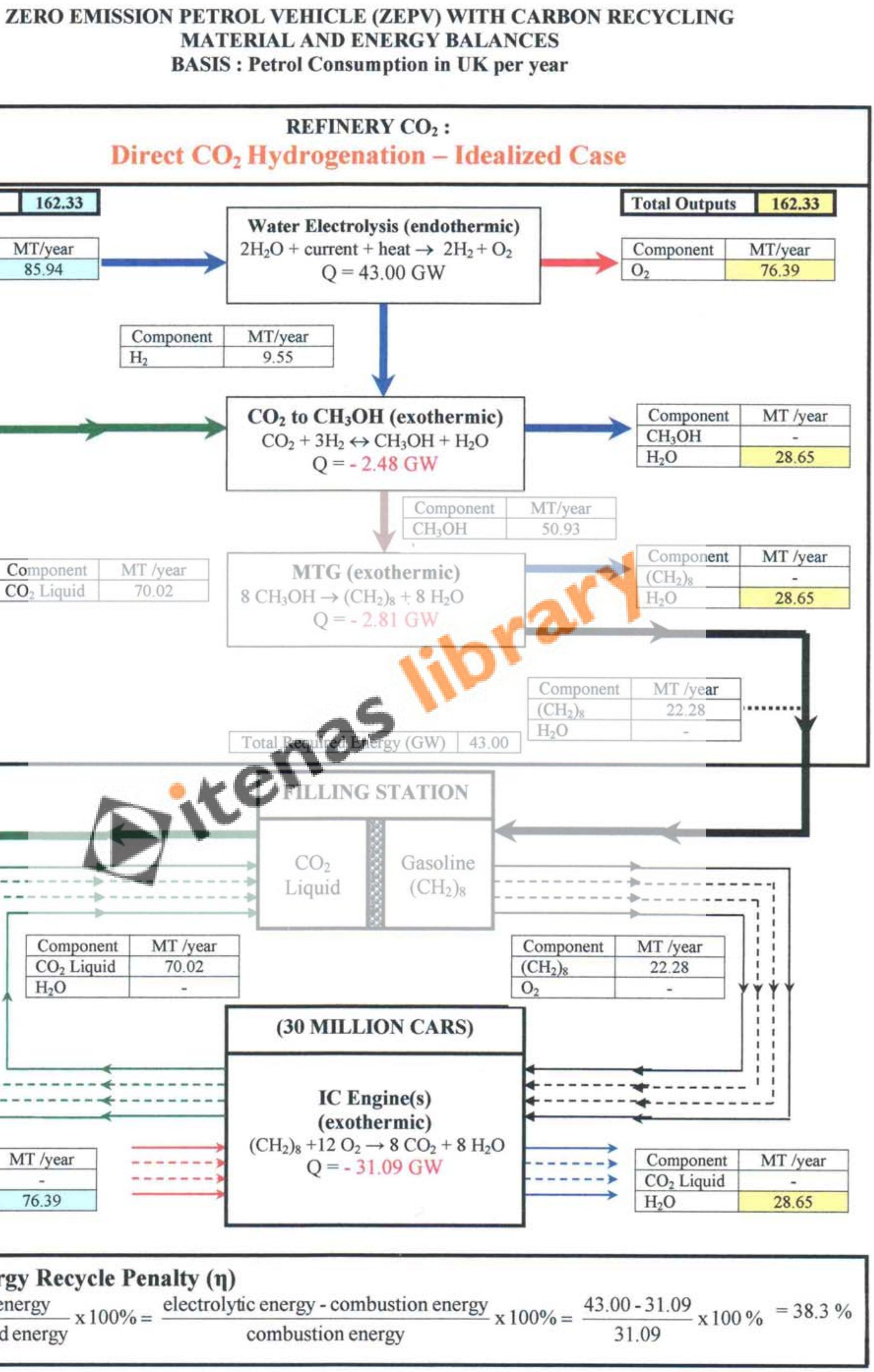
Different from these chemical pathways, in the H_2O-CO_2 electrolysis, CH_3OH is synthesised by CO hydrogenation. The CO is produced from the CO_2 recycle and H_2O by electrolysis at $650^{O}C$ (Jensen et al., 1999). Therefore, the electrolysis process chemical pathways consist of electrolysis of recycled CO_2 and H_2O, water electrolysis, CO hydrogenation and the methanol to gasoline process.

4 RESULTS AND DISCUSSION

4.1 UK MATERIAL AND ENERGY BALANCES

The calculation of material and energy balances is observed for initial analysis to explore the best chemical pathway. The gasoline consumption per year in United Kingdom is used. According to the transport statistics for Great Britain, the number of vehicles now in UK, the average gasoline consumption and the distance on average a British resident now travels by car are 30 million, 30 mpg (6.6 miles/L) and 6,800 miles a year respectively. Based on these data, the gasoline consumption per year in the United Kingdom is about 22 Mt/year. This value is used as a "1 year" basis of the calculation of UK overall material and energy balances. For example, the result of material and energy balances calculation for the direct CO_2 hydrogenation chemical pathways can be seen in Figure 3 for the idealized case.

For every chemical pathway, the energy balance is observed by using two cases, an idealized case and a practical case. The idealized case considers solely the energy change (Hess's Law) which is involved in the chemical reactions. The practical case describes not only energy for the chemical reaction but includes also energy in the less efficient practical process, especially energy which is involved in the heating, cooling or distillation processes.



$$\eta = \frac{\text{extra energy}}{\text{produced energy}} \times 100\% = \frac{\text{electrolytic energy - combustion energy}}{\text{combustion energy}} \times 100\% = \frac{43.00 - 31.09}{31.09} \times 100\,\% = 38.3\,\%$$

Fig 3. Direct CO_2 hydrogenation chemical pathway for thermodynamically “idealized” case

Therefore, energy consumed in the practical case will be more than in the ideal thermodynamic case.

4.2 ENERGY RECYCLE PENALTY (η)

The next analysis is to calculate the energy recycle penalty (η) for each possible chemical pathway. The energy recycle penalty (η) is the extra energy needed to produce the equivalent gasoline. This value highlights the relative need of extra energy for the recycle chemical pathways. Based on the energy balance observations, there are two kinds of energy recycle penalty (η), which are

$$\eta_{ideal} = \frac{Q_T - Q_C}{Q_C} \times 100\% \qquad (1)$$

$$\eta_{practical} = \frac{Q_P - Q_C}{Q_C} \times 100\% \qquad (2)$$

Q_T is the required thermodynamic energy in the re-synthesis reactions, Q_C is the gasoline combustion energy and Q_P is the required practical energy in the “real” reaction processes.

The energy recycle penalties (η) for three chemical pathways are summarised in Table 1. Based on the energy recycle penalty, the the H_2O-CO_2 electrolysis is not recommended because it appears to need relatively much more extra energy. Direct CO_2 hydrogenation and the Camere process could be considered for gasoline re-synthesis from recycled CO_2.

TABLE 1. Required energy (Q_T and Q_P) and Energy recycle penalty (η)

Chemical pathway	Q_T (GW)	Q_P (GW)	Q_C (GW)	η_{ideal} (%)	$\eta_{practical}$ (%)
Direct CO_2 Hydrogenation	43	53	31	38	72
Camere process	45	64	31	45	105
H_2O-CO_2 electrolysis	73	89	31	135	160

4.3 ENERGY REQUIREMENT

According to the practical energy balance for all chemical pathways, regenerating gasoline from the recycled CO_2 will obviously require energy. The energy requirement (Q_P) and the rate of this energy (Q'_P) for each chemical pathway can be seen in Table 2.

For a truly sustainable process, demands for this energy must be met by renewables, such as solar thermal energy, solar photo-voltaic, bio-energy, hydroelectricity, tidal power, wind energy, wave energy and geothermal energy. Wind energy possibly represents the nearest term cost-competitive renewable source. The energy intercepted at a wind speed of 7 m/s is 210 kW/m^2, assuming an efficiency of 20 – 40%, so the output of a typical single turbine is about 0.5 – 2.5 MW for on-land wind power and can be up to 5 MW for offshore (Williams et al., 2004). For example, the energy requirement for gasoline synthesis via direct CO_2 hydrogenation chemical pathway is 190 TWh/year. This energy can be supplied from around 21,000 x 3 MW offshore wind turbines which are installed (out of sight offshore) at a separation spacing of 500 metres.

TABLE 2. The required energy per year for alternative chemical pathways

Chemical pathways	**Q_P (GW)**	**Q'_P (TWh)**
Direct CO_2 hydrogenation	53	190
Camere process	64	230
H_2O-CO_2 electrolysis	89	320

GW = giga watt ; TWh = tera watt hour

As an illustration, the 190 TWh/year of energy requirement is only about 6 % of the total energy which could be produced from proposed offshore wind turbines in UK (Taylor, 2004). The 21,000 offshore wind turbines for re-synthesis can be installed in the proposed three strategic areas in UK, 30 TWh/year from the Thames Estuary (3,500 turbines), 95 TWh/year from the Greater Wash (10,500 turbines) and 65 TWh/year from the North West (7,000 turbines), see Figure 4. This utilization would not significantly reduce the potential energy supply in UK, because if the wind energy projects are a success, an overall total of 3,200 TWh/year of energy could be produced from these three areas. So, there is in principle no energy problem for powering the gasoline re-synthesis from recycled CO_2. There are however some remaining issues on the scale of diverted capital investment that would be required.

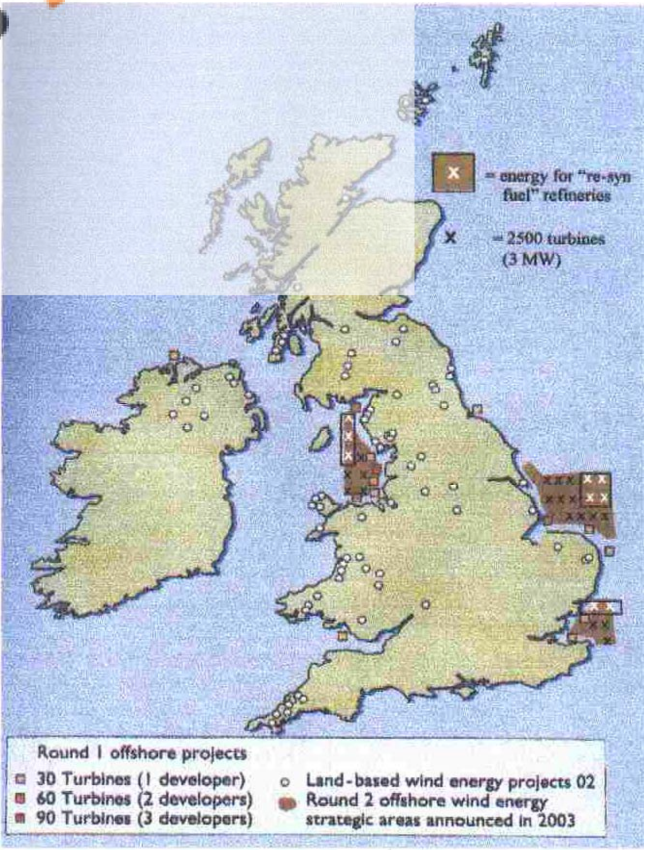


Fig. 4. Distribution of wind energy resources for the “re-syn fuel” refineries

The much discussed intermittency problem with wind power is no longer a problem here. This is because the fuel storage capacity in the "re-syn fuel" refinery as well as in 30 million vehicle fuel tanks provides an intrinsic capacity buffer.

4.4 INITIAL ECONOMIC ANALYSIS

The total required energy for producing typically 10 Mt of hydrocarbon products per year in a typical conventional oil refinery is 0.3 GW (Gary, 2001). This typical required energy is much less than needed for the proposed "re-syn fuel" refineries, see Table 3. The difference between the required energy in the proposed "re-syn fuel" refinery ($Q_{P,10}$) and for the typical oil refinery is indicated by Q_{excess}. The direct CO_2 hydrogenation chemical pathways needs energy around 80 times of the baseline required energy in the typical oil refinery while the Camere process chemical pathway needs more at around 95 times.

TABLE 3. Comparison of energy consumption for gasoline production
(per 10 Mt gasoline production per year)

Chemical Pathways	$Q_{p,10}$ (GW)	Q_{excess} (GW)	Excess Energy Factor
Direct CO_2 Hydrogenation	24	23.7	80
Camere Process	29	28.7	95
Typical Oil Refinery	**0.3**	**0**	**0**

Although a "re-syn fuel" refinery needs much more energy than the typical oil refinery, these processes should still be considered because there would be no limitation of raw material, no further requirement or "expense" for exploration, production and refining of feedstock crude oil and most importantly no carbon emission. For example, re-synthesizing 10 Mt/year of gasoline from recycled CO_2 using direct CO_2 hydrogenation needs around 24 GW/year (or 86.4 TWh/year) of energy. If offshore wind were to be used as the energy resource in this proposed re-syn fuel refinery, with the cost of offshore wind power currently around 5.5 p per kWh (SDC, 2005), the re-synthesis energy expense should overall be 34.2 p per litre gasoline. This cost is higher than the production plus refining costs for the typical conventional oil refinery, which are currently around 18 p per litre (see Table 4), but this re-synthesis refinery would be sustainable because it uses recycled CO_2 as a feed stock instead of crude oil.

Although the coal (IGCC, Integrated Gasification Coal Combustion) energy cost is only around 3.2 p per kWh, the carbon value (£10 – £ 30 / tCO_2) should be added to this cost because using coal energy releases CO_2 to the environment. Thus, the coal energy cost (IGCC) should be around 5.7 p per kWh (UIC, 2005). This cost is now actually somewhat more expensive than the offshore wind energy cost and the re-synthesis power expense would be 35.4 p per litre gasoline if the coal (IGCC) were used as the energy source.

The use of the offshore wind energy in the proposed refinery is an appropriate idea because it is estimated that the cost of offshore wind power will almost inevitably fall over time and it is predicted that the cost (at today's prices) should be around 2 – 3 p per kWh by 2020 (SDC, 2005). Consequently, the mid-range cost of petrol in the (mid-term) future could fall to around 16 p per litre with a change to renewable wind energy. This cost will be somewhat cheaper than the present production plus refining costs for the typical conventional oil refinery (see Table 4). And this cost is still less than the cost for the "re-syn fuel" refinery using coal as an alternative source of energy, which should be 21.8 p per kWh.

5 CONCLUSIONS

The combination of the ZEPV concept, catalytic hydrogenation of CO_2 and MTG process, which is referred to as gasoline re-synthesis from recycled CO_2 (to produce re-syn fuel), is one of the possibilities to eliminate CO_2 emissions from the transportation sector. There are three possible chemical pathways for this re-synthesis : direct CO_2 hydrogenation, the Camere process and the electrolysis process. According to the magnitude of the "ideal" and

TABLE 4. The present (2005) and future (2020) gasoline production costs

Refinery	Energy Cost P per kWh	Cost (p per litre)		
		Exploration + Production	Refining	Overall production cost
Present : 2005				
Typical oil refinery		12.8	5.5	**18.3**
Re-syn fuel refinery – Coal (IGCC) energy	5.7	Zero	35.4	**35.4**
Re-syn fuel refinery – Offshore wind energy	5.5	Zero	34.2	**34.2**
Future : 2020				
Re-syn fuel refinery – Coal(IGCC) energy	3.5	Zero	21.8	**21.8**
Re-syn fuel refinery – Offshore wind energy	2.5	Zero	16.0	**16.0**

"practical" energy recycle penalty (η), the electrolysis process is not recommended because it needs relatively much more extra energy.

According to this initial economic analysis, this re-synthesis using offshore wind energy is almost a competitive process today and will be in the future because this refinery needs no further "expenses" for exploration and production of crude oil, no limitation of raw material and being carbon neutral there will be no cost penalty for emitted carbon.

Although the present (2005) total production costs per litre for the "re-syn fuel" refinery using offshore wind energy (34.2 p per litre) is more expensive than the total cost for the typical oil refinery (18.3 p per litre), in the future (2020) the total production costs for the "re-syn fuel" refinery using offshore wind energy (16 p per litre) will be cheaper than this total cost for the conventional oil refinery.

Comparing with the present (2005) and future (2020) total production costs for the "re-syn fuel" refinery using coal energy (35.4 and 21.8 p per litre), total production costs for the "re-syn fuel" refinery using offshore wind energy (34.2 and 16 p per litre) are cheaper. In the future (2020), it is predicted that the energy cost of offshore wind and coal would be reduced as low at 2.5 and 3.5 p per kWh, respectively.

Finally, by the re-synthesis of gasoline from recycled CO_2 using offshore wind energy, several problems can be solved all at once, such as CO_2 emission, the limitation of fossil fuels for conventional gasoline production and the economic cost of gasoline made by re-synthesis. The concept is readily extended to diesel, thereby also providing carbon neutrality for the heavy road transport sector.

NOMENCLATURE

Q	energy	[GW]
Q_C	gasoline combustion energy	[GW]
Q_P	required practical energy in the "real" reaction processes	[GW]
$Q_{P,10}$	Qp for 10 Mt of gasoline product	[GW]
Q_{excess}	difference between the required energy in the proposed "re-syn fuel" refinery and for the typical oil refinery	[GW]
Q'_P	rate of required practical energy (Q_P)	[TWh]
Q_T	required thermodynamic energy in the re-synthesis reactions	[GW]
η_{ideal}	energy recycle penalty for idealized case	
$\eta_{practical}$	energy recycle penalty for practical case	

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