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Atmospheric Chemistry Research

Rick D. Saylor

Global environmental changes are occurring all around us, and the energy industry is a major player in the changes that are taking place. Wise energy policy can only be generated from a position of informed enlightenment and understanding about the environmental consequences of energy production and utilization. The atmospheric chemistry research being conducted at the University of Kentucky's Center for Applied Energy Research is geared toward providing the knowledge necessary to allow industrial and legislative officials to make responsible energy decisions in the 1990's and beyond.

Introduction

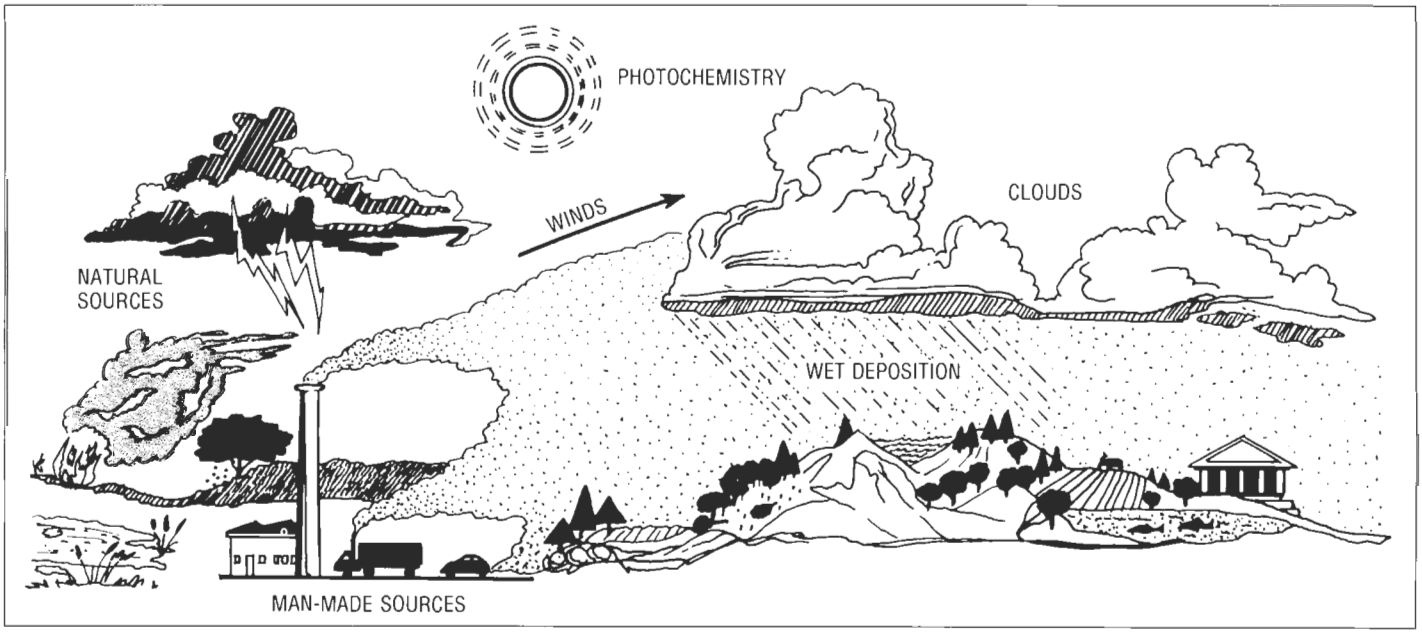
One of the major challenges facing the energy industry in the 1990's and into the 21st century is the effect of energy utilization on the environment. As stated recently by the presidents of the National Academy of Sciences, National Academy of Engineering, and the Institute of Medicine: "We believe that global environmental change may well be the most pressing international issue of the next century." Energy utilization and the resultant release of combustion products into the atmosphere seem to be playing a significant role in the changes that are taking place in the Earth's environment. The general public, as it becomes more aware of environmental issues, is beginning to add its voice to previously isolated environmental groups calling for major changes in the relationship between human activities and the global environment. Some sectors of the public domain even seem ready to pay the high costs necessary to clean up and keep the environment in a protected state. Thus, for the energy industry, this is a problem that is not going to go away, but rather, it is a challenge that must be faced head on. The only way to make intelligent decisions concerning energy policy in the next decade and the next century will be to be fully informed on the environmental consequences of energy production and utilization.

The overall objective of the University of Kentucky's Center for Applied Energy Research (CAER) Atmospheric Chemistry program is to provide information to the energy industry and to the general scientific community about the effect of energy production and utilization on the Earth's atmosphere. Currently, there are three major efforts underway at the CAER to come to a better understanding of atmospheric chemistry. This article will briefly present an overview of each of these efforts, while succeeding articles will discuss each program in greater detail.

Kentucky Acid Deposition Program Precipitation Chemistry Network

The Kentucky Acid Deposition Program (KADP) precipitation chemistry network was initiated in 1983 with the goal of providing a statewide monitoring system to document and characterize the occurrence of acid deposition in Kentucky. The KADP network consists of nine monitoring stations located across the Commonwealth. Each station consists of a precipitation collection device and rain gauge surrounded by a six-foot high chain link fence. The precipitation samples are collected every Tuesday and sent to the CAER Atmospheric Chemistry Laboratory for analysis.

The precipitation chemistry data obtained from the KADP network are used to advance the understanding of acid deposition along many fronts. These areas include: (1) elucidating the important chemical and physical atmospheric mechanisms responsible for the formation of acid



Cycle of acid production and deposition.

deposition; (2) determining the statewide variation of acid deposition; (3) investigating the role of local emissions sources on deposition within and beyond the state's borders; (4) monitoring the temporal trend of acid deposition as more stringent emissions control legislation is enacted and imposed; and (5) providing empirical data for the development and validation of numerical acid deposition models. The KADP data is important for Kentucky in that it shows us the extent of the acid deposition problem now and should help us to predict the severity of the problem in the years to come.

Modeling of Regional and Urban Photochemistry and Acid Deposition

Acid precipitation falling into lakes and streams has been found to increase pH levels of surface waters, possibly resulting in the eventual death of aquatic ecosystems. Many lakes and streams in the northeastern U. S., Canada, and Europe have been acidified by the uptake of acid deposition, and many have been severely damaged. High deposition acidities may also enhance the release of metals such as aluminum, cadmium, and mercury from soil compounds. This leaching of toxic metals into water supplies is certainly hazardous to aquatic organisms and may be hazardous to human health. Acid deposition has also been implicated in the decline of forest populations in Europe and recently in North America. Scientists are not yet certain of the exact role that acid deposition plays in forest declines, but in combination with other factors such as increased ozone levels, it seems clear that acid deposition has a significant impact on the health of forest populations.

In light of the facts already known about the effects of acid precipitation on the environment, it is essential that we better understand the chemical and physical atmospheric processes that lead to the formation and removal of acidic substances so that meaningful control strategies may be suggested to mitigate the effects of man's activity. The goal of this project is to achieve this kind of improved understanding through computer modeling of the important acid deposition forming mechanisms.

STEM-II is a 3-dimensional numerical model that simulates the emission, transport by winds, chemical reaction, and removal of pollutants in the atmosphere. It is one of only three models of its type in the United States, and it has been extensively tested and applied to various regional and urban acid deposition situations. Numerical models of this kind serve as tools by which a better understanding of atmospheric processes can be obtained. The STEM-II model has recently been applied to a region in the lower Ohio River Valley which encompasses Kentucky and portions of the surrounding states. Predictions of acidic deposition from the STEM-II model have been compared with actual measurements obtained from the KADP network and from the National Atmospheric Deposition Program -National Trends Network and found to be in relatively good agreement. Plans are underway for STEM-II to be used as part of a national program investigating the formation of ozone in the Southeastern U.S.

Modeling of Global Tropospheric Chemistry

Much public interest has recently been focussed on the so-called global "greenhouse effect," which refers to the possible climatic warming of our planet due to increased atmospheric concentrations of CO_2 (carbon dioxide), CO (carbon monoxide), CH_4 (methane), and chlorofluorocarbons. Another recent global concern has been the occurrence of the Antarctic ozone "hole" and the projected future deterioration of the stratospheric ozone layer at lower latitudes. Atmospheric scientists from many specialties are converging on the idea that a full understanding of the Earth's environment will only be gained by considering the atmosphere as a whole. Over the last three decades air pollution has gone from being only an acute local problem (smog in urban areas), to being a chronic regional problem (acid deposition in Europe and the NE U.S.), to now finally being recognized as a truly long-term global phenomenon.

The overall objective of this project is to determine the effects of fossil fuel combustion (and the resultant emission of pollutants) on global tropospheric chemistry. We will attempt to examine the changes in magnitude and distribution of pollutants in the global troposphere as fossil fuel combustion continues and increases in the next century. Additionally, we will examine the perturbations of global tropospheric chemical cycles resulting from a future change in climate as well as from changes expected in solar radiative flux due to decreases in stratospheric ozone. This work will largely be carried out by employing a numerical model known as GLOBAL, which is an Eulerian, 3-dimensional model that simulates the emission, transport, chemistry, and surface interactions of trace chemical species in the Earth's troposphere. The current version of GLOBAL simulates the worldwide distribution of CH_4 and CO in the atmosphere. GLOBAL has previously been used to simulate the worldwide increase of CH_4 and CO due to increased fossil fuel combustion.

Rick D. Saylor, a native Kentuckian, holds a doctorate in Chemical Engineering from the University of Kentucky. He is employed as a scientist at the CAER, and is the author of several journal articles in engineering and atmospheric science. He has broad expertise in the use of high-performance computers for the modeling of physical and chemical systems.

Fluidized-Bed Combustion and Energy Production

John M. Stencel

Fluidized-bed combustion (FBC) provides the potential for expanding the use of coal. The technology is extremely flexible and able to meet environmental standards for a wide range of feedstocks. Low and high sulfur coal and even mine refuse can be combusted, and sulfur dioxide emissions limited by trapping with added limestone. This article provides an overview of the current status of FBC.

Introduction

Coal resources in the Commonwealth of Kentucky have made a significant contribution to industrial and economic development in Kentucky and in the United States. Currently, about one-fifth of the total amount of coal used in the United States is produced in Kentucky; almost 95 percent of this coal is used for power production in utilities and industrial boilers. Continued and expanded use of Kentucky coals will depend to a great degree on their ability to be burned under stricter state and federal regulations governing sulfur and nitrogen oxide emissions.

The Combustion Research Program at the Center for Applied Energy Research (CAER) is developing and applying advanced combustion processes and techniques which will be applicable to an expanded use of coal as 21st century energy needs and regulations approach. One of these techniques is fluidized-bed combustion (otherwise known as FBC). Since 1983, the CAER has been at the forefront of research and development in this rapidly expanding and increasingly more important combustion effort.

Briefly, the fluidized-bed combustor at the CAER is a 1.2 MW pilot plant which has a typical configuration like that shown in the figure on the following page. Coal, limestone and air are co-fed into the combustor at the bottom of the bed. The combustion air imparts a fluid-like character to the coal and limestone, thereby promoting mixing and intimate contact between the particles of burning coal and limestone. At the temperatures normally employed in this fluidized combustion zone (about 1550°F), the limestone is converted to calcium oxide which reacts with the sulfur that is released during coal burning. This sulfur is in the form of sulfur dioxide (SO_2) which forms the reaction product calcium sulfate. Calcium sulfate, or gypsum, is a stable, dry and potentially usable by-product.

The cyclone at the top of the combustor is used to capture particulates exiting the combustion zone and enables recycle of the particulates to increase the efficiency of sulfur capture and carbon utilization. The in-

EDITORIAL COLUMN

Frank Derbyshire
Director
Center for Applied Energy Research

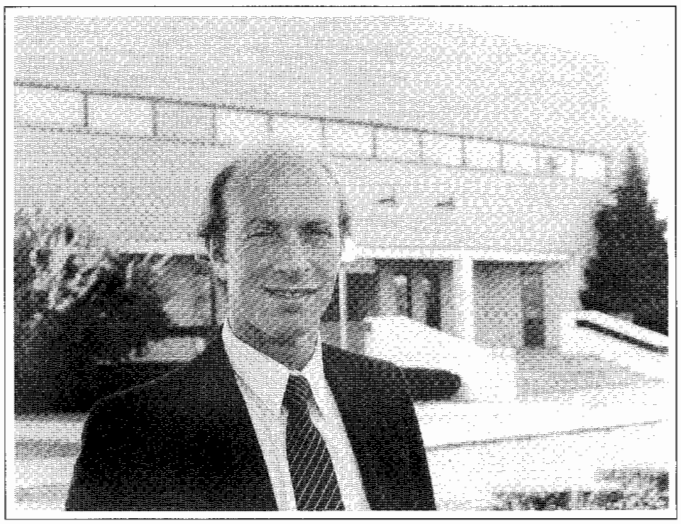
This is the first issue of this newsletter - beginning appropriately and one hopes auspiciously at the start of not just a New Year but a new decade. It is my intention to write an editorial column in selected issues. On this occasion it seems appropriate to say something about the newsletter and it's aims.

Published by the University of Kentucky Center for Applied Energy Research - CAER for brevity - the newsletter is intended to be a companion publication to the Institute for Mining and Minerals Research's (IMMR) longstanding "Highlights." While Highlights focuses on technical matters relating to mining and minerals processing, this newsletter, "Energeia," will deal with energy technology and environmentally related topics, and will appear in alternate months. The articles will be contributed by researchers from various UK academic Departments, Centers and Institutes and occasionally from other sources.

The name "Energeia" was selected after considering a number of suggestions, some of which were actually polite. Inspiration was finally supplied by consulting a dictionary. Energeia is the Greek word which is the root of our English word "energy." To our thinking, the choice of this name conveys an attractive simplicity and at the same time gets to the point.

The newsletter is being published for a number of reasons. First, a wide audience in Kentucky should be made aware of the energy research which the state is supporting. They need to be kept informed of what this work is doing or will do for their prosperity, and to understand the significance of changing energy technologies and their effect upon the environment. In turn, the continuation of this research relies upon the support of this same audience.

Second, the newsletter provides a means to extend contact beyond the immediate state boundaries. Essentially all of the problems of energy supply, demand and use have worldwide implications and are shared in common by other states and countries. Working to their solution requires the involvement and interaction of scientists and technologists at national and international levels.



Frank Derbyshire has recently joined the University of Kentucky as Director of the Center for Applied Energy Research. He has a Ph.D. in Chemical Engineering, and brings to the Center extensive experience in fuel research from both university and industry.

Third, the newsletter provides a vehicle by which individual researchers can describe their activities and express their opinions.

Turning to the present and the future, we are now on the run up to the millennium. This is an exciting and, to a degree, intimidating prospect. There is an aura of mystique and expectancy associated with the year 2000. The very wholeness of the number seems to confer a unique stature and significance.

What will the decade bring in terms of changes and developments in the pattern of energy use? It seems that there are at least two factors which are destined to exert a strong influence on the national energy situation over the next several years. These are the increasing emphasis

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Fluidized-Bed Combusion and Energy Production (continued)

bed tube bundles (see figure) are also an important feature of FBC in that they allow heat extraction from the combustor at three times the rate typical of those in pulverized coal combustors. Hence, the size of the heat exchangers needed for removing combustion heat in FBC units is significantly smaller than for other combustors.

Experience at the CAER and elsewhere in the world has shown that FBC is a tremendously flexible technique in terms of the types of fuels that can be effectively burned. For example, at the CAER we have burned fuels having sulfur contents as high as 12 percent with heating values as low as 4000 Btu/lb, in addition to coals having sulfur contents as low as 0.5 percent and heating values as high as 13,000 Btu/lb. In either case, and in all intermediate cases, 90 percent sulfur capture and 98 percent carbon burn-off are easily attained. Hence, emission regulations can be effectively satisfied with a large variety of fuels, offering to energy users and producers a flexibility which was previously not available.

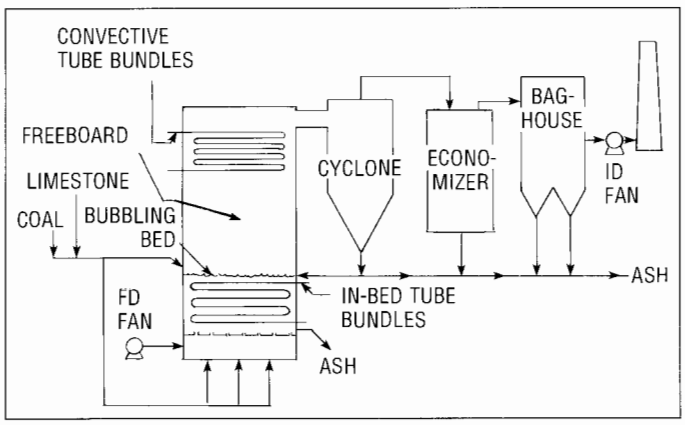

Diagram of typical fluidized-bed combusion system.

The CAER is addressing how to increase the efficiency of sulfur capture by the limestone injected into the combustor. Currently, the limestone utilization is near 40 percent, thereby leaving substantial calcium in the sorbent particles yet available for creating calcium sulfate. If the used limestone is made into concrete or applied as an agricultural liming agent this 40 percent utilization is near an optimal value. However, if it is to be disposed in a landfill, there is no overriding reason why the calcium should not be fully converted to the sulfate. An increase in the amount of sulfur in the particles will decrease the amount of limestone needed to attain 90 percent sulfur capture and, simultaneously, the amount that is subsequently to be disposed. In our view, it may be possible to use nearly 100 percent of the available calcium in limestone and to produce valuable by-products other than those mentioned. These research efforts will be described in future editions of this newsletter.

Other combustion topics to be presented in future editions of this newsletter include research that the CAER is performing in cooperation with EPRI, industrial and governmental agencies that address potential and new markets for coal and other solid fuels using FBC technology.

For example, liquid and gaseous fuels are used increasingly for power production in industrial and other small-scale combustors. According to the U.S. Department of Energy, the amount of energy used in these industrial and commercial boilers is nearly equivalent to the annual coal production of the United States. Data in the table provide a glimpse at sizes and markets for these combustors.

Estimated power requirements for small-scale combustors currently burning oil or gas.

Power (Quads)	Unit Size (Steam Production)
3.5	larger than 200,000 lb/hr
9.0	50,000 to 200,000 lb/hr
1.5	less than 50,000 lb/hr

* One Quad is 10^{15} Btu

Energy needs that develop into the 21st century may require the replacement of these liquid and gaseous fuels by other domestic U.S. energy resources. In this event, small-scale FBC is an extremely attractive technology that could help to maintain and even expand markets for coal. There are areas of development which have to be addressed for such expanded FBC utilization. Some of these, such as convenience of operation, ease of control, and aesthetics of construction will be addressed by the boiler and combustor industry. Other areas, such as emission control and safety have clearly been proven by existing technology. Aspects yet to be proven are the relative cost, maintenance and ash and sorbent handling. These latter three topics are related to advanced engineering designs and other improvements in fluidized-bed combustor components currently under scrutiny at the CAER.

John M. Stencel has a Ph.D. in Physics and has conducted research in fossil energy within university settings and with the U.S. Department of Energy, Pittsburgh Energy Technology Center. In 1985, Dr. Stencel joined the CAER where he is currently an Acting Associate Director of the Environmental and Materials Research Division.

Editorial Column (continued)

on environmental problems and the long-term stability of the supply of petroleum crude.

Acid deposition and global warming are the foremost environmental issues. Significant advances are being made in flue gas desulfurization and coal cleaning which are opening the way to the acceptable use of high-sulfur fuels, although at a cost. The phenomenon of global warming is a rather different problem. Although the reality of the "greenhouse" effect and its connection with carbon dioxide emissions are still the subject of much debate, the public perception is that a problem and its cause have already been defined. It also seems somewhat incongruous that the awareness of climatic change has grown to huge proportions in only a few short years when the period over which the changes have occurred, or could be reversed, spans generations. At this time, the situation calls neither for despondency nor wild optimism. Rather, it requires accurate evaluation, good judgement, and common sense.

On the subject of petroleum crude, over the last twenty years, there have been wide swings in the total energy consumption. Essentially, these swings have been accommodated by changes in import levels. Domestic crude production has been at best steady and for the last few years it has gradually been declining. The present trend is towards increasing import levels and increasing prices. If the trend continues, petroleum crude prices will continue to increase, following an upward movement in imports which began around 1984-85. An escalation in price will conceivably introduce incentives for the expanded use of indigenous energy resources and for the revival of synfuels technologies.

Of course, there is always the possibility that these tentative prognostications will be proved completely incorrect by the emergence of a revolutionary new energy technology, such as cold fusion might have been. Whatever the case, it promises to be an interesting time between now and 2001.

Energeia and **Highlights** are published on alternating months by the Center for Applied Energy Research (CAER) and the Institute for Mining and Minerals Research (IMMR), both of the University of Kentucky. The publications feature complementary aspects of mineral and energy resource development and environmentally related topics. Subscriptions are free and may be requested as follows: Judith M. Hower, Editor of **Energeia**, CAER, 3572 Iron Works Pike, University of Kentucky, Lexington, KY 40511-8433, (606) 257-0262; David Lazar, Editor of **Highlights**, IMMR, 233 Mining and Minerals Resources Bldg., University of Kentucky, Lexington, KY 40506, (606) 257-8636,

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