

Carbon Sequestration and Chemical Synthesis

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1. Introduction

Fossil energy supports industrial economies both in providing energy for mobile and stationary applications and raw materials for the petrochemical industry. Natural gas and petroleum currently account for the majority (~62%) of our energy consumption, followed by coal/peat (21%) and combustible renewables and wastes (3.9%) [1,2]. Non-energy uses in 2006 accounted for 10.9% of the consumption of gas and 16.5% of the consumption of oil, including use as feedstocks for petrochemicals (chemical feedstocks account for 3% of the global oil and gas market). The consumption of fossil energy does not mirror the availability of the energy resources; the current ratios of reserves to production in 2007 [1], are 41.6 years for oil, 60.3 years for gas and 133 years for coal, showing the preferential consumption of oil and gas over coal that has exacerbated the rate of depletion of oil and gas reserves.

The future use of fossil energy will face major challenges both in the power generation and chemical synthesis fields as a consequence of the increasing pressures to reduce carbon dioxide emissions, diminishing reserves of oil and gas, and the rising costs of fossil energy. These are broad issues and this presentation will be restricted to the consideration of climate change and technologies proposed for its mitigations, including a limited discussion on its implication to the use of biomass for chemical feedstocks.

2. Key Features

Global Warming: There is contention of whether man's activities contribute to increases in the concentration of atmospheric CO₂, and whether these activities influence climate change. The International Climate Change Panel (IPCC) [3], an international body of experts that provides a consensus of the peer-reviewed literature on climate change, concluded that "the global increases in carbon dioxide concentration are due primarily to fossil fuel use and land-use change". The increase in concentrations of CO₂, other greenhouse gases, aerosols, as well as changes in land use have been estimated to contribute 1.85 W/m² to the radiative forcing function (corresponding effectively to increasing the average incoming solar radiation of 341.5 W/m² by 0.55%) [4]. Carbon dioxide is the most important contributor to the radiative forcing function, accounting for approximately 50% of the impact of gas contributions with CH₄, N₂O, CFCs, and O₃ contributing the balance [4]. Other important contributors to the radiative forcing function are aerosols; these include soot which increases the forcing function and sulphates and forced cloud that decrease it. Land use changes are estimated by Hansen *et al.* [4] to exert a small cooling effect. Although the values of the forcing functions for aerosols and land use have a high uncertainty, that of carbon dioxide is fairly well known. Carbon dioxide concentrations have been recorded at Mauna Loa, Hawaii since 1958; the recorded daily average has increased from 313 ppm in March, 1958 to 387 in May 2008 [5]. The increase in CO₂ concentration correlates well with the cumulative addition to the atmosphere from fossil fuel consumption and cement manufacture, with the concentration increases corresponding approximately to 57% of the cumulative emissions of CO₂ to the atmosphere [5], consistent with the conclusions of the IPCC.

The impact of the radiative forcing on climate change is less well established, since model predictions vary widely between different research centers. Based on recent data, the IPCC [3] concluded that "Warming of the climate system is unequivocal, as is now evident from observations of increase in global average air temperature..., rising global average sea level,...widespread melting of snow and ice...". The observed increases were about 1°C for the global average temperature over the time interval of 1850 – 2000, an increase of about 200 mm in the global average sea level in the interval 1870 – 2000, and a decrease of about 2 million km² in the Northern Hemisphere snow cover. The rates of change have been increasing in recent years and projections have led to the strong recommendation for action on the decrease of the emission of CO₂ as well as the other contributors to the radiative forcing function.

CO₂ Mitigation Strategies. The contributions to the CO₂ emissions by fuel type in 2006 were 19.4% gas, 38.5% oil, and 41.7% coal [1]. China is now the dominant emitter of CO₂, having caught up with the U.S.A. in 2006 (5697 Mt for U.S.A. and 5606 MT for China [1]), with both countries accounting for 40.3% of the global emissions [1]. Various goals have been proposed for the reduction guided by the desire to stabilize global CO₂ concentrations at levels that would constrain the global temperature rise above pre-industrial levels to 2°C, levels above which the impacts on climate change are projected to be severe. Attaining this goal will be extremely difficult and will take a multiplicity of actions.

An example is a scenario developed by the Electric Power Research Institute (EPRI) to reduce CO₂ emissions from the U.S. electric sector in 2030 by 45% below the Energy Information Agency (EIA)'s projections [6]. The EPRI analysis indicates that the following technologies, if aggressively developed and deployed, could achieve this goal:

- i. Reduction in the load growth from the EIA estimate of 1.7% to 1.1% by increased end-use energy efficiency
- ii. Increase in renewables from a projected 30 GWe to 70 GWe
- iii. Increase in nuclear generation from 12.5 to 64 GWe
- iv. Advanced coal generation including plant upgrades for 150 GWe, increase in efficiency for new plants to 46% by 2020, and to 49% in 2030
- v. Widespread deployment of carbon capture and sequestration (CCS) after 2020
- vi. Replacement of 10% of new vehicles by plug-in hybrid electric vehicles by 2017, with 2% yearly increase thereafter
- vii. Contribution of 5% of the base load of distributed energy resources (including distributed solar) in 2030.

An aggressive approach of this magnitude will not be achieved without legislation, prospects for which do not seem likely. A major component of the portfolio of technologies is carbon capture and sequestration (CCS), which will be briefly reviewed in this paper in order to provide their state of development, projected costs, and barriers to their implementation. The most advanced of the technologies, although being pursued most aggressively for application to coal-fired plants, can be applied to any large scale concentrated CO₂ stream independent of fuel type, and are:

- **Post-combustion.** The scrubbing of the flue gas with a solvent to remove CO₂ with the CO₂ recovered from the solvent by steam stripping. The most common solvent is mono-ethanol amine (MEA), but it requires a large amount of steam for the stripping operation. This process is widely used in industry and has been applied to capture and sequester CO₂ from natural gas in Sleipner, Norway since 1996 [7]. The project is capturing CO₂ using two MEA scrubbers and injecting the CO₂ into an aquifer at a rate in excess of a million tones per year.
- **Combustion.** Oxy-fuel combustion using a mixture of oxygen with recycled flue gas in place of air. In this way, the nitrogen is eliminated from the flue gases from which the CO₂ can be easily recovered and is available for sequestration or enhanced oil recovery. This process has been tested at pilot-scale, and a 30MWe plant has recently started operation at the Vattefall plant in Schwarze Pumpe [8], with tentative plans for a commercialization in a 250 MWe plant at Jämschwalde by 2015.
- **Pre-combustion.** In pre-combustion applications, the fuel is gasified with oxygen to provide a syngas comprised mainly of mixtures of CO and H₂, with varying amounts of CO₂ and H₂O. In cases of hydrogen or electricity production with CO₂ capture, the CO is catalytically converted to CO₂ by reaction with controlled amounts of H₂O (water-gas-shift equilibrium). The CO₂ is separated from the H₂. In electricity production the H₂ provides the fuel for a combined cycle; the integration of the gasifier with the combined cycle is known as an Integrated Gasification Combined Cycle (IGCC). IGCC without the water-shift conversion has been demonstrated in the pilot Coolwater project commissioned in 1984 and has since been demonstrated in full scale units at Puertollana, Spain; Bugenum, Netherlands; and Wabash River and Polk Power Plant in the USA [9]. Gasification of a variety of fuels for chemical and fuel production has been used in numerous plants for the chemical synthesis and fuel production, as will be summarized below.

CO₂ capture by scrubbing has been used for enhanced oil recovery for many years. An example is the Great Plains Synfuels Plant in North Dakota, U.S.A., where CO₂ captured by scrubbing the syngas from a Lurgi type gasifier, is transported 320 kilometers for use in enhanced oil recovery (EOR) in Weyburn [10]. More than seven million tons of CO₂ have been sequestered. However, if CO₂ sequestration is going to be used on the large scale needed to impact climate change, the volumes used for EOR will not suffice. Assessment of potential geological reservoirs indicate that the capacity needed is available in underground saline formations at depths of one to several kilometers [9]. Examples of large scale sequestration of CO₂ at scales of a million tones per year in saline aquifers include the projects at Sleipner, Norway [7,9] and in Salah, Algeria [11].

Numerous studies have been conducted of the cost of CO₂ capture and sequestration for the three technologies provided above, but costs are difficult to compare because of the plant specific variations. The MIT study [9] provides a comparison of costs with common assumptions for 500 MW_e subcritical and supercritical pulverized coal boilers with and without carbon capture, but costs of material, labor, and fuel have escalated significantly since its publication. However, many of the conclusions they reached are still valid. Order of magnitude increases in capital costs and costs of electricity for the addition of CCS with 90% CO₂ capture are in the range of 40 to 80%. The costs decrease with increasing efficiency of the plant. A major factor in the increase in cost is that the significant decrease in the efficiency of the plants, is of the order of 25%, as a consequence of the energy needed for the compression of the CO₂ to about 15 MPa for sequestration i) for the steam needed to regenerate the sorbent for post-combustion; ii) to operate the air separation unit (ASU) for oxy-fuel, and iii) for the ASU (oxy-fuel because of the reduced O₂ requirement), the losses in the gasification process, and for the relatively low availability of gasifiers for precombustion. If CCS is to be implemented on a scale needed to mitigate the impact of CO₂ emissions on global climate change, the following are needed: i) a reduction in costs through technological developments, ii) the construction of full-scale demonstration plants that integrate carbon capture and sequestration for combustion systems, and iii) the development of regulations, long-range liability coverage, and validation and verification data of the ability to capture CO₂ capture at very large scale [9].

Examples of technological developments aimed at reducing the cost of capture are: for post-combustion, the development of new solutions such as the proprietary K-1 solvent by Mitsubishi, chilled ammonia by Alstom, and potassium carbonate and piperazine among others by Rochelle; for oxy-fuel combustion the reduction or elimination of external flue gas recycle by use of fluidized beds or by using internal gas recycle driven by the burner jet momentum, as well as the thermal integration of the ASU and the boiler; for pre-combustion through the reduction of oxygen costs by the use of ion transport membranes and by feeding the hydrogen produced by the gasifier to a fuel cell in lieu of a gas turbine. In the longer term, major larger reductions in cost may be possible by development of technologies such as chemical looping, which eliminates the need for an expensive ASU by use of an oxygen carrier that is reduced in a fluidized bed by the fuel to produce a CO₂ product stream, and then oxidized by air in a separate fluidized bed.

Some of the technological developments are being advanced by developments in other fields. Gasification for example is being extensively developed for chemical and fuel production, as will be discussed in the next section.

Organic Chemical Feedstocks: Gasification has a long history of being used for generating producer gas from the 1850s, until it was displaced by natural gas in the 1940s; for the production of Fischer-Tropsch fuels starting in WWII, since the 1950; to produce syngas from residual fuels and coke in the petroleum industry; and since the 1970s, as a consequence of the spikes in fuels costs, to produce chemicals. By 2007 there were 397 gasifiers with a total syngas production of 57 GW (or 42 mtoe). These gasifiers were fueled by 49% coal and coal/coke blends, 36% heavy resid feeds, and the balance biomass, gas, and petcoke feeds with a product distribution of 44% chemicals, 28% Fischer-Tropsch liquids, and 20% power generation [12]. A majority of the output is from entrained flow gasifiers (GE, Shell, ConocoPhillips, Siemens designs) with 32% from Lurgi-type moving bed units. Although the production of syngas in 2007 was widely distributed globally (Europe 28%, South Africa 26%, China 18%, U.S.A. 15%, Rest of World 13%), the start-ups in 2007 were dominated by China (60%).

Gasification by providing syngas with high concentrations of CO and H₂, whose ratio can be adjusted by use of the water-gas-shift reaction, provides an alternative path to chemicals from difficult fuels such as coal, biomass, petroleum resids and coke. CO₂ produced in such processes is readily captured since physical sorbents with small energy requirements for regeneration are effective at the high pressures of gasification. Gasification is complemented by pyrolysis processes for the production of chemicals, particularly ethylene and propylene from gas and oil, and by fermentation for biomass. An elegant analysis of the relative profitability of these feedstocks, including the influence of a CO₂ tax, has been presented by Banholzer and co-workers [13] which takes into consideration the cost of the feedstock, capital costs, and on the profitability of olefin production. In their analysis of the impact of placing a cost on CO₂, they assume that the mass of CO₂ emission per mass of olefin produced is 5 for coal-based processes, 2 for natural gas fractionation and cracking, and 1 for ethane cracking. As would be expected, the impact of CO₂ taxes was greatest for coal. Without CO₂ taxes, the greatest profitability for olefin production was for chemical feedstocks from the Middle East, as a result of the large differential in feedstock cost. This differential explains why in the U.S.A. only one or two large scale plants (> a billion dollars) are now under consideration for organic chemical production, and both are based on the use of syngas from coal/coke-fired gasifiers [14,15]. The profitability of ethylene production from various integrated ethanol plants from biomass are considered for three sources of biomass: corn (USA), cellulosic

biomass (USA), and sugarcane (Brazil). The analysis indicates that coal as a feedstock becomes competitive with cellulosic-ethanol (USA) at a CO₂ cost of \$25/tonne, with that corn-ethanol (USA) at about \$40/tonne, and that sugarcane-ethanol (Brazil) is competitive with coal even without a CO₂ tax. However, Banholzer *et al.* [13] point out that capital costs and land mass requirements present disincentives to the use of biomass. A conclusion that may also be reached from reading their paper is how valuable gas and oil are as feedstocks, and one can appreciate the sentiment sometimes expressed that these resources are too valuable to burn.

3. Conclusions

Fossil fuels remain the principal source of our energy as well as our organic chemical feedstocks. The evidence for the impact of man's activities on the increase of ambient CO₂ concentrations, and the effect of that increase together with those of other anthropogenic gases and aerosols on climate change, is incontrovertible. It will take a multiple of approaches, including carbon capture and sequestration (CCS), to mitigate the effect of these emissions. Technologies have been developed and demonstrated for CCS, but not with the integration of capture and sequestration at the scales needed to demonstrate that CCS is commercially viable and that will satisfy the public that sequestration is safe. Technological challenges remain to overcome these gaps in our knowledge as well as to reduce the high cost of CCS. CCS being developed primarily for the energy industry is also applicable to the production of petrochemicals, which although representing a small percentage of the CO₂ emissions, will be subject to any regulations placing a cost on carbon emissions.

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Speaker's Biography

Adel Sarofim obtained a B.A. in Chemistry from Oxford University, an S.M. and Sc.D. from M.I.T. He is currently a Presidential Professor and co-Director of the Utah Clean Coal Program at the University of Utah, to which he transferred after serving on the MIT faculty from 1961 to 1996. He has been involved in teaching, research, and consulting in the energy field since 1996 specializing in heat transfer and pollutant formation and control in fossil-fuel-fired plants. He has co-authored one book and over 200 peer-reviewed publications. He has served on advisory committees to the Environmental Protection



Agency, Department of Energy, the Environmental Protection Agency, the National Institute of Health, the National Institute of Standards and Technology, and the National Research Council. He has received a number of awards including Egerton Gold Medal (Combustion Institute); Kuwait Prize; Ahstrom Prize (Finnish Academies of Technology); Lowry Medal (Department of Energy); Larry Cecil Award (American Institute of Chemical Engineers); Westinghouse Medal (American Society of Mechanical Engineers); Doctorate in Chemical Engineering, Honoris Causa, University of Naples "Federico II. He was elected to the U.S. National Academy of Engineers in 2003.