The Selective Activation of Methane

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INTRODUCTION

It is safe to predict that increasing attention will be focused on energy production from natural gas. The energy content of the gas is high (the heat of methane combustion is 1223 kJ/standard mol) and carbon dioxide emissions are about 30% less than gasoline for production of a unit of energy.

The use of natural gas as a transport fuel is limited by storage problems. High pressure storage requires a weight penalty associated with cylinders, and this limits the application to larger vehicles. Lower pressure adsorption beds are being studied, but adsorption capacities are too low (but only by a factor of ca 2-5) for vehicle application. As a result, it is not surprising that the conversion of methane to other fuels has been the subject of much study.

Methane is an unreactive molecule; and methane activation is not easy. Essentially, the gas can be converted to other products either by direct or indirect reaction into components followed by reassembly of new molecules.

\[
\Delta \text{H}_\text{g} \quad x \text{CH}_4 \rightarrow \text{C}_x \text{H}_y + \text{H}_2 + \text{CO} + \text{N}_2 \quad (1)
\]

2\text{CH}_4 \rightarrow 2\text{C}_x \text{H}_y + \text{H}_2 \quad (2)

\text{CH}_4 + \text{H}_2 \text{O} \rightarrow \text{CO} + \text{H}_2 \text{O} \quad (3)

\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2 \text{O} \quad (4)

\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4 \text{OH} \quad (5)

or by insertion - for example of oxygen or chlorine.

\text{CH}_4 + \text{O}_2 \rightarrow \text{CH}_2 \text{O}_2 \quad (6)

\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_2 \text{Cl}_2 + \text{HCl} \quad (7)

These direct insertion reactions have an obvious appeal, but the stability of the methane molecule, the energy needed to disrupt the molecule and the low yields and selectivities of the insertion reactions have, to date, made such processes uneconomical. Similarly, the low yields and selectivities have argued against pyrolysis (reaction 4) and oxidative coupling (the essential reaction of which is shown in reaction 2). Rather it has been the degradation of the molecule by steam reforming (reaction 3) or partial oxidation (reaction 4), followed by reassembly (e.g. reaction 5) that has proven to be of commercial interest.

Although both reactions are operated industrially, the high operation temperature pose economic and scientific penalties. Thus, for example, the production of syngas accounts for ca 25% of the cost of methanol - a fact that has focused attention on more economic routes to carbon monoxide and hydrogen. In this context, recent studies by Asbeck have suggested that syngas can be produced at lower temperatures by partial oxidation. Although possibly open to question, interest in the results reflects the desire to develop a more economical process.

In the context of steam reforming, the catalyzed reaction of methane with steam requires high temperatures. At such temperatures, carbon formation can occur, and sufficient steam must be added to react with methane and to minimize coke formation. Both high temperatures and the provision of steam under reaction conditions are major cost penalties.

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Environmental Aspects of Coal Trace Elements

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INTRODUCTION

The increasing use of coal, especially for power production, means that more attention is being given to environmental aspects. Some matters, for example, acid mine drainage, acid deposition and the relevance of coal-derived carbon and nitrogen oxides to the greenhouse effect are still being investigated in order to find methods of mitigation. However, much less attention has been given to possible untoward effects from trace elements in coal during mining, preparation and use. Occasional emotional outbursts, based on insufficient evidence, focus attention on arsenic, lead, cadmium, mercury and uranium. The best way to counter such claims is to provide proper information as a basis for more informed judgements. The comments contained in this article are mostly based on work done at the Commonwealth Science and Industrial Research Organization CSIROB.

There is a good deal known about the contents of a wide range of trace elements in coals from the USA, Australia, Canada and limited areas in some other countries.

Although there is some information on the modes of occurrence of certain elements, much more research is needed.

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Although small additions of sulfur have been shown to be beneficial, such additions must be made continuously owing to the possibility of sulfur desorption from the surface (e.g., as H₂S). It is possible to minimize coking using other more permanent doping agents such as copper. Experiments show that ensemble size control can be achieved in this way — but at the cost of activity. Copper covers most of the nickel surface and, although coking is reduced, so is steam reforming activity. Similar experiments are still being carried out with agents that cover the surface and are catalytically active in their own right. Preliminary experiments show that it is possible to maintain steam reforming activity while minimizing coke formation.

Another approach which is also showing promise is to dope the nickel catalyst with other metals. It is believed that the deposition of carbon precursors via the formation and subsequent decomposition of nickel carbonate. The question then arises as to whether it is possible to dope the active catalyst in such a way that steam reforming can occur while coke formation does not.

Such dopants have been identified and are now being patented. It appears that the dopants react preferentially with orbitals responsible for the formation of nickel carbonate, although this has yet to be proven. The net result is, however, that steam reforming activity is reduced slightly and coke formation is reduced markedly. The consequent economic gains look most interesting.

There is little doubt that continuing attention will be focused on cost reduction in the production of syngas. In the absence of economic routes for the direct reduction of desired chemicals from methane, the major opportunity for cost savings lies in the production of syngas. Whether, in the long run, this will involve improvements in steam reforming or in partial oxidation remains to be seen. The selective activation of methane is too complex a problem to make accurate predictions.

David Trimm was born in England and worked at Imperial College, London for many years. He moved to Australia in 1979 where he is Head of the School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney. His main interest is in Applied Catalysis and is a Regional Editor for the journal of that name.

Visiting Professors at the CAER

DR. KENNETH KUHN was a visiting professor for the past four months at the CAER. He was on sabatical from Western Kentucky University, where he is an Associate Professor of Geology. He performed fine-coal agglomeration studies with the petrography group here. His presence was a tremendous asset and complement to the Center’s research activities in analyzing the partitioning of materials in coal during beneficiation.

Ken is a leading expert on the technology and characterization of charcoal briquets and has worked internationally to promote industry standardization in this area. Presently, he is in China where he is presenting lectures on the geology and petrology of United States coals.

DR. BASIL JOHN is working at the CAER while on a sabatical from the University of Melbourne in Australia until July. He is investigating the creation of activated carbons from coal and brings with him an international reputation. He has been a Professor of Organic Chemistry at the University of Melbourne since 1973.
Environmental Aspects, (continued)

especially on the mineral matter that is a primary site for many elements which may occur as discrete minerals, as replacement ions in minerals and are adsorbed on minerals, particularly clays. In this regard, micron- and submicron-sized particles closely associated with the organic coaly matter are being recognized as an important part of the total mineral matter in many coals. A geochemical approach has shown the association of manganese with siderite and calcite and of cadmium with sphalerite.

Of the 70 trace elements that have been found in coal, about 22 can be regarded as environmentally interesting, and of these, most attention should be given to arsenic, boron, cadmium, fluorine, lead, manganese, mercury, molybdenum, selenium, thorium, uranium and zinc. These suggestions are based on the concentrations of the elements found in most, say about 90% of, coals (Swaine 1980).

During underground mining there could be releases of some elements from coal and associated rocks, especially if there is pyrite oxidation giving solutions with relatively low pH. With surface mining there is more likelihood of pyrite oxidation with consequent mobilization of some elements. However, increased solubility does not necessarily mean increased concentration in solution, because removal by adsorption on clays may occur. In the case of acid mine drainage, the acid solutions may well mobilize some elements, but the precipitation of hydrated iron oxides, which are an insightful feature of some streams, would remove appreciable amounts of some trace elements.

Rehabilitation after mining may involve the establishment of vegetation, which may be affected by too much boron and manganese. If forage plants are envisaged, the levels of selenium and molybdenum must be kept low enough to avoid opentopping grazing animals. The best approach is to carry out plant trials prior to rehabilitation. It may also be prudent to check that the run-off water from the mining area is not adding unwanted amounts of trace elements to nearby waters.

Beneficiation of many coals is carried out to reduce the total mineral matter, especially pyrite, but at the same time the concentrations of some trace elements are also reduced, as shown in Figure 1.

It is clear that the rejects will have enhanced contents of elements that have been leached in the washed coal and these must be taken into account during disposal.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As</th>
<th>Cl</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-of-mine</td>
<td>2.1</td>
<td>0.09</td>
<td>255</td>
</tr>
<tr>
<td>Washed</td>
<td>0.5</td>
<td>0.06</td>
<td>64</td>
</tr>
<tr>
<td>Reject</td>
<td>4.5</td>
<td>0.21</td>
<td>502</td>
</tr>
</tbody>
</table>

Figure 1. The beneficiation effect of a bituminous coal from the Sydney basin, Australia (results are in ppm).

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Contact Theresa Wiley for more information.
Environmental Aspects, (continued)

During coal combustion, trace elements are released into bottom ash and flyash. A small proportion of flyash as very fine particles plus some elements in the vapor state are emitted to the atmosphere with the stack gases. A four-year study published in 1983 around an Australian 1260 MW power station gave much information about the contents of trace elements in food soil, bottom ash, flyash and the deposition of trace elements in the environs of the power station (Swain et al 1983). The Deposition collection was by the use of cleaned Sphagnum moss held in fine-mesh envelopes with 4 compartments each containing 2 g of moss (Figure 2).

The fine particle retention by the moss is because of the structure of the moss, which is made up of holes, up to 10 μm diameter, and folds. Flyash particles, mostly spherical, and soil particles, mostly angular, were seen by scanning electron microscopy.

Marked content variations in elements deposited at a particular location were found at different times of samplings (Figure 3). It should be stressed that the amounts of trace elements deposited from the atmosphere in the environs of a power station vary greatly with sampling time. The distance and direction from the power station were also found to be important. In other words, there is a space-time relationship.

The disposal of flyash and bottom ash from the power station hoppers should be monitored to check that leachates are not adding unwanted amounts of trace elements to nearby surface and underground waters.

Further studies of some coals are needed, i.e., trace-element associations with mineral matter, the effect of beneficiation, the amounts of trace elements deposited around power stations and mobilization of trace elements during mining and waste disposal. In general, “if proper care is taken, then it seems most unlikely that trace elements from coal mining and usage should be harmful” (Swain 1989). Dr. Stuart is an Honorary Research Fellow at CSIRO and a Professorial Fellow at the University of Sydney. Most of his research is on trace-element geochemistry—related to rocks, soils and coals, especially environmental aspects.
A CONGRESSIONAL STAFFER’S PERSPECTIVE ON DOMESTIC ENERGY POLICY

by Nancy Jeffrey

There is good news and bad news. The good news is that this year energy is finally receiving the attention it has lacked for a decade. The bad news is that no one has yet presented a coherent energy strategy to solve current and future problems. The need for an energy policy and the effects of the lack of policy has finally been recognized as a problem to be resolved. The benefits of such a policy as well as the economic impacts of the want of policy make it imperative that the United States establish a national energy strategy. A great opportunity is at hand to do that. Much work on energy policy has been accomplished to date by the Congress. We should build on that information and not let the country languish for the next decade without a responsible plan for our energy future.

I can’t overemphasize the importance of long-term goals in research and development. However, those goals must be responsive to national economic, environmental, and energy security issues. While I doubt that many would disagree with these goals in the abstract, the reality of reconciling energy needs with economic policy is a daunting task.

There is a tremendous competition for research dollars; and regional technology concerns must be reconciled (e.g., coal versus oil or nuclear). Short-term needs must be weighed against long-term benefits. Very expensive programs like the superconducting super collider are competing with programs like Eastern oil shale for federal funding.

It is incumbent upon those concerned to let their representatives know about the long-term benefits and needs for continued research and development funding for fossil fuels. Until representatives understand the importance, it is difficult to provide adequate funding needed for the projects. Politicians and scientists often have different agendas. The differences are understandable and each is justified. Communication among interested parties is a way to bring separate agendas closer together.

It is difficult to quantify what impact the lack of a coherent energy research and development policy has had on our domestic energy situation. Clearly, the absence of an energy strategy has translated itself in terms of research funding and a lack of a long-term commitment by federal research part ners. Understanding the deleterious impacts of the lack of a research and development policy and how it affects the energy policy for the greater good are different problems. Policy makers are recognizing the need to restructure or at least improve the way we look at research, development and demonstration in this country.

Throughout the FY 1992 budget submission hearings, many of our witnesses stressed the need to set a comprehensive research agenda and in doing so, evaluate the ongoing projects and set appropriate criteria before continuing. Projects should have proper goals and milestones. Many of our current projects have not been properly peer reviewed to ensure research integrity.

One of my job’s benefits is visiting university research laboratories and private-sector research institutions. I am always impressed by the caliber and dedication of the research scientists I meet. They are remarkably committed considering the vagaries of research funding. University research scientists provide the foundations of national research and development activities. These solid foundations allow us to accomplish much as a nation for what is relatively speaking, a small investment.

A vigorous research, development and demonstration program is the insurance policy for our future. I hesitate to mention the overused word competitiveness, but as our budget deficit grows, and our economy becomes less healthy, competitiveness is a real issue. Foreign capital is coming into this country in the form of large

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real estate purchases as well as the purchase of smaller technology development companies. I won’t go over simplify the problem by attempting to resolve its complexities here. But I do believe that we can do more to help our domestic energy technology development companies.

Federal funding partners should stay with developing technologies until they are proven. We cannot foresee whether each research and development program will come to fruition, nor can we tell the industry which product to purchase. We can, however, ensure that by continuing our federal funding commitment through the demonstration stage, the technologies will be on the commercialization track, not languishing in the laboratory for want of adequate funding.

Remarks expressed here are the author’s opinions and do not necessarily represent the opinions of the other committee staff members.

Nancy Jeffery has been a professional staff member on the energy subcommittee of six subcommittees of the Committee on Science, Space, and Technology for fourteen years. Her responsibilities have focused on forest fuels, renewable energy and energy conservation research and development.

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