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Potential sources of CO_2 and the options for its large-scale utilisation now and in the future

J.H. Edwards *

CSIRO Division of Coal and Energy Technology, PO Box 136, North Ryde, NSW 2113, Australia

Abstract

The current emissions of CO_2 to the atmosphere through man-made activities are outlined and the options for recycling CO_2 for some useful purpose, as distinct from simply storing or disposing it in an environmentally-benign manner, are discussed. It is shown that for CO_2 recycling to have any significant impact on reducing emissions of this gas, it must form part of some large-scale energy conversion process which is based on a non-fossil-fuel energy source such as solar or nuclear energy. Since the quantities of undiluted CO_2 available for recycling are relatively small, the cost of recovering CO_2 from sources such as power station flue gas must be taken into account in the overall CO_2 recycling/energy conversion scheme.

1. Introduction

Carbon dioxide is the most important greenhouse gas arising from human activities. Increases in CO_2 concentrations in the atmosphere contribute over half of the enhanced greenhouse effect, the rest being mainly due to increases in the concentrations of methane, halocarbons and nitrous oxide [1].

New energy forecasts being prepared by the International Energy Agency (IEA), based on inputs from member countries, show that fossil fuels will continue to be the prominent energy source well into the 21st century [1]. In addition there are expectations of substantial growth in fossil-fuel use, particularly coal, in non-OECD regions [1]. Since fossil fuels are a major source of CO_2 emissions to the atmosphere, the CO_2 concentration in the atmosphere will continue to rise unless measures are taken to reduce net emissions. Consequently, since global warming can be directly attributed at least in part to the increase in atmospheric levels of CO_2, the need to reduce CO_2 emissions will become a matter of increasing priority. Studies to date suggest that emission reductions through energy efficiency improvements, whilst initially substantial, will progressively become limited, as will the option of fuel switching where a high-carbon-containing fuel such as coal is replaced with a lower carbon-containing fuel such as natural gas.

It is expected that over the medium to longer term future there will be growing interest in new technology options to capture, use or otherwise dispose of CO_2. In fact the recovery of CO_2 from stationary sources, such as power station flue gas, and the evaluation of the options for its long-term disposal (e.g. deep ocean disposal, forest sequestration and storage in geological formations etc.) are already the subjects of considerable interest [2].

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* Corresponding author.

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One other option which might help in reducing overall atmospheric CO_2 emissions is to recover and recycle existing CO_2 for the production of marketable products and for use in applications where the CO_2 is currently generated from fresh sources. This paper summarises the current uses for CO_2 in the production of industrial chemicals and other saleable products and considers how this CO_2 might be derived from the existing sources of CO_2 which are currently generated through human activities and emitted to the atmosphere. It then discusses the scope for potential new uses for CO_2 to produce saleable materials, as well as assessing the impacts that any such uses would have on the overall CO_2 emissions if this CO_2 was derived from existing, rather than new, sources. The paper does not address the much wider subjects of storing and disposing of CO_2 as means of helping to stabilise the concentration of this gas in the earth's atmosphere.

2. Current sources and uses for CO_2

The estimated 1990 worldwide production of CO_2 from man-made sources is given in Table 1 [3]. It does not include the CO_2 generated by natural processes such as animal metabolism, which is essentially a CO_2 recycling process in itself. The total produced from fossil fuels (22 Gt) is split 41%, 43% and 16% between coal, oil and natural gas, respectively. The CO_2 generated during cement manufacture is a surprisingly high figure (0.6 Gt) in the context of the total production and comes largely from the decomposition of limestone ($CaCO_3$). To put the figures in Table 1 into perspective, the atmosphere is estimated to contain about 2750 Gt of CO_2 [3].

Table 1
1990 world production of CO_2 from man-made sources [3]

Source	Gt CO_2
Coal	9.0
Oil	9.4
Natural gas	3.6
Total fossil fuel	22.0
Cement manufacture	0.6
Deforestation and land exploitation	7.4
Total	30.0

The CO_2 from fossil fuels can be subdivided into the following categories:

(i) Flue gas from stationary fossil fuel-based combustion processes (electricity generation, process and industrial heat).
(ii) Automobile exhaust gases.
(iii) CO_2 associated with natural gases and coal seam gases.
(iv) Metallurgical processes (e.g. Al smelting, iron and steel production).
(v) Byproduct from chemical processes (e.g. NH_3, H_2, CO-based syntheses, fermentation processes etc.).

The current uses for CO_2 are mainly for chemical and fertiliser manufacture (e.g. urea), beverage carbonation and food preservation, secondary recovery of petroleum and various other minor uses (e.g. firefighting, greenhouses, inert gas, etc.). The worldwide consumption of CO_2 for these purposes is difficult to estimate. However, the consumption of CO_2 is clearly only a very small proportion of that generated through the use of fossil fuels which are used to supply the major portion of the world's energy requirements.

Both the current and any future large-scale uses for CO_2 require it to be in a relatively pure form. With the exception of certain chemical processes (e.g. NH_3 and H_2 production) and natural gas treatment operations, most of the CO_2 is only available in heavily diluted forms. However, the quantity of CO_2 available from the aforementioned undiluted sources is more than enough to satisfy the current demand for CO_2. In some cases the CO_2 is derived from these sources and is thus already effectively recycled, whilst in other cases it has been found to be more cost-effective to produce the CO_2 from fresh feedstock (e.g. by combustion of fossil fuel at the point of end-use, followed by recovery and purification of the CO_2). In either case, since the CO_2 consumption is so small compared to its global production rate, it has essentially no impact on the overall contribution by CO_2 to the greenhouse problem.

3. Potential new uses for CO_2

Carbon dioxide can be used as feedstock in new routes for the production of a number of organic chemicals, and the options available here have been dealt with in some detail by Aresta [4] and Aresta et al. [5]. However, in the case of the production of chemicals, as distinct from fuels, the CO_2 which could be recycled and consumed in this application is insignificant in comparison to the total CO_2 emissions to the atmosphere.

On the other hand, since the quantity of fossil fuels used in combustion and other energy conversion processes is so very much greater than that consumed, or likely to be consumed in the future, in the production chemicals, the situation might be somewhat different if CO_2 could be recycled and used in the production of fuels. In this context the following reactions deserve consideration:

Gasification of carbon:

$$C + CO_2 + 171\ \mathrm{kJ} \rightarrow 2CO \qquad (1)$$

Reforming of methane:

$$CH_4 + CO_2 + 247\ \mathrm{kJ} \rightarrow 2CO + 2H_2 \qquad (2)$$

Enhanced photosynthesis:

$$6CO_2 + 6H_2O + \mathrm{energy} \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (3)$$

The main problem here is that CO_2 is at the bottom of a potential energy well and its use in the above reactions requires a very large energy input. The source of this energy is crucial in determining the impact that the large-scale application of reactions (1)–(3) could have on the overall global CO_2 emissions. If the energy is derived from a carbon-containing fossil fuel then CO_2 is inevitably generated to produce this energy and it must be included in the overall CO_2 mass balance for the process. This can be illustrated by considering the CO_2/CH_4 reforming reaction (2). If the 247 kJ of energy required for this reaction is supplied by the combustion of CH_4 at an overall thermal efficiency of say 80%, about 0.35 mols of CO_2 are generated per mol of CO_2 consumed by the reforming reaction.

A further consideration here is that the CO_2/CH_4 reforming reaction theoretically produces a synthesis gas with a 1/1 H_2/CO ratio. Whilst there are some applications requiring 1/1 H_2/CO feeds (e.g. the OXO synthesis reactions), the conventional processes for producing synthetic fuels generally need a feedstock with higher H_2/CO ratios. For example, the synthesis of methanol, a major contender as a future synthetic liquid fuel, requires a feed with a 2/1 H_2/CO ratio viz:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (4)$$

In practice the H_2/CO ratio of synthesis gas can be increased by conducting the water–gas shift reaction (5) which also produces CO_2:

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (5)$$

If this reaction is applied in conjunction with CO_2/CH_4 reforming to produce a 2/1 H_2/CO gas for methanol production, a further 0.67 mols of CO_2 are generated per mol of CO_2 consumed by the reforming reaction. When this is combined with the CO_2 produced in the energy production step, slightly more than 1 mol of CO_2 is generated per mol of CO_2 consumed, resulting in a net production, rather than a reduction, of this greenhouse gas. It would then most likely be preferable to use the widely employed steam/CH_4 reforming reaction (6) for the production of synthesis gas when products such as methanol are required. The surplus mol of H_2 from reaction (6), over that required for methanol synthesis by reaction (4), could be combusted to supply more than enough heat to drive reaction (6) without any net production of CO_2.

$$CH_4 + H_2O(g) + 206\ \mathrm{kJ} \rightarrow CO + 3H_2 \qquad (6)$$

One exothermic reaction involving CO_2 which is being seriously considered in Japan for CO_2 recycling and utilisation is methanation:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O(g) + 90\ \mathrm{kJ} \qquad (7)$$

It is claimed [6] that a Rh–Mn/Al_2O_3 catalyst can attain a 90% conversion of CO_2 at 300°C, and that this reaction will allow CO_2 emitted from power stations to be recycled as a source of fuel.

However, what must be considered here is the source of H_2 for reaction (7). Once again, applying the above analysis to include the CO_2 generated from the H_2 production step (taken here as the steam/CH_4 reforming reaction (6) combined with the water–gas shift reaction (5)) and allowing for the CO_2 generated by CH_4 combustion to supply the heat for reaction (6), about 1.3 mols of CO_2 are formed to produce 4 mols of H_2. The overall reaction scheme then is a net producer of CO_2 and thus there is no benefit to be gained in recycling CO_2.

It might be argued that this would not apply if the H_2 could be generated from some renewable energy source or nuclear power. However, if such H_2 is available and CH_4 is not specifically required, there is no point in conducting reaction (7) at all. Rather, it would be preferable to use the H_2 directly as a fuel. This argument is further strengthened by the fact that, as discussed later, substantial energy is required to recover CO_2 from power station flue gases and the provision of this energy can also produce more CO_2 which has not been included in the above analysis.

This very simple analysis can also be done for other reactions involving CO_2 and it illustrates the very important point that unless the energy (and in some cases the hydrogen) required for the CO_2 conversion processes is derived from non-fossil fuel sources, there is little or no benefit to be gained in recycling CO_2 from existing sources from the viewpoint of reducing CO_2 emissions.

On the other hand, if the energy for these reactions could be derived from a renewable source such as biomass or solar energy, or nuclear energy, the situation changes considerably. The photosynthesis reaction (3), with energy supplied directly from sunlight, could have application in the longer term if the major current problems with this route namely, the development of catalysts and high-capacity processing techniques to both accelerate the kinetics of photosynthesis and to increase process efficiency, could be solved.

The intermittent nature of renewable energy sources in general, and solar energy in particular, is a major impediment to their large-scale around-the-clock utilisation in industrial process heat and power applications. A comparison of the options for energy storage and transmission clearly shows that using reversible chemical reactions with large reaction heat effects is an efficient method for accomplishing these tasks. Since the energy can be stored efficiently in a chemical form at ambient temperature, it enables the solar energy to be harvested at the most effective sites (e.g. arid areas with high solar insolation) which are almost invariably located remotely from the industrial sites and large population centres where the energy is required.

Of the several alternative reversible chemical reactions being studied for this purpose, the CO_2/CH_4 reforming reaction (2) and its reverse CO/H_2 methanation reaction are now considered to be the frontrunners for thermochemical heat pipe (TCHP) applications in the storage and transmission of solar energy [7,8].

The CO_2/CH_4 reforming reaction in a high-temperature solar energy-driven reaction system is perhaps a shorter term prospect where the large-scale recycling of existing CO_2 could substantially reduce the net emissions of this gas to the atmosphere during the production of electricity and process heat and power.

The TCHP concepts based on CO_2/CH_4 reforming are shown in Fig. 1. They involve using a high-temperature source of focussed solar energy to supply the heat for the strongly endothermic CO_2/CH_4 reforming reaction. The reaction products (CO/H_2) can be then stored or transported to a separate site and subsequently used for the reverse reaction (i.e., CO/H_2 methanation), thereby releasing the stored chemical energy. The products of the reverse reaction are then sent back to the endothermic reactor to complete the closed loop cycle (Fig. 1a). A simpler open-loop cycle (Fig. 1b) is also possible. Here the product gas is directly combusted (e.g. in a gas turbine) to produce heat and power. However, unlike in the former case, where in principle all of the energy produced by the heat-pipe can be derived from the primary energy source with zero CO_2 emissions to the atmosphere, only part (up

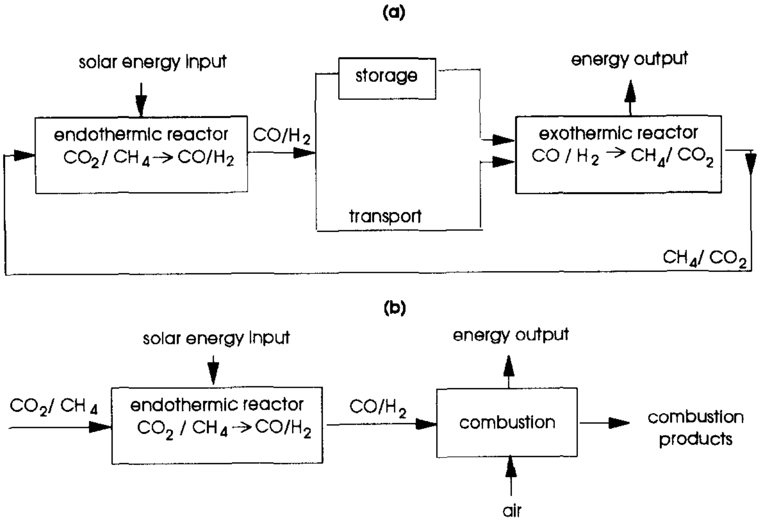

Fig. 1. Concepts for (a) closed and (b) open-loop thermochemical heat-pipes based on CH_4/CO_2 reforming and solar energy.

to around 40%) of the energy is derived thus in the open-loop configuration. Also, the open-loop cycle would require a source of cheap CO_2.

The direct linkage of reactors employing the CO_2/CH_4 reforming reaction with high-temperature solar energy is being studied at the technical scale in Israel at the Weizmann Institute of Science [9,10], and it is now part of the International Energy Agency Solar Power and Chemical Energy Systems (SolarPACES) R&D programme [11]. To date the experiments have concentrated on the technical problems associated with linking the reactor directly to the solar energy source, rather than optimising the catalyst and reactor design. To this end the research has employed fixed-bed reactors and commercial Rh-based catalysts which have been developed for reactions other than CO_2/CH_4 reforming.

Research on developing catalysts and practical reaction systems for carrying out the CO_2/CH_4 reforming reaction using solar energy is being conducted in Australia by CSIRO in collaboration with Pacific Power, Australia's largest electric power utility. This work is being partially financially supported by the Commonwealth Energy Research and Development Corporation and the New South Wales State Energy Research and Development Fund.

4. Sources of CO_2 for potential new uses

As outlined in the previous section, the scope for potential new applications for recycling CO_2 is somewhat limited. However, in the medium to longer term future the widespread application of solar-driven TCHP's based on CO_2/CH_4 reforming could create a situation in which the existing quantities of relatively high-grade CO_2 cannot completely satisfy demand. It should be emphasised here that the impetus for CO_2 recycling and its large-scale use in TCHP's would be considerably increased if carbon emission taxes were to be introduced, a situation already existing in some countries and being seriously considered in others [12]. Under these circumstances it is necessary to determine the most cost effective method of overcoming this shortfall in CO_2 through its recovery from sources where it is largely in a diluted form, due in most cases to the presence of varying amounts of N_2 which comes from the air used in the fossil fuel combustion process.

The major sources of CO_2 emissions from fossil fuel combustion are automobile exhausts and power station flue gases. Due largely to the highly dispersed and mobile nature of automobile exhaust gas, it is difficult to imagine any practical system ever being developed for the recovery and recycle of CO_2 from this source. On the other hand, power station flue gas, which is the largest single point and stationary CO_2 source, is the most likely candidate on which to base any evaluation of the various options for CO_2 recovery.

An extensive evaluation of the options for recovering CO_2 from selected alternative fossil fuel-based power generation technologies is currently in the final stages of completion by the IEA as part of its Greenhouse Gas R&D Programme [3]. Although this study is being conducted as part of a broader evaluation of CO_2 disposal options, its results will also be directly applicable to the recycling of CO_2.

The costs of CO_2 recovery are not only dependent on the type of technology employed but also on the CO_2 partial pressure in the gas being processed. The IEA study [3] addresses both of these issues by considering alternative recovery technologies (adsorption, absorption, cryogenic and membrane systems) as well as four different power generation schemes which were chosen to represent a wide range of CO_2 concentrations and conditions in the exhaust gas to be presented for downstream processing. The power generation schemes studied were:

(a) A modern pulverised coal-fired plant with flue gas desulphurisation facilities (PF + FGD) and operating with a subcritical high-temperature steam cycle.

(b) A modern natural gas-fired gas turbine combined cycle (GTCC) plant.

(c) An integrated gasification combined cycle (IGCC) plant in which a coal slurry is fed to an oxygen-blown Texaco entrained flow gasifier. This technology was selected as being representative of emerging coal-based power generating technology in the near future.

(d) Power generation based on a scheme of burning pulverised coal in oxygen (rather than air) using recycled CO_2 to moderate the combustion temperature (CO_2 recycle). This processing route concentrates CO_2 in the exhaust gas to the extent that further processing is governed by CO_2 purity requirements, rather than CO_2 recovery. The technology has not been demonstrated and must be regarded as a long-term option.

In each case the net power output, after allowing for the additional power required for CO_2 recovery, is 500 MWe. Table 2 gives the overall thermal efficiency (on a net or lower heating value (LHV) basis), specific capital cost (all costs given here are in first quarter 1992 US$) and the CO_2 level in the flue gas for each of the base cases (i.e. before inclusion of any CO_2 recovery technology). The relatively low CO_2 concentrations in the effluents from the IGCC and GTCC plants are due to the need to use high-excess air levels in the gas turbines in order to keep their inlet temperatures below the maximum limit dictated by the turbine materials of construction. Note that, whilst the CO_2 recycle option produces by far the highest concentration of CO_2, its specific capital investment is estimated to be around 2.7 times that required for the PF + FGD case and its thermal efficiency is substantially lower.

The IEA study has shown that each CO_2 recovery technology has its own particular advantages and disadvantages which depend to a large extent on the power generation scheme with which it is being linked. Whilst the number of options evaluated is too large to be included here, Table 3 gives a summary of the changes in power plant thermal efficiencies, electricity costs and how these translate into costs of recovering CO_2 for some of the more favoured options. The costs are based on a consistent set of economic parameters detailed in Appendix H of reference [3]. They

Table 2
Power station thermal efficiencies, capital costs and flue gas CO_2 levels for the base cases evaluated in the IEA Greenhouse R&D Programme [3]

Case	Fuel	Efficiency (% LHV)	Specific capital costs ($/kW)	CO_2 level in effluent (% v/v)
PF + FG D	Coal	39.9	1058	14
GTCC	Gas	52.0	750	4
IGCC	Coal	41.7	1563	7
CO_2 recycle	Coal	32.8	2712	91

Table 3
Summary of the costs of recovering CO_2 from power station flue gas for selected options evaluated in the IEA Greenhouse Gas R&D Programme [3]

Power system	Efficiency (% LHV)	Power cost (cents/kWh)	Cost of CO_2 recovered ($/tonne)	CO_2 recovery efficiency (%)
PF + FGD base case	39.9	4.9	–	0
PF + FGD plus gas scrubbing (MEA)	28.8	7.4	24	90
GTCC base case	52.0	3.5	–	0
GTCC plus gas scrubbing (MEA)	42.0	5.3	42	85
GTCC plus gas absorption membrane (MEA)	46.6	4.5	28	80
IGCC base case	41.7	5.3	–	0
IGCC plus gas scrubbing (MEA)	28.2	11.2	34	90
IGCC plus gas absorption membrane (MEA)	32.3	7.6	30	80
CO_2 recycle base case	32.8	7.8	–	0
CO_2 recycle plus gas scrubbing (Selexol)	30.4	9.4	15	99
CO_2 Recycle plus membrane	31.8	8.4	8	80

have been calculated using coal and natural gas costs of $2 and $3/GJ, respectively, and include a discounted cash flow (DCF) rate of return of 10% per annum with zero inflation.

Of the many commercial CO_2 scrubbing processes available the Econamine process, using monoethanolamine (MEA) as solvent, was the preferred one for the PF + FGD, GTCC and IGCC plants whilst the Selexol process was chosen for the CO_2 recycle case. For both the GTCC and IGCC options, where the CO_2 levels are relatively low, it was found to be cost effective to use gas absorption membranes with MEA as the absorption medium on the liquid side of the membrane. The extent to which this reduces the cost of recovering CO_2 can be seen in Table 3 which shows that using MEA gas absorption membranes reduces the recovery costs from $42 to $28/tonne and from $34 to $30/tonne for the GTCC and IGCC cases, respectively.

As expected, the CO_2 recycle case has the lowest CO_2 recovery costs ($8–15/tonne). However, it is by far the most expensive of the base cases and this, combined with the fact that it is not likely to reach commercial application in the foreseeable future, makes it a very much longer term proposition. As such it is probably inappropriate to compare it directly with the other base cases at this stage.

The results in Table 3 serve to illustrate that when CO_2 for recycling needs to be recovered from existing dilute sources, such CO_2 has a substantial cost which must be taken into account in the economic assessment of the subsequent utilisation process.

5. Concluding remarks

The current uses for CO_2 are equivalent to only a very small fraction of the total emissions of this greenhouse gas to the atmosphere through fossil fuel-based energy production and conversion processes. For CO_2 recycling to make any significant impact in the longer term reduction in atmospheric CO_2 concentrations, the recycling process must be part of an energy conversion process which is based on some form of non-fossil fuel source such as solar or even nuclear energy. Since most of the CO_2 is currently released into the atmosphere in heavily diluted forms, the not insignificant cost of recovering the CO_2 must be taken into account in the overall recycling process. At this stage power station flue gas would appear to be the most suitable source of CO_2 for recovery.

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