Energy & Environmental Science

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/ees

Analysis Article

The Feasibility of in-situ Geological Sequestration of Supercritical Carbon Dioxide Coupled to Underground Coal Gasification

David J Schiffrin, Chemistry Department, University of Liverpool, Liverpool L69 7ZD, UK
d.j.schiffrin@liv.ac.uk

Based on the thermophysical properties of supercritical carbon dioxide and available power plant engineering information, it is shown that the maximum achievable efficiency of carbon dioxide sequestration in underground cavities left after in-situ coal gasification is approximately only 14%. Available evidence indicates that the claim that the syngas thus produced can be employed to synthesise "green" liquid fuels is over-optimistic. In addition, a brief analysis is presented of environmental issues relating to the potential contamination by carcinogenic polycyclic aromatic compounds dissolved by supercritical carbon dioxide. An estimate of the solubility of the carcinogenic compound benzo[a]pyrene based on molecular polarizability is presented.

Broader context

The concern about long term security and reliability of energy supplies has triggered intense search and discussions on energy sources and production methods. Policy makers and the general public are faced with conflicting demands that appear irreconcilable between environmental issues, global warming, quality of life and international obligations. The exploitation of coal that cannot be extracted by conventional mining methods employing Underground Coal Gasification coupled to carbon capture and sequestration has been presented as a long term "green" solution to ensure security of energy supply for several centuries. This article analyses some of the claims made regarding CO_2 underground storage and liquid fuel production highlighting the complexity of some of the environmental issues related to this technique.

1. Introduction

Concerns about energy supplies, CO_2 emissions and consequential environmental issues have triggered a justifiable renewed interest in alternatives to the extensive current use of oil and natural gas. For example, in the case of natural gas, the UK North Sea gas production has been in decline for several years as shown by the increase in UK natural gas imports (Figure 1).[1] Coal gasification was used for many years for the production of manufactured gas and the UK pioneered this technology.[2] A return to coal gasification as a source of energy presents, however, severe environmental concerns related both to the need for decreasing global CO_2 emissions and environmental pollution risks. The former is currently being addressed through international agreements on greenhouse effect emissions abatement.[3] In support of the policies required to reach CO_2 emission targets, a recent comprehensive analysis of the carbon budget projections to keep global warming below the 2 ^{o}C limit concludes that 80 % of coal reserves should remain unused.[4]

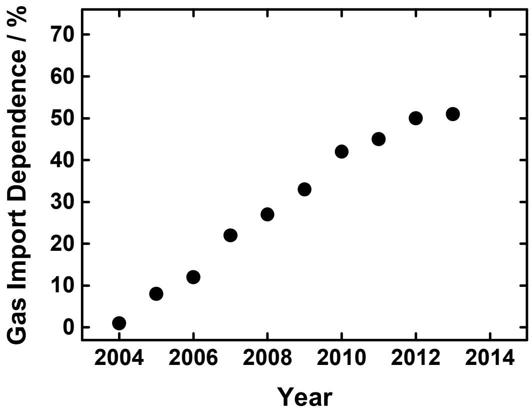

Figure 1. Natural gas UK imports

It has been argued, however, that underground coal gasification (UCG) is an acceptable solution to supply energy requirements, by tapping the very large coal reserves that cannot be mined by conventional methods.[5] The principles of this method have been extensively described,[6.7] and a schematic diagram of the process is shown in Figure 2.

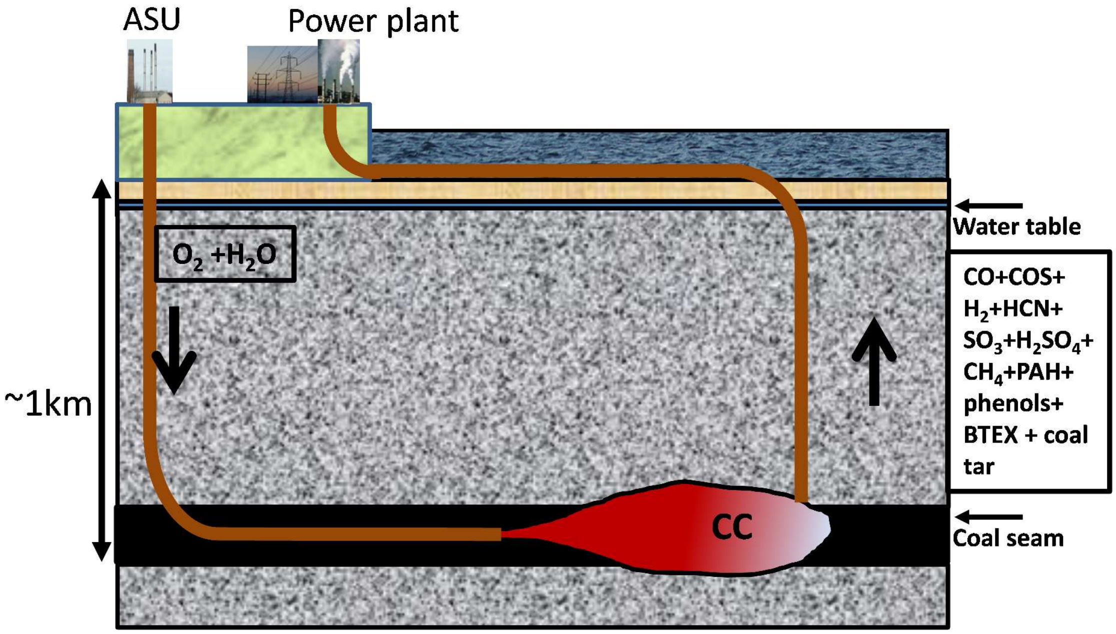

Figure 2. Schematic diagram of an UCG plant. ASU is the air separation unit for the production of oxygen required for an efficient carbon dioxide sequestration; CC = underground combustion cavity. Diagram not in scale. Penetration within the coal seam can be in the km or greater range. Diagram is not in scale

In summary, a coal seam underground is accessed by directional drilling to reach a production pipeline and the oxidant, oxygen (either diluted or at a high concentration), is injected and the coal adjacent to the production well is ignited. Combustion takes places with insufficient O_2 so as not to burn completely the carbon content of the coal to CO_2 thus producing a gas mixture ("syngas") with the components indicated in Fig. 2. The main idea is that this gas is burnt in a power station to produce electricity thus employing the residual calorific value of the coal gasified underground or using the latter in other applications that still result in similar high CO_2 emissions (see below). An alternative proposed application is as feed-stock for chemical plants.

In order to retain a partially carbon-based economy, capture and sequestration (CCS) as a way of storing CO_2 either underground or in depleted oil reservoirs have been proposed.[8] The technical feasibility of doing so in saline aquifers in the North Sea has been demonstrated in the Snøhvit and Sleipner facilities in the Usira reservoir in the Norwegian sector,[8, 9, 10] although the long term suitability of this CCS technique will have to await post-injection monitoring.[11] The average yearly sequestration rate in these reservoirs has been estimated as 1.7 Mt CO_2/year but since the total UK CO_2 release for 2013 was 464.3 Mt CO_2, this only represents 0.37% of the total yearly emissions.[12] The current status of the requirements for geological storage of CO_2 and field results has been recently critically reviewed.[13]

A combination of UCG and CCS has been proposed as the "green" solution for the exploitation of underground coal for the in-situ manufacture of syngas that can be used as fuel in electricity power stations. It has been argued that this will allow the use of inaccessible coal reserves whilst at the same time avoiding large emissions of CO_2. CCS requires CO_2 purification and then storage as supercritical carbon dioxide (sCO_2). Claims about how much carbon can be sequestered in this way vary widely but a justification for the use of the UCG technology is that the cavities left after burning the underground coal seams can be employed directly to store some or all the carbon dioxide produced as sCO_2.[5]

The purpose of this article is to provide a physicochemical basis for quantifying the percentage of produced CO_2 that can be expected to be sequestered with this approach by considering the thermophysical properties of sCO_2 and process energy requirements. The conditions considered here are presented as a typical example of the degree of storage that could be achieved. A second important issue relates to the solubility in sCO_2 of the polycyclic aromatic hydrocarbons (PAH) products of coal gasification and the consequent potential environmental pollution impact of UCG, which is also quantified. Finally, a brief analysis of the overall atmospheric CO_2 discharge that can be expected from UCG is presented by taking into account the different usages of the gas produced: electricity generation from its residual calorific value, or conversion to liquid fuels by the Fischer-Tropsch process.

2. Carbon sequestration in UCG cavities

It has been proposed many times that an advantage of UCG is that the cavities formed after the coal seam is gasified could be employed for CO_2 sequestration, thus not only allowing the production for many years of cheap "clean" energy from otherwise inaccessible coal seams (200 years are often quoted) but also providing the underground sites for geological CO_2

sequestration. [14-18] Indeed, it has been stated that there is "no a priori engineering barrier to developing CCS in UCG voids".[18]

The percentage of CO_2 produced that could be sequestered in this way depends on the temperature and density of sCO_2 in the underground cavities, the volume of non-volatile products remaining after gasification and the maximum pressure that can be safely applied to the supercritical fluid while ensuring that the integrity of the cavities to be used for the containment of the high pressure fluids is maintained.

3. Conditions prevailing in UGC cavities

To determine the amount of sCO_2 that can be stored, the properties of sCO_2 in the cavities formed by UCG must be quantified at the temperature and pressure at which it will be present. A key factor to be recognised is that the coal seams that are being considered for UCG in the UK are at depths greater than 800 m. For example, the conditional operation licenses granted in the estuary of the river Dee and in the heavily populated Wirral and Merseyside coastline involve the in-situ gasification of coal deposits present at approximately 1000 m underground. The equilibrium temperature at this depth has been estimated at ~37^{o}C.[19] In order to avoid gas leakage from the thermally fractured cavities left after gasification, the storage pressure should probably not exceed the hydrostatic pressure at this depth.

Vertical connectivity through the whole formation leads to hydrostatic equilibrium conditions for the overlying fluids that are hydraulically connected. For pure water at a constant temperature and pressure throughout, the hydrostatic pressure at a depth z, $P_H(z)$, is given by:[20]

$$P_{\mathrm{H}}(z) = \mathrm{g}\, z\, \rho_{\mathrm{w}}(z) \qquad (1)$$

g is the acceleration due to gravity and ρ_w is the density of water. The temperature is however, a linear function of depth up to approximately 1000 m and for instance, in the Wirral/North Wales region, the gradient is approximately 27 ^{o}C/km.[19,21] The density of water (or of saline solutions) is also a function of pressure and these two effects can contribute to the hydrostatic pressure that will have to prevail within the underground cavities to be used for sCO_2 storage. Thus, the hydrostatic pressure calculations refer to a fluid of non-uniform density.

The influence of a variable water density on underground flow direction and flow rates has been comprehensively discussed by Kooi et al[22] and the case of a static column of water by Oberlander.[23] In what follows, pressure will be reported in the usual units employed in physicochemical measurements instead of the water head terminology preferred by hydrogeologists.[22] The hydrostatic pressure is given by:

$$P_{\mathrm{H}}(z) = P_{\mathrm{H}}(0) + \mathrm{g} \int_0^z \rho_{\mathrm{w}}(z) dz \qquad (2)$$

where $P_H(0)$ is the pressure at ground level taken as a reference point.

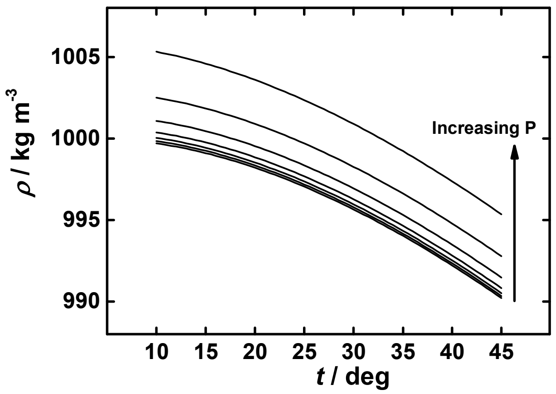

Figure 3. Temperature dependence of the density of water at different pressures. From bottom to top, P = 1, 4, 8, 15, 30, 60, 120 bar. Data taken from Reference 24.

The temperature dependence of the density of water at different pressures is shown in Figure 3[24], where it can be seen that pressure and temperature have opposite effects. In consequence, the water density in the range of interest (310 K, 100 bar) has a maximum spread of only 1 %. For greater depths, the corresponding non-linear differential equations describing hydrostatic pressure must be solved. For the purpose of the following calculations an average density of 1,000 kg m^{-3} was assumed. From the above discussion, the maximum pressure of sCO_2 that will be in equilibrium with the hydrostatic pressure in the cavities (Eqn. 1) would be ~98 bar. A pressure higher than this will result in uncontrolled pressure-assisted leakage in the formation with the consequent loss of the sequestered gas and/or release of contaminants. To simplify the following calculations, a pressure of 100 bar has been considered throughout.

4. Sequestration efficiency

4.1 Volume of UCG cavities

In order to determine the expected percentage sequestration of the overall CO_2 produced, the densities of coal and CO_2 must be considered. The average density of UK bituminous coal is 1,300 kg m^{-3} [25] and the corresponding elemental carbon content is in the range 80-90 %. After combustion, non-volatile components, mainly inorganic solids (ashes) and coal tar, will be left in the cavities.[6] The amount of ash left after gasification will depend strongly on the source of the coal. The typical inorganic ash content of British coals lies between 1.2 and 4.5 % [25] and their mean density is approximately 3,000 kg m^{-3}.[26] Although the coal tar residues from coal gasification contain potent carcinogenic compounds, for the purpose of the analysis below, their contribution to available cavity volume will be ignored. Therefore, for a coal containing ~3 % of inorganic matter, the cavity volume available for sCO_2 storage is ~0.97 m^3 for each m^3 of coal gasified.

It is expected that the voids formed by coal gasification will be heavily fractured due to roof collapse with shedding of broken rocks,[6] known in the UK mining industry as goaf.[15, 16, 27] Simple overburden collapse is unlikely, however, to increase the total void volume, it just redistributes its location. If this were not the case and the fracturing of the overburden were to extend far beyond the estimates calculated employing isotropic properties of the formation and based on safe mining recommendations beneath water bodies,[27] the resulting increase in overall porosity would make the feasibility of CO_2 sequestration rather dubious. In this respect, an important difference between classical mining and UCG should be highlighted. Unlike classical mining, UCG generates large thermal stresses within the formation since local operating temperatures in excess of 1,300 ^{o}C are expected.

4.2 Oxygen requirements

A justification for the deployment of UCG has been the suggestion that gasification coupled to CCS will lead to a “green” usage of coal. There are significant differences between UCG and modern power plants operating above ground and relying on coal gasification, in that the gasification for the latter is carried out in well-defined, controlled and thermally insulated pressurised gasification reactors. In both cases, however, the use of high concentration oxygen instead of oxygen from air as the oxidant (the so-called oxy-fuel technology) is advantageous for the efficient separation and sequestration of the carbon dioxide produced as well as increasing energy efficiency.[28] The use of air instead of oxygen results also in more complex and inefficient separation processes with the added complication of the formation of NOx gases.

The use of oxygen in power generations plants, either retro-fitted or fully integrated with CCS units,[28] has been comprehensively analysed and different plant designs and configurations have been published. [29-33] Oxy-combustion technologies are advantageous for implementing CO_2 capture and storage since product separation is simplified by the production of flue gases with very high concentrations of CO_2 that can be sequestered without significant further processing, thus decreasing the overall CO_2 footprint. Recent short term laboratory tests also indicate that oxy-fuel combustion might also be successfully employed for the in-situ gasification of high-ash content coals.[34]

The large throughput of O_2 required can only be achieved by cryogenic distillation of liquid air for which the technology and plant engineering is well-known. Since the use of oxy-fuel combustion cycles involves large volumes of relative pure oxygen (purity greater than 95 %) efforts have been made by plant manufacturers to decrease the separation energy employed by the Air Separation Unit (ASU) for its inclusion in advanced power generation plants. For example, the separation energy quoted by two plant manufacturers are 201[35] and 200[36] kWh/t of O_2 but for the latter, improvements to take this value down to 160 kWh/t of O_2 have been predicted if the ASU is fully integrated within the power plant operations.[36] Unfortunately, in this case, the comparison of overall efficiency is not clear since the published information indicates that the compressors’ drive efficiency and other power requirements are excluded from the definition of estimated power.[36] Therefore, a separation energy of 200 kWh/t of O_2 will be considered here.

A detailed assessment of the efficiency of CO_2 sequestration in the voids left after combustion requires, however, a thorough knowledge of the overall process, for which full data is lacking. Nevertheless, from the information available in the open literature, the oxy-fuel combustion power cycle is recognised as the most effective technique to achieve CO_2 sequestration coupled to fossil fuel utilisation[28-33,37] and therefore, published operation parameters derived from these studies will be employed.

4.3. CO_2 balance and sequestration efficiency

The so-called “syngas” produced is a mixture mainly of CO_2, CO, H_2, H_2O and CH_4. In addition, many other chemicals and pollutants are produced such as COS (carbon sulphide) and coal tar. Moreover, coal tar contains many carcinogenic polycyclic aromatic hydrocarbons, benzene and derivatives, phenols, hydrogen cyanide, SO_3 and SO_2 (sulphur trioxide and dioxide); and SO_3 reacts with the water content of the produced gas to give sulphuric acid. The products are typical of the production of manufactured “town” gas, prior to its replacement by natural gas.

The syngas produced can be employed in a variety of applications.[5,18] After purification, the immediate market is its use as feedstock fuel for electricity generation. Making use of the residual calorific value of the coal gasified in this way leads to CO_2 and H_2O as final reaction products. In consequence, in this case, the CO_2 emitted per m^3 of coal gasified underground is no different from the same amount of coal burnt, for instance, in a power station albeit with a lower energy yield. Burning coal in two stages, however, does not alter the environmental loading due to CO_2 but is impacted by any additional CO_2 burden resulting from all the unit operations involved in a two-stage process. Oxygen enrichment from air, compression of gases, purification operations and the energy required to carry out the gasification process itself at temperatures of above 1,300 ^oC using the underground coal must also be taken into account.

Another proposed use of the syngas produced is to transform it into liquid fuels for transport.[5,18] The consequent larger CO_2 loading from this route is discussed below (See Section 6) and results in even larger CO_2 emissions than burning it to generate electricity. The carbon monoxide content of the “syngas” can also be employed to generate hydrogen through catalytic conversion in the water shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(I)}$$

H_2 is an important industrial gas but it should be noted that reaction (I) entails the production of CO_2 in molar stoichiometric amounts to the H_2 produced. It can be concluded that none of the proposed applications of the “syngas” produced will reduce CO_2 emissions.

The questions now are: how much CO_2 is actually produced and how much of this can be stored in the volume of the voids left behind after coal combustion? Due to the lack of published plant modelling data, the analysis presented below greatly ***overestimates*** the efficiency of the proposed UCG-CCS processes. Taking the average carbon content of bituminous coal as 80 %,[38] then burning 1 m^3 of this coal will produce 1,320x0.8x44/12 = 3,872 kg of CO_2. This is not, however, the full carbon footprint of the gasification process since the CO_2 emitted in the generation of the electrical power required to drive the gasification process must also be considered. In the absence of detailed UCG-CCS engineering information, only two major energy requirements will be taken into account, O_2 separation from air as discussed above and gas compression energy. The estimation of the latter presents some uncertainties related, for example to compressor efficiency, pressure drops due to the length of piping through which the gases will be injected and extracted, the possible pressure loss in the production tubing caused by coal tar condensation and the resulting two-phase flow, and losses resulting from the recirculation of syngas or high pressure steam into the oxygen supply to moderate flame temperature and improve calorific value.[31-33]

Chiesa et al[32] have modelled the various contributions to the energy requirements to run an oxy-coal fired power station and calculated the O_2 compression energies at two operating pressures of 60 and 120 bar. Note that this section of a power station will be functionally similar to a well-engineered UCG-CCS operation. From the results presented in Reference 31 (Tables 5a and 5b) a minimum overall average compression energy of 0.175 kWh/t of O_2 can be calculated. Therefore, a conservative estimate of the electrical energy specifically required for the underground oxy-combustion process is approximately 200+175=375 kWh/t of O_2.

The O_2/C molar combustion ratio for a coal of similar rank to that used in the present calculations is 1.02,[37] which corresponds to an O_2 consumption of 2.2 t of O_2 per t of coal. Consequently, the energy required for producing the oxygen used and the compression energy for injection into the underground gasification cavity is approximately 375x2.2=825 kWh/t of coal burned. This conservative estimate can be related to the CO_2 emissions from the underground gasification operation and the electrical power required with the corresponding CO_2 emissions. The median CO_2 emissions per kWh of power output in the UK have been estimated at 0.87 kg CO_2/kWh[39] and therefore, an additional energy consumption of 825 kWh will be required to gasify 1 m^3 of coal (see above), which will lead to an additional emission of 718 kg of CO_2. The total mass emission of CO_2 calculated per cubic metre of coal gasified is, therefore, 3,872 + 718 = 4,590 kg.

In order to be able to sequester all the CO_2 produced, a pressure at which the density of CO_2 is 4,590/0.97=~4,732 kg m^{-3} would have to be employed. The pressure dependence of the density of sCO_2 at different temperatures and pressures has been carefully measured by Span and Wagner[40] and the calculated density-pressure data at 37 ^oC are presented in Figures 4 and 5 for the high and low pressure ranges, respectively. It is clear that such densities are inaccessible for sCO_2 and in fact, at the maximum pressure investigated, of 8,000 bar, a solid CO_2 phase is formed with a density of 1,496 kg m^{-3}.[40]

These Figures also show that there is an abrupt change in the density-pressure dependence around 90 bar. This is a consequence of the onset of strong intermolecular repulsive forces as the average distance between molecules in the gas phase decreases with increasing pressure.[41] The density of sCO_2 at a sequestration pressure of 100 bar is 686 kg m^{-3} [40] and therefore, it would only be possible to re-inject 665 kg of CO_2 in the UCG cavity at the equilibrium temperature and pressure at the depth of the cavities, i.e*, **only14 % of the total carbon dioxide from the combusted coal**.* However, due to the simplifications mentioned above, the real proportion of emitted carbon dioxide that could be stored will be significantly smaller than this.

.

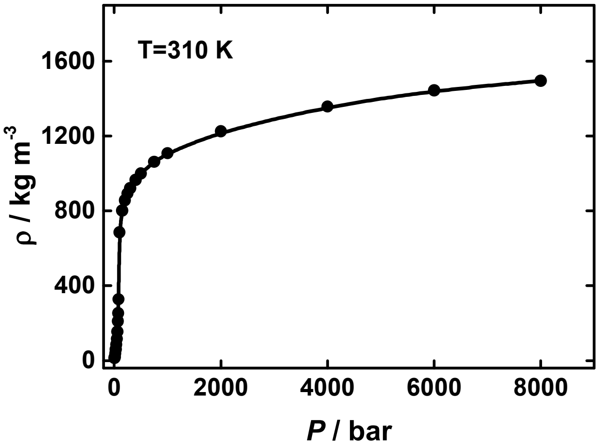

Figure 4. Pressure dependence of the density of sCO_2 at 37 °C. High pressure range.[40]

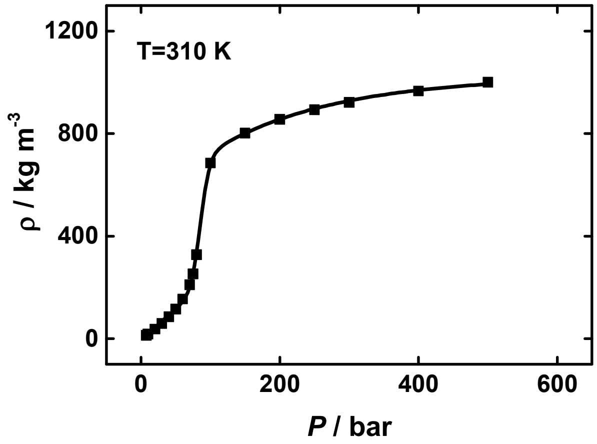

Figure 5. Pressure dependence of the density of sCO_2 at 37 °C. Low pressure range.[40]

The problem highlighted here is common to all sequestration strategies since the volume of the CO_2 molecule is an important factor determining the maximum CO_2 concentration that can be achieved either in underground cavities or in saline reservoirs. Previous work by

Bondi in 1964[42] gave an estimate of the molecular volume for CO_2 of 4.48×10^{-4} m^3kg^{-1}. This value has been recalculated in the present work using a more modern approach employing Density Functional Theory with the B3LYP model using several basis sets (6-311 G*, 6-311+G*, 6-311++ G** and 6-311++G(2df, 2p))[43] and a value of $5.24x10^{-4}$ m^3kg^{-}has been estimated. Although the results from these calculations depend on the energy repulsion distances defining the molecular volume, they provide a good estimate of the volume fraction in the gas phase. From this, the volume fraction occupied by the sequestered CO_2 at 100 bar in the case discussed above is approximately 36 %. Due to the pressure dependence of the density of sCO_2 (Figs. 4 and 5), very high pressures would have to be applied to increase the sequestration efficiency. For instance, to achieve a modest 50 % occupancy by CO_2 in the available cavity volume, a pressure of 400 bar would be necessary. This is well above the hydrostatic pressure at the depths of the coal seams to be exploited and outside the pressure range that can be safely employed to prevent CO_2 leakage.

5. Environmental issues

5.1 Contaminants mobilisation by sCO_2

The toxicity of coal tars and other coal pyrolysis products, e.g., BTEX (benzene, toluene, ethylbenzene and xylenes) in relation to chemical carcinogenesis has been known for a long time.[44] Although initially this was related mainly to occupational hazards,[45] extensive research has demonstrated the intricate relationship between molecular structure, specific reactivity to DNA and chemical carcinogenesis.[44] In particular, the polycyclic aromatic hydrocarbons (PAH) have emerged as the most important group of chemicals that present serious health risks to human populations.[46] For example, an important result of this has been the establishment beyond dispute of the relationship between tobacco smoking and lung cancer, and PAHs have now been clearly identified as some of the major chemicals responsible for genetic mutations in growth control genes.[47] PAH have pernicious effects in many other areas of human health and an example of this is the indication that exposure to PAH greatly increases the risk of preterm delivery of babies and leads to reduction of foetal growth.[48]

The PAH compounds that have shown greatest carcinogenic activity are benzo[a]pyrene (BaP), various benzofluoranthenes and chrysene and its derivatives.[49] BaP is the most harmful compound to human health in this group and the International Agency for Research on Cancer (IARC) of the World Health Organization has concluded that: "Benzo[*a*]pyrene is *carcinogenic to humans (Group 1*) (See Ref. 49 and the many references cited therein related to the toxicity of PAH in coal tar pitch and other products related to the coal gasification industry). From the available evidence this compound has been chosen as a marker to assess the degree of air contamination by PAH.[50] The effect of these contaminants is cumulative and in order to reduce the detrimental health and environmental effects of PAH the EU Environmental Directive on contaminants in ambient air establishes a yearly concentration target for BaP in PM_{10} particles in air of ***1.0 ng/m³***.[51] The UK has a more stringer target, of 0.25 ng/m^3. The EU Directive mandates the measurement of PAH concentrations in air at different locations and in the UK, the National Physical Laboratory runs a network including a maximum of 31 stations operating at any one time for monitoring air-born PAH.[50,52] The existence of this extensive Network provides a wealth of experience for monitoring PAH air emissions and provide alerts to the presence of dangerous contamination levels.

There is a significant difference between coal gasification when carried out in-situ, within an underground coal seam, or in advanced coal-fired power stations. For the latter, the combustor has evolved from the crude 19th century devices to designs engineered to ensure uniform and total access of the oxidant to the coal and consequently, greatly decreasing the formation of coal tars since these are consumed during an efficient and controlled gasification process. This is achieved, for example by employing fluidised bed or other reactors.[53] In addition, water content is regulated to ensure maximum yield in calorific value with the minimum conversion to CO_2. It is interesting to notice that although the total amount of coal used in the UK for electricity production was 55 Mt in 2012[54] the estimated emission of BaP during that year represented only 0.51 % of all emissions of this PAH (Estimated 18 kg compared with a total of 3,510 kg of BaP emitted).[55] Thus, abatement of PAH production and emissions by controlled gasification conditions in hermetically sealed and insulated pressurised combustion chambers coupled to purification of the gaseous products integrated next to the combustor substantially decreases the environmental loading with PAH.

By contrast, in underground coal gasification, the oxidant accesses the coal seam at a distance of more than one km away from the processing plant in a very irregular fashion through non-uniform gasification channels, partially determined by the simultaneous roof collapse of the gasification cavity (See Ref. 6 and references cited therein). The resulting irregular gas flow leads to complex temperature profiles and the formation of coal tars, a good proportion of which are left in the cavity after gasification. The long term contamination left in the UCG cavities has been investigated, for example, in the experiments in Hoe Creek, Wyoming, US, where the presence of 135 organic compounds was identified. This contamination persisted for 15 months after coal gasification and significantly, all the PAHs, characteristic of coal tar formed in the old gas manufacturing plants were observed.[56]

5.2 Solubilisation of PAH in sCO_2.

In addition to the very low sequestration efficiencies of the combined *in-situ* UCG-CCS approach, when discussing this alternative it is not usually recognised that supercritical carbon dioxide, although a gas, not only mobilises viscous organic fluids entrapped in porous media but is also a good solvent of organic compounds. The former property has been employed in Enhanced Oil Recovery (EOR) by virtue of its dissolution within residual oil trapped in the pores of the formation with the corresponding increase in the volume of the trapped oil and also decreasing both oil viscosity and surface tension at the oil/aqueous phase interface. The injection of sCO_2 in the UCG cavities will have two effects; first, the mobilisation of coal-tar oils, produced by the pyrolysis of coal and trapped within the UCG cavities by similar mechanisms to those used for EOR and secondly, the dissolution of PAH within the supercritical fluid phase. The ensuing potential dangerous environmental issues of the latter have already been mentioned in the UCG literature.[15,27] The high solvent power of sCO_2 is well-known and used industrially, for example, in the manufacture of decaffeinated coffee.

The excellent solvent properties of sCO_2 present some insidious issues regarding the dissolution of carcinogenic compounds left in the gasification cavities following combustion. sCO_2 is known to dissolve coal tar and extract the various organic contaminants present. For this reason sCO_2 have been tested for the remediation of soils contaminated from manufactured gas plants and the selective extraction of PAH from coal tars has been clearly demonstrated.[57] In what follows, the extraction of PAH by sCO_2 under the conditions discussed in this paper is quantified.

Table 1 shows the solubility of some important PAH containing 3, 4 and 5 benzene rings calculated from literature sources at 310 K and 100 bar. For compounds for which sufficient solubility data are available at different pressures and temperatures, the mole fraction of PHA data ($y_{2)}$ was first fitted for different pressures at constant temperature to a second order polynomial to obtain the value at 100 bar and then a second fit was carried out at constant pressure in order to obtain the solubility at 310 K. This procedure was followed for fluorene, phenanthrene, pyrene and flouranthene.

For the analysis of the dependence of the solubility on the solute molecular structure, temperature and pressure it is convenient to employ the enhancement factor (E_e) defined by:[59]

$$E_{\mathrm{e}} = \frac{y_2 P}{p_2^{Subl}} \qquad (3)$$

y_2 is the mole fraction of the solute dissolved in sCO_2, P is the pressure of sCO_2 and p_2^{Subl} is the vapour pressure of the solute. E_e is therefore, the ratio of the partial pressure of the solute and to that of the solute in the absence of sCO_2. For compounds such as anthracene, for which data was available only at temperatures outside the range of interest, the method employed by Méndes *et al*[59] was followed. These authors demonstrated that for a given compound, the function $T \ln(E_e)$ depends linearly on the density of sCO_2:

$$T\ \ln(E_{\mathrm{e}}) = \mathrm{A} + \mathrm{B}\rho_{\mathrm{CO_2}} \qquad (4)$$

where A and B are temperature independent constants specific to the compound and $\rho_{\mathrm{CO_2}}$ is the density of the supercritical fluid. An example of the applicability and reliability of Equation (SI-3) to describe supercritical solubility is shown in Figure 6 for fluorene from data reported between 303-343 K and 83.6-484 bar.[59] This provides access to reliable solubility information for a very wide range of conditions and data for chrysene and perylene were fitted to Equation 4 to calculate values of E_e. The solubility, y_2, was calculated employing the reported vapour pressure data of the pure compounds. Table 1 gives the references for the data employed in these calculations.

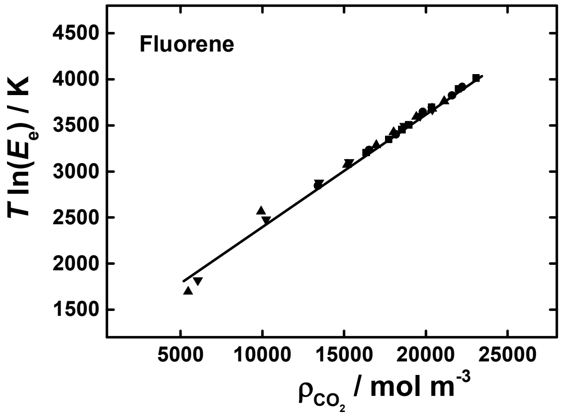

Figure 6. Dependence of the enhancement factor for fluorene on the density of sCO_2 (Eqn (4)) at four different temperatures. Results taken from Reference 62.

No solubility data for BaP in sCO_2 corresponding to the conditions of interest could be found in the literature. A semi-empirical approach to predict solubility of BaP was followed here based on general solubility trends of PAH molecules containing different number of aromatic rings. For very dilute solutions, as is the case for PAH compounds dissolved in sCO_2, the interaction between solute molecules can be ignored. The work of introducing a molecule of a solute in a fluid can be divided in two steps: (1) Opening a cavity of appropriate size within the fluid (solvent) and (2) Introducing a solute molecule into this cavity.[63] For a liquid solvent, the energy required for the first step is determined by the strong intermolecular forces between solvent molecules but for a supercritical fluid, the applied external pressure will be a main contribution to the work of cavity formation. The second and more important contribution is determined by dispersion (or London) interactions between the PAH molecule and CO_2. For a clear discussion of these questions, see Reference 63.

E_e is related to the Gibbs energy of solute-solvent interaction corresponding to the transfer of one mole of solute from an ideal gas (no intermolecular interactions) to the supercritical fluid. For the range of pressures considered here, the Poynting correction to the standard Gibbs energy of formation of the PAH can be safely ignored and therefore, the Gibbs energy component due to the gas phase solvation of the solute, $\Delta G_\mathrm{interact}$, is given by:

$$\Delta G_\mathrm{interact} = -\mathrm{R}T\ln(E_\mathrm{e}) \qquad (5)$$

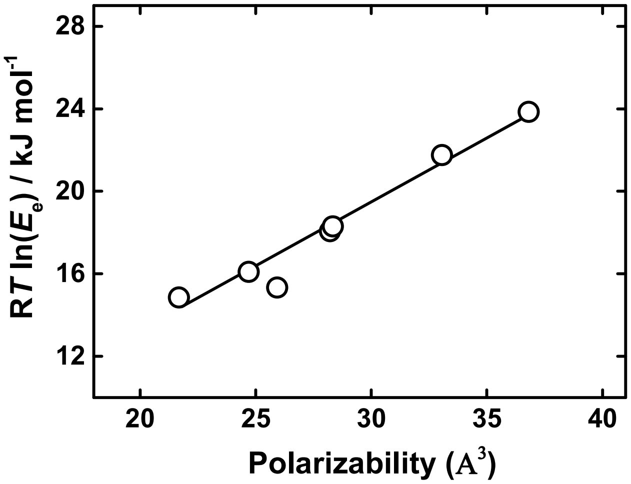

Figure 7. Dependence of the solubility enhancement factor on the polarizability for several polycyclic aromatic compounds in sCO_2 at 100 bar and 310 K. The data points correspond, in increasing order, to: (1) fluorene,[66] (2) phenanthrene,[66] (3) anthracene,[66] (4) pyrene,[66] (5) flouranthene,[67] (6) chrysene[66] and (7) perylene.[67]

Extensive computer simulations have been carried out employing *ab-initio* calculations to determine atom potentials in PAH and employ these to model molecular interactions.[63] A simpler semi empirical approach, according to the analysis by Pierotti[64] and others,[65] has been followed here, recognising that for molecules with no permanent dipole, the solute-supercritical solvent interaction energy will depend on the molecular polarizability and hard sphere radii and therefore, the enhancement factor of a family of hydrocarbons would be expected to show well-defined trends depending mainly on the polarizability/molecular volume of the solute.[63]

The simplest choice to consider is to use the molecular polarizability (α) as a global variable for estimating the solubility of non-polar PAH molecules in sCO_2.[63] A practical advantage of this approach is that values of α are readily available in the literature or can be obtained from quantum chemical calculations. Figure 7 shows the dependence of the enhancement factor on molecular polarizability for some PAH. The source of the data analysed is given in the legend to this Figure and the experimental values of α are in good agreement with the theoretical calculations by Alparone et al.[68] From the linear fit shown in Fig. 7, a value of $RT \ln(E_e)$ of 24.1 kJ mole^{-1} was estimated for BaP using $\alpha_{BaP} = 37.44$ Å^3.[69] The vapour pressure of the compounds analysed was taken from references 70-72. The vapour pressure of BaP at 310 K was calculated from the analysis by Oja[70] from which $p_{BaP}^{Subl} = 1.42\times10^{-11}$ bar and therefore, the mole fraction solubility of BaP is $y_2 = 3.7\times10^{-7}$. There are few reliable measurement of the generally low vapour pressure of the high molecular weight members of the PHA series and the results by Oja[70] were employed for this compound since the enthalpy of sublimation quoted in Ref. 71 was at variance with results from other sources.

The above analysis refers to the incorporation of PAH dissolved in the supercritical gas phase. No literature information could be found on the additional solubilisation contribution by PM_{10} particles containing adsorbed PAH.

Table 1. Calculated solubility of PAH in sCO_2 at 310K and 100 bar

Compound	**Mole fraction, y_2**	**Solubility / ng m^{-3} ***	**References**
Fluorene	8.73×10^{-4}	2.26×10^{12}	58
Phenanthrene	4.97×10^{-4}	1.38×10^{12}	58
Anthracene	1.67×10^{-5}	4.63×10^{10}	59
Pyrene	6.37×10^{-5}	2.01×10^{11}	58
Fluoranthene	1.58×10^{-4}	4.98×10^{11}	59, 61
Chrysene	1.36×10^{-6}	6.62×10^{9}	59, 61
Perylene	1.24×10^{-7}	4.88×10^{8}	59, 60
Benzo[a]pyrene (BaP)	3.7×10^{-7}	1.5×10^{9}	#

*For comparison, the solubility in sCO_2 is expressed in the same units as used for the recommended air contamination concentration limit of BaP stated in the EU Environmental Directive (1 ng $m^{-}3$)[51] and in the UK (0.25 ng m^{-3}).[50,52] # Present work.

The results in Table 1 demonstrate quantitatively that these compounds are dissolved by sCO_2 and that there would be significant solubilisation of the PAH products left in the UCG cavities. Importantly, ***their solubility is over 10 orders of magnitude greater*** than the maximum target concentration recommended in the UK. It is therefore reasonable to conclude that migration of PAH compounds through the overburden dissolved in the supercritical gas at high pressure and their release into the environment cannot be safely ignored. Their migration in the long (or short!) term due to fractures in the formation, both naturally occurring or as a results of the thermal stresses caused by the high temperature gasification process, must be carefully assessed to avoid the uncontrolled emission of carcinogenic compounds, in particular considering the pressures required for an efficient CO_2 sequestration. This is a very important consideration if, as is the case for the licenses granted in the UK, UCG exploitation is supposed to take place under the sea where remediation measures would not be easily implemented and in some cases, the operations will take place close to coastal towns and villages in quite heavily populated areas.

The expectation of a successful CCS operation is that the sequestration method of CO_2 should "deposit the gas underground with 99% permanence over at least 100 years".[73] Ii is concluded that in the case of UCG cavities, the leakage of stored carbon dioxide ***is only part of the problem*** and the likely release of contaminants by supercritical gas migration containing dangerous concentrations of carcinogenic products is a matter of grave concern.

6. Production of liquid fuels from "syngas"

It has been argued[5] that UCG is a "clean coal" technology and that it can provide liquid fuels by employing the syngas produced to subsequently manufacture liquid fuels employing the Fischer-Tropsch (F.-T.) process. The corresponding full environmental impact in terms of CO_2 equivalent emissions has been carefully analysed[74] and an average emission of ~4 kg

CO_2 per dm^3 of F.-T. liquid fuels produced has been calculated (See Table 6 in Ref. 63). In addition, when used as a transport fuel, the full carbon content will be discharged anyway, thereby adding to the CO_2 emitted during production. Although there might be some very exceptional circumstances that might justify the acceptance of this large environmental carbon loading, it is unlikely that this is a reasonable solution for the supply and decarbonisation of transport. In this respect, it is relevant to note that transport is responsible for 20% of all CO_2 emissions in the UK[12] and the use of such fuels, if extensively adopted, would represent an unacceptable increase in atmospheric CO_2 release.[3]

Conclusions and Final Comments

The analysis presented here indicates that some key arguments which have previously been employed to justify as environmentally safe a combined *Underground Coal Gasification – Carbon Capture and Storage"* approach to syngas generation, by using the cavities generated underground (by coal-seam combustion) for supercritical CO_2 storage are found to be seriously over-optimistic. *First,* calculations here indicate that it would be impossible to store in such cavities (typically) more than approximately 14 % of the CO_2 produced by the coal-seam combustion. *Secondly,* it is shown that the likely mobilisation of coal-tar and carcinogenic polycyclic aromatic hydrocarbons dissolved in sCO_2 presents significant risks both to the environment and to human health. Thus, the use of the UCG-generated cavities for sCO_2 storage is highly controversial and their application in the "decarbonisation" of UCG for energy production appears to be not only physically unfeasible but is attended by unacceptable environmental and health risks.

Moreover, the proposed advantage of employing the produced syngas for the synthesis of liquid fuels requires re-evaluation, since there is already solid evidence available indicating that this route for the utilisation of underground carbon resources will result in the atmospheric release of high levels of CO_2, which is clearly incompatible with policies and international agreements on CO_2 emissions abatement.[3]

The analyses presented in this paper relate only to a few specific risk aspects associated with the process and do not touch upon a variety of other concerns about UCG. New industrial activities involving incompletely explored areas of technology, especially in extremely problematic locations where effective monitoring is particularly challenging, can have unintended consequences that are difficult or even impossible to remedy, as has been argued here is the case with UCG. Besides the obvious problem of the production and mobilisation of dangerous concentrations of potent carcinogenic compounds, there are practical unanswered questions relating to the structural integrity of the thermally-damaged geological formations surrounding UCG syngas production that need to be addressed, since the behaviour of compressed gasses at high pressure and temperature in a fractured formation cannot easily be predicted.

Moreover, the thermal stresses to which the steel tubing and sealants in the gas transport system will be subjected may have a detrimental impact on the integrity of the casing of the production well and hence, uncontrolled gas injection within the formation may occur. In addition, the produced gases will contain sulphuric acid so that corrosion of the steel tubing becomes a matter of concern not only due to the acidic conditions but also as a consequence of the inevitable presence of chloride anions and the consequent danger of the onset of localised pitting corrosion. This is very different from the conditions found in the conventional oil and gas industry, where corrosion, for instance in sour wells can be controlled by the incorporation of corrosion inhibitors. No such possibility exists in UCG since the high temperatures involved preclude their stability.

Although some of these problems might be ameliorated by intensive research programmes, the main difficulties with UCG relate not only to the local environmental issues discussed in this paper, but also to the more generic problem of the continued use of coal as a source of energy. In addition to the lower calorific value of the syngas produced by UCG compared to that of mined coal used in modern power stations, it is now widely accepted that urgent global action must be taken to ***decrease*** the current international dependence on fossil fuels. Rather the focus of the discussion and all available scientific, technological and industrial resource should be directed towards practical and safe methods of achieving this objective.

Investing in a return to 19th century energy sources does not seem a reasonable alternative to address some of the greatest challenges ever to face human societies.

Conflict of Interests

The author declares no commercial, financial, investment, consultancy or employment relationship with any concerns dealing with Underground Coal Gasification, Carbon Capture and Sequestration or related technologies.

Acknowledgements

The author gratefully acknowledges the help, advice and critical analyses during the preparation of this manuscript on questions about unconventional gas extraction (UGE) and related energy issues by Professor Denis R. Hall, School of Engineering & Physical Sciences, Heriot-Watt University, Edinburgh.

References

1 DECC, UKCS Oil and Gas Production Projections, https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/287001/production_projections.pdf

2 T. I. Williams, A History of the British Gas Industry, Oxford University Press, 1981.

3 UK Climate Change Act, 2008

4 C. McGlade and P. Ekins, The geographical distribution of fossil fuels unused when limiting global warming to 2 ^{o}C, *Nature*, 2015, **517**, 187-190.

5 P. L. Younger, D. J. Roddy and G. González, King coal: restoring the monarchy by underground gasification coupled to CCS, *Petroleum Geology Conference series* 2010, **7**, 1155-1163.

6 D. W. Gregg and T. F. Edgar, Underground coal gasification, *AIChE J.*, 1978, **24**, 753-781.

7 A. W. Bhutto, A. A. Bazmi and G. Zahedi, Underground coal gasification: From fundamentals to applications, *Prog. Energ. Combust.,* 201, **339**, 189-214.

8 A. Hosa, M. Esentia, J. Stewart and S. Haszeldine, Injection of CO_2 into saline formations: Benchmarking worldwide projects, *Chem. Eng. Res. Des*., 2011, **89**, 1855-1864

9 S. L. Nooner, O. Eiken, C. Hermanrud, G. S. Sasagawa, T. Stenvold, M. A. Zumberge, Constraints on the in situ density of CO_2 within the Utsira formation from time-lapse seafloor gravity measurements, *Int. J. Greenh. Gas Con*., 2007, **1**, 198-214.

10 R.A. Chadwick, G.A. Williams, J.D.O. Williams and D.J. Noy, Measuring pressure performance of a large saline aquifer during industrial-scale CO2 injection: The Utsira Sand, Norwegian North Sea, *Int. J. Greenh. Gas Con*., 2010, **10**, 374-388.

11 R. A. Chadwick and O. Eiken in J. Gluyas and S. Mathias (Eds.), *Geological Storage of Carbon Dioxide (CO2)*: Geoscience, Technologies, Environmental Aspects and Legal Frameworks, Ch 10, p. 227-250, Elsevier Science 2013.

12 2013 UK Greenhouse Gas Emissions, Final Figures, UK Department of Energy and Climate Change, 3rd February 2015.

13 S. J. Altman, Chemical and Hydrodynamic Mechanisms for Long-Term Geological Carbon Storage*, J. Phys. Chem.* C, 2014, **118**, 15103-15113.

14 E. Shafirovich and A. Varma, Underground Coal Gasification: A Brief Review of Current Status, *Ind. Eng. Chem. Res*., 2009, **48**, 7865-7875.

15 D. Roddy and G. González. Underground Coal Gasification (UCG) with Carbon Capture and Storage (CCS) in R.E. Hester and R.M. Harrison, Eds., *Issues in Environmental Science and Technology*, *Carbon capture: sequestration and storage,* The Royal Society of Chemistry, 2010, **29**, Ch. 4, p. 102-125.

16 D. J. Roddy and P. L. Younger, Underground coal gasification with CCS: a pathway to decarbonising industry*, Energy Environ. Sci*., 2010, **3**, 400-407.

17 DTI Report, Review of the Feasibility of Underground Coal Gasification in the UK, September 2004 (See p. 32).

18 P. Younger, J. Gluyas, M. Cox and D. Roddy, Underground Coal Gasification, *Ingenia*, 2010, 43, 42-46.

19 J. Busby, A. Kingdon and J. Williams, The measured shallow temperature field in Britain*, Q. J. Eng. Geol. Hydroge.*, 2011, **44**, 373-387,

20 K. M. Hiscock and V. F. Bense, *Hydrogeology***,** *Principles and Practice, 2nd Ed.,* Wiley 2014

21 http://www.bgs.ac.uk/research/energy/geothermal/

22 V. Post, H. Kooi and C. Simmons, Using Hydraulic Head Measurements in Variable-Density Ground Water flow Analyses, *Ground Water*, 2007, **45**, 664-671. See also references cited therein.

23 P. L. Oberlander, Fluid Density and Gravitational Variations in Deep Boreholes and Their Effect on Fluid Potential, *Ground Water*, 1989, **27**, 341-350.

24 Thermophysical Properties of Fluid Systems, NIST, National Institute of Standards and Technology, US, http://webbook.nist.gov/chemistry/fluid/

25 W. Francis, *Coal; its formation and Composition*, Edwards Arnold (publishers) Ltd, London, 1961,Ch. XI.

26 D. W. van Krevelen, *Coal*, Elsevier Publishing Company, Amsterdam, 1961, p. 315.

27 P. L. Younger, Hydrogeological and Geomechanical Aspects of Underground Coal Gasification and its Direct Coupling to Carbon Capture and Storage. *Mine Water Environ*., 2011, **30**, 127-140.

28 M. E. Boot-Handford, J. C. Abanades, E. J. Anthony, M. J. Blunt, S. Brandani, N. Mac Dowell, J. R. Fernández, M.-C. Ferrari, R. Gross, J. P. Hallett, R. S. Haszeldine, P. Heptonstall, A.

Lyngfelt, Z. Makuch, E. Mangano, R. T. J. Porter, M. Pourkashanian, G. T. Rochelle, N. Shah, J. G. Yao and P. S. Fennell, Carbon capture and storage update, *Energy Environ. Sci*., 2014, **7**, 130-189.

29 K. Damen, M. van Troost, A. Faaij and W. Turkenburg, A comparison of electricity and hydrogen production systems with CO_2 capture and storage. Part A: Review and selection of promising conversion and capture technologies *Prog. Energ. Combust*., 2006, **32**, 215-246.

30 K. Andersson and F. Johnsson, Process evaluation of an 865 MWe lignite fired O_2/CO_2 power plant, *Energy Conv. Manag*., 2006, **47,** 3487-3498.

31 H. Zebian, M. Gazzino, A. Mitsos, Multi-variable optimization of pressurized oxy-coal combustion, *Energy* 2012, **38**, 37-57.

32 P. Chiesa, S. Consonnia, T. Kreutz, R. Williams, Co-production of hydrogen, electricity and CO_2 from coal with commercially ready technology: PartA: Performance and emissions, *Int. J. Hydrogen Energ.*, 2005, **30**, 747-767.

33 J. Hong, R. Field, M. Gazzino, and A. F. Ghoniem, Operating pressure dependence of the pressurized oxy-fuel combustion power cycle. *Energy* 2010, **35**. 5391-5399.

34 V. Prabu and S. Jayanti, Laboratory scale studies on simulated underground coal gasification of high ash coals for carbon-neutral power generation. *Energy* 2012, **46**, 351-358.

35 P. Higginbotham, V. White, K. Fogash and G. Guvelioglu, Oxygen supply for oxyfuel CO_2 capture*, Int. J. Greenh. Gas Con*., 2011, **5S**, S194-S203.

36 J.-P. Tranier, R. Dubettier, A. Darde and N. Perrin, Air Separation, flue gas compression and purification units for oxy-coal combustion systems, *Energy Procedia*, 2011, **4**, 966-971.

37 M. B. Toftegaard, J. Brix, P. Glarbor and A.D. Jensen, Oxy-fuel combustion of solid fuels, *Prog. Energ. Combust*., 2010, **36**, 581, 625.

38 C. Higman and M. van der Burgt, Feedstocks and Feedstock Characteristics in *Gasification*, Ch.4, p. 50, 2008, Elsevier Inc., 2nd ed.

39 *Carbon Footprint of Electricity Generation*, The Parliamentary Office of Science and Technology, UK, Postnote Update, Number 383, June 2011.

40 R. Span and W Wagner, A New equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point temperature to 1100 K at Pressures up to 800 MPA, *J Phys, Chem. Ref. Data*, 1996, **25**, 1509-1596.

41 P. Atkins and J de Paula, *Physical Chemistry*, Oxford University Press, Oxford, 2002.

42 A. Bondi, van der Waals Volumes and Radii *J, Phys. Chem.*, 1964, **68**, 441-451.

43 *Spartan'14,* Wavefunction, Inc. Irvine, CA, USA.

44 R. G Harvey, Historical overview of Chemical Carcinogenesis, in T.M. Penning (Ed.), *Chemical Carcinogenesis*, *Current Cancer Research*, Chapter 1, , New York, Springer, 2011.

45 P. Ross, Occupational Skin Lesions Due to Pitch and Tar, *Brit. Med. J.,* 1948, 369-375.

46 A. Dipple, Polycyclic Hydrocarbons and Carcinogenesis, in R. G. Harvey (Ed.), American Chemical Society: Washington, DC, *ACS Symposium Series*, 1985, **283**, 1-17.

47 S. S. Hecht, Tobacco Smoke Carcinogens, and Lung Cancer, in T.M. Penning (ed.), *Chemical Carcinogenesis*, *Current Cancer Research*, Springer, 2011, Chapter 3, P. 53-73.

48 H. Choi, V. Rauh, R. Garfinkel, Y. Tu and F. P. Perera, Prenatal Exposure to Airborne Polycyclic Aromatic Hydrocarbons and Risk of Intrauterine Growth Restriction *Environmental Health Perspectives*, 2008, **116**, 658-665.

49 Chemical Agents and Related Occupations, *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, Benzo[a]pyrene, 2012, **100F**, 111-144.

50 A. S. Brown and R. J. C. Brown, Correlations in polycyclic aromatic hydrocarbon (PAH) concentrations in UK ambient air and implications for source apportionment, *J. Environ. Monit*., 2012, **14**, 2072-2082.

51 Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Publication date: 26.1.2005.

52 D. Sarantaridis, S. L. Goddard, D. Hussain, K. J. Whiteside, P. Hughey, A. S. Brown, R. J. C. Brown and S. Brennan, Annual Report for 2012 on the UK PAH Monitoring and Analysis Network, January 2014, National Physical Laboratory, UK.

53 D. A. Bell, B. F. Towler and Maohong Fan, *Coal Gasification and Its Applications*, Chapter 4, Gasifiers, Elsevier, 2011.

54 https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/338716/coal_since_1853.xls

55 http://naei.defra.gov.uk/data/data-selector?view=air-pollutants

56 D. H. Stuermer, D. J. Ng, and C. J. Morris, Organic Contaminants in Groundwater near an Underground Coal Gasification Site in Northeastern Wyoming, *Envlron. Sci. Technol*. 1982, **16**, 582-587.

57 I. K. Barker, K. D. Bartle, A. A. Clifford, J. P. Kithinji, G. F. Shilstone, T. R. Phillips and G. Thomas, Separation of compounds from gasifier tars by extraction with supercritical carbon dioxide, *Fuel*, 1989, **68**, 601-606.

58 K. D. Bartle, A. A. Clifford, and S. A. Jafar, Measurement of Solubility in Supercritical Fluids Using Chromatographic Retention: the Solubility of Fluorene, Phenanthrene, and Pyrene in Carbon Dioxide, *J. Chem. Eng. Data* 1990, **35**, 355-360.

59 J. Méndez-Santiago and A. S. Teja, The solubility of solids in supercritical fluids. *Fluid Phase Equilibria* 1999, **158–160**, 501-509.

60 G. Anitescu, L. L. Tavlarides, Solubilities of solids in supercritical fluids-I. New quasistatic experimental method for polycyclic aromatic hydrocarbons (PAHs) + pure fluids, *J. Supercrit. Fluid*, 1997, **10**, 175-189.

61 L. Barna, J. M. Blanchard, E. Rauzy, and C. Berro, Solubility of Flouranthene, Chrysene, and Triphenylene in Supercritical Carbon Dioxide, *J. Chem. Eng. Data* 1996, **41**, 1466-1469.

62 K. P. Johnston, D. H. Ziger and C. A. Eckert, Solubilities of Hydrocarbon Solids in Supercritical Fluids. The Augmented van der Waals Treatment, *Ind. Eng. Chem. Fundam*., 1982, **21**, 191-197.

63 R. A. Pierotti, A Scaled Particle Theory of Aqueous and Nonaqueous Solutions, *Chem. Rev.*, 1976, **76,** 717.

64 E. Wilhelm and R. Battino, Estimation of Lennard-Jones (6,12) Pair Potential Parameters from Gas Solubility Data, J. Chem. Phys. 1971, 55, 4012- 4017.

65 Z. Su and M. Maroncelli, Simulations of solvation free energies and solubilities in supercritical solvents, J. Chem. Phys. 2006, **124**, 164506

66 K. T. No, K. H. Cho, M. S. Jhon and H. A. Scheraga, An Empirical Method To Calculate Average Molecular Polarizabilities from the Dependence of Effective Atomic Polarizabilities on Net Atomic Charge, J. *Am. Chem. Soc*. 1993 **115**, 2005.

67 C. M. White and C. E. Schmidt, Polarizability of coal liquefaction product d. Insight into intermolecular forces. *Fuel*, 1987, **66**, 1030.

68 A. Alparone, V. Librando and Z. Minniti, Validation of semiempirical PM6 method for the prediction of molecular properties of polycyclic aromatic hydrocarbons and fullerenes, *Chem. Phys. Lett.*, 2008, **460**, 151.

69 P. Lazzeretti and F. Taddei, Uncoupled and Coupled Hartree-Fock Calculations of Dipole Polarizabilities of Condensed Hydrocarbons. *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1153.

70 V. Oja and E. M. Suuberg, Vapor Pressures and Enthalpies of Sublimation of Polycyclic Aromatic Hydrocarbons and Their Derivatives*, J. Chem. Eng. Data* 1998, **43**, 486

71 K Nass, D. Lenoir and A. Kettrup, Calculation of the Thermodynamic Properties of Polycyclic Aromatic Hydrocarbons by an Incremental Procedure, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1735.

72 J. L. Goldfarb and E. M. Suuberg. Vapor Pressures and Enthalpies of Sublimation of Ten Polycyclic Aromatic,Hydrocarbons Determined via the Knudsen Effusion Method, *J. Chem. Eng. Data* 2008, **53**, 670-676.

73 A. Burant, G. V. Lowry, and A. K. Karamalidis, Partitioning Behavior of Organic Contaminants in Carbon Storage Environments: A Critical Review, *Environ. Sci. Technol*. 2013, **47**, 37-54.

74 J. J. Marano and J. P. Ciferno. *Life-Cycle Greenhouse-Gas Emissions Inventory for Fischer-Tropsch Fuels*, U.S. Department of Energy, National Energy Technology Laboratory, June