

Carbon Neutral Gasoline Re-synthesised from On-board Sequestered CO₂

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CO₂ emissions are one of the main causes of the greenhouse effect. Catalytic hydrogenation of CO₂, such as methanol synthesis and methanation, could play an important role in reducing these emissions. By using a combination of the Zero Emission Petrol Vehicle (ZEPV) concept, catalytic hydrogenation of CO₂ and methanol to gasoline (MTG) process gasoline can be re-synthesised from recycle CO₂. However the low methanol yields, both selectivity and conversion, is the main problem in the methanol synthesis. The objectives of research in the University of Manchester are to examine the methanol synthesis behaviour in the lab scale tubular catalytic reactor, to investigate the effect of molecular Sieve 4A (MS 4A) on this synthesis and to analyse the feasibility study for a re-syn fuel refinery.

The experimental results showed that a maximum CO₂ conversion was reached at 190°C, 1 bar, 3600 h⁻¹ and H₂/CO₂ = 4 and MS 4A adsorbed water hence the conversion of CO₂ increased from 1.13% to 2.12%. The numerical model results predicted that the initial rate of methanol synthesis increases sharply at pressures into 50 atm and is then relatively constant at pressures above 50 atm. At 50 atm, the initial rate ratio is predicted to increase 35 – 45 times than the initial rate at 1 atm.

Finally, material and energy balances were calculated for four possible chemical pathways for this re-synthesis (the direct CO₂ hydrogenation, the Camere process, the methane to methanol process and the electrolysis process) to determine energy requirements in the re-syn fuel refineries. By using the ZEPV concept, some 70 MT/year of CO₂ from the combustion of about 22 MT/year of gasoline in around 30 million vehicles in UK can be liquefied at 70 bar and stored on board. This liquid CO₂ is available to be converted back to gasoline via methanol. The 30% conversion, which was obtained from combination of experiment and numerical model results, was applied for direct hydrogenation of CO₂. For the other chemical pathways, the conversion used was based on previous studies. Carrying out this recycling in a set of geographically distributed “re-syn fuel” refineries using offshore wind energy has no further requirement for exploration of crude oil, no limitation of raw material and furthermore no cost penalty for the emitted carbon value. The economic analysis shows that the present (2008) forecourt price for the typical oil refinery (98 p/l) is lower than this forecourt price for the “re-syn fuel” refinery using the offshore wind energy (109 p/l). By predicting that the wind energy cost will be reduced to as low as 2.5 p/kWh in the future (2020), it is estimated that the forecourt price of gasoline from this futuristic sustainable re-synthesis refinery would be decreased to 89 p/l.

1. Introduction

Emissions of CO₂ have been linked to the greenhouse effect and global warming. These emissions have, over the past decade, become the subject of many government incentives and sparked major clean-up process initiatives throughout the motoring world. Although CO₂ emissions are not solely from transportation, this sector produces approximately 24% of the UK's total carbon emissions and road transport contributes 85% of this. From 1995 to 2005, CO₂ emissions from transport sector increased by approximately 6.5% (Foster and Ramaswamy, 2007). If there are no new initiatives, these emissions will continuously increase. The development of electric, hydrogen fuelled and plug-in hybrid cars have provided evidence that vehicles can be manufactured to achieve low emissions on the street, while still providing the car with sufficient power. The consideration of the ZEPV (zero emission petrol vehicle) concept, a closed-cycle on-board combustion process, is not only zero emission but also sustainable through the use of carbon recycling, via renewable energy sources.

Today, around 30 million vehicles in UK consume about 22 MT/year of petrol and will thus produce some 70 MT/year of CO₂. By using a combination of the ZEPV concept, catalytic hydrogenation of CO₂ and the methanol to gasoline (MTG) process, this CO₂ is available to be converted back to petrol/gasoline. This process, called gasoline re-synthesis from recycled CO₂ (to produce "re-syn fuel"), using offshore wind energy becomes in principle a sustainable and wholly renewable process. According to a preliminary economic assessment, this process is potentially competitive both for today and in the future. Moreover, a clean and promising technology for delivering perfect sustainability of the transportation energy sector could be achieved by a combination of the ZEPV concept and the plug-in hybrid electric vehicle (PHEV) concept.

Recently, many studies have been undertaken to synthesize methanol from CO₂/H₂ catalyst. The apparently low conversion of CO₂ to methanol is a problem in this hydrogenation. The presence of water is one of the reasons of this problem. Therefore, the objectives of this study are to design and examine the behaviour of methanol synthesis in a lab scale tubular catalytic reactor and in particular to investigate the effect of a water removal desiccant (molecular sieves 4A, MS 4A) on the reversible methanol synthesis and to analyse the feasibility study for a re-syn fuel refinery.

2. Zero Emission Vehicles

Transportation is one of the main sectors that generate CO₂ emissions in the UK. According to Professor Julia King, Vice-Chancellor of Aston University and formerly of Rolls-Royce, the emissions from cars could be reduced by 25% now and by up 80% by 2050 (Smith, 2007). One of the technologies which can be used to achieve those values is zero emission vehicle, such as battery driven cars (Electric Vehicles, EVs), hydrogen fuelled cars, Zero Emissions Membrane Piston Engine System (ZEMPES), Zero Emission Petrol Vehicle (ZEPV), hybrid electric vehicle (HEV) and plug-in Hybrid Electric Vehicle (PHEV). EVs use an electric motor and chemical batteries, fuel cells, ultra-capacitors or flywheels for traction and energy sources, respectively. This vehicle has no emissions, high efficiency, independence from petroleum and quiet and

smooth operation (Ehasani et al., 2005). But the limited range and long charge times of them 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. 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 infrastructure and a conventional internal combustion engine (ICE), but by closed cycle combustion, it is possible to store/sequester liquefied CO₂ on-board. No CO₂ release to the atmosphere because this gas will be traded in at the filling station, returned to a re-synthesis 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 O₂ “locally” separated for fuel combustion in the engine (Mann and Dutton, 2005; Yantovski et al., 2004).

In recent years, there has been a lot of advanced vehicle technology research in the hybrid electric vehicle (HEV) concept. This concept combines an electric drive with a heat engine using a fossil fuel energy source (Westbrook, 2001; Ehsani et al., 2005; Fajri and Asaei, 2008). As a comparison to a solely ICE vehicle, a HEV could save 30% gasoline consumption (sometimes more).

The next generation of hybrid electric vehicle is a plug-in hybrid electric vehicle (PHEV) which has a clear advantage over the current hybrid car. It has a large high-capacity battery that can be plugged into a typical home power socket and also charges the battery by the electricity from the grid when the vehicle is not used. By using the capability of plug-in, it is possible for plug-in hybrid electric vehicle to operate all electric for most short and commuting trips and then functions like a normal hybrid vehicle for longer distances. Plug-in hybrid electric vehicle can travel only by using its electric motor and battery generally 15 to 100 km in which during this period there is no fuel consumption, resulting in zero emissions. Compared to a non plug-in hybrid, a plug-in hybrid can reduce 25 – 55% NO_x, 35 – 65% greenhouse gases and 40 – 80% gasoline consumption. And also by charging the battery in the off-peak time, it can save an electricity cost to operate the vehicle (Bradley and Frank, 2009). Finally, combination between zero emission petrol vehicle concept and plug-in hybrid electric vehicle concept would become a clean technology and a promising technology for delivering perfect sustainability of the transportation energy sector.

3. The Possible Re-synthesis Chemical Pathways

The CO₂ produced by the ZEPV could be re-processed back into gasoline via four possible existing practical chemical pathways, direct CO₂ hydrogenation, the Camere process; the methane to methanol process and the H₂O-CO₂ electrolysis. The overall principle of these chemical pathways is depicted in figure 1. The difference between the chemical pathways lies in the configuration of the “re-syn fuel” refinery, especially the methanol synthesis.

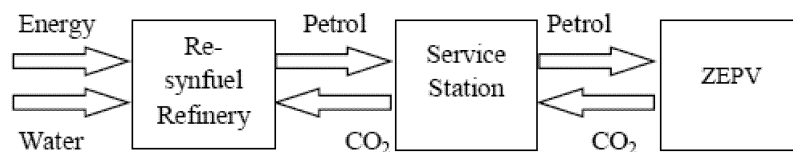


Figure 1: The Principle of Recycle Chemical Pathways for Gasoline Re-synthesis from CO₂ in The Transportation Sector (Mann and Dutton, 2005)

The direct CO₂ hydrogenation is the simplest pathway for gasoline re-synthesis from recycled CO₂. In a re-synfuel refinery stage, this chemical pathway involves water electrolysis, the subsequent hydrogenation of CO₂ and the final methanol to gasoline conversion. The Camere process chemical pathway is a combination of hydrogenation of CO₂ and reverse water gas shift reaction (RWGS reaction). Therefore, this pathway involves more processes than reactions in the direct CO₂ hydrogenation. In the “re-syn fuel” refinery stage, the required processes are water electrolysis, RWGS reaction, hydrogenation of CO₂ and methanol to gasoline. In the methane to methanol process, CO₂ is hydrogenated into CH₄ at 205^oC and then CH₄ is oxidised into CH₃OH at 180^oC. This chemical pathway consists of methanation, oxidation of CH₄ and the methanol to gasoline process. Different from the other chemical pathways, in the electrolysis process, CH₃OH is synthesised by CO hydrogenation. The CO is produced from the CO₂ recycle and H₂O electrolysis at 650^oC. Therefore, the electrolysis process pathways consist of electrolysis of recycled CO₂ and H₂O, water electrolysis, CO hydrogenation and finally methanol to gasoline.

4. Results and Discussions

4.1 Experimental Work

The objectives of these experiments were to design and examine the lab scale tubular catalytic reactor for methanol synthesis behaviour and in particular to investigate the effect of a water removal desiccant on the methanol synthesis. For this, different composition of CuO/ZnO/Al₂O₃ catalyst and molecular sieve 4A (MS 4A) were used.

First, the stainless steel catalytic tubular reactor, with dimension 0.10 m in length, 3/8 inch outside diameter and 0.006 m inside diameter, was designed and then was examined at 190 – 220^oC, 1 bar, 3600 – 7200 h⁻¹ and H₂/CO₂ = 3 - 4. The results indicated that methanol was produced from reaction between H₂ and CO₂ at those conditions. The maximum conversion was reached, 1.13%, at 190^oC, 1 bar, 3600 h⁻¹ and H₂/CO₂ = 4. This conversion is lower than the equilibrium conversion, 1.74%. By using numerical model, this conversion at 50 atm is predicted to increase 30 times than the conversion at 1 atm. Similar to the previous studies, the conversion achieved of CO₂ to methanol in methanol synthesis was lower than the equilibrium conversion although the reaction was carried out at high pressure, 10 – 50 atm.

To reduce the effect of water on the active site of catalyst, then methanol synthesis with different composition of a CuO/ZnO/Al₂O₃ catalyst and molecular sieve 4A (MS 4A) as a desiccant were carried out at 190^oC, 1 bar, 3600 h⁻¹ and H₂/CO₂ = 4 for 20 hours. The

results showed that MS 4A adsorbed the water with the consequent increase conversion of CO₂, from 1.13 to 2.12%. The latter conversion is higher than equilibrium conversion. This increase, 180%, is higher than the increase in Camere process and methanol synthesis using a membrane reactor. Joo (1999) reported that the combination of direct hydrogenation of CO₂ and reverse water gas shift (RWGS) reaction, the conversion increased 120%, from 69% to 89% (Joo et al., 1999), while Sea and Lee (2003) reported that by using the silica/alumina composite membrane reactor, the conversion improved 150% of the value in the conventional reactor (Sea and Lee, 2003).

4.2 Preliminary Economic Analysis

The last objective of this thesis was to analyse the feasibility study for a “re-syn fuel” refinery by comparing with a typical oil refinery. This analysis based on the comparison of the required energy and economic analysis in those refineries.

First, the calculations of material and energy balances for four possible chemical pathways in re-synthesizing gasoline were performed. The basis chosen was annual gasoline consumption in the UK, which are around 22 MT/year. According to the material balance, the combustion of this gasoline in the vehicles will produce some 70 MT/year of CO₂. The conversion 30% of CO₂, which was obtained from the combination of the experiment result and the extrapolation result by using numerical model, was applied for direct hydrogenation of CO₂.

The re-synthesis chemical pathways were then analysed by energy balance to determine the energy requirement for each chemical pathway. According to this analysis, the energy requirement for the direct CO₂ hydrogenation, the Camere process, the methane to methanol process and the electrolysis process are 90, 120, 134 and 210 TWh/year respectively. These required energies are only about 3 to 6.5% of the total energy which could be produced from the already proposed offshore wind turbines in UK, 3213 TWh/year.

Finally, economic analysis for the re-synthesizing of gasoline from recycled CO₂ using offshore wind energy was performed based on the energy requirement for today (2008) and future (2020). The analysis shows that the present (2008) forecourt price for the typical oil refinery (98 p per litre) is lower than this forecourt price for the “re-syn fuel” refinery using the offshore wind energy (109 p per litre) and the “re-syn fuel” refinery using coal energy (110 p per litre). By 2020 the forecourt price for re-syn fuel using the offshore wind energy (88 p per litre) and coal energy (95 p per litre) would in fact be cheaper than the present forecourt price for gasoline from typical oil refinery. It is likely that the conventional forecourt price will increase by 2020 due to the fact that the worldwide crude oil supplies will become scarcer and the carbon taxation issue.

5. Conclusions

The combination of the ZEPV concept, catalytic hydrogenation of CO₂ and MTG process, which is referred to as gasoline re-synthesis from recycled CO₂ (to produce re-syn fuel), is one of the possibilities to eliminate CO₂ emissions from the transportation sector.

The results of experiments clearly show that methanol was produced at the proposed conditions and compares to another technologies, Camere process and membrane reactor, the usage of MS 4A in methanol synthesis to remove the water from the active site of catalyst is very recommended.

According to preliminary economic assessment shows that it is feasible to re-synthesize gasoline from recycled CO₂ using offshore wind energy. And also with this re-synthesizing, the problem of CO₂ emission, the limitation of raw material for petrol synthesis and a feasible economic cost of transportation petrol can be solved together.

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