

Pursuing Carbon Capture with Glassy Thermoplastic Polymeric Membranes

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Earth's Atmosphere

We can debate whether there is scientific evidence for global warming. We can debate human contributions, the role of the sun, and the atmosphere's composition today versus a million years ago. But rather, let us say that man's expulsion of greenhouse gases alters atmospheric make-up faster than nature can restore the balance. With the industrialized world's dependence on fossil fuels to power our factories, our cars and our homes, and a growing middle class beyond the western world in China, India and Russia, there is no question that carbon dioxide (CO₂) emissions are rapidly increasing. Data confirm atmospheric concentrations are rising. Let's start our conversation by asking ourselves, "Do we wait for scientific proof of man's impact on the environment, or do we take reasonable steps to curb emissions now?"

Fossil Fuels and CO₂

The Energy Information Administration's (EIA) 2005 International Energy Annual showed that CO₂ emissions by member countries in the Organization for Economic Cooperation and Development (OECD) totaled 14 billion metric tons that year and that worldwide all nations totaled 28 billion metric tons!¹ In 2008, EIA projected the output to grow to 16 billion metric tons and 42 billion metric tons, respectively in 2030.¹ The EIA also reported that in 2007, U.S. energy consumption was 101.6 quadrillion BTU's and that 85% was fossil fuels.² The report goes on to state that U.S. consumed 42.1 quadrillion BTU's in all forms during 2007 to generate electricity, 70% of which came from fossil fuels.³ Coal, one of our most abundant and valuable fuels comprised 21 quadrillion BTU's of our nations' electricity flow (prior to conversion losses).³

We see clearly that we are dependent on fossil fuels and coal in particular for electricity. In representing half of the BTU inputs for the generation of our electricity, with a high CO₂/BTU output ratio and relatively few point sources for emissions, coal combustion offers an attractive source for capture. The make-up of coal does vary from region to region, but in general terms it is very carbon rich, 35-45% for subbituminous and 45-86% for bituminous⁴ – the two grades dominantly used for U.S. electricity generation.^{4,5,6} Through the oxidation (i.e. combustion) of this carbon, energy is released. Part and parcel to that process is the generation of CO₂, wherein the stoichiometry of the reaction shows that 12 grams of pure carbon will convert to 44 grams of CO₂ if fully combusted.

According to the Union of Concerned Scientists, a typical 500 megawatt coal plant produces 3.5 billion kilowatt-hours of electricity per year, enough to power a city of about 140,000 people; it burns 1.4 million tons of coal and emits 3.7 million tons of carbon dioxide plus a number of other pollutants⁷ which include, although frequently mitigated by scrubbing, nitrous oxides and sulfur oxides. Adding to the emissions concern is the efficiency issue of these plants. With the median age of the U.S. online conventional coal-fired plants now at 45 years,⁸ and the limitations of their pulverized coal (PC) fired steam turbine-generators, efficiencies are fairly low. EPA reported in 2006 that PC plants operate at 34.8 -38.3% net thermal efficiency – the lower performance typical for subcritical steam PC plants with subbituminous coal, the higher for supercritical PC plants with bituminous coal.⁹

First Step

Modern technology improves the situation and is getting us on the right path. New plant designs utilize coal more efficiently while providing better opportunity to separate and capture SO_x, NO_x and CO₂. This new technology is called Integrated Gasification Combined Cycle (IGCC). By converting the coal to

synthesis gas (syngas), the IGCC process generates electricity in two stages, thereby improving efficiency. In this process, coal is gasified through partial combustion and enriched through a water-gas-shift; the inputs are converted to Hydrogen (H₂) and CO₂. The CO₂ is available for pre-combustion capture, the subject of this paper, and the H₂ is used to produce energy. Electricity is generated in the first instance from the combustion of H₂ in a combustion gas turbine-generator. The heat in the gas turbine's hot exhaust goes on to a heat recovery steam generator to superheat the steam produced in the gasification plant to drive a steam turbine-generator for production of additional electricity.¹⁰ EPA's 2006 study of IGCC plants calculates their efficiency at 40.0 % with subbituminous coal feed and 41.8% with bituminous.⁹ On balance an IGCC process boosts efficiencies 2.1-3.5% over the supercritical PC process and 5.2-5.9% over subcritical PC plants assuming the same coal feed.⁹

Getting Down to Business

While almost no one would oppose the capture of carbon if it could be done inexpensively, it has thus far proven to be anything but. Post-combustion capture is particularly expensive. In post-combustion capture, chemical solvents such as monoethanolamine (MEA) in particular, or alternately diethanolamine (DEA) or other amines are considered the best available technology to capture CO₂ from the low pressure flue gas.^{11,12} Efficiencies improve when CO₂ is captured pre-combustion from syngas.^{11,13,14} Physical solvents such as Rectisol and Selexol are under study for this purpose and are a choice for CO₂ capture, pre-combustion.^{14,15,16} According to the EPA's 2006 report on this matter, use of these technologies to capture CO₂ would add 66% to the cost of electricity for supercritical coal plants (post-combustion) and 38% to the cost of electricity generated by IGCC plants (pre-combustion).¹³

It is widely agreed that even a 25% surcharge for electricity would be economically untenable. So to the end of reducing carbon emissions for an acceptable price, the Department of Energy has initiated a Carbon Sequestration Program, whose overall goal is to develop by 2012, fossil fuel conversion systems that achieve 90 percent CO₂ capture with 99 percent storage permanence at less than a 10 percent increase in the cost of energy services.¹⁷ The initiative is focused on capturing CO₂ from coal fired power plants, the largest stationary sources of CO₂.

This program has many challenges, the largest being the cost of carbon capture. There are several parallel research paths that address capture in unique ways. Post-combustion, pre-combustion and oxy-combustion capture technologies are all under development, or are already commercial. None are close to what those of us in the commercial sector would call affordable.

A Better Way

Maybe membranes are the answer. Membranes are of interest because the thermodynamics of the system presented to us works in their favor. Membranes are simple, energy efficient, low maintenance and are used without chemical solvents. There is just one problem – we don't have one that's good enough yet.

For years now, polymeric membranes have been fashioned to conduct separations in liquids and gases. Polymers are of interest because scientists and engineers have developed the technology to create micro, ultra or nanopores in polymeric membranes precisely as the situation requires, allowing permeation of one component of the feed stream while excluding another. The design flexibility enabled by polymeric membranes holds great promise for separating CO₂, but their performance has been restrained by chemical resistance, thermal resistance or the tradeoff of selectivity vs. flux. A good

membrane for capturing CO₂ will be heat and chemical resistant; it will also have high selectivity with necessarily high flux to be cost effective. In very simple terms, selectivity is achieved by engineering the proper pore size and replicating it many times over across one surface of the membrane to create what's known as an asymmetric membrane. The thin film layer of tiny pores becomes the selective layer. To be functional, any unnecessary pressure drop imposed by the film's selective layer and support structure must be eliminated. Finally, the flux of the system must be maximized with the large driving force of a hot, high pressure gas feed stream.

Separating CO₂ from H₂ in syngas pre-combustion is ideal because the gases are already hot and pressurized. If we enact the separation here without costly intermediate cooling, we use the available driving forces of the hot gas to maximize flux. The ideal polymer for a membrane in this situation would be highly heat tolerant, dimensionally stable in this high heat, and resistant to the steam, sulfuric and nitric components of the gas stream. The polymer must be formable into a very thin membrane to minimize pressure drop, and it must be strong. The class of polymers that fits these requirements best is the glassy thermoplastics.

Scientists at several National Laboratories in conjunction with universities and commercial entities have made significant progress in the development of thin polymeric films for H₂/CO₂ separation. Significant strides have been made by a Los Alamos National Laboratory (LANL) led team using polybenzimidazole-based membranes. In a pre-pilot test lasting over 300 days at 250C, their polybenzimidazole-metallic composite membranes successfully demonstrated the membrane's thermal stability in a separation involving a mixture of H₂, CO₂, CH₄, N₂, CO and H₂S.¹⁸ The PBI-based composite membrane outperformed any polymer-based membrane available commercially or reported in the literature for separations involving H₂.^{18,19}

More Work to Do

Polybenzimidazole (PBI) films have shown great promise because of their high glass-transition temperature (427C), excellent strength, hard glassy structure and low coefficient of thermal expansion.²⁰ These films demonstrate pore size stability at high temperature and over a broad temperature range. This and PBI's chemical and hydrolysis resistance make it a very promising candidate amongst the class of glassy thermoplastics. Yet, while membranes based on PBI have shown great promise for carbon capture, they still lack sufficiently high flux to meet DOE's Carbon Sequestration Program goals for keeping the incremental cost below 10 percent. This is our challenge.

To advance we must create a next generation product. We'll do so by modestly re-engineering the membrane. We'll optimize the membrane's selective layer, simultaneously strengthening it and thinning it as much as possible. The free volume architecture will be opened to reduce pressure drop while tweaking the pore size to enhance selectivity. Through molecular manipulation, adjustment of polymer chain spacing and conversion to a hollow fiber membrane structure, new morphologies will be evaluated. The permselectivity of the new variants will be tested and the best elements will be incorporated into the next generation membrane.

It is with great hope and confidence that a rigorous effort to optimize the permselectivity of a thin film polymeric membrane based on PBI will result in a technology that meets DOE's objective. The optimization of this membrane, subsequent pilot scale evaluation, and production of commercial test systems will take several more years. We should know in two to three years after this next phase of development begins whether we can succeed. The fruits of this labor and investment will be several

more years away as commercialization will add time. Still, we're encouraged with the progress to date and we believe the goals are achievable. Our optimism is fed by the progress of those whose contributions brought us to this point and by our belief that our dreams are within reach.

One Day

We began this conversation by asking ourselves if there were "reasonable steps" we could take to reduce greenhouse gas emissions. It may turn out that a collective we holds the answer. The problem waits to be solved, and a solution appears within reach. If we succeed in developing a truly transformational technology, the burden of adapting to carbon constraints will be easy. And the reasonable steps will have been worthwhile. Sooner or later we will have to replace our aged PC power plants. It is none too early to plan for that. With some hard work and some innovative thinking, clean coal technology could be available to us and we will then be enabled to capture one major source of greenhouse gases.

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