Chemistry for Energy

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ACS Symposium Series

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

The main purpose of the Chemistry for Energy Symposium was to identify where advances in chemical knowledge and understanding are required for the development and diversification of energy sources. The contributors were invited to review the chemistry and chemical engineering aspects of various sectors of energy production from Canadian sources and to indicate important areas for research and development. With a view to encouraging participation by University chemists and engineers in energy research and development, authors were asked to select areas where expansion of fundamental chemical knowledge and basic chemical data are needed.

The symposium was divided into three sectors: fossil fuels; perpetual and renewable sources; and electricity production and storage. This publication contains a selection of papers that were presented at the symposium.

The symposium provided ample evidence that, while Canada is very well endowed with energy resources of various kinds, it will require much effort by chemists and others to make them available in useful form and at moderate price. Even with the best possible efforts and stringent conservation measures, we are unlikely to avoid shortages and importation of large amounts of oil in the 1980s. Forms of energy and energy conversions which are not economic at present then may begin to compete effectively.

Energy is distributed in several quite distinct and not readily interchangeable forms. Electricity can perform work with near 100% efficiency (it is essentially pure Gibbs free energy) but cannot be efficiently and economically stored. Fuel oil is a very compact and convenient energy store which is readily released as heat (enthalpy) that can be only partly converted to work, where so required, in some form of heat engine. Fuel gas has some characteristics of both. Thus liquid fuel and electricity have complementary functions and both are required. The distinction was occasionally overlooked by some speakers. The coming energy crisis is a deficit of liquid fuel. Supplies of cheap electricity can be maintained but can only be substituted for liquid fuel to a limited extent.

Chemistry research can help a great deal to minimize the deficit in energy supplies and the rise in energy costs and to facilitate and shift to new sources. There are three main branches of energy technology:

energy collection and concentration, conversion and storage, and application and waste-product control. The R&D emphasis is concentrated in the first two areas for novel energy sources and in the latter two for established energy sources. Fluidification is a dominant theme—the conversion of various raw energy sources, new or old, to liquid fuels.

Some papers are quite explicit as to the new chemical knowledge required for progress; in others, the requirements are implicit. Many of the chemical topics are specific to particular energy sources and to particular aspects of the technology. However, certain common threads and general requirements can be perceived, which are noted below, followed by brief discussion of some of the more specific aspects from the respective sectors of the symposium.

Surface and interface chemistry is the key to progress in many areas of energy technology. Recovery of oil from the Alberta tar sands involves separating oil–water–sand with an interfacial area of approximately 1 m^2/g. Furthermore, several authors noted the major wastes problem of separating and stabilizing the solids from the residual sludge. Adhesion of fly ash to superheater tubes, which reduces the efficiency of coal use, is a problem in surface-charge phenomena. Coal can be used to extend fuel oil supplies directly if dispersions of coal in oil can be stabilized sufficiently. Conversely, knowledge of destabilization of carbonaceous colloids could lead to improvements in the dewatering of peat so that it may be used more readily as an energy source. Other aspects of surface chemistry come into the improvement of catalysts for the liquefaction or gasification of coal. Improved knowledge of various electrode interfacial processes is important in the development of better batteries and fuel cells. A specific example is the need for improved electrocatalysis to lower the overpotential for oxygen reduction. Another form of surface chemistry, the science of membranes, cellular and synthetic, is likely to be important in developing methods for trapping solar energy in chemical-stored form. Knowledge of the adsorption of dissolved radionuclides on rock can be used to provide extra assurance of retention underground of the wastes from the use of nuclear energy.

Improved knowledge of chemistry at elevated temperatures is a general requirement since all energy use and transformation processs involve temperatures higher than normal. Requirements include thermochemical and kinetic data at the temperatures of combustion and conversion reactions of fossil fuels and at the more moderate temperatures of hot aqueous solutions. Improvements in theoretical models or empirical methods are required to allow more accurate extrapolation of knowledge and data from ordinary temperatures.

Many aspects of sulfur chemistry are of concern if we are to reverse the apparent trend to increasingly acid rain while continuing to use all forms of fossil fuel whatever their sulfur content—35% H_2S in some sour gas wells. Perhaps even more important than sulfur recovery and control of emissions is to find constructive uses or innocuous methods of disposal and to determine the long-term effects of the sulfur which is prevented from immediate dispersal in the atmosphere—currently in excess of 25,000 tonnes per day accumulating on the ground in Alberta.

Improved knowledge of the structure and transformations of certain solids is desired. Notably coal, it was said, is still very imperfectly understood, despite its long use as an energy source. Improvements here would aid development of processes for conversion to liquid fuels and for recovery of solid residues in a form suitable for metallurgical coke. For new ways to tap energy sources, development of solids with high photoelectric conversion efficiency for sunlight could provide a major breakthrough. In relation to nuclear energy, knowledge of the solid-state transformations of glass and other solids is being developed to ensure that nuclear wastes are well locked into appropriate solids until they are no longer hazardous.

Advances in knowledge of the chemistry of fermentation processes will aid the exploitation of biomass energy, e.g. a more concentrated fermentation process for the production of sugar from cellulose is required if alcohol from Canada's very extensive forests is to compete with other sources of liquid fuel.

Fossil Fuels

The fossil fuel program was highlighted by five invited papers dealing with coal conversion, oil sands, desulfurization, peat, and the federal government's R&D program. In total, there were a dozen papers pertaining to Canada's fossil fuel resources, coal (four papers) and oil sands (three papers) receiving the greatest attention. Seven of these papers appear in this volume.

N. Berkowitz (Alberta Research Council) provided a stimulating account of the potential of coal in Canada's energy future. Coal can be used directly as an industrial fuel or be converted to other combustible hydrocarbons. Berkowitz described the three different conversion techniques: gasification, liquefaction, and partial conversion techniques to produce gases, oils, and solid fuels.

M. Greenfeld described unique laboratory experiments designed to stimulate and understand the complex chemistry of in-situ coal gasification. Developed at the Alberta Research Council, the gasification simulator was heavily instrumented with calorimeters and gas chromatographs to determine the enthalpy, composition, and kinetics of formation of the product gases. Computer techniques were used to calculate mass and heat balances and to test kinetic models.

K. Belinko, M. Ternan, and B. N. Nandi of the Canada Centre for Minerals and Energy Technology (CANMET) discussed the formation of mesophases during the liquefaction of noncoking coals. R. D. Humphreys (Alberta Oil Sands Technology and Research Authority) focussed on the huge energy potential of Alberta's Athabasca, Wabasca, Cold Lake, and Peace River oil-sands deposits. A staggering 2.5 trillion barrels are locked in these deposits of sand and underlying carbonate rock. About 5% of the Athabasca deposit can be extracted by mining while 30% or more is recoverable by in-situ technology. With a $150 million budget and by collaborative action with industry and university, AOSTRA's goals are to help improve surface extraction technology and land rehabilitation, to increase the efficiency of in-situ recovery, and to develop efficient processes to convert the oil sands into higher-value materials (petroleum and minerals). Humphreys described the licensing arrangements for joint AOSTRA–industry ventures and the depth of interaction with university where some 30 projects are now being funded.

A paper contributed by J. E. Desnoyers, R. Beaudoin, G. Roux, and G. Perron described the use of microemulsions as a possible tool for the extraction of oil from tar sands. Using a technique called flow microcalorimetry recently developed at the University of Sherbrooke, these researchers studied the structure and stability of organic microphases in aqueous media. These microphases can be stabilized by surfactants and can dissolve large quantities of oil. In a similar vein, D. F. Gerson, J. E. Zajic, and M. D. Ouchi (University of Western Ontario) described the extraction of bitumen from Athabasca tar sands by a combined solvent–aqueous-surfactant system.

Desulfurization of fossil fuels was the subject of an authoritative review by J. B. Hyne (Alberta Sulphur Research Institute). This is a topic of increasing importance as Canada relies more and more on sulfur-containing fuels such as tar sands and heavy oils. Hyne reviewed the present state of the chemistry and technology for both precombustion desulfurization of natural gas and crude oils and postcombustion tail-gas clean up of coals and cokes. He clearly identified areas of possible future research such as the high temperature–high pressure chemistry pertaining to in-situ desulfurization processes.

Perpetual and Renewable Sources

BIOMASS. The potential of biomass to contribute to Canada's energy needs was discussed in papers by C. R. Phillips, D. L. Granatstein and M. A. Wheatley (University of Toronto), R. Overend (Canada Department of Energy, Mines, and Resources), and M. Wayman, J. Lora, and E. Gulbinas (University of Toronto). The most energy-efficient and least costly use of biomass is the direct burning of wood, followed by gasification and liquefaction, respectively. It was estimated that 2–3% of Ontario's liquid-fuel consumption could be replaced by wood liquefaction based on 500,000 hectares of available forest. The potential would increase to 8–10% if 1.5×10^6 hectares were available. C. R. Phillips, D. L. Granatstein, and M. A. Wheatley recommended an energy program having the following order of priority: crude-oil exploration, oil sands, possibly coal liquefaction, then wood liquefaction. The need for more R&D in the wood liquefaction areas was stressed since Canada has an abundant supply of wood.

The use of anaerobic bacterial systems for conversion of animal manure into methane gas was discussed by H. M. Lapp (University of Manitoba) who described operating characteristics and factors affecting anaerobic digestion plants. M. Wayman and M. Whiteley (University of Toronto) reported on the interaction of photosynthetic and sulfate reducing bacteria in a membrane-separated anaerobic culture. This autotrophic microbial system is capable of producing a high protein biomass in one fermenter, while the other produces a high energy biomass.

SOLAR. J. Bolton (University of Western Ontario) discussed thermodynamic and kinetic limits on photochemical conversion and storage of solar energy. He stated that 25–28% efficiency should be attainable for conversion of solar energy to electricity. Some guidelines and objectives were given for research to foster development of workable fuel and electrical-generation systems using solar energy. B. L. Funt, M. Leban, and A. Sherwood (Simon Fraser University) have constructed a 100-cm^2 CdSe photoelectrochemical cell which uses a large part of the sun's energy spectrum. They assessed factors relevant to the scaling up of their cells, with the objective of attaining 1% conversion efficiency in a large converter. F. R. Smith (Memorial University) stressed that if photoelectrolysis of aqueous solutions is to become an economical process for hydrogen and oxygen production, it will be necessary to develop semiconductor anodes having band gaps matched to the solar spectrum.

Electricity Production and Storage

The final session of the Conference was devoted to discussion of the main methods of producing and storing electrical energy (batteries and fuel cells) and to a discussion of some of the chemical problems encountered during nuclear generation of electricity.

E. J. Casey (Defense Research Establishment, Ottawa) reviewed the selection of anodes and electrolytes for high-energy density storage batteries. The present state of development of batteries by using light metal anodes in nonaqueous, molten salt and solid electrolytes was reviewed, and suggestions were made on the feasibility of novel systems.

Another prospect for efficient energy conversion is the fuel cell. The different types of fuel cells presently under study or development were reviewed by G. Bélanger of Hydro-Québec, who concluded that commercial availability of such units is now in sight. However, the need to develop cheap, efficient electrocatalysts for oxygen reduction remains.

The next presentations discussed chemical problems encountered in the nuclear power industry. S. R. Hatcher (Atomic Energy of Canada Ltd., Pinawa) gave a general review covering the chemistry of established and novel nuclear fuels, heavy-water production, and reactor operation.

M. Tomlinson (Atomic Energy of Canada Ltd., Pinawa) described how advances in chemical knowledge can help to assure long-term containment of nuclear wastes in underground formations.

In conclusion, the conference indicated the diverse nature of the chemical research and development which is required in order to benefit from Canada's abundant energy sources.

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