

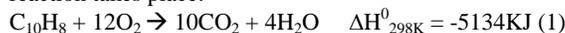
# The Potential of the CO<sub>2</sub> reforming of CH<sub>4</sub> as a method of CO<sub>2</sub> mitigation. A thermodynamic study.

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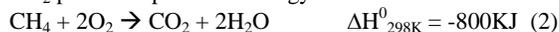
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## 1. Introduction.

Carbon dioxide (CO<sub>2</sub>) has been identified as the most significant greenhouse gas arising from anthropogenic activities. Presently, atmospheric levels of CO<sub>2</sub> are thought to be about 25% higher than in pre-industrial times [1]. It is of great importance to reduce anthropogenic CO<sub>2</sub> emissions in order to counteract global warming. In many countries (7 in the EU) a tax related to CO<sub>2</sub> emissions has been introduced in order to encourage better plant efficiency and/or create increased investment in CO<sub>2</sub> mitigation. One method of accomplishing a reduction in CO<sub>2</sub> emissions is fuel switching. As an example, if naphtha is used as a fuel, the following combustion reaction takes place:

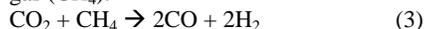


and 0.085g of CO<sub>2</sub> is released per KJ of energy produced. If the naphtha is replaced with a low-carbon containing fuel such as natural gas the energy:CO<sub>2</sub> ratio becomes more favourable with 0.055g of CO<sub>2</sub> produced per KJ of energy released.



In the long term one must consider more innovative options for anthropogenic CO<sub>2</sub> reduction. One such method, which is presently being extensively investigated, is the sequestration of CO<sub>2</sub> produced by concentrated sources (such as industry and power stations) and the subsequent disposal of the trapped CO<sub>2</sub> in reservoirs such as the deep sea or in aquifers [3,4]. Ocean disposal is seen as the method with the greatest long-term application possibilities. However there are a number of relevant concerns about this method of CO<sub>2</sub> disposal: how much of the sequestered CO<sub>2</sub> will be returned to the atmosphere and when will it be returned? According to Adams *et al.* [5] the atmosphere and the ocean eventually equilibrate on a timescale of about 1000 years regardless of where the CO<sub>2</sub> is originally discharged. Wong *et al.* [4] estimated that the disposal of CO<sub>2</sub> in to the intermediate waters of the North Pacific would buy only 20-50 years of CO<sub>2</sub> reduction. Another option which may aid in the reduction of CO<sub>2</sub> emissions is the fixation of CO<sub>2</sub> as a chemical. The advantage of CO<sub>2</sub> utilisation (fixation) over CO<sub>2</sub> disposal is that the production of chemicals with an economic value is possible. Aresta *et al.* [6,7] have done extensive research in this area. They have shown that the production of materials such as carbamic esters, urea and methylamines can be produced from CO<sub>2</sub> feedstocks.

Another reaction which consumes CO<sub>2</sub> is the dry reforming of natural gas (CH<sub>4</sub>).

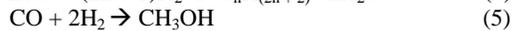
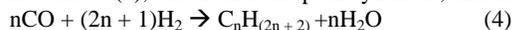


This paper assesses whether dry reforming can be viably used as a method of CO<sub>2</sub> mitigation. We have calculated all-over energy balances for a number of all over process scenarios involving the production of synthesis gas followed by the production of some other product (methanol, sulphur-free diesel and carbon).

## 2. Methods of Analysis.

Much of the work carried out on dry reforming of CH<sub>4</sub> has been justified by the argument that the reaction offers a route for the conversion of large amounts of CO<sub>2</sub>. The product of reaction (3), synthesis gas, is an equimolar mixture of CO and H<sub>2</sub>. Synthesis gas

can be used to produce higher value products, most notably sulphur free diesel (4), via Fischer-Tropsch synthesis, and methanol (5).



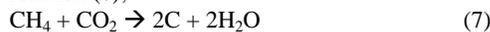
Both of these reactions ((4) and (5)) require H<sub>2</sub> to be added to the reactant synthesis gas feed in order to establish the correct reactant ratio. This hydrogen would usually be supplied by the steam reforming of CH<sub>4</sub> (6).



CO<sub>2</sub> and CH<sub>4</sub> are both relatively stable compounds with low potential energies. As a result the dry reforming reaction is highly endothermic and so energy has to be provided in order to drive it in the forward direction. Similarly, the steam reforming of CH<sub>4</sub> is also an endothermic reaction. The most likely energy source to drive these reactions will be the combustion of natural gas (2) and this process, in itself, produces CO<sub>2</sub>.

In these calculations we assume CO<sub>2</sub> and steam reforming operate in parallel to form the necessary ratio of synthesis gas to produce; (i) methanol, (ii) sulphur free diesel, represented simply as C<sub>6</sub>H<sub>12</sub>, and (iii) carbon.

In the case of carbon production the process could occur directly via reaction (8);



or more likely by the production of synthesis gas (3) followed by the reduction of CO (9).

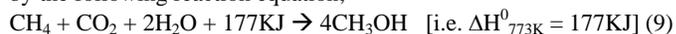


The carbon all-over process does not require additional steam reforming, as the synthesis gas ratio required for reaction (8) is 1.

In these calculations we assumed an all-over energy efficiency of 80%, i.e. 80% of the energy released from the exothermic final reaction step (e.g methanol synthesis) can be recycled to drive the endothermic reforming steps. The remainder of the energy required can be attained from the combustion of natural gas (also at an 80% energy efficiency). For simplicity, we have calculated the enthalpies for the processes involved at a single temperature of 773K. This temperature represents a compromise between the low and high temperature steps (the final reaction and the reforming steps respectively) likely to be involved in the all-over process. For example, methanol is produced by the Syntex (formerly ICI) process in the temperature range 473-573K [7], while reforming reactions are usually carried out in the temperature range 973-1223K [8].

### (i) Methanol Synthesis.

In this study methanol is assumed to be produced in two steps. The first step involves the formation of synthesis gas via the combined steam and CO<sub>2</sub> reforming of CH<sub>4</sub> (reactions (3) and (6)). Following the reforming step, methanol is synthesised by reacting the resultant synthesis gas (CO and H<sub>2</sub>). This all-over process can be summarised by the following reaction equation;



When the heat efficiency of the system is assumed to be 80%, the heat required to drive the reaction increases to 221KJ. This means for 1 mole of CO<sub>2</sub> to be consumed by reaction (9), a heat input of 221KJ is required from an external source. This usually is obtained by combusting natural gas;



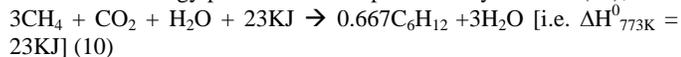
This implies that 0.34 moles of CO<sub>2</sub> will be released so as to provide the required energy to drive the all-over methanol synthesis reaction (9).

Therefore the all-over amount of CO<sub>2</sub> consumed in methanol synthesis process is 0.66 moles per mole of CO<sub>2</sub> consumed by the initial reforming of CH<sub>4</sub>.

### (ii) Sulphur Free Diesel (Fischer-Tropsch Synthesis).

Again this reaction occurs in two steps; the first being the reforming of CH<sub>4</sub> to produce synthesis gas while in the second step the resultant synthesis gas is reacted to produce higher hydrocarbons (C<sub>6</sub>H<sub>12</sub>).

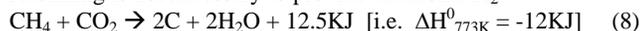
This all over energy process can be represented by reaction (10);



At an energy efficiency of 80%, the amount of energy required to drive reaction (10) is 28.8KJ. This energy is supplied by combusting CH<sub>4</sub> at the expense of 0.05 moles of CO<sub>2</sub> per mole of CO<sub>2</sub> consumed in the Fischer-Tropsch process. Therefore 0.95 moles of CO<sub>2</sub> are mitigated in this process per mole of CO<sub>2</sub> consumed in the initial reforming step.

### (iii) Carbon production

This all-over reaction scheme differs from the previous two, as steam reforming is not necessary to provide additional H<sub>2</sub>.



$\Delta H^0 < 0$  at the reaction temperature examined (indeed  $\Delta H^0 < 0$  for all temperatures) and as a result there is no need for additional CH<sub>4</sub> combustion. For every mole of CO<sub>2</sub> consumed in reaction (11) one mole of CO<sub>2</sub> is mitigated.

## 3. Discussion.

Although there were a number of gross approximations made in calculating the all-over energy results presented in this paper, the results are very informative and may inevitably lead to one gaining a greater understanding of the environmental benefits, if any, of CO<sub>2</sub> reforming.

### 3.1 Methanol Synthesis.

CO<sub>2</sub> reforming when used in parallel with steam reforming can produce synthesis gas with a CO/H<sub>2</sub> ratio suitable for methanol synthesis or in Fischer-Tropsch synthesis. The all-over methanol synthesis process enables, theoretically, 0.66 moles of CO<sub>2</sub> to be mitigated per mole of CO<sub>2</sub> consumed in the initial reforming stage. A 66% reduction of CO<sub>2</sub> per mole of CO<sub>2</sub> reacted seems a favourable result in terms of CO<sub>2</sub> mitigation. Methanol is a very useful commodity, with a worldwide annual production of approximately 30 million tonnes [7,9]. Industrially methanol is synthesised in a process where synthesis gas is produced solely by the steam reforming of CH<sub>4</sub> [7]. If all the methanol production in the world were to be shifted to a process which combined CO<sub>2</sub> and steam reforming, 10 million tonnes of CO<sub>2</sub> could be consumed in this process. This would correspond to the mitigation of 6.6 million tonnes of CO<sub>2</sub> annually. However this amount of CO<sub>2</sub> is rather insignificant in comparison to global CO<sub>2</sub> emissions; excluding deforestation and land use change CO<sub>2</sub> emissions amounted to 23.9 giga tonnes in 1996 [10]. Therefore an equivalent reduction in global CO<sub>2</sub> emissions of 0.0027% is possible by producing methanol via the CO<sub>2</sub> reforming of natural gas. Unless vast new markets are created for methanol, this method does not constitute a viable potential method of CO<sub>2</sub> mitigation.

### 3.2 Fischer-Tropsch Synthesis.

Fischer-Tropsch synthesis date back to the nineteen twenties when Fischer and Tropsch first published results concerning the reaction of H<sub>2</sub> and CO over Co, Ni and Fe catalysts to produce paraffins, olefins, waxes and oxygenates. The present and, most likely long term, application of the Fischer-Tropsch (FT) process concerns the conversion of natural gas to liquid transportation fuels (green diesel). The advantage of green diesel fuel over more conventional diesel is that green diesel has a higher cetane rating. Green diesel also contains virtually no sulphur compounds and is low in aromatics, thus greatly reducing soot and particulate emissions. The FT process is highly exothermic: the heat released per mole of CO is approximately 1000 KJ (if one assumes the composition of the end product is primarily

C<sub>6</sub>H<sub>12</sub>). From an engineering aspect this highly exothermic reaction causes a number of problems in the design of an effective FT reactor [11]. However, if this heat can be rapidly transported from the reactor to heat exchangers it can be used to provide energy the endothermic CH<sub>4</sub> reforming reactions (3 and 6). The calculations carried out in this study show that the all-over reforming and FT process is slightly endothermic ( $\Delta H = 23$  KJ). A small quantity of CH<sub>4</sub> combustion is therefore required to drive the all-over process. This occurs at the expense of 0.05 moles of CO<sub>2</sub> per mole of CO<sub>2</sub> consumed in the reforming-FT all-over process. Therefore, for every mole of CO<sub>2</sub> which is consumed in these all-over process, 0.95 moles of CO<sub>2</sub> can be mitigated. This method however only offers an effective method of short-term CO<sub>2</sub> mitigation (or fixation), as the green diesel will eventually be burnt in an engine consequently releasing the "fixed" CO<sub>2</sub> back into the atmosphere.

### 3.3 Carbon Production.

The all-over process of CO<sub>2</sub> reforming followed by carbon production is an energy efficient process at 773K. The production of carbon enables 1 mole of CO<sub>2</sub> to be mitigated per mole of CO<sub>2</sub> reacted initially in the reforming reaction. The carbon formed, in principle, can be used for a number of purposes; for example as an adsorbent or as a catalyst support. The carbon could also be used, in theory, in the production of synthetic diamonds. Ni/Fe alloys, which catalyse the diamond synthesis reaction, are also active for reaction (9) (i.e. carbon production from syngas) [12,13]. However, if the aim is solely to remove CO<sub>2</sub> from a flue gas and the cost of CH<sub>4</sub> required is not a serious factor, the carbon formed can be disposed of easily. If we consider this all-over process as a suitable potential method of CO<sub>2</sub> mitigation it becomes interesting to consider types of catalyst which can be used to carry out the CO<sub>2</sub> reforming and C production reaction steps.

### 3.4 CO<sub>2</sub> reforming.

The CO<sub>2</sub> reforming of CH<sub>4</sub> has been extensively studied in the literature. The most active catalysts contain either the active phase Ni, Co, noble metals or Mo<sub>2</sub>C. A review of these catalysts is carried out elsewhere [8]. One of the main problems with CO<sub>2</sub> reforming is the risk of catalyst deactivation due to coke deposition. This will also be discussed [8].

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