

**The Opportunities for Reducing GHG Emissions
through the capture of Carbon Dioxide during the
Production of Bioethanol: ‘Pumping Carbon from the
Atmosphere’**



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The Opportunities for Reducing GHG Emissions through the capture of CO₂ during the
Production of Bioethanol: 'Pumping Carbon from the Atmosphere'

ICEPT report for British Sugar

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EXECUTIVE SUMMARY

For each tonne of bioethanol produced from wheat grain 970 kg of gaseous carbon dioxide is emitted during fermentation. This carbon dioxide is a biological product of the fermentation process of which, about 90% can viably be captured, purified and then liquefied (compressed and cooled) for sale into industrial gas markets, e.g. for use in fizzy drinks. Should urgent action be required to mitigate climate change, the CO₂ could also be captured, transported and finally stored in long-term or permanent reservoirs i.e. sequestered.

This report presents the findings of a study into the environmental implications of the capture and possible uses of carbon dioxide (CO₂) produced during the fermentation of wheat grain or sugar beet for bioethanol production destined for use as a transport fuel. The work builds on earlier studies by Mortimer *et. al.* (2004) and Rickeard *et. al.* (2004) which assessed the life-cycle energy balances and greenhouse gas (GHG) emissions arising from wheat and sugar beet-based bioethanol production in the UK using current technologies. We were not asked to carry out an economic evaluation.

This study evaluates the potential GHG impacts of fermentation-derived CO₂ capture when used for:

- (i) sale into the UK industrial gas market as liquid CO₂, or;
- (ii) long term or permanent sequestration in oil or gas wells as part of a national GHG mitigation strategy.

We conclude that:

1. Evaluating the potential for GHG emissions abatement through market substitution is complicated, but significant market opportunities may exist. Two possibilities arise depending on the fate of the CO₂ being displaced:
 - (i) Where CO₂ is produced as a by-product of bioethanol production and displaces production of CO₂ by dedicated fossil-fuel-based generators, a net reduction in GHG emissions would be attained.
 - (ii) Where any CO₂ displaced is a by-product of another process such that the loss of market for that CO₂ leads to it being vented, the capture and sale of fermentation CO₂ would have no effect on net GHG emissions.

The 'broad boundaries' and uncertainty resulting from complex gas-market interactions made delivery of a quantified estimate of net GHG impacts of CO₂ sales impossible. Therefore, claiming GHG benefits from market sales of fermentation-derived CO₂ would be difficult to justify without further work. However, CO₂-capture for sale as an industrial gas would be at worst, GHG-neutral.

2. In the case of sequestration, the opportunities could be attractive should a significant value for sequestered carbon develop from changes in Government policy.
3. By coupling bioenergy (bioethanol in this case) with carbon capture and sequestration (BECS) an opportunity exists to develop new systems that would be net atmospheric CO₂ absorbers i.e. they act as 'carbon pumps', pumping carbon from the atmosphere into long-term below-ground sinks.
4. Early indications are that this BECS option would be significantly cheaper than flue-gas decarbonisation coupled to oil or gas well sequestration.
5. The potentials for reducing GHG emissions from UK-based bioethanol production with and without BECS are illustrated in table E1 below. The levels of GHG benefits shown in the table would result from the substitution of 5.75% of UK 2002 gasoline consumption with wheat-based bioethanol requiring about 2.2 billion litres of bioethanol per year. The EU Biofuels Directive's encourages all EU member states to achieve a 5.75% share of total transport energy from biofuels by 2010.
6. The additional energy inputs and associated GHG emissions resulting from the capture, purification and liquefaction of fermentation-derived CO₂ are minimal. For example, capturing the 32 kg liquid CO₂ per GJ ethanol arising during fermentation (670g per litre ethanol) is estimated to require about 3% (30MJ/GJ ethanol) of the energy content of the ethanol output. The GHG emissions resulting from the energy inputs required to capture the CO₂ depend on the method of its supply. However, these emissions would add equivalent of approximately 2% to the net GHG emissions arising from the

bioethanol production. The net benefit of coupling bioethanol with CO₂ capture is significant, as shown in Table E1.

Table E1: Ethanol as a tool for reducing national GHG emissions

Conversion Plant Energy Supply Model	Without BECS				With BECS			
	GJ primary energy input per GJ ethanol output ^a	Net GHG emissions from ethanol supply	National CO ₂ savings ^b	Share of 2002 transport CO ₂ emissions	GJ primary energy input per GJ ethanol output	Net GHG emissions	CO ₂ savings	Share of 2002 transport CO ₂ emissions
	GJp / GJ EtOH	Kg CO ₂ eq / GJ EtOH	MtCO ₂	%	GJp / GJ EtOH	Kg CO ₂ eq / GJ EtOH	MtCO ₂	%
Natural Gas Boiler + Heat Recovery	-0.36	26.30	2.83	1.98	-0.35	-1.77	4.16	2.91
Straw + Boiler	-0.56	22.86	2.99	2.09	-0.55	-5.10	4.32	3.02

Notes:

a Energy balance. A negative figure denotes that the energy content of the ethanol produced is greater than the primary energy required to produce that ethanol. 1 GJ anhydrous ethanol = 47 litres

b GHG savings arising from the substitution of 5.75% of the energy content of UK 2002 Petrol Consumption.

7. The use of bioethanol offers the potential for rapid and significant reductions in transport-based GHG emissions. Simply by diverting current UK wheat grain exports to fuel-ethanol production, virtually the entire EU Biofuels Directive's 2005 target for the UK could be met and a reduction in transport sector GHG emissions of 0.65% is projected. Together, wheat-based fuel-ethanol production coupled to CO₂ capture and sequestration would lower transport sector emissions by 1.12% (see Table E2).

Table E2: Potential Fuel- Ethanol Production from UK Wheat or Beet Production and Resulting GHG Impacts

Agricultural Feedstock ^a	Without BECS				With BECS					
	Potential ethanol production	Share of total 2002 transport energy	Share 2005 transport CO ₂	Share 2010 transport CO ₂ emissions	Net CO ₂ capture from biofuel production	Share 2005 transport CO ₂	Total CO ₂ reduction ^b	Share 2005 emissions from UK transport	Share 2010 transport CO ₂ emissions	
	t EtOH	Energy basis %	CO ₂ avoided MtCO ₂	Emissions avoided %	MtCO ₂	Emissions avoided %	Substitution + capture MtCO ₂	%	%	
Wheat	Total	4 682 900	8.03	4.14	2.90	3.52	2.46	7.66	5.36	4.79
	Share	1 050 600	1.80	0.93	0.65	0.79	0.55	1.72	1.20	1.12
Beet	Total	739 100	1.27	0.65	0.46	0.56	0.39	1.21	0.85	0.79
	Share	165 800	0.28	0.15	0.10	0.12	0.09	0.27	0.19	0.18

Notes:

a 'Total' = all current (3 year average) UK wheat or beet production used exclusively for ethanol production. 'Share' = wheat or beet currently exported is used exclusively for UK ethanol production.

8. Rickeard *et al.* (2004) confirm in their consensus report to the UK Low Carbon Vehicle's Partnership that the use of ethanol produced from wheat in the UK as a transport fuel could result in significant reductions in GHG emissions of approximately 70% per litre of petrol replaced. For a vehicle with an average unleaded petrol consumption of 2.00 MJ/km (just under 40 miles per gallon) typical life-cycle GHG emissions would be 172 gCO₂ equivalent per km (144 gCO₂ per km). As shown in table E3, **if the vehicle was powered by ethanol produced with conventional production technologies (e.g. natural gas boiler with heat recovery), the GHG emissions would drop to 53 gCO₂ equivalent per**

km. Adopting more advanced bioenergy-only systems where, for example, the wheat straw is used to provide the energy inputs to the ethanol plant, would further reduce vehicle emissions to 46 gCO₂ equivalent per km; a 76% reduction compared to normal unleaded petrol. It is worth noting that the EU's aspirational target for 2008 is 120 gCO₂/km.

Table E3: LCA GHG vehicle emissions – with and without BECS^a

Energy Supply Model for fermentation & distillation plant	Without BECS			With BECS		
	GHG Emissions			GHG Emissions		
	2 MJ per Litre					
	Kg CO ₂ eq / GJ EtOH	g CO ₂ eq / km	% of petrol	Kg CO ₂ eq / GJ EtOH	g CO ₂ eq / km	% of petrol
Natural Gas Boiler + Heat Recovery	26.3	53	27.4%	-1.77	-4	-2.1%
Straw + Boiler	22.9	46	23.8%	-5.1	-10	-6.1%

Notes:

^a - based on a vehicle consuming 2.00 MJ per km; equivalent to an unleaded petrol fuel efficiency of 38.8 miles per gallon.

- By coupling BECS to fuel-ethanol production and use, ethanol-fuelled vehicles could become Zero-Emissions Vehicles (ZEV) and possibly Negative Emissions Vehicles, the use of which would actively remove CO₂ from the atmosphere.

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1 Introduction and scope of the study

Imperial College London, Centre for Energy Policy and Technology (ICEPT) was commissioned in February 2004 to investigate the potential implications of the capture of carbon dioxide (CO₂) produced during the fermentation of wheat grain or sugar beet for bioethanol production destined for use as a transport fuel. This scoping study includes evaluating the energy requirements for capturing the CO₂ and the resulting GHG emissions arising from the supply of that energy; it does not include an economic evaluation.

Although any likely CO₂ capture, purification and liquefaction system (CC&S) can be regarded as a discrete sub-system of the ethanol (EtOH) production chain, it can not be analysed in complete isolation from the rest of the chain. As a result, and for the purposes of life cycle analysis (LCA), it was agreed that the outputs of an earlier LCA study for British Sugar by Mortimer, Elsayed and Horne (2004) on bioethanol production in the UK would be used in parallel with outputs from a Woods and Bauen (2003) LCA study for UK-DTI and a WTW¹ study for ethanol production from wheat by the fuels working group of the Low Carbon Vehicles Partnership (Rickeard et. al. 2004)

1.1 Background

The publication of the International Panel on Climate Change's Third Assessment Report (TAR), effectively removed the scientific uncertainty from the analysis of 'if' human induced global warming is occurring (IPCC, 2001). In the UK, the publication of the influential Royal Commission on the Environment's report on Energy and the Environment, which stated the requirement for a 60% reduction in GHG emissions relative to 1990 levels by 2050 if serious climate change impacts were to be avoided, caused the UK government to adopt the same long term target within the Energy White Paper. Such a significant and severe reduction in national CO₂ emissions requires a very radical switch to low or zero carbon provision of energy services. To date, two major possibilities are being considered as follows:

- 1) A substantial switch to renewable energy
- 2) De-carbonisation of fossil energy supplies.

However, a third and even more radical option is emerging which is only applicable to certain bioenergy provision routes:

¹ WTW = Well to Wheels

3) Bioenergy with carbon-capture and sequestration (BECS).

In the recent 2004 budget announcement, the Chancellor of the Exchequer, Gordon Brown, re-confirmed the UK government's commitment to renewable energy (RE) and to bioenergy by continuing the 20p/l duty derogation on renewable transport biofuels for at least the next three years. Whilst this derogation may be an insufficient fiscal stimulus to encourage the development of a significant fuel-bioethanol industry, the government's intention to participate in the EU Biofuels Directive has been clearly signalled (EU, 2003; DfT, 2004). This is further re-enforced by the recent revision to the Energy Bill as it is currently passing through parliament for the inclusion of a Renewable Transport Fuels Obligation Certification scheme (TOC) and supported by UK government as reported in the DfT response to the EU biofuels directive (DfT, 2004).

Together these three actions will further develop the markets in biopower (electricity, heat, and CHP) and renewable transport fuels. Furthermore, as the primary driver is the reduction of greenhouse gas (GHG) emissions, particularly CO₂, options for the permanent removal of CO₂ are likely to become increasingly valuable as the very significant scale of national GHG reduction targets - 20% by 2010 and 60% by 2050 - are realised.

Table 1-1: Forecast of UK Transport and Total CO₂ Emissions (Mt Carbon): 1990 to 2010

	1990	2000	2005	2010
Low Fuel Prices				
Transport	35	36	39	41
Rest of the Economy	124	112	105	106
Total	159	148	145	148
High fuel Prices				
Transport	35	36	39	41
Rest of the Economy	124	110	108	108
Total	159	147	147	149

Notes: adapted from DfT (2003) - quoting DTI Energy Paper 68.

Despite the lack of a sufficiently large incentive for potential bioethanol producers to start the construction of production facilities, the potential impacts of carbon capture from bioethanol fermentation for transport fuel production were deemed sufficiently large by British Sugar to warrant further investigation. Terms of reference were drawn up between British Sugar and ICEPT to carry out this investigation as outlined below.

1.2 Technical scope

In order to evaluate the potential for CO₂ capture from bioethanol production, a model system has been developed based around a 100 000 t_{EtOH}/yr plant located in the UK. A base year of 2002 was

adopted and it is assumed that the energy for the processing and conversion of the wheat grain (or sugar beet) to ethanol is supplied by either:

- 1) Natural Gas-fired Combined Heat and Power (CHP) plant with a gas turbine and heat recovery steam generator (Low Carbon Vehicles Partnership (LCVP) model b21).
- 2) Wheat Straw-fired Combined Heat and Power (CHP) plant with a steam turbine (LCVP model c1)
- 3) Grid electricity (LCVP model a)

It is further assumed that the captured carbon dioxide could have three eventual fates:

- 1) Capture, purification and liquefaction for supply to premium industrial CO₂ gas markets in the UK.
- 2) Capture and sequestration – analogous to systems under evaluation for removing carbon from the flue-gases of coal and gas-fired electricity power stations. Transport of CO₂ to final destination (gas or oil well) is via existing low pressure pipelines.
- 3) Venting to atmosphere.

The net impact on atmospheric GHG levels and the certainty with which the fluxes can be calculated is highly sensitive to which of the three ‘eventual fate’ options above are considered and the boundaries which are drawn to carry out the evaluation as discussed below.

1.2.1 System boundaries

The conceptual system for evaluating the impacts of CO₂ capture from fermentation is provided in Figure 1. In this framework, two possible CO₂ sinks exist, one of which is a physical ‘sequestration’ sink, most probably in exhausted oil or gas wells or for enhanced oil recovery (see section 3). The second potential sink is a market ‘substitution sink’ through sales of the captured CO₂ into the industrial gas market. Both sinks are highlighted in figure 1 and are assumed to require the recovery of CO₂ as outlined in chapter 2.

1.3 Resources and potential demand

Although ethanol can be blended with diesel in the presence of an additive, its main use as a transport fuel would most probably be restricted to blending with petrol at least during the early stages of implementation. In temperate climates, such as the UK’s, the most viable feedstocks for ethanol production are currently wheat grain and sugar beet. Ethanol production from lignocellulosic materials such as wheat straw and other agricultural and forestry residues is an emerging technology, but large-scale commercial ethanol production from these resources is unlikely for the next five years at least. Cellulosic ethanol production is not considered further in this report.

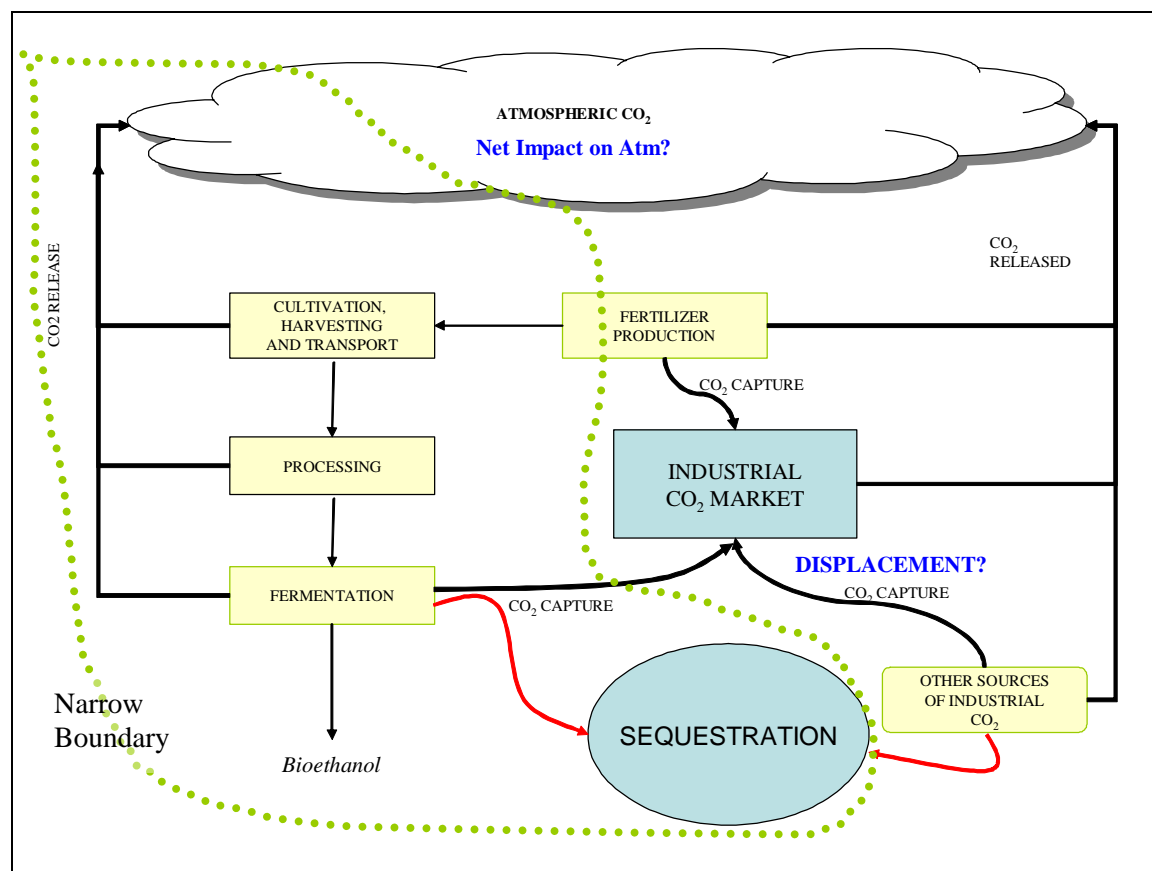


Figure 1: Conceptual Systems Framework for Carbon Dioxide Capture from an Ethanol Fermentation Plant

In 2002, according to the Department for Transport (DfT), total non-aviation transport energy consumption in the UK amounted to 1.81 EJ² (42.3 Mtoe; DfT, 2003), resulting in the release of approximately 36 Mt³ of carbon. Of this total transport energy, road transport consumption accounted for 1.56 EJ. ‘Motor spirit’ (Petrol) consumption in 2002 amounted to 0.827 EJ. Therefore, 47.5 PJ or 1.77 Mt (2.2 Bl⁴) of ethanol would be required to meet the EU Biofuels Directive target of 5.75% (energy basis) of the ‘motor spirit’ (petrol) fraction of consumption. The supply of fuel-ethanol at this scale would result in the production of 1.71 MtCO₂ from fermentation of which about 80% could be captured, representing approximately 3 times the current total industrial gas market for carbon dioxide in the UK (see section 3). The effective capture and sequestration of this fuel-ethanol fermentation

² An EJ (Exa Joule) = 1x10¹⁸ Joules; Mtoe = Million tonnes of oil equivalent (1 toe = 42 GJ); 1 GJ = 1x10⁹ Joules

³ Mt = million metric tonnes = 1x10⁶t

⁴ Bl = Billion litres = 1x10⁹l

derived CO₂ alone could result in a reduction of approximately 1.12% of predicted 2005 transport emissions (including aviation), even at this relatively low blend.

For comparison, out of a total average production of 14.4 Mt wheat grain, the UK exports on average, 3.2 Mt (22% of total production) using 430kha of arable land. Were all this exported grain diverted to ethanol production, 1.1 Mt EtOH would be available (Table 1.2). If a similar share of sugar beet production i.e. 22%, was diverted to ethanol, 165 kt EtOH could be produced on 40kha of land. Therefore almost all of the potential biofuels demand that would be created by the EU Biofuels Directive could be met in this way.

Table 1-2: UK Wheat and Beet Resources for Ethanol Production

		Ethanol (t)	Land (Mha)	ha/tEtOH	tEtOH/ha	Gross lEtOH/ha
Wheat	Total ^a	4,682,915	1.920	0.410	2.44	3071
	Share ^b	1,050,624	0.431	0.410	2.44	3072
Beet	Total ^a	739,143	0.180	0.244	4.11	5169
	Share ^b	165,829	0.040	0.244	4.11	5169

Notes:

Total UK annual production of wheat grain and sugar beet (10 year average; 1992-2002)

Based on share of wheat grain exported from the UK (10 year average; 1992-2002) of 3.2 Mt or 22% of total production. For beet, it is assumed that 22% of total production is made available for ethanol production

Source: Wheat production data from HGCA, 2004; Sugar Beet data from FAOSTAT, 2004.

2 Industrial CO₂ Recovery from Fermentation

Carbon dioxide recovered from fermentation processes has constituted a relatively small but important part of the merchant CO₂ market for many years. Breweries, distilleries and fuel ethanol plants are able to capture carbon dioxide gas generated as a by-product of their operations and produce high-purity liquid CO₂ to meet the standards required by the market. The technical capabilities and limitations of commercial CO₂ recovery plant are well known, and several manufacturers supply CO₂ recovery package plants to meet the needs of fermentation ethanol producers. Nevertheless, fermentation sources have not been the most economical for commercial CO₂ production. Many breweries choose to purchase the CO₂ they require for beer production from external sources in preference to capturing the gas generated in their own fermenters. Generally in the fermentation ethanol industry, CO₂ capture has only been practised by those plants located close to CO₂ markets and with throughputs high enough to justify the capital and operating costs of capture and purification equipment (Toromont, 2004).

To date, none of the large demonstration projects for carbon dioxide capture and storage has been based on CO₂ from fermentation plants. Fermentation is generally seen as high quality but low quantity source of CO₂ for sequestration. A demonstration project in Russell, Kansas in the USA, which has been using the CO₂ produced by a corn-ethanol plant for enhanced oil recovery (EOR) since December 2003 is claimed to be the first of its kind (Griekspoor 2003; Carr, et. al. 2004). EOR effectively sequesters a large fraction of the carbon dioxide injected (how much and for how long depends largely on whether or not the reservoir is “blown down” at decommissioning), and the CO₂ specifications for EOR would be similar to those for other forms of geological sequestration. Purity specifications for CO₂ that is destined for sequestration would be less stringent than those for CO₂ destined for the liquid market, but sequestration would require compression to higher pressures.

Outlined below is an evaluation of a CO₂ recovery plant of an appropriate scale to capture the bulk of CO₂ arising from a 100 000 t per year batch fermentation-based ethanol production facility in the UK. The analysis estimates the energy input requirements and GHG emissions resulting from the recovery of CO₂ to produce a CO₂ product to meet the specifications of a) the liquefied gas market, and b) sequestration.

2.1 Process Overview

The equipment and processes required for any CO₂ recovery scheme depend on the nature and quantities of the contaminants present in the raw carbon dioxide source and on the specification of the

final CO₂ product. Typical compositions and physical properties of CO₂ coming off a fermenter and of the required CO₂ product for the liquid market and for sequestration are described below. This is followed by descriptions of the processes involved in producing CO₂ with the required specifications given the conditions of the fermentation source.

2.1.1 Raw gas purity

Fermentation sources produce carbon dioxide with high purity, typically around 99%. The main contaminants in the carbon dioxide stream leaving a fermenter are air, water, alcohols (mainly ethanol), aldehydes, ketones and sulphur compounds (hydrogen sulphide, dimethyl sulphide and carbonyl sulphide). The amounts of contaminants present depend in part on the feedstock and the process, but a general list of impurities identified by the European Industrial Gases Association (EIGA) as being potentially associated with CO₂ from fermentation sources is given in Appendix 2.1 (Ringo, 2002). Section A2.1 also provides a typical analysis of the raw gas from a fuel ethanol plant (EIGA, 1999).

2.1.2 CO₂ Product Specification

The beverage industry is responsible for about 5% of total commercial CO₂ consumption and demands the most stringent purity specifications of all the major users of CO₂ (Johnson Matthey, 2004). Following on from a number of CO₂-related quality scares in the US and UK beverage industries in the late 1990s, the International Society of Beverage Technologists (ISBT) developed a set of guidelines for maximum contaminant levels in carbon dioxide (Ringo, 2002). These guidelines recommend even stricter purity levels than had previously been accepted in the industry. The purified liquid CO₂ specifications of the ISBT are shown in section A2.2. These are also the food and beverage CO₂ specifications of the EIGA and the American Compressed Gas Association (CGA). The main specifications of concern for purification of carbon dioxide coming off a fermenter are a minimum 99.9% CO₂ purity, moisture less than 20 ppm, oxygen less than 30 ppm and sulphur compounds less than 0.1 ppm. Carbon dioxide is generally stored and shipped at temperatures and pressures ranging from 1.4 MPa and -29°C to 2.4 MPa and -12°C (CGA, 2003).

Purity specifications for carbon dioxide destined for sequestration are less stringent than those for the liquefied CO₂ market. Hendriks et. al. (1995) give a moisture content of less than 10 ppm and permanent gases of less than 5% as the purity specifications of carbon dioxide suitable for pipeline transport and underground storage. Depending on reservoir temperature and original pressure, CO₂ can be stored in geological media either as a gas, as a liquid or in the supercritical phase (Bachu, 2001). In most cases, the supercritical state is seen as the most economically preferable for pipeline transport (Davison and Gale, 2002).

2.1.3

Typical Process Flow

Given a typical analysis of the raw CO₂ gas stream from fermenters and the required levels of final product purity, the set of purification processes shown in the process flow diagram of Figure 2 is typically used to recover carbon dioxide from fermentation and produce food-grade liquid CO₂. It follows from the raw gas and product specifications described above that for sequestration, only the dehydration and compression steps of this process will generally be required.

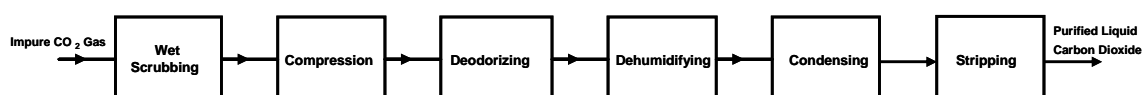


Figure 2: Typical Process Flow for Recovery of Liquid CO₂ from Fermentation

Some less advanced liquid CO₂ plants may not include a stripping section. Such plants are not able to recover as much CO₂ or to purify to the high levels as those with a stripping column.

Different manufacturers have different approaches to practical implementation of the above purification steps. Figure 3 illustrates the main components in a plant designed for high recovery and purity. It includes a set of purification steps designed to remove the contaminants normally present in raw CO₂ gas from fermentation, and produce CO₂ to food-grade purity standards as specified in the industry guidelines. The purpose of each major component is explained below.

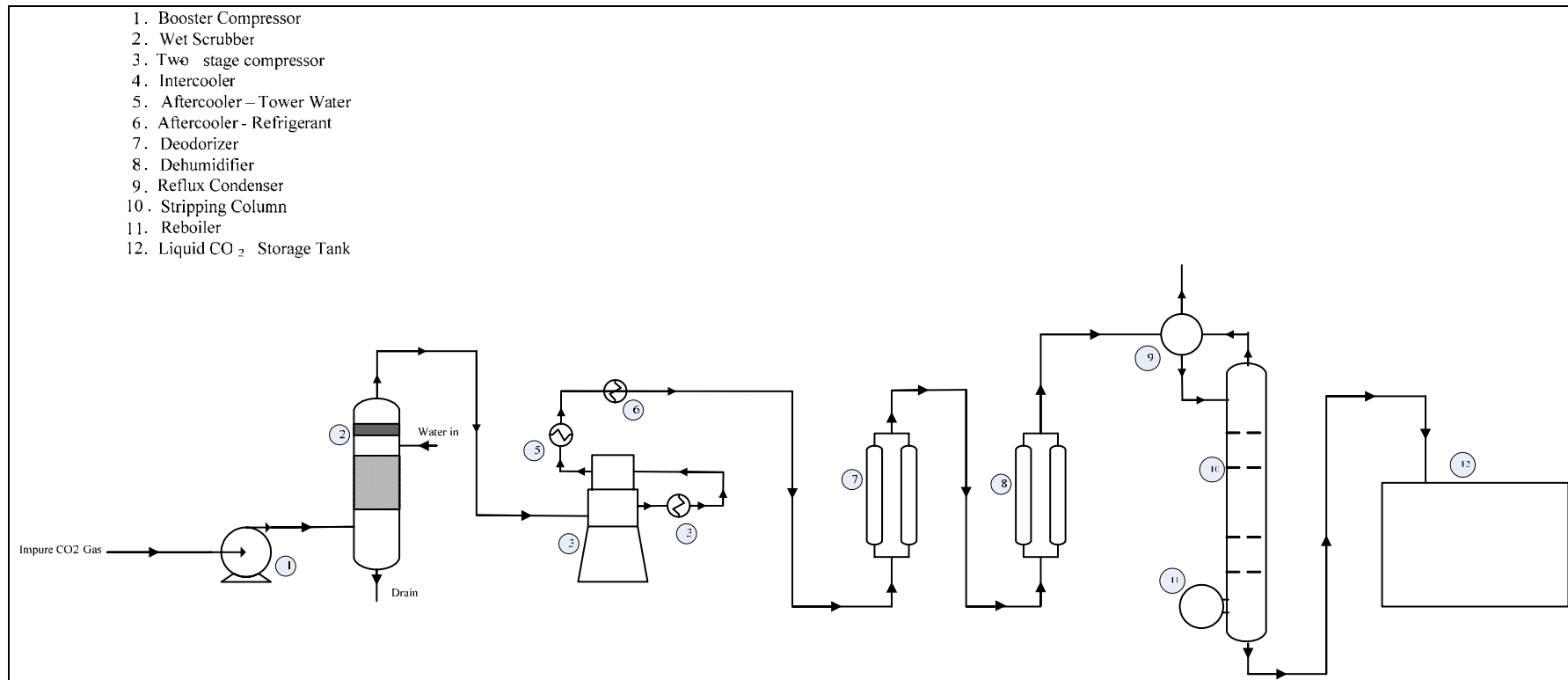


Figure 3 Generic CO₂ Capture Plant Scheme

Booster Compressor

The booster compressor provides enough gas pressure to deliver the required flow rate of gas through the scrubber and at a positive pressure at the intake of the main compressor. Because of the low pressure drop across the scrubber and the need to keep the temperature of the gas going into the scrubber low in order to maximize the solubility of the contaminants in the water stream, the pressure delivered by the booster compressor is quite low (usually less than 150 kPa).

Wet Scrubber

The scrubber removes water-soluble impurities, mainly alcohols, aldehydes and ketones. High efficiency counter-current packed bed water scrubbers are normally used. These use packing with high packing factor and once-through water feed (no recirculation). Ethanol is the soluble impurity present in the greatest concentration here, and its efficient removal in the scrubber is very important, since any ethanol remaining in the gas after the scrubber effectively competes with hydrogen sulphide (H₂S), dimethyl sulphide (DMS) and other impurities as adsorbates in the activated charcoal deodorizer further downstream. Removal of the odour-causing H₂S and DMS is especially important for food and beverage grade CO₂.

Compressor

The compressor, along with cooling and liquefaction, achieves the very large reduction in volume required for practical storage of the CO₂ (overall volume reduction achieved is in the order of 550 in a typical installation). CO₂ gas is compressed from atmospheric pressure to between 1.4 and 2.4 MPa in two stages, with inter-cooling between stages. The compressor is either a non lubricated reciprocating compressor or a screw compressor with a lubricant separation system. Total electricity requirements for compression are of the order 80 kW/t CO₂.

Aftercoolers

The high-pressure gas exiting the compressor must be cooled in order to maximize the effectiveness of the downstream adsorption columns. Cooling is normally accomplished using a water-cooled heat exchanger followed by a refrigerant-cooled heat exchanger.

Deodorizer

The activated carbon deodorizer removes a range of impurities including sulphur compounds, remaining alcohols, aldehydes and acetates. Regeneration of the activated carbon is achieved by means of hot air; and the columns are double mounted to allow regeneration of one column while the other is in operation.

Dehumidifier

The dehumidifier uses alumina or similar adsorbent to remove water down to a dew point of around -60°C (about 10 ppm). Regeneration is normally by means of electric heating elements and vent gas from the CO_2 condenser. The columns are double mounted to allow regeneration of one while the other is in operation.

Condenser

The condenser is a shell-and-tube heat exchanger in which the carbon dioxide is condensed at between -20°C and -30°C . Oxygen, nitrogen, methane and other gases with low boiling points are vented from the condenser to atmosphere.

Stripping Column and Reboiler

The stripping unit enables higher recovery rates and the production of higher purity CO_2 by stripping dissolved low boiling point gases from the CO_2 liquefied in the condenser. Liquid CO_2 from the condenser flows down the stripping column counter-current to an upward flow of pure CO_2 gas which has been generated in the reboiler. The upward-flowing CO_2 gas strips the low boiling point impurities from the downward-flowing liquid CO_2 . The CO_2 and the stripped gases flow to the condenser, where the CO_2 is re-condensed and the stripped gases are vented.

It is normal to vent the gas stream from the fermenter to the atmosphere until the CO_2 purity has built up to a level that can be processed by the purification equipment. For systems without stripping, the required input purity is around 99.7%, and around 20% of the CO_2 gas is lost through venting the fermenter and recovery system (Lewis, 2001). Even at such high inlet purity, a further 20% of the CO_2 entering the recovery system is lost through condenser venting (Sloesen, 2000). With typical stripping systems, condenser venting losses at 99.7% inlet purity are less than 1% and it is normal to collect CO_2 at 95% inlet purity, while still achieving 99.998% liquid CO_2 purity (ibid.). The CO_2 equipment supplier Wittemann claims that its best recovery systems can accept inlet gas purity as low as 80% and still produce 99.998% purity liquid CO_2 (Wittemann, 2004), but other suppliers claim that this is not economical (Brueren, 2004; Youngs, 2004).

Storage tank

The liquid CO_2 is stored in an insulated storage tank at a pressure between 1.4 and 2.4 MPa and -30 and -10°C .

2.2 Energy inputs and associated GHG emissions

The primary energy requirements and greenhouse gas emissions associated with the capture, purification and liquefaction of each tonne of liquid CO₂ from bioethanol production were determined. This involved first a determination of the total delivered energy requirements for this recovery process, and then calculation of the required primary energy and greenhouse gas emissions associated with production of this amount of delivered energy using specific power generation options previously specified and analysed by Mortimer et. al. (2004).

2.2.1 Methodology

In order to determine the delivered energy requirements for CO₂ recovery from bioethanol production, a representative plant model was analysed. As discussed earlier, there are a number of variations of the typical CO₂ plant arrangement, with differing CO₂ capture efficiencies and energy requirements. For this study, a system designed to achieve an 80% recovery rate and 99.998% liquid CO₂ purity level was considered. Figure 4 shows the basis of the analysis with the following main assumptions made:

- 1) The plant is designed with a capacity to capture 80% of the CO₂ gas generated in a 100 000 t per year bioethanol plant.
- 2) The fermenters are switched from atmospheric venting to CO₂ recovery when the CO₂ purity of the off-gas reaches 95%.
- 3) The recovery plant peak capacity is 125% of its average capacity.
- 4) Impure CO₂ gas is received at the recovery system intake at 50°C and 101 kPa.
- 5) A booster compressor delivers this gas at 140 kPa to a water scrubber with 99.75% efficiency in removing ethanol, of which the level in the impure gas is 1500 ppm.
- 6) A two-stage compressor compresses the gas exiting the scrubber to 1.5 MPa, using inter-cooling provided by a cooling tower.
- 7) The gas is cooled using water-cooled and refrigerant-cooled heat exchangers to 50°C.
- 8) Each deodorizer operates for 12 hours before being regenerated for 8 hours, using activated charcoal.

A spreadsheet model of the specified CO₂ recovery process was developed and used to calculate the energy and GHG impacts for each of the five stages of the process as shown in Figure 4. Calculations were based on the specifications for the unit operations as described above and on data provided by plant manufacturers (Brueren, 2004; Youngs, 2004).

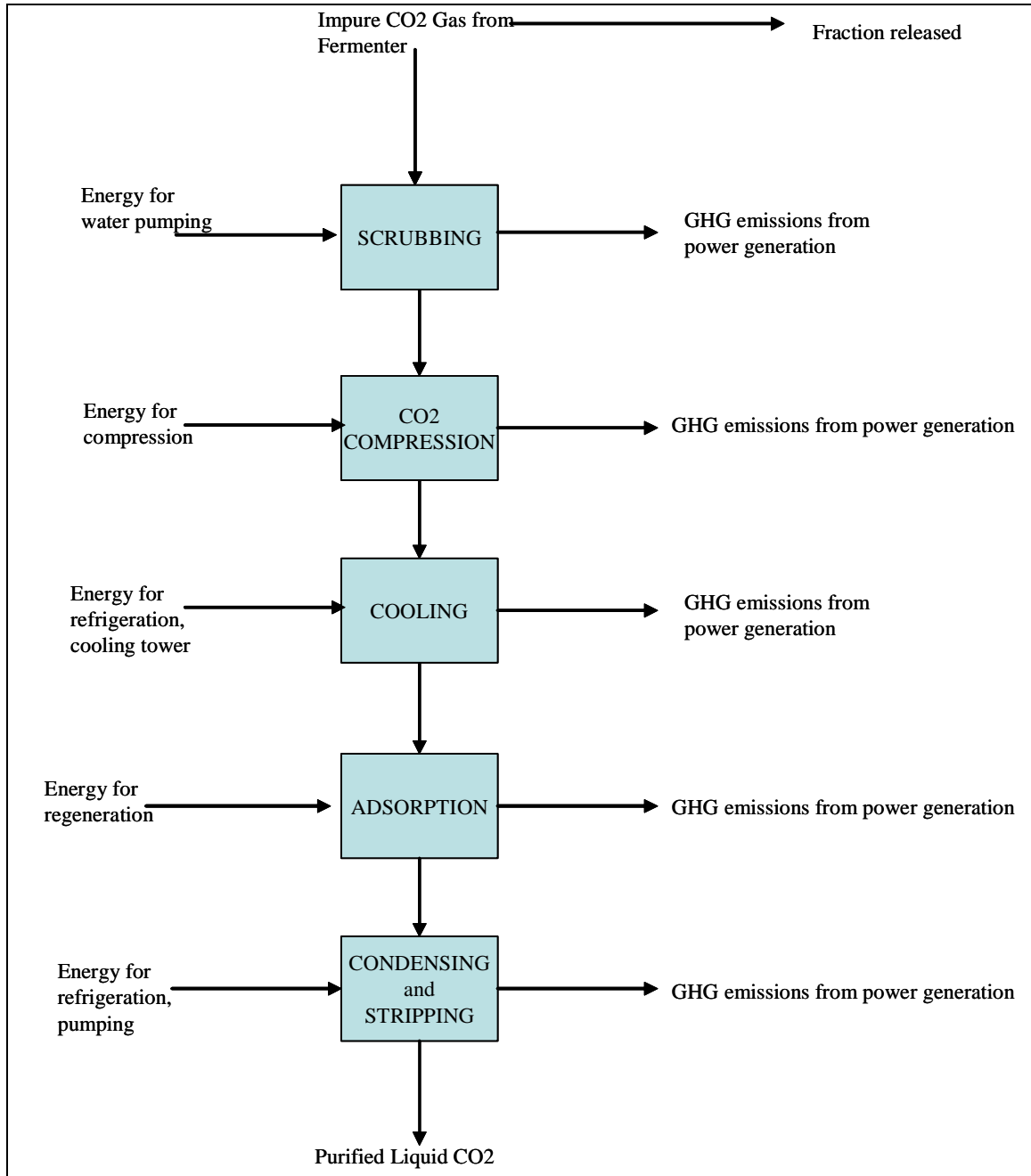


Figure 4 Overview of energy inputs and GHG outputs of CO₂ capture process

2.2.2 Summary of CO₂ Recovery Primary Energy Requirements and GHG emissions

The energy required for the CO₂ recovery is supplied entirely using electricity. Using the spreadsheet model, this electricity requirement was determined and the primary energy and greenhouse gas impacts of consuming this amount of electricity were calculated for alternative means of energy production. The primary energy and GHG balances determined by Rickeard et. al. were used in the calculations. The results are summarized in tables 2.1 and 2.2 below.

Table 2-1: Delivered energy requirements for recovery of food grade liquid CO₂

	Per t liquid CO ₂	Per t ethanol	Per GJ ethanol
Delivered energy requirements (MJ)	616.1	478.6	17.9

Table 2-2: Primary energy and GHG emissions for recovery of food grade liquid CO₂

Energy Supply	grid electricity	CHP: Natural gas-fired gas turbine + unfired HRSG + Backpressure Steam turbo-generator	CHP: Straw-fired steam boiler + Backpressure steam turbo-generator
Primary energy requirements			
MJ/t CO ₂	1897.6	875.9	965.1
MJ/t EtOH	1474.1	680.4	749.7
MJ/GJ EtOH	55.0	25.4	28.0
Total GHG Output (kg eq CO₂)			
kg eq CO ₂ /t CO ₂	98.6	53.3	58.7
kg eq CO ₂ /t EtOH	76.6	41.4	45.6
kg eq CO ₂ /GJ EtOH	2.9	1.5	1.7

As mentioned earlier, only dehydration and compression are likely to be required for recovery of carbon dioxide for geological storage. Hendriks et. al. (1995) present an analysis of the energy requirements for recovery of CO₂ from ammonia production. They calculate a total requirement of 409 kJ/kg CO₂ for compression and dehydration. The purity and physical conditions of the inlet gas described are very similar to those for CO₂ from fermentation, and

the energy requirements given can be considered a good approximation for recovery from fermentation. On this basis, table 2.3 provides the delivered energy requirement for the recovery of CO₂ from the ethanol plant with compression to 110 bar (the standardised delivery pressure used in IEA GHG calculations (Freund and Davison, 2004)). Table 2.4 shows the corresponding primary energy requirements and GHG emissions.

Table 2-3: Delivered energy requirements for recovery of CO₂ for sequestration

	Per t liquid CO ₂	Per t ethanol	Per GJ ethanol
Delivered energy requirements (MJ)	409.0	317.7	11.9

Table 2-4: Primary energy and GHG emissions for recovery of CO₂ for sequestration

Energy Supply	grid electricity	CHP: Natural gas-fired gas turbine + unfired HRSG + Backpressure Steam turbo-generator	CHP: Straw-fired steam boiler + Backpressure steam turbo-generator
Primary energy requirements			
MJ/t CO ₂	1259.7	581.4	640.6
MJ/t EtOH	978.6	451.7	497.7
MJ/GJ EtOH	36.5	16.9	18.6
Total GHG Output (kg eq CO₂)			
kg eq CO ₂ /t CO ₂	65.4	35.4	39.0
kg eq CO ₂ /t EtOH	50.8	27.5	30.3
kg eq CO ₂ /GJ EtOH	1.9	1.0	1.1

3 Options for CO₂ capture and use

This section considers two main scenarios: i) current and potential options for CO₂ capture and use, (major options for CO₂ capture, storage and sequestration; green energy), and ii) current and potential market options for CO₂ applications.

There are basically two possible CO₂ sinks existing, one of which is a physical ‘sequestration’ sink, possibly in exhausted oil or gas wells or for enhanced oil recovery. The second potential sink is a market ‘substitution sink’ through sales of the captured CO₂ into the industrial gas market (see Figure 1 for further details) thus displacing/avoiding dedicated production for this purpose.

Evaluating the potential for the sequestration sink requires a comprehensive, but methodologically simple, quantification of the mass and energy inputs and outputs for each stage in the production, capture and storage chain. Evaluating the market or ‘substitution sink’ is considerably more complex and theoretically challenging. The complexity arises because of the need to estimate and quantify the impact on the existing market of the availability of new supplies of CO₂ and therefore on the existing suppliers. Because of the uncertainties inherent in the analysis surrounding the industrial CO₂ market sink the detailed quantitative analysis carried out in this project is limited to the narrow boundary system implicit in the sequestration sink.

Globally, atmospheric CO₂ emissions continue to rise despite concerted national and international efforts to curb them. CO₂ abatement efforts will take many years to succeed at any significant scale because of the fundamental changes entailed in the way energy is generated and used. In comparison to global emissions, current CO₂ markets are very small (i.e. equivalent to 0.1% of the CO₂ released into the atmosphere by anthropogenic activities⁵). Only premium markets e.g. high quality CO₂ obtained from fermentation or as a by-product of other chemical processes are commercially attractive.

3.1. Major options for CO₂- capture, storage and sequestration

Most atmospheric CO₂ is generated by man’s activities; but it is also formed naturally by combustion and through biological processes e.g. from the combustion of organic matter if sufficient amounts of oxygen are present and by animal and plant metabolism (respiration); it is important in the life cycles of both animals and plants. It is present in the atmosphere in

⁵ In the case of Europe, markets represent 0.07% of CO₂ emitted from combustion (www.eiga.org/).

relatively small quantities (0.03%, by volume, or 375 ppm)⁶; and is found in high concentrations in underground formations⁷.

For most man-made CO₂ there are currently few viable options for non-atmospheric disposal and historically it has been regarded as a low impact zero-disposal cost pollutant. Indeed, as a result of the low environmental impact of venting CO₂ and the relatively high costs entailed in capturing and purifying it for sale in markets, there has been little incentive to do anything but vent. Longer term alternatives are actively being researched that will impact on CO₂-market development. These include: i) biological sequestration (e.g. growing and protection of forests), and ii) carbon capture and sequestration (CC&S). These options are briefly discussed below.

3.1.1 Carbon capture and storage (CC&S): market implications

CC&S is a major political priority in many countries e.g. hydrogen could be obtained extracting it from fossil fuels and capturing the carbon, with resulting very low net GHG emissions. By using carbon capture technologies in the future, it may be possible to produce near zero, or even CO₂-free energy systems based on fossil fuels. Although at present the CO₂ mitigation sector is relatively immature and risks to industry are too large and protracted to make implementation viable (Singh et al 2003), there are many new technologies under development and entirely new options are possible. Currently there is no commercial electricity generation plant in the world using CO₂ CC&S technologies (DTI, 2003a) because of the punitive costs of implementing flue-gas de-carbonisation.

Developing cost-effective CO₂ capture and sequestration is an increasingly essential element in reconciling the need for fossil fuels and combating climate warming. For the EU, the unit cost of sequestering CO₂ needs to be reduced to below Euros30/t in the short to medium term, and to below Euros20/t in the medium to long term⁸. Given these types of cost reductions, the scope for reducing CO₂ emissions in the EU is significant e.g. an ECCP report identified 42 possible measures which could lead to reductions of between 664 to 765 Mt CO₂ equivalent that could be achieved at less than Euros20/t CO₂ equivalent⁹.

Current levels of global fossil fuel consumption for power production alone would require the disposal of 2-3 GtC annually to avoid further contributions to increased atmospheric CO₂

⁶ For the fundamentals of CO₂ see, for example, www.ieagreen.org.uk/doc2b.htm; www.en.wikipedia.org/wiki/Carbon_dioxide, and <http://cdiac.esd.ornl.gov/trends/co2/sio-mlo.htm>. See also Appendix 3.1.

⁷ Natural wells can contain up to 97% by of CO₂ and may be piped hundreds of miles away. See for example, www.ugi.com/carbondioxide.html and www.ieagreen.org.uk/doc2b.htm

⁸ See for example EC leaflet- CO₂ Capture and Sequestration- Clean Power from fossil fuels

⁹ See European Climate Change Programme (ECCP)- www.europa.eu.int/comm/environment/climate/eccp.htm

from this sector. An obvious solution would be to increase both the industrial applications and CC&S at the same time. However, it is clear that the relative very large scale of the emissions compared to the small size of the CO₂ market, makes even enhanced industrial use markets unlikely to have a measurable impact e.g. the CO₂ currently traded globally is estimated at 89 Mt/yr¹⁰. Although increasing, the number and volume of new products that can be obtained from CO₂ are still relatively small. Nevertheless, it seems clear that there cannot be a market solution for disposing of such large quantities of CO₂ and therefore, avoiding emissions in the first place and CC&S remain the most realistic option. CO₂ disposal and utilisation potentials are summarised in Appendix 3.3

The UK has a substantial CO₂ storage capacity in the North Sea, approximately 16.34 GtC¹¹, (DTI, 2003a) associated with deep saline aquifers and depleted gas fields. Using existing oil and gas fields to store CO₂ is attractive because much of the necessary infrastructure is already in place e.g. existing pipelines from gas and oil fields to mainland power stations can be used in reverse to carry the CO₂ from the power stations to the gas fields. The primary driver is to use CC&S in conjunction with EOR to prolong the life of existing oil fields. Although the current costs are too high¹² to couple CC&S to EOR, CO₂-based EOR is already being carried out in the North Sea on an experimental basis. A DTI (2003a) study has estimated the cost for CC&S in depleted gas reservoirs at £34-93 t/CO_{2eq}; and £6-50/t CO_{2eq} in the case of EOR, which would add 1.0-2.3p/kWh to the cost of electricity. Such estimates are preliminary and may be optimistic. The level of economic support needed for EOR is particularly uncertain and this may take quite a bit of time to be determined¹³.

3.1.2 Biological options for CO₂ utilisation

New developments in this area, and indeed the impacts on vegetation of the land use changes that are currently underway, can have major impacts in CO₂ emissions. Considerable amounts of research continue to estimate the biological options for sequestering, avoiding and utilising CO₂. This is because biological CC&S systems offer options with the greatest scope and flexibility for dealing with CO₂. These options may include biological processes that can directly use CO₂ in conventional power station flue gas systems, or in demonstrating the feasibility of using microalgae-based processes to reduce CO₂ emissions from power plants.

Forests are of particular importance as they hold about 740Gt (90%) of the above ground terrestrial carbon. Because of the massive size of this forest carbon-pool, relatively small

¹⁰ See www.ieagreen.org.uk/utill.htm and http://www.grida.no/climate/ipcc_tar/wg3/pdf/TS.pdf for details.

¹¹ This corresponds to 2.6 Gt to depleted oil fields; 4.9 Gt to depleted gas fields; 8.6 Gt to deep saline aquifers, and 0.24 (closed and open, respectively).

¹² See for example www.pointcarbon.com/article (13 April 2004)

¹³ The EOR capacity is estimated at 700 Mt, a mere six years of UK's emissions.

changes to the net primary productivity (NPP) can have very significant changes in total annual carbon storage rates. This is one reason why forestry options are considered amongst the most effective and cheap options e.g. costs are about \$12/tC sequestered (US\$3.3/t CO₂), with an annual potential to remove 700 MtC. For comparison, the costs of carbon-capture in the power generation sector are estimated to at \$71 to 165 for natural gas CCGT and \$159 for coal per tC captured (US\$19 to 45/t CO₂)¹⁴. The carbon sequestration potential estimates vary from 0.5 to 5.4 GtC/year¹⁵, with the upper level roughly equivalent gross global annual GHG emissions. Currently one of the major potential resources of CO₂ for CC&S is from fermentation ethanol, but investment to recover CO₂ from the process remain an important limiting factor to its full utilisation (EIGA, 2003).

Other alternatives include incremental enhancement to the carbon uptake by photosynthetic systems and harnessing naturally occurring; non-photosynthetic microbiological processes capable of converting CO₂ into useful forms, such as methane and acetate. An advantage of biological systems is that they do not require pure CO₂, and thus do not incur in costs for separation/purification, capture, and compression of CO₂ gas¹⁶ (see also section 3.2).

Most of these options are long-term alternatives and of limited impacts with regard to the total amount of CO₂ that can be absorbed. For the UK, the most promising short to medium term alternatives are:

- Bioethanol production- mainly from wheat and sugar beet.
- Co-firing of biomass with coal i.e. agro-forestry residues and fast-growing plantations.
- Carbon sequestration through fast growing plantations e.g. willow and poplar.

3.2 Green energy and the implications for CO₂

The greening of the energy market has the potential to influence the CO₂ production and use in two main ways:

- 1) by reducing the CO₂ supply in a lower carbon economy;
- 2) by increasing the availability of premium CO₂ (i.e. through increased use of renewable energy, particularly via fermentation-based supplies).

¹⁴ http://www.grida.no/climate/ipcc_tar/wg3/pdf/TS.pdf ; The Technical Summary of IPCC Working Group III on Mitigation Strategies.

¹⁵ See for example, www.ieagreen.org.uk/util5.htm

¹⁶ See www.fossil.energy.gov/sequestration/novelconcepts

Green energy¹⁷ has been increasing its market share over the last decade as consumers become more aware of the health and environmental implications of energy use. The green energy market is becoming an international reality particularly in countries with the most liberalised energy regulation, where energy security issues in particular are forcing them to turn to renewable energy alternatives

The market for green energy EU-wide is estimated to be worth between Euros 20-30 billion by 2010, of which biomass (for supplying heat, electricity and transport) and wind will make the greatest contribution¹⁸. Promotion tools are moving from being technology-based (subsidies, feed-in-tariffs, tendering schemes, etc) to more market-based policies as demand for green energy increases. The UK market for green energy is one of the most promising because the strong government commitment to reducing GHG through a greater market share being provided by renewable energy.

In the case of the UK market, there are various pricing schemes e.g. green funds, surcharges, additional price per kWh, etc. Green energy, to be successful, would need to be considered EU-wide to justify investment costs. The industry is already responding to this market fragmentation through various instruments e.g. the Renewable Energy Certificates System (RECS), created by parties involved in the green energy market in Europe (see www.recs.org). In the UK, the existing Renewables Obligation support is likely to be augmented by two new schemes, including a Renewable Heat Obligation Certification (HOC) scheme and a Renewable Transport Obligation Certification (TOC) scheme in addition to the existing 20p/l duty derogation for renewable transport fuels.

Emissions or Carbon Trading (CT), trading is widely recognised as the best way to assist business in identifying the most cost effective options to reduce emissions. Currently, a major difficulty is the lack of infrastructure for international emissions trading. Although the full impacts of CT are still to be felt, it is becoming evident that a market for carbon reduction is rapidly emerging, and this will have implications for the overall CO₂ premium market.

UK is leading the way in implementing domestic trading systems for abating GHGs, particularly CO₂. The UK has launched the National Allocation Plan (NAP) after consultation with DEFRA and the DTI. This represents an important step in the UK implementation of the EU GHG Allowance Trading Scheme Directive (2003/87/EC)¹⁹.

¹⁷ Currently the term “green energy” refers to electricity obtained from renewable sources. However, in the future it may be possible to buy “green gas” or “green heat”; and on a longer term hydrogen and other biofuels could become part of the green energy market.

¹⁸ See www.reutersbusinessinsight.com

¹⁹ See www.defra.gov.uk/corporate/cosult/eu-etsnap/index.htm

However, despite the increasing importance of green energy/CT, the effect on the overall CO₂ market appears to be marginal. The strength of the green market alone would not be able to bring down CO₂ supply in any significant scale. The pressure to reduce CO₂ levels will continue in many industrial sectors, but a reduction in any significant scale will be over a long-term period of time.

3.3 Major industrial applications of CO₂

This section deals primarily with the industrial applications of CO₂²⁰, both current and future. It sketches out the existing supply and demand for industrial CO₂ and its relevance to the dynamics of new supplies of CO₂ entering the market from a premium biological source i.e. fermentation-capture from wheat or sugar beet fuel-ethanol production. However, it is not possible to provide a comprehensive analysis of the CO₂ market for two fundamental reasons: i) a large amount of CO₂ market-related data is commercially sensitive and therefore confidential, and;

ii) a detailed analysis would be too complex to be included within the scope of this study.

CO₂ is used in literally thousands of industrial applications. It finds uses in all its physical forms:

- solid (dry ice) used in refrigeration and cooling,
- liquid, also used as in solid,
- gaseous, used in chemical processes, in the storage of carbon powder and in fire extinguishers,
- supercritical, as a solvent in decaffeination, pharmaceuticals, dry cleaning, etc.

At the triple point, the pressure-temperature combination at which carbon dioxide can exist simultaneously in its three phases, it is possible to change the physical characteristics of CO₂ e.g. if the pressure is reduced the liquid changes to gas and snow; and if increased, the liquid boils to generate gas. It is the versatility of CO₂ in any of its three forms that makes it suitable for so many industrial applications.

Worldwide industrial gases, of which CO₂ is a major sub-sector, were worth \$US17.8 billion (Euros 14.83B)²¹ in 2000²², forecast to reach 225 Bm³ in 2005, worth US\$24 billion annually

²⁰ CO₂ was first discovered by Van Hekmont in 1577 who detected it in the products of both fermentation and charcoal burning; but CO₂ was not used until after 1754 when Joseph Black rediscovered it. See www.boc.com/education/gases/co2.html

²¹ Using an exchange rate of Euro = \$US1.20

(Euros 20 B), expanding at an average of 4.8% (see Freedonia Group, 2001)²³; the growth estimate for the UK market is between 5-6% (see footnote 3).

Commercial CO₂ is typically manufactured by separation and purification from relatively CO₂-rich gases produced by both combustion and biological processes. Table 3.1 summarises the major applications of carbon dioxide. Currently most of the CO₂ used in industry is not derived from flue gases, but usually from the processes specific to that industry. Over 80% of CO₂ recovered in Europe by the gas industry is obtained from waste gases from chemical processes (EIGA, 2003).

The largest CO₂ applications are in the production of urea and methanol, enhanced oil recovery, hydrogen, phosphate, ethylene oxide; carbonate soft drinks, and beer, freezing (food storage and distribution), and fire-fighting. It is also used in supercritical fluid extraction to decaffeinate coffee and for the extraction of a large number of aroma products from plants. More recent extraction applications include oils from berries and seeds, fractioning of marine and vegetable oils, removing oils from machine parts, etc. It is estimated that there are more than 100 commercially operating supercritical extraction plants globally²⁴.

The manufacturing techniques for CO₂ applications have advanced rapidly in recent years. CO₂ purity is of prime importance because higher purities raise the capital cost in equipment for recovery, purification and liquefaction. High purity CO₂ has many applications and can be sold at a premium, particularly in the food and beverage industry. Modern technologies can clean up almost any gas stream to provide liquid product, making it possible to obtain very high quality of CO₂ from many sources, but this involves additional costs. For these reasons, CO₂ recovery from fermentation processes, for example, can fetch a high value, despite the additional investment cost for recovery. Another source of high purity CO₂ is from naturally-occurring CO₂ wells and springs.

There are many types of CO₂ manufacturing plants, but the most common are:

- 1) Liquefying CO₂ from high purity sources (95%+).
- 2) Fermentation-based CO₂ recovery.
- 3) Generation of CO₂ from hydrocarbon fuels.
- 4) Recovering CO₂ from boiler stack gas (flue-gas de-carbonisation)

²² In fact this industry was worth B\$34 (B\$17.8 represents gases and B\$16.2 equipment, services and distribution). See www.chemicalprocessing.com/

²³ In Europe this industry employs 55,000 people, and gas production is about 200 000 t/day (www.eiga.org/industrialgases/)

²⁴ See for example, www.vtt.fi/pro/pro6/compressed/indappl.htm

5) Natural CO₂ recovery (wells and springs)²⁵.

Despite the growing industrial applications, the high cost of CO₂ together with other potential feedstock alternatives are still major barriers for large scale industrial applications. Access to good quality CO₂ is the key issue for the development of the premium CO₂ market. The applications can be divided into two major categories:

- i. applications that use CO₂ temporarily (i.e. bubble, cooling, etc), and;
- ii. applications that remove CO₂ permanently from the atmosphere (pH control of waste water, etc). Currently the CO₂ market represents about 0.1% of the CO₂ released into the atmosphere.

Table 3-1: Major industrial uses of CO₂

Metals	Used in large scale as shield gas in MIG/MAG welding to protect the weld puddle against oxidation. A mixture of argon and CO ₂ is commonly used to achieve a higher welding rate and to reduce the need for post welding treatment. Also used in the manufacture of casting moulds to enhance their hardness.
Manufacturing & construction	Dry ice pellets are used to replace sandblasting when removing paint from surfaces; this done to reduce the cost of disposal and clean up, etc
Chemicals, pharmaceutical & petroleum	Large quantities of CO ₂ are used as a raw material in the chemical process industry, especially for methanol and urea production. CO ₂ is used to prime oil wells for oil extraction and maintain pressure within a formation. When CO ₂ is pumped into the oil well, it is partially dissolved into the oil, rendering it less viscous facilitating its extraction from the bedrock; considerably more oil can be extracted using this process
Rubber and plastics	Flash is removed from rubber objects by tumbling them with crushed dry ice in a rotating drum
Food and beverages	Used in large quantities both in solid and liquid forms, for quick freezing, surface freezing, cooling and refrigeration in the transport of food. CO ₂ is used to carbonate drinks, beers, and wine to prevent bacterial and fungal growth; it is used also to displace air during canning, cold sterilization, etc. Approx. 1Mt/yr of CO ₂ is used in the beverage industry alone
Health care	Used as an additive to oxygen for medical use as a respiration stimulant
Environmental	CO ₂ is widely used as a propellant in aerosol cans; paint removal, etc
Water treatment	Water treatment is a rapidly growing market for CO ₂ . For example, is the preferred method for lowering pH because it is easy to control; elimination of hazardous acids from the treatment site, and the wide availability of CO ₂ . Also, a minimum of CO ₂ is added to potable water
Nuclear industry	Cooling medium for power plant cooling
Others (there are many other applications not listed)	Use on greenhouses to increase yields e.g. a 20% increase has been reported. A typical CO ₂ level would be about 1000 ppm.

Sources: UIGI (2003); www.uigi.com/carbondioxide.html; www.toromontprocess.com; Vansant (2004).

²⁵ See www.toromontprocess.com/

Many countries are currently investigating new applications of their natural and by-product sources of CO₂. As a recycled product of many natural and industrial processes, CO₂ offers many commercial opportunities that are environmentally more friendly than many other similar products. For example, CO₂ is a cost and effective replacement for other less environmentally friendly products such as many cleaning products, solvents, volatile organic compounds (VOCs), methylene chloride, n-propyl bromide (bPB), perchloroethylene, trichloroethane, etc. CO₂ is already supplied as a liquid in cylinders, mini-bulk tanks, and bulk storage tanks²⁶. This market's full potential has not been achieved yet.

- The most important growing markets for CO₂ include²⁷:
- Food freezing and chilling
- Beverages
- Oil wells (EOR) and refining
- Plant growth
- Fire extinguishers
- Medicals
- Waste treatment
- Mould setting
- Tobacco

For example, the CO₂ market in the soft drink industry in Europe has been estimated at between 206 520 and 346 354 t, in 1998²⁸. In 1996, the food market in the USA consumed 3.1 Mt of CO₂, or 58% of the CO₂ market. If Europe were to use the same level of CO₂ this market could reach 2Mt/yr. The total merchant market in Europe is about 2.12 Mt compared to its production capacity of 3.28 Mt (see Vansant 2004).

Therefore, the forces driving market growth are being determined by demand for more environmentally friendly products, improved product quality, increase in productivity and lower costs (see www.boc.com).

3.3.1

Quality versus Quantity

For most industrial applications, quality and nearness to market are fundamental prerequisites over quantity. Even where large quantities of CO₂ are available from local sources, logistics and economics may mean that the resource remains un-tapped and CO₂ is purchased on the open market. Conversely, CO₂ is bulky and therefore expensive to transport making access to geographically dispersed markets difficult.

²⁶ See for example, www.deflex.com/

²⁷ See www.boc.com

²⁸ Assuming 8 g CO₂ per litre of soft drinks produced, and population of 370 million

Despite considerable efforts to curtail pollution levels, continuous growth is being experienced and EU-15 emissions are predicted to rise from 3.14 Gt CO₂ in 2000 to 3.23 Gt CO₂ by 2015 (see Table 3-2). There are some industries which offer better prospects for CO₂ recovery than others due to their specific characteristics. For example, despite emitting over 900 Mt CO₂ in 2000, EU power plants do not necessarily represent a viable supplier to industrial CO₂ markets for two main reasons:

- i. The flue-gas CO₂ concentration is very low (3-12%), making CO₂ recovery very expensive, and;
- ii. The quality of CO₂ is poor with need to remove many impurities adding considerably to purification costs.

The same applies to other substantive CO₂ -emitting industries such as cement manufacture, oil and gas refineries, steel & coke manufacturers, etc. Therefore, industries that produce naturally high-concentration, high-quality CO₂ have an advantage in terms of inherently cheaper recovery and purification of CO₂. Such industries include: fermentation, ammonia, ethylene oxide, etc, that have a high CO₂ concentration in the raw gas (Vansant, 2004).

Ammonia and ethylene oxide manufacturing already play an important role in the CO₂ market. This is because these manufacturing processes produce high purity CO₂ waste streams (95%+ for ammonia). Ammonia and ethylene production in the EU-15 is about 11.80 and 2.55 Mt/yr (Vansant, 2004).

An apparently simple way of utilising CO₂ from power stations is to replace in-house CO₂ generation by the chemical industry with CO₂ from power stations or fermentation. However, this option needs careful consideration since the production of CO₂ in many chemical industries is often a by-product of the chemical process itself. In addition, as more stringent environmental legislation is put in place, CO₂ currently vented to the atmosphere would have to be recycled and used.

The advantages of fermentation-derived CO₂ from a wheat-based bioethanol plant is that high CO₂ concentration and low impurities of the feed-gas means that it may be sufficiently low-cost to be sold for high quality applications in a premium CO₂ market.

Table 3-2: Estimated CO₂ emissions in the EU-15 in 2015 (Mt)

Sector	Total
Industry	431.0
Iron & steel	113.8
Non ferrous metals	17.1
Chemicals	58.8
Building materials	86.2
Paper and pulp	28.7
Food, drinks, tobacco	21.9

Engineering	46.2
Textiles	7.8
Others	50.7
Tertiary	202.7
Household	476.9
Transport	987.9
Electricity steam production	1,021.1
District heating	10.5
New fuels (hydrogen)	0.3
Energy branch	104.8
Grand total	3,235.4

Note: Based on projections from all anthropogenic activities for the years 1990-1999, and on a Business as Usual Scenario.

Source: Vansant (2004), Table 18.

3.3.2

New chemicals from CO₂

The chemical industry offers an alternative for absorbing additional CO₂ in new industrial applications. If new and improved processes can be developed, CO₂ usage in this industry could be increased significantly. However, this option offers only a limited solution for premium CO₂ since the market as a whole is considered to be too small e.g. 89 MtC/yr²⁹ (equivalent to 326Mt CO₂), in comparison with the potential availability of CO₂ if all options are taken into account, as illustrated in A3.I. Some products are particularly promising as shown in Table 3.3. Two of the most promising chemical pathways are magnesium carbonate and CO₂ clathrate³⁰. The processes for removal of CO₂ are summarised in Appendix 3.2.

Table 3-3: New Chemicals manufactured from CO₂

Reduction of CO₂ by alkanes	The catalytic reduction by methane or higher alkanes requires less energy than traditional routes since production of hydrogen is not needed. Production of aromatic mixtures of Benzene, Toluene and Xylene (BTX) could be increased by increasing the addition of CO ₂ to the alkaline feed. If this method was adopted e.g. for all Japan's BTX market, CO ₂ emissions would be reduced by 2.2 Mt/yr (see source for further details)
Oxidative coupling of methane with CO₂	This reaction is, a reverse water gas shift reaction where methane is used as a reducing agent for CO ₂ converting it to hydrogen and carbon monoxide; process could use large amounts of CO ₂
CO₂ polymers	CO ₂ is not normally regarded as a useful monomer but it can take part in a number of reactions, particularly to form alkylene oxides and alkylene poly-carbonates. New developments indicate that such new polymers may substitute more conventional oil-based polymers. The predicted market is about 100t/yr.
Dimethyl carbonate	A process to produce DMC from CO ₂ is already commercial using cobalt catalysts. New low and high temperatures systems/catalysts are being

²⁹ This is the amount of CO₂ that could be prevented in the chemical industry by replacing the CO₂ currently used in the industry with recycled flue gas.

³⁰ For example, it is estimated that the entire global emissions of carbon in 1990 could be contained as magnesium carbonate in a space 10 km x 10 km x 150 m.
(www.fossil.energy.gov/sequestration/novelconcepts/)

(DMC)	developed. If accepted as a gasoline additive, the potential for CO ₂ utilisation could be vast. Globally, at least 1-2 Mt/yr of CO ₂ might be used in the production of DMC. Overall production costs of DMC from CO ₂ appear to be lower than current costs of additives only if CO ₂ is subsidised
Others	CO ₂ could also be used to replace other chemicals and solvents which are currently marketed commercially.

Source: www.ieagreen.org.uk/util3.htm

3.3.3

The UK Market

It is not possible to provide a detailed analysis of the UK carbon dioxide market for reasons already outlined above. The CO₂ market is highly specialised and competitive, with a high emphasis on the premium markets. The current UK market is about 0.5 Mt of CO₂ annually with an estimated growth of 5-6%³¹ per year, although the real potential may be closer to 1 Mt. Yet, despite a number of potential biological CO₂ suppliers existing, the UK remains a major net importer of high quality CO₂. This indicates that there are likely to be complex supply and demand factors at play in this market even where, at face value, it would appear to make economic sense to increase domestic production of premium CO₂ from existing sources. However, it is important to consider that if bioethanol fuel is introduced in to the EU or elsewhere on a large scale, the availability of high quality CO₂ will increase dramatically with significant market implications³². Since the UK is a major net importer of premium CO₂, this raises some questions about market structure, size of potential suppliers, quality, etc.

Therefore further details are required with regard to:

- Market structure e.g. monopoly of supply
- Quality of supply
- Size threshold for CO₂ suppliers to enter into viable production
- Fate of C CO₂ O₂ currently obtained as a by-product from other processes that might be substituted by new supplies
- Fate of dedicated existing CO₂ producers were significant amounts of fermentation-derived CO₂ to enter the market
- Transport costs

The fertiliser industry is a significant supplier of CO₂ into the UK. However, it is going through a difficult phase, the outcome of which will have a direct bearing on current suppliers of CO₂. If as a consequence this industry shrinks, then this may present a new market opportunity for new suppliers e.g. producers of bioethanol, and thus it may make good

³¹ There are no official growth figures. The 5-6% is based on global growth (4.8%) and the dynamism of the UK market.

³² For example, Brazil produces about 9.2 Mt of CO₂ from its ethanol production facilities. Currently only a small proportion is used in the premium market, the rest is vented out partly because lack of a domestic market and the high cost of equipment needed to recover CO₂ and to transport it international markets.

economic sense to put in place a strategy to capture fermentation- CO₂ for supply into the UK industrial gas market. However, as the EU is stimulating the introduction of large scale fuel-ethanol schemes, a possibility of oversupply of good quality CO₂ might emerge, in a similar way that the increased production of biodiesel has resulted in large volumes of glycerol entering the market and suppressing prices. UK manufacturing sales, net supply, imports, exports, prices, and imports by country of origin are summarised in the Appendix 3, Tables A3.3, Nos. I to IX.

3.3.4

CO₂ and fertilizer production

Fertiliser production has changed considerably in the past decade. The fertiliser industry has been transformed from high energy-intensity e.g. from about 400 GJ/t nitrogen in 1910 to about 25 GJ/t in 2000 (see Brentrup, 2003a). In West Europe, which has the world's more advanced ammonia (NH₃) production facilities, energy inputs have been reduced even further to about 15 GJ/tNH₃ which is close to the theoretical minimum energy input requirement (Table 3-4). At the same time, modern farming systems have increased their knowledge on fertiliser application and are now maximising productivity whilst lowering fertiliser application rates.

Table 3-4: Energy consumption in ammonia production ^a

	Regional Average energy consumption ^b		Percentage compared to West Europe
	GJ/t ammonia	GJ/t N	
West Europe	15.1	18	100
North America	17.0	23	113
Former Soviet Union	19.0	21	126
Central European Community	22.7	28	150
World average	18.5	23	123

Notes:

- (a) Excluding the feedstock for chemical transformation to ammonia e.g. the stoichiometric value.
- (b) Based on energy benchmarking by Plant Surveys International and British Sulphur Consultants, 1998 and 2000; energy levels expressed in LHV; stoichiometric value of ammonia = 20.9 GJ/t NH₃

Source: adapted from EFMA, 2004.

The use of fertilizers increased dramatically with the green revolution because high yielding varieties required large inputs e.g. total fertilizer use increased from 14 Mt in 1950 to 143 Mt in 1990. However, fertilizer use per capita began to decrease from the 1980s e.g. from 28 kg/person in 1989 to under 23kg/person in 1993. In general, this decrease has been due to various factors ranging from low commodity prices, to high debts of many developing countries; more directly related to agriculture.

The fertiliser industry is going through a difficult phase and this outcome will influence the market for CO₂ particularly in the UK.

3.4 Conclusions

The main points are summarised below.

Section 3.1: CC&S

- CC&S remains best option for climate change mitigation but does not preclude the development of premium CO₂ markets.
- Recovering CO₂ from bioethanol could make good economic sense since the UK is a major net importer of high quality CO₂.
- R&D in CC&S will eventually reduce cost and improve CO₂ quality significantly thus increasing the supply of premium CO₂
- Green energy has the potential to influence the CO₂ market in two main ways:
 - i) by reducing the CO₂ supply as a result of a lower carbon economy;
 - ii) by increasing the availability of premium CO₂ (i.e. through increase use of RE³³). But in neither case will the green market solve the problem of CO₂ in climate change. CO₂ is simply too abundant and cannot be absorbed by the industrial gas market.

Section 3.2: Market options

- The greatest value of CO₂ is in the premium market (food, beverages, supercritical fluid extraction, etc).
 - This is a specialised, healthy, and expanding market (i.e. in the UK approx. 5-6% annually) as new CO₂-based industrial applications are found
- Most CO₂ in the market arises as a by-product of other processes³⁴ (over 80% in Europe)
 - The industrial gas market will remain small in comparison to the overall potential supply of CO₂. Viability will depend on the development of the fertiliser industry in EU.
- The large potential source of CO₂, captured from power station flue-gases, would not be able to compete directly with CO₂ captured from ethanol plants because the higher purification and separation costs. Better value would result from its utilisation in greenhouses that do not require high quality CO₂.
- However, two major factors should be taken into account:
 - i. a strong possibility that the EU will embark in large scale bioethanol production to supply part of the demand required to be blended transport fuels;
 - ii. a significant reduction in transportation costs³⁵ of CO₂ which are considered quite possible, could increase quite significantly the supply of premium CO₂ e.g. Brazil produces about 9 Mt annually which is currently mostly vented to

³³ Other sources of good quality CO₂ are natural streams. These streams are often ignored if they are not close to major markets due to high transportation costs. If these costs are reduce this open new possibilities

³⁴ The best of our knowledge there are not any dedicated CO₂ plants, except those using natural CO₂ (wells and springs)

³⁵ No detailed composition of transportation costs are provided in this report

atmosphere. However, CO₂ market will be strongly determined by location of CO₂ production to avoid transport costs.

Overall, bioethanol production represents an excellent opportunity to replace fossil fuels-based CO₂ in the UK gas market but the market is likely to be very small compared to the likely production of CO₂.

4 CO₂ equivalent balances from bioethanol and carbon capture

Capturing CO₂ either for sequestration or to substitute for fossil-fuel-use or other CO₂ - emitting activities will have significant implications for assessing the overall impacts of the use of bioethanol as a transport fuel. In this section the integration of the CO₂-capture system into the whole LCA of the wheat and sugar beet bioethanol production chains is assessed, based on the analysis of wheat and beet by Mortimer et al. (2004).

4.1 Overview of CO₂-capture and disposal system

The detailed analytical evaluation carried out here assesses the energy inputs and associated GHG emissions for the capture, purification and liquefaction of fermentation-derived CO₂. Where the CO₂ is being captured for supply into the industrial gas market, the purification and liquefaction are pre-requisites in meeting the relevant market standards and regulations.

However, the capturing of the carbon for long-term sequestration will involve less purification and will not require the refrigeration needed to produce liquid CO₂. Transport will be by pipeline, using existing gas and oil network infrastructure. This would avoid expenditure and emissions from purification and liquefaction and expensive transport by truck. For example, the distribution of compressed hydrogen by tube tanker is estimated to result in GHG emissions of 5.78 kg CO₂ eq./t.km (roundtrip) and a similar level of emissions could be expected from liquid CO₂ distribution (Woods and Bauen, 2003). Although gas pipelines ar2.2 billion litres of ethanol Baseline ethanol production facilities and factors

The CO₂ is provided free-of-charge from 100 000t per year ethanol production facility using UK-produced wheat grain as the primary feedstock (see Figure 5). A similarly specified facility using sugar beet as its primary feedstock is also considered. The ethanol and CO₂ - capture facilities operate for 24 hours per day, 7 days a week and 336 days per year; a total capacity factor of 92%. The carbon dioxide gas and energy input requirements to the CO₂ - capture plant are provided by the ethanol production facility's power plant, as assessed by Mortimer et al., 2004; and described in section 1.2. Mortimer et al. (2004), and Rickeard et al. (2004) provide LCA GHG and energy balance data for these facilities which are used in this evaluation (see tables 4-1 and 4-2).

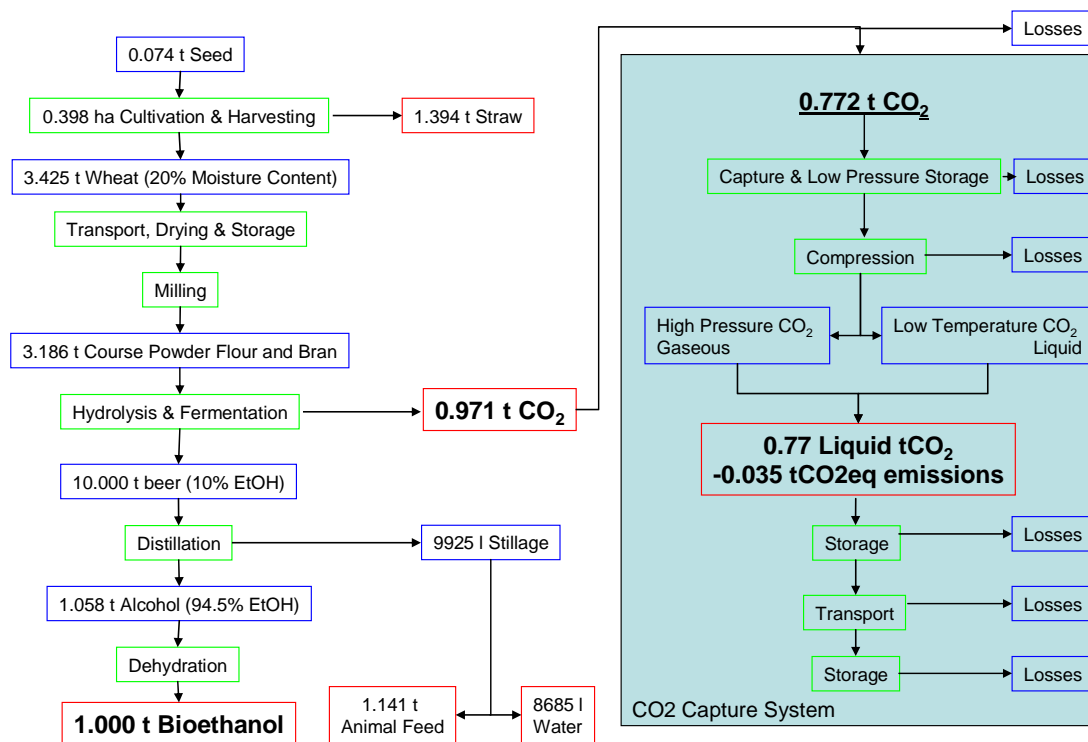


Figure 5: Integrated CO₂-capture and bioethanol production system (Wheat)

It is clear from the GHG emission factors provided in tables 4-1 and 4-2 that source(s) of energy used to provide heat and electricity for the ethanol production facility have a very significant impact on the overall net GHG emissions per unit ethanol production. Extremely low or even negative GHG emissions, arising from the production of ethanol are possible when the plant is powered by renewable biomass fuels, in this case wheat straw and co-products e.g. DDGS. Estimating the net LCA GHG emissions is sensitive to the co-product allocation methodology used. However, even without the allocation of a share of energy inputs and therefore emissions to co-products the use of natural gas CHP coupled to gas turbines will result in net GHG emission reductions of about 50% compared to unleaded petrol and less than 20% where straw is used.

Table 4-1: Reference & Model GHG emission factors from Wheat and Sugar Beet Ethanol Production (Based on Mortimer et al., 2004)

Model System	System Model	Configuration	kg CO ₂ equivalent per GJ ethanol	CO ₂ emissions as % of reference	Energy Input Requirement GJ/GJ EtOH
unleaded petrol			81	100%	
Wheat	1	NGH+GE	44	54%	0.644
Wheat	3	NG-CHP ST	44	54%	0.597
Wheat	3a	NG-CHP GT	33	41%	0.404
Wheat	7	Straw-CHP ST	14	17%	0.070
Sugar Beet	2	NGH+GE	47	58%	0.828
Sugar Beet	4	NG-CHP ST	39	48%	0.678
Sugar Beet	4a	NG-CHP GT	22	27%	0.360
Sugar Beet	8	Straw-CHP ST	-109	-135%	-0.521

Notes: NG = Natural Gas, H = Heat, CHP = Combined Heat and Power (electricity), ST = Steam Turbine, GT = Gas Turbine, GE = Grid Electricity

By-product allocation based on price

Source: Mortimer *et al.* 2004

Table 4-2: Reference & Model GHG emission factors from Wheat Ethanol Production with DDGS by-product credited as fuel for power generation (based on study for LCVP [Rickeard et. al. 2004])

Model System	System Model	Configuration	kg CO ₂ equivalent per GJ ethanol	CO ₂ emissions as % of reference	Energy Input Requirement GJ/GJ EtOH
unleaded petrol			85.5	1	
Wheat	a	NG boiler + grid NG GT+HRSG	54.3	64%	0.240
Wheat	b21	+BPSTG Straw boiler	26.3	31%	-0.363
Wheat	c1	+ BPSTG	22.9	27%	-0.564

Notes: NG = Natural Gas, GT = Gas Turbine, HRSG = Heat Recovery Steam Generator, BPSTG = Back-Pressure Steam Turbo-Generator

Source: Rickeard et. al. 2004

4.2 LCA Energy Inputs and GHG emissions from CO₂ capture

As described in section 2, the CO₂-capture facility requires electricity to power the pumps, compressor and scrubbers. This electricity is assumed to be provided from a Natural Gas Turbine configured in combined cycle mode as described in section 2. If a straw-fired CHP

unit were to be used as per Mortimer et al. (2004), models 7 and 8 or LCVP (Rickeard et al, 2004) model c1, the emissions associated with the electricity requirements for CO₂ -capture would be virtually zero.

The total primary energy requirement for the capture of one tonne of purified food-grade liquid CO₂ using electricity supplied by the natural gas-fired CHP plant of LCVP model c1 (straw-fired steam boiler and backpressure steam turbo-alternator) is calculated as 0.965 GJ. For every tonne of ethanol produced, 0.971t of CO₂ is generated and 80% of this is captured as liquid. Therefore, with an additional energy input of 0.750 GJ per tonne of ethanol produced, 777 kg liquefied CO₂ can be captured. This is equivalent to 29.0 kg CO₂ per GJ ethanol. The provision of 0.750 GJ of primary energy in the form of natural gas per tonne of ethanol produced results in GHG emissions of 45.7 kg CO₂eq./t ethanol or 1.71 kg CO₂eq./GJ ethanol. Thus the net capture of carbon dioxide per GJ of ethanol is 29.0-1.71= 27.3 kg CO₂ per GJ ethanol. This is summarised in table 4-3.

Table 4-3: GHG emissions from carbon dioxide capture with LCVP model c1 energy source

	Value	Unit
GHG emitted per t liquid CO ₂ product	58.9	kg CO ₂ eq/t CO ₂
GHG emitted per t ethanol produced ^a	45.7	kg CO ₂ eq/tEtOH
CO ₂ captured per GJ ethanol produced	29.0	kg CO ₂ /GJ EtOH
GHG emitted per GJ ethanol produced ^b	1.71	kg CO ₂ eq/GJ EtOH
Net CO₂ capture per GJ ethanol produced	27.3	kg CO₂ eq/GJ EtOH

Notes:

a. Assumes 80% of CO₂ produced by fermentation is captured and accounts for GHG emissions resulting from NGCC-derived electricity.

b. Ethanol energy density = 26.8 GJ/t anhydrous. 777kg CO₂ recovered from fermentation vessels per t ethanol produced.

The calculation shows that the level of greenhouse gas emissions associated with CO₂ capture is low compared with the total amount of CO₂ captured. How much of the net GHG abatement benefit is ultimately realized will depend on how much of the captured CO₂ is ultimately sequestered or how much displaces CO₂ directly generated by burning fossil fuels.

Table 4-4 summarises the potential GHG benefits from capturing CO₂ for sequestration (dehydration and compression to 110 bar) using energy supplied as per the LCVP models a, b21 and c1. Note that the primary energy and GHG emissions factors used assume credits for distillers dried grains and solubles (DDGS) used as a source of energy (Rickeard et. al., 2004)

Table 4-4: Effect of BECS on primary energy and GHG performance of bioethanol production with DDGS credits for energy

Energy Supply Model	Without BECS				With BECS			
	GJp/GJ EtOH	kg eq CO ₂ /GJ EtOH	Mt CO ₂ savings	% of 2002 UK Transport emissions	GJp/GJ EtOH	kg eq CO ₂ /GJ EtOH	Mt CO ₂ savings	% of 2002 UK Transport emissions
a (natural gas boiler b21)	0.24	54.32	1.50	1.05%	0.28	27.12	2.79	1.95%
(natural gas boiler + heat)	-0.36	26.30	2.83	1.98%	-0.35	-1.77	4.16	2.91%
c1 (straw boiler +)	-0.56	22.86	2.99	2.09%	-0.55	-5.10	4.32	3.02%

4.3 CO₂ and ethanol distribution

A detailed evaluation of the energy inputs and emissions resulting from the distribution of the captured carbon dioxide to its final destination or point of use is beyond the scope of this evaluation. However, based on the work of Woods and Bauen (2003) which evaluated the options for hydrogen distribution as an alternative transport fuel, it is possible to provide some rough comparative estimates for the distribution of carbon dioxide, either as a compressed liquid in tube tanker trucks or as a gas in low pressure pipelines.

Whilst the low pressure (1-3MPa) pipeline is expensive to install, it requires virtually zero energy inputs and therefore emissions to transport a gas. Transport of compressed gases by truck is energy intensive and therefore incurs emission penalties when transport over long distances is required. For the example of compressed hydrogen transport in a tube-truck with a payload capacity of 460kg the energy required is 79 GJ per km (roundtrip) resulting in the emissions of 5.8 kg CO₂ eq. per t.km (roundtrip) travelled if fuelled by diesel. If liquid CO₂ transport results in similar energy inputs and therefore emissions, delivery to a market 50 km from the CO₂ capture plant (100km round trip) would result in 580 kg CO₂ eq per tonne CO₂ delivered- a 100km delivery distance (200km round trip) would result in the emissions of more GHG than the carbon contained in the CO₂ delivered.

5 Conclusions: does CO₂ capture allow bioethanol production in the UK to be a net carbon sink pathway?

The main conclusions of the work are provided below:

- CO₂ capture from fuel-ethanol production offers a significant opportunity for both sales of food-grade premium carbon dioxide and for sequestration given appropriate economics.
- The total market for CO₂ is about 1 Mt per year in the UK which is virtually insignificant compared to the 143 Mt CO₂ total predicted emissions from UK transport in 2005 (including aviation).
- Energy and GHG emissions resulting from capture, purification and liquefaction of CO₂ are minimal.
- The production and use of bioethanol, most likely as a blend with petrol, offers the potential for rapid and significant reductions in transport-based GHG emissions. Simply by diverting UK wheat grain exports for fuel-ethanol production, the resulting 1Mt EtOH would meet virtually meet the entire EU Biofuels Directive 2005 target and result in reduction in projected Transport sector GHG emissions of 0.65%. See Table 5-1 for details.

Table 5-1: Potential for Reducing Transport-based UK CO₂ Emissions with Bio-Ethanol

		Potential Ethanol Production	Ethanol Energy Content as Share of 2002 Transport Energy (energy basis)	CO ₂ Avoided	Share 2005 Transport CO ₂ Emissions Avoided
		t EtOH	%	MtCO ₂	%
Wheat	Total	4,682,915	8.03%	4.142	2.90%
	Share	1,050,624	1.80%	0.929	0.65%
Beet	Total	739,143	1.27%	0.654	0.46%
	Share	165,829	0.28%	0.147	0.10%

Notes: See section 2 for details on basis of ethanol production potential

- Sequestration could result in notable reductions in transport-based GHG emissions on top of the emissions directly avoided by using bioethanol to substitute for petrol. The

capture and sequestration of the CO₂ emissions during fermentation of the 3.2 Mt wheat grain that would have gone to exports would remove an additional 0.79 MtCO₂ or the equivalent of 0.55% of predicted 2005 Transport sector GHG emissions. See Table 5-2.

- Coupling bioethanol production and CO₂ capture and sequestration would virtually meet the EU 2005 Biofuels Directive and result in a Transport sector emissions reduction of 1.12%. See Table 5-2. Diverting all of the UK's wheat production to bioethanol would result in a reduction of 1.44% of UK's total predicted GHG emissions for 2005.

Table 5-2: Potential for Reducing Transport Emissions with Bio-Ethanol and CO₂ Capture

		Net CO ₂ Capture From Biofuel Production	Share 2005 CO ₂ Emissions	Total CO ₂ Reduction Substitution + Capture	Share 2005 CO ₂ Emissions from UK Transport	Share 2010 CO ₂ Emissions
		Mt CO ₂	%	Mt CO ₂	%	%
Wheat	Total	3.52	2.46	7.660	5.36	4.97
	Share	0.79	0.55	1.719	1.20	1.12
Beet	Total	0.56	0.39	1.209	0.85	0.79
	Share	0.12	0.09	0.271	0.19	0.18

Evaluating the comparative economics for biological carbon capture and sequestration from bioethanol production relative to fossil-based carbon sequestration options was not in the scope of this study. However, retrofitting existing fossil-power stations with flue-gas decarbonisation equipment and transporting the carbon dioxide to existing oil and gas fields is likely to be expensive. Indeed, the capture and sequestration of carbon dioxide from biological bioenergy conversion plants is likely to be significantly cheaper, even allowing for the greater economies of scale of large power plants, and **will result in the active removal of carbon from the atmosphere**. Such biological routes are the only routes available for the physical pumping of carbon from the atmosphere and deserve very detailed investigation.

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APPENDICES

A2.1 Impurities in raw carbon dioxide gas generated by fermentation

The European Industrial Gases Association document IGC Doc 70/99/E identifies the following as possible trace impurities in carbon dioxide derived from fermentation sources, in addition to air gases and water (ISBT, 2004; EIGA, 1999).

- Aldehydes
- Benzene
- Carbon Monoxide
- Carbonyl Sulphide
- Dimethyl Sulphide
- Ethanol
- Ethers
- Ethyl Acetate
- Hydrogen Sulphide
- Ketones
- Mercaptans
- Methanol
- Nitrogen Oxides
- Sulphur Dioxide
- Toluene
- Volatile Hydrocarbons
- Xylene

Toromont Process Systems, a supplier of CO₂ recovery plants, gives the following as a typical analysis of the CO₂ gas stream from the fermenter of a fuel ethanol plant (Toromont, 2004):

Table A2-1: Typical Analysis of Carbon Dioxide Gas from Fermenter

CO ₂	98.5%
Air	1.3%
Acetaldehyde	300 PPMV
Sulphur Compounds (H ₂ S, CS ₂)	35 PPMV
Ethanol	1500 PPMV
Methanol	200 PPMV
Ethyl Acetate	80 PPMV
Acetic Acid	10 PPMV
Amyl Alcohol	50 PPMV
Isopropanol	25 PPMV
Butanol	25 PPMV
Methane	20 PPMV

A2.2 Purity specifications for liquid carbon dioxide product

The International Society of Beverage Technologists (ISBT) purity guidelines for beverage-grade liquid carbon dioxide are given in the table below. These guidelines were developed in conjunction with the European Industrial Gases Association (EIGA) and the American Compressed Gas Association (CGA), and the EIGA and CGA specifications for food-and-beverage grade carbon dioxide are identical (Ringo, 2002).

Table A2-2 Purity Specifications for Food and Beverage Grade Liquid Carbon Dioxide

Parameter	Guideline	Rationale^a
Purity	99.9% v/v min.	Process
Moisture	20 ppm v/v max.	Process
Oxygen	30 ppm v/v max	Sensory
Carbon monoxide	10 ppm v/v max	Process
Ammonia	2.5 ppm v/v max	Process
Nitric oxide/nitrogen dioxide	2.5 ppm v/v max. each	Regulatory
Non-volatile residue	10 ppm w/w max	Sensory
Non-volatile organic residue	5 ppm w/w max	Sensory
Phosphine	To pass test (0.3 ppm v/v max.)	Regulatory
Total volatile hydrocarbons (as methane)	50 ppm v/v max., including 20 ppm v/v max. as total nonmethane hydrocarbons	Sensory
Acetaldehyde	0.2 ppm v/v max	Sensory
Aromatic hydrocarbon	20 ppb v/v max	Regulatory
Total sulphur content ^b (as S)	0.1 ppm v/v max	Sensory
Sulphur dioxide	1 ppm v/v max.	Sensory
Odour of solid CO ₂ (snow)	No foreign odour	Sensory
Appearance in water	No colour or turbidity	Sensory
Odour and taste in water	No foreign taste or odour	Sensory

^aRationale definitions: sensory = any attribute that negatively impacts the taste, appearance, or odour of beverage; process = any attribute that defines a key parameter in a controlled process and an important consideration in the beverage industry; regulatory = any attribute whose limit is set by governing regulatory agencies.

^bTotal sulphur-containing impurities excluding sulphur dioxide.

A3.1 Global Carbon Dioxide Storage Potentials

Table A3-1: Global Carbon Dioxide Storage Potentials

Options	Potential for global CO ₂ storage capacity, GtC	
	<i>IEA GHG studies</i>	<i>Others + remarks *</i>
Use methods		
Enhanced oil recovery	65 (0.4 Gt /yr)	17 to 63 GtC/yr
Direct	0.15 GtC/yr	No estimates
Indirect	1.2 GtC/yr	500-620 Mha
Chemicals	0.089 GtC/yr	
Disposal methods		
Ocean disposal	No estimate	2x10; 1400 GtC
Terrestrial disposal	No estimate	No estimate
Aquifers	<87GtC	87; 116 ; 2700 GtC
Exhausted gas wells	140GtC (a)	83; 142; 314 GtC (b)
Exhausted oil wells	40 GtC	42; 187 GtC (c)

*Summary only. For further details see source.

(a) Maximum value for depleted fields + proven reserves

(b) Based on proven reserves, assuming all reservoirs can be refill; based on proven reserves and depleted reservoirs assuming all can be refill; and including unproven fields, respectively

(c) Based on proven reserves, assuming all reservoirs can be refill; based on proven reserves and depleted reservoirs assuming all can be refill, respectively

Source: www.ieagreen.org.uk/util7.htm

A3.2 CO₂ Removal Technologies

Table A3-2: Processes for Removal of Carbon Dioxide from Flue Gases

System	Solvent	Corrosion inhibitor	Acid gas content in treated gas	Heat required	Comments (brief- see sources for further details)
MEA*	15-20% mono-ethanol amino	None	Less than 50 ppmv	High	High utility consumption; alloy material needed to combat corrosion
Inhibited MEA	25-35% MEA + UCAR amine guard	Yes	Less than 50 ppmv	Medium	Inhibitor allows higher CO ₂ loading, reducing circulation & consumption
TEA/MEA	Triethanol + monoethanol amine	None	Less than 50% ppmv	Low	Used in several NH ₃ installations. Separate absorption & stripping systems required
AMDEA	40-50% MDEA + additive	None	100-10000 ppmv	Low	Two-stage configuration mostly used in ammonia plants
Benfield **	25-30% K ₂ CO ₃ + additives	Yes	500-1000 ppmv	Low	Used extensively in ammonia. Low operating costs
Catacarb	25-30% K ₂ CO ₃ + additives	Yes	500-1000 ppmv	Low	Used in ammonia plants up to 1,540 t/day capacity
Carsol	K ₂ CO ₃ + additives	Yes	500-1000 ppmv	Low	Used as single stage or two-stage system. Used in NH ₃ plants up to 1360 t/day
Flexsorb HP	K ₂ CO ₃ + additives	Yes	500-1000 ppmv	Low	Recently commercial. In a 1640 & 472 t/c ammonia plant
Lurgi	25-30% K ₂ CO ₃ + additives	Yes	500-1000 ppmv	Low	Used in various installations e.g. Germany + others
Vetrocoke	K ₂ CO ₃ + As ₂ O ₃	Arsenic inhibits	500-1000 ppmv	Low	Use of arsenic presents disposal and pollution problems
Vetrocoke	K ₂ CO ₃ + glycerine & Secondary amine	Yes	250-1000 ppmv	Low	Low energy, uses 2-pressure regeneration- heat reduction by 50%
Sulfanol	Sulfolane, di-isopropanol-amine solution	None	Less than 100 ppmv	Low	Process can be used for CO ₂ & H ₂ S removal applications in synthesis gas & natural gas services. Cost relatively high
Purisol (NMP)***	N-methyl-2 pyrrolidone	None	Less than 50 ppmv	Low	Used in high pressure processes e.g. partial oxidation
Rectisol	Methanol	None	Less than 10 ppmv	Low	System circulates refrigerated methanol. Can be used for CO ₂ , H ₂ S & COS removal
Flour Solvent	Propylene carbonate	None	Dependent on pressure	Low	Has high degree of solubility for CO ₂
Selexol	Propylene glycol dimethyl ether	None	Dependent on pressure	Low	Suitable for high pressure absorption services. Part of CO ₂ lost during flash

Notes: * Chemical type systems amine-based

** Potassium-carbonate based

*** Physical absorption systems

Sources: **Handbook of Fertilizers, Brentrup (2003)**

**A3.3: UK Statistical Tables of CO₂ markets (imports and exports)
(Manufacturing sales, net supply, values, imports-exports, prices, and imports by country of origin)**

Statistical information on CO₂ presents additional difficulties because it has many and different applications (i.e. as an inert gas for welding, as carbonate for beverages and beers, or in solid or liquid forms, as a refrigerant). Depending of the uses the quality varies e.g. if used in the beverage industry it must be of the highest quality (odourless and tasteless), as compared if used to shrink metals. These Tables provide rough estimates and thus should be read with caution.

Table III provides estimates of manufacturing sales and net balance of UK supply of CO₂ for the years 2000 and 2002, and partial data for 2001 and 2003. Tables III to VII show UK imports and exports of CO₂ from 2000 throughout 2003. They show that UK was a large importer of CO₂ over this period, although there seems to be a tendency to decrease toward the end of this period, when exports actually exceeded imports for the first time. The second factor is that the price of exports far exceeded the price of imports which has remained low over this period.

The second set of Tables, Tables VIII- XI, show UK imports of CO₂ by main country of origin and price fro the periods 1999-and 2001 to 3rd quarter of 2003. The Netherlands and Norway are by far the two largest and cheapest suppliers of CO₂ to the UK market. Prices over this period have remained more or less constant. As indicated, there are difficulties withy the data and hence discrepancies are common. These tables are intended to give an overall view of the market, not a detailed analysis.

Table A3.3-I: UK manufacturing sales, net supply and value of Carbon Dioxide, 2000 -2003

	2000	2001*	2002	2003*
Volume (kt)				
- Manufacturing sales	511.6	111.0	407.0	92.6
- Net supply	571.4	130.0	488.0	96.8
Value (£M)				
- Manufacturing sales	17.3	3.8	12.4	3.0
- Net supply	19.1	3.6	13.0	2.6

* Includes data for the first quarter of 2001 and 2003 only. For further details consult the National Statistics –Product Sales and Trade PRQ 24110 –Industrial Gases, from which this table has been compiled.

Table A3.3-II: UK Imports and exports of Carbon Dioxide, and average value (£/Kg) in 2000

Volume(Kg)	1st quarter	2nd quarter	3rd quarter	4th quarter
Total exports	915,842	1,001,052	1,300,743	1,136,126
Total imports	28,874,936	25,367,125	5,595,536	4,230,434
Net balance	27,959,094	24,366,073	4,294,793	3,094,308
Value/Kg				
- total exports	0.53	0.76	0.56	0.60
- total imports	0.04	0.06	0.20	0.20

Source: National Statistics- Product Sales and Trade; PRQ 24110 (Industrial Gases)

Table A3.3-III: Imports and exports of Carbon Dioxide, and average value (£/Kg) in 2001

Volume(Kg)	1st quarter	2nd quarter	3rd quarter	4th quarter
Total exports	2,994,044	2,343,281	4,339,046	4,033,053
Total imports	21,913,924	22,969,503	24,240,261	26,721,444
Net balance	18,919,880	20,636,222	19,901,215	22,688,391
Value/Kg				
- total exports	0.38	0.51	0.29	0.28
- total imports	0.04	0.04	0.04	0.04

Source: National Statistics- Product Sales and Trade; PRQ 24110 (Industrial Gases)

Table A3.3-IV: UK Imports and exports of Carbon Dioxide, and average sale value (£/Kg) in 2002

Volume(Kg)	1st quarter	2nd quarter	3rd quarter	4th quarter
Total exports	3,500,009	2,017,621	2,110,789	4,885,572
Total imports	23,318,040	21,978,083	16,562,528	32,443,185
Net balance	19,818,031	19,960,462	13,451,739	27,557,613
Value/Kg				
- total exports	0.27	0.48	0.27	0.21
- total imports	0.05	0.05	0.05	0.04

Source: National Statistics- Product Sales and Trade; PRQ 24110 (Industrial Gases)

Table A3.3-V: Volumes and Values of UK Imports and exports of Carbon Dioxide (2003)

Volume(Kg)	1st quarter	2nd quarter	3rd quarter	4th quarter
Total exports	5,199,798	6,536,878	8,666,852	N/A
Total imports	9,317,761	2,026,086	1,550,059	N/A
Net balance	4,117,963	-4,510,792	-7,116,793	N/A
Value: £/Kg				N/A
- total exports	0.19	0.15	0.09	N/A
- total imports	0.07	0.21	0.31	N/A

Source: National Statistics- Product Sales and Trade; PRQ 24110 (Industrial Gases)

Table A3.3-VI: United Kingdom imports of CO₂, 1997 – 1999, total and by major country (Kg)

<i>Country</i>	<i>1997</i>	<i>1998</i>	<i>1999</i>
World total	130,197,031	140,648,734	148,071,290
Netherlands	121,587,788	132,897,985	145,358,626
Austria	4,272	1	98,516
Germany	200,004	567,814	641,714
Italy	325,407	183,043	109,410
Sweden	0	10,560	16,202
Ireland	38,104	1,310,786	905,989
France	8,314	3,506	15,795
United States	19,735	6,056	13,407
Israel	0	0	935
Japan	116	3,073	4,083
Belgium	0	0	16,156
Norway	7,842,613	4,200,369	868,126
Denmark	0	337,379	0
Belgium-Lux.	167,128	1,127,252	0
Greece	0	0	478
Spain	0	0	3,132
Switzerland	3,550	810	18,182
Canada	0	0	250

Source: H.M. Customs and Excise, World Atlas UK Imports (281121 Carbon Dioxide)

Table A3.3-VII: Total and by country United Kingdom imports of CO₂, 1997 – 1999 (Average price £/kg)

<i>Country</i>	<i>1997</i>	<i>1998</i>	<i>1999</i>
World average	0.04	0.03	0.04
Netherlands	0.03	0.02	0.03
Austria	18.00*	*	0.12
Germany	1.20	0.53	0.82
Italy	0.41	0.52	1.37
Sweden		0.82	0.16
Ireland	0.12	0.19	0.07
France	1.57	3.69	1.53
United States	5.92	12.83	6.90
Israel			5.12
Japan	22.57	4.79	6.25
Belgium			0.61
Norway	0.03	0.06	0.06
Denmark		0.08	

Belgium-Luxem.	0.06	0.02	*
Greece			5.81
Spain			0.66
Switzerland	6.52	4.83	5.08
Canada			6.01

Note: For Denmark, the price quoted for 1998 was 0.08. For 1999 the figure is 3,185.00 which seems to be a mistake)

Source: H.H. Customs and Excise, World Atlas UK Imports (281121 Carbon Dioxide)

Table A3.3-VIII: United Kingdom imports of CO₂, 2001– 2003, total and by major country (Kg)

<i>Country</i>	<i>2001</i>	<i>2002</i>	<i>2003</i>
<i>World total</i>	<i>95,845,141</i>	<i>94,301,836</i>	<i>13,894,320</i>
Netherlands	84,790,729	89,275,931	7,521,913
Austria	545,531	171,996	2,949,108
Germany	346,918	2,223,028	1,242,299
Italy	106,479	133,442	977,719
Sweden	0	101,160	552,672
Ireland	297,418	361,285	356,159
South Korea	60,248	214,905	150,635
France	12,358	3,421	23,165
United States	36,580	5,240	21,165
Israel	0	10,615	16,435
Japan	25,173	19,555	16,435
Belgium	34	1,135	9,075
Norway	9,558,144	1,748,780	4,246
Luxemburg	51,673	0	43
Spain	12,319	1	0
Poland	0	22,290	0
Hungary	1,525	11,131	0

Source: H.H. Customs and Excise, World Atlas UK Imports (281121 Carbon Dioxide)

Table A3.3-IX: United Kingdom imports of CO₂, 2001– 2003.

<i>Country</i>	<i>2001</i>	<i>2002</i>	<i>2003</i>
<i>World total</i>	<i>0.04</i>	<i>0.05</i>	<i>0.13</i>
Netherlands	0.03	0.03	0.03
Austria	0.32	1.72	0.13
Germany	0.63	0.16	0.18
Italy	1.61	1.54	0.25
Sweden		1.51	0.19
Ireland	0.41	0.24	0.14
South Korea	0.79	0.76	0.99
France	2.06	17.26	1.07
United States	3.50	10.26	8.42
Israel		5.59	4.77
Japan	4.86	4.96	6.43
Belgium	30.38	13.13	2.58
Norway	0.03	0.03	2.56
Luxemburg	1.87		21.88
Spain	0.72	*	
Poland		0.25	
Hungary	3.05	4.22	

Source: H.H. Customs and Excise, World Atlas UK Imports (281121 Carbon Dioxide)