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Applications of Laser Diagnostics in Energy Conservation Research

R. A. Hutchinson

February 1985

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

APPLICATIONS OF LASER DIAGNOSTICS
IN ENERGY CONSERVATION RESEARCH

R. A. Hutchinson

February 1985

Prepared for
Energy Conversion and Utilization
Technologies Division
Office of Energy Systems Research
Conservation and Renewable Energy
U.S. Department of Energy
under Contract DE-AC06-76RLO-1830

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Richland, Washington 99352

PREFACE

This study was completed for the Division of Energy Conversion and Utilization Technologies (ECUT) in the Department of Energy. The division's mission is to identify and research long-range technology concepts for more efficient energy use. To meet its goals, the ECUT staff established a planning and systems analysis project that was responsible for conducting this study.

This report is one of a series of studies in support of the ECUT research planning effort. This volume examines potential research applications for a powerful new set of measurement techniques--laser diagnostics--in energy conversion systems. This and a companion volume, Capabilities of Laser Diagnostics for Combustion and Flowfields (PNL-5280), also fill a role in technology transfer, providing ideas and information to potential users of laser diagnostic techniques. Other documents in the series contain assessments of energy conservation technology areas, appraisal of research projects for support, and data reference sources. Publications from this project include the following:

Abarcas, R., and D. Johnson. 1984. ECUT Data Reference Series: Lightweight Materials for Ground Transportation. PNL-5192, Pacific Northwest Laboratory, Richland, Washington.

Abarcas, R., and D. Johnson. 1984. ECUT Data Reference Series: High-Temperature Materials for Advanced Heat Engines. PNL-5193, Pacific Northwest Laboratory, Richland, Washington.

Bomelburg, H. J. 1983. Efficiency Evaluation of Oxygen Enrichment in Energy Conversion Processes. PNL-4917, Pacific Northwest Laboratory, Richland, Washington.

Chockie, A., and D. Johnson. 1984. ECUT Data Reference Series: Boilers. PNL-5195, Pacific Northwest Laboratory, Richland, Washington.

Hane, G. 1983. Efficiency Evaluation of the DISC, DHC, and DI Diesel Engines. PNL-4568, Pacific Northwest Laboratory, Richland, Washington.

Hane, G., et al. 1983. A Preliminary Overview of Innovative Industrial Materials Processes. PNL-4505, Pacific Northwest Laboratory, Richland, Washington.

Hane, G., et al. 1984. A Review of Studies of Research Opportunities in Energy Conservation. PNL-4571, Pacific Northwest Laboratory, Richland, Washington.

- Hane, G. and D. Johnson. 1984. ECUT Data Reference Series: Otto Cycle Engines in Transportation. PNL-5191, Pacific Northwest Laboratory, Richland, Washington.
- Hopp, W., et al. 1981. An Overview of Energy Conservation Research Opportunities--Executive Summary. PNL-3944, Pacific Northwest Laboratory, Richland, Washington.
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- Hopp, W., et al. 1982. Identification of Energy Conservation Research Opportunities: A Review and Synthesis of the Literature. PNL-3966, Pacific Northwest Laboratory, Richland, Washington.
- Hutchinson, R. A. and H. J. Bomelburg. November 1984. Capabilities of Laser Diagnostics for Combustion and Flowfields. PNL-5280, Pacific Northwest Laboratory, Richland, Washington.
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- Young, J. K., E. A. Griffin, and J. A. Russell. November 1984. Opportunities for Energy Conservation Through Biotechnology. PNL-5295, Pacific Northwest Laboratory, Richland, Washington.
- Young, J., and D. Johnson. 1984. ECUT Data Reference Series: Ammonia Synthesis Energy Use and Capital Stock Information. PNL-5194, Pacific Northwest Laboratory, Richland, Washington.

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Project Manager

ACKNOWLEDGMENTS

The author extends his appreciation to the many people who contributed to bringing this report to completion. In particular, the authors would like to thank the staff at Sandia-Livermore's Combustion Research Facility, especially Bill Robinson, Mike Dyer, and Taz Bramlette, for their advice throughout this project. Russ Barnes and Tony Boiarski at Battelle Columbus, Dave Crosley at SRI International, Paul Hedman at BYU, and Ron Hanson and Mark Allen at Stanford were also very helpful at various stages of the work.

SUMMARY

During the past decade, intensive research and development has demonstrated the feasibility, checked the accuracy, and extended the sensitivity of laser diagnostics for combustion systems. Combinations of diagnostics can now provide in-situ, time-, and space-resolved measurements of temperature, velocity, and species concentration.

Although these tools are powerful, they also can be exceedingly difficult to use, and their application remains largely in the hands of specialized instrument developers rather than problem-oriented researchers. This report outlines a variety of applications for existing diagnostics that may interest both instrument developers and researchers in particular fields. A companion report^(a) briefly discusses the capabilities and limitations of many diagnostic tools, to aid researchers in developing further applications based on their own interests.

The two reports are the product of an effort to enhance the application of laser diagnostics to basic research problems involved in energy conversion systems. The work was carried out for the Energy Conversion and Utilization Technologies (ECUT) Division of the U.S. Department of Energy (DOE). ECUT, which has spearheaded the practical application of laser diagnostics to energy conversion through its investigations of internal combustion engines, engages in a variety of basic and applied research projects to develop knowledge about energy processes and materials of potential importance in multiple future applications. This generic focus is a vital element of the program's philosophy, as the economic leverage of multiple applications is extremely important in expensive work such as laser diagnostics measurements.

Because of this expense, and their difficulties and limitations, diagnostics applications must be carefully chosen. In addition, developing successful measurement strategies requires a great deal of planning. Laser diagnostic measurements, which are by nature specific and detailed, must be utilized by

(a) Hutchinson, R. A. and H. J. Bomelburg. November 1984. Capabilities of Laser Diagnostics for Combustion and Flowfields. PNL-5280, Pacific Northwest Laboratory, Richland, Washington.

models of the processes being examined to be most effective. Diagnostics can be viewed as tools for model development and verification. In addition, simple preliminary models must often be used in planning diagnostic experiments. The interactive nature of this relationship between modeling and laser diagnostic applications is a very important concept. This interaction is often difficult to achieve in an investigation, however, because of the differences in outlook between modelers and experimentalists.

The relationship between modeling and laser diagnostics was utilized in developing this report. Modeling research needs provided input, as did energy consumption data, diagnostics literature, and considerable contact with researchers. The search emphasized finding generic processes that needed modeling and could be examined with laser diagnostics. Further study of the concepts included consideration of a problem's scientific significance, its energy impact and the chances for success. The objective was to find a range of research applications, from basic (though system-oriented) research to immediately practical measurements. The possible results of a given piece of research helped determine its energy impact, although the implementation of findings was not rigorously analyzed.

The various research areas selected for this report do not include much combustion work, for two reasons. First, well-established and successful programs in combustion diagnostics already exist, including important ECUT investigations of internal combustion engines and pulse combustion. A comprehensive review of diagnostics use in coal combustion and conversion was recently published by Sandia National Laboratories-Livermore.^(a) Second, during the many years of developing laser diagnostics for combustion, it has become clear that much of the relevant critical development research is very basic, delving into the fundamentals of chemistry and physics. Although basic work is suggested in this report (in areas not being emphasized by others), applications of most interest to ECUT must have a certain basis in practicality, and a hope of improving understanding sufficiently to influence equipment design and, thus, energy consumption.

(a) Hardesty, D. R. 1984. "Advanced Diagnostics in Fossil Fuel Combustion Studies." Lecture at the Short Course on Advanced Diagnostics for Particle-Laden Flows, Sandia National Laboratories, Livermore, California.

The research applications discussed in this report cover a considerable range from basic to applied, and are presented in that order in Table S.1 and the main report. All of the basic work is in materials and surface science. New understandings of materials can very quickly be translated into design, as the engineers need not assimilate the full body of research knowledge. Thus, fundamental investigations in the areas of tribology and catalysis are attractive prospects for diagnostics work, with possibilities in corrosion and fouling as well. On a somewhat more applied level is the investigation of a generic mixing and reacting mechanism called a fluidized bed. This mechanism is already used in a tremendous range of processing and conversion devices, and as pollution regulations, use of dirty fuels, and need for precise control increase, its popularity will continue to rise. However, further understanding is necessary to optimize such a diverse set of applications. The third major area discussed in this report is cavitation. This phenomenon of bubble formation and collapse is more familiar to civil engineers and ship designers than those interested in energy conservation. Cavitation has proved to be very difficult to understand, and its presence in pumps and valve systems can severely limit the performance and reliability of these important components. Finally, the short-term diagnostics impacts on (and use in) industry are discussed. Diagnostics have been applied to important types of industrial conversion equipment but have yet to have significant impact. The role of the tool in American industry is therefore examined on a general level, emphasizing important needs for diagnostics.

Table S.1 gives a detailed listing of all the research suggestions provided in this report. The most important prospects for ECUT are the suggestions in tribology and catalysis. The most attractive non-surface-science investigation involves using diagnostics to determine generic details of fluidization behavior. However, such work should be coordinated with other government programs (e.g., the Fossil Energy Division) investigating fluidization. Many simpler investigations using laser doppler anemometry (LDA) and flow visualization are underway, which should, if effectively planned, provide valuable information on flow details in many critical energy conversion applications.

TABLE S.1. Summary of Possible Laser Diagnostic Applications

Research	Diagnostic(s) Used	Possible Result
<u>Tribology</u>		
In-situ monitoring of tribological processes	Surface Raman	Breakdown and failure mechanism models leading to design improvements and predictive maintenance
<u>Catalysis</u>		
Residence times of chemical intermediates on catalytic and noncatalytic surfaces	Surface Raman	Residence time models, perhaps leading to higher output rates
Active sites and species migration	Surface Raman	Information on role of active sites and migration in catalysis
Electrocatalysis-cathode reactions	Surface Raman	Process models for fuel cells
Fuel conversion and combustion catalysis	Surface Raman plus CARS, LIF, spontaneous Raman	Selective combustion and coal conversion catalysts
Catalyst deactivation	Surface Raman	Models and avoidance methods for major deactivation processes
<u>Corrosion and Fouling</u>		
Combustion chemistry of impurities	LIF, CARS, inverse RAMAN	Models of development of impurities that accelerate environmental attack
Deposition - particle sizes and local temperatures	Particle sizing, Raman	Models of particle dependence on time/temperature/pressure histories
Adhesion and retention	Raman, surface Raman, CARS	Models of deposition processes, including overall rates of deposit
Corrosion initiation	Surface Raman	Knowledge of changes in chemistry preceding rapid environmental attack
In-situ localized fouling measurements	LDA, particle sizing	Design data illuminating fouling dependence on local conditions
Anti-scaling additive chemistry	Raman, surface Raman	More effective anti-scalants
Corrosion fouling initiation	Surface Raman	Models of, and perhaps designs to avoid, initiation of corrosion fouling
<u>Fluidization</u>		
Entrainment and elutriation mechanics	LDA, particle sizing	Data on freeboard flows and heat transfer for use in fluidization modeling and reactor design
Freeboard reactions	CARS	Design input for role of freeboard reactions in a fluidized reactor
Bed flow mechanics and influence on heat transfer and mixing	LDA, LDA probes	Improved mixing and heat transfer models for designers

TABLE S.1. (contd)

<u>Research</u>	<u>Diagnostic(s) Used</u>	<u>Possible Result</u>
<u>Fluidization (contd)</u>		
Sulfur-Limestone reactions	LIF, Raman microprobe	Improved efficiency of sulfur make-up by sorbents in a variety of combustors
Fast fluidized bed flow characterization	LDA, LDA probe	Improved fast (circulating) fluidized bed designs
Pressurized fluidized bed flow characterization	LDA, LDA probe	Improved pressurized fluidized bed designs
<u>Cavitation</u>		
Scaling experiments with special modeling fluids	Holographic methods, LDA	Decreased uncertainty in scaling of cavitation experiments results
Boundary layer and viscous effects	Holographic methods, LDA	Models of viscous effects on cavitation
Vortex effects	Holographic methods, LDA	Models of effects of vortex flows on cavitation
Turbulence effects, including possible feedback loops	Holographic methods, LDA	Limited ground rules for design and operation
Cavitation nuclei	Holographic methods, particle sizing, LDA	Models of effect of nuclei size and distribution on cavitation
<u>Turbines</u>	LDA probe, holographic interferometry	Local flow measurements and models
<u>Plasma Processes and Chemical Vapor Deposition</u>	Vary	Improved control and efficiency in a variety of processes
<u>Probes and Fiber Optics</u>	--	Simplified diagnostics usable in industrial environments

Although laser diagnostics are primarily instruments for basic laboratory research, these tools (especially LDA) are beginning to be applied in more practical situations. However, diagnostics work may never be simple. It can require expertise in many very complex technologies that have not been customarily intermingled in the past, such as optics, high-speed computing, spectroscopy, electronics instrumentation, and laser optics. A successful measurement in a new environment can take years of preparation by experts. Therefore, this report focuses on relatively fundamental research efforts in new areas where results will have the greatest possible impact.

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1.0 INTRODUCTION

During the past decade, intensive research and development efforts have demonstrated the feasibility, checked the accuracy, and extended the sensitivity of laser diagnostics for combustion systems. Combinations of diagnostics are now capable of measuring temperature, velocity, and species concentration. Improvements in diagnostic systems are reported regularly, driven by developments in laser, detector, and computer technology and increased participation in the field.

Laser diagnostics are now mature enough to be truly useful in combustion research. Although the techniques can be both expensive and difficult, they are key to solving the critical problems that currently face combustion researchers. These problems center on the need for a deeper understanding of combustion mechanisms. Many related areas within the field of energy conversion demand in-situ measurement as well. A wide variety of both combustion and noncombustion measurements is needed to help build and validate process models that can be used in design and control of energy conversion systems. The lack of effective models is a primary limitation in the effort to promote energy conservation by increasing the efficiencies of conversion systems.

Successful applications of laser diagnostics can be expanded in two ways. The first would involve broadening the "user base" by introducing nonexperts (and even student researchers) to diagnostics capabilities so that they could consider using diagnostics in pursuing their own interests. This might be done by providing user-oriented information on the various techniques. Such an effort should heavily emphasize the strengths and limitations of, as well as the physical basis for, each method. Potential users could begin the process of applying a technique to a problem by consulting diagnosticians. The second approach to expanding applications would be to search specifically for applications, on the bases of important needs and current diagnostics capabilities. Such an approach would be especially useful in noncombustion areas where the tools have received little notice.

Pacific Northwest Laboratory (PNL)^(a) has contracted with the U.S. Department of Energy (DOE) to study the application of laser diagnostics to novel and nontraditional problems. The investigation was developed for the Energy Conversion and Utilization Technologies Division (ECUT), which conducts long-term research in processes and materials in order to strengthen the technology base for energy conservation. The program's trailblazing use of laser diagnostics to probe in-cylinder processes for internal combustion engines is an example of ECUT's pragmatic approach. In keeping with the pioneering nature of ECUT, PNL has focused on developing ideas for application. The results of the work are presented in two volumes. One volume, Capabilities of Laser Diagnostics for Combustion and Flowfields, provides background on the physical principles and inherent operational drawbacks of diagnostics (Hutchinson and Bomelburg 1984). Its purpose is to acquaint nonspecialists with these tools, enabling them to develop applications in their own areas of interest. This companion volume presents new or little-used diagnostics applications that have been collected or developed by PNL with the aid of numerous external advisors.

Many important problems in energy conversion might benefit from an improved understanding resulting from diagnostic tools; however, the costs and benefits of most such undertakings are unclear. The goals of this report are to provide perspective and to suggest further ideas for ECUT research programs. Because of the significant quantity of high-quality combustion work underway, spearheaded by the Combustion Research Facility at Sandia National Laboratories-Livermore, noncombustion and combustion-related topics are emphasized in this report, rather than further combustion work. Many of the difficulties encountered in making conventional combustion measurements, and the resulting need for in-situ work, also are found in other processes. The power of laser diagnostics in treating these other processes is a primary focus of this report.

This power has disadvantages. Laser diagnostics are generally difficult and expensive to use, and require precise direction in order to produce useful results. They should only be applied to a problem when there is no easier

(a) PNL is operated for the Department of Energy by Battelle Memorial Institute.

alternative method, and when there is a strong knowledge framework (often based on preliminary theoretical efforts) for planning the measurement effort and using the result. PNL's search for applications emphasized identifying generic processes that needed and deserved modeling that could be examined with laser diagnostics. The generic focus was derived from the philosophy of the ECUT program; because of the expense and difficulty of laser diagnostics research, the economic leverage of multiple applications is an important factor in selecting suitable research topics.

Another factor that proved to be important in developing and selecting ideas was the interrelationship of modeling and laser diagnostics. This intermingling can start very early, before diagnostics are used or even selected, because preliminary models of a phenomenon selected for study are often integral to planning the measurement effort. The preliminary models help guide day-to-day experiment planning and operational decisions toward producing specific results. These results, in turn, aid in constructing detailed models of the process. Further results validate those models for application to equipment design or control systems for new situations in which the same process occurs. Thus, interactions with modeling efforts essentially define the scope and justify the hardships of laser diagnostic measurement efforts. Unfortunately, close cooperation between modelers and experimentalists is difficult to achieve because they have different viewpoints. Interaction must be encouraged because models provide the connection between a given experiment, the experimental results, and their application. In fact, modeling needs provided many potential diagnostics applications described in this report.

The results of this report are meant to help focus the role of laser diagnostics in solving energy problems. Although the results will provide planning input to ECUT, they do not represent current specific ECUT program objectives. The topics in the report were developed through selective examination of the literature and discussions with researchers. Because energy consumption data were used to help guide the search, the topics cover a wide range of research areas, but are not intended to be complete. Other suggestions from researchers may prove to be just as important. The problems outlined here have

been selected, however, to have significant scientific content, high impact on energy consumption, a generic nature, and significant chances for successful resolution.

The various research topics are presented in an order determined by their character. The initial material, on surface and interface processes, is judged to be more basic, or at least less well-developed, than the topics in the following chapters. The surface work in Chapter 2, which relies predominantly on the in-situ capabilities of surface Raman diagnostics, is categorized into discussions on tribology, catalysis, and corrosion and deposition. Chapter 3 discusses the generic phenomenon of fluidization as used in a variety of combustors, reactors, and materials-handling situations. Chapter 4 covers cavitation, which occurs in bearings and in many kinds of equipment for handling liquids (e.g., pumps and valves). This equipment itself is used in many energy conversion systems. Chapter 5 focuses on industry, where the impact of laser diagnostics will eventually be determined. It reviews the use of laser diagnostics in important, universal industrial applications, such as boilers and heat exchangers, and examines the role of diagnostics in developing new industrial processes and in industrial process control.

2.0 SURFACE STUDIES

There is currently a boom in surface science, the discipline based on probing the details of interactions at interfaces between solids and other phases. This boom is generating almost explosive advances in knowledge. It is driven in part by the increasing realization that every interaction with a solid deals with its surface--and that this interaction is generally the limiting step in the process of interest. The other development is that new tools, singly and in combination, make precision probing of surfaces easier than ever. Important surface-sensitive tools are listed in Table 2.1. Some of these tools can even monitor reactions in-situ. One laser method, Raman spectroscopy, can provide in-situ information in a wide variety of applications. Raman may be most valuable when used as the in-situ component of a multi-instrument measurement effort, since different tools provide different types of information. Raman itself can be used in combination with a microscope to make measurements with extremely accurate (1 micron) spatial precision (Rosasco and Etz 1977).

Raman techniques could also potentially be used in developing and implementing advanced industrial processes--surface etching, vapor deposition, formation of high-temperature surface coatings, or electrochemical processes. Many of these areas could significantly affect energy conservation (e.g., high-temperature coatings). Industrial processes are briefly discussed later in this report; this chapter will focus on basic surface-related research in three areas: tribology, catalysis, and corrosion and deposition processes. These areas are discussed individually following a review of surface Raman capabilities. The discussions will emphasize the need for understanding in these areas and how various Raman and other laser diagnostic methods can help develop that understanding.

2.1 SURFACE RAMAN

Surface Raman diagnostics utilize the Raman light-scattering phenomenon. This phenomenon, which has been known for over 50 years and is well understood, is outlined in the companion report (Hutchinson and Bomelburg 1984). Raman

TABLE 2.1. Surface Analysis Tools

Method	Typical Pressure (torr)	Possible in Aqueous Solution	Min. Observable Film Thickness (Å)	Information Gained
Raman Spectroscopy	760	Yes	50	Compound identity
Infrared Spectroscopy	760	No	10	Compound identity
Ellipsometry	760	Yes	10	Film thickness
Differential Reflectometry	760	Yes	5	Compound identity
X-Ray Diffraction	760	No	500	Compound identity
Low Energy Electron Diffraction (LEED)	10^{-10}	No	Monolayer	Compound identity
Auger Electron Spectroscopy (AES)	10^{-9}	No	Monolayer	Elemental composition
Secondary Ion Mass Spectrometry (SIMS)	10^{-10}	No	Monolayer	Elemental composition
Electron Microprobe Analyzer	(10^{-5}) - (10^{-10})	No	200	Elemental composition
Scanning Electron Microscope	(10^{-4}) - (10^{-9})	No	50	Surface topography
Electron Spectroscopy for Chemical Analysis (ESCA)	$10(-^7)$ - $10(-^{10})$	No	5	Elemental composition, electronic states

Adapted from Thibreau et al. 1980.

scattering is the inelastic scattering of light with a frequency shift due to the light's interaction with the molecule. The frequency spectrum resulting from energy transfer to molecular vibration modes is characteristic of a particular molecule. Once the spectrum of a given molecule is known, it can be identified in-situ if a signal can be obtained that is free of overlapping spectra or other scattered light. Raman scattering from solids is stronger than that from gases, because of solids' increased density, but it is nevertheless quite weak. The primary focus of interest in this report is a relatively new development--the use of laser surface Raman tools to make in-situ measurements. These measurements require advanced detectors to detect Raman spectra from a single laser pulse, permitting time resolution on the order of nanoseconds. The measurements can also be as spatially precise as laser focusing will allow. Limiting the in-situ capability allows measurements with a microscope, as noted above.

There are several difficulties with making Raman measurements from solid surfaces. First, light interferences can be a major problem. Fluorescence at measurement frequencies is often far more serious than in gases. Moreover, it generally cannot be predicted because it results from uncharacterized impurities, the presence of which can only be determined with a "try and see" experiment. Second, signal extinction can be significant in many environments. Third, reference spectra must be measured or synthesized for all the solids, mixtures and phases involved. A thorough knowledge is required of the surface under study and all other species that may deposit or react with it. Such knowledge can often only be gained by extensive preliminary experimental work with general-purpose analytical techniques, such as Fourier transform infrared spectroscopy (FTIR). Fourth, the sensitivity of a given measurement and the resulting value of the data yielded are very difficult to predict. This sensitivity is dependent on the success of the experimental approach in reducing interferences and eliminating overlaps of spectra from the various materials under study. It is also important to note that Raman is only sensitive to the very thin layer close to a material's surface (between 100 microns and 0.01 microns thick). This thickness, for opaque materials, depends on the material absorption coefficient (Hamilton 1984). Finally, care must always be taken not to overheat or otherwise change the sample with the incident laser light (see Figure 2.1).

FIGURE 2.1. Surface Raman Configuration for Measurements of Metal Oxide

The most effective approach to actually performing a measurement involves three steps. First, a quick trial run is made to determine whether fluorescence and other interferences are going to be a problem and, if so, how they might be avoided. Second, a great deal of preparation takes place. All the relevant spectra must be found, and a measurement strategy must be developed to maximize signal quality and signal strength within time and budget constraints. Finally, if a suitable approach has emerged, the measurements are made. In general, crystalline and amorphous phases can yield Raman spectra, while metals do not exhibit Raman scattering. Surface Raman thus requires an interdisciplinary approach in deciding what is important to measure and deciding how to measure it. Knowledge of the surface is intimately related to developing an optical approach to measuring its properties. Fortunately, the first trial runs can (far more definitively than with gases) show when a measurement is impossible. This "negative inference" capability is an important and valuable attribute of surface Raman diagnostics.

Before the applications of surface Raman are discussed, the technique should be put in slightly better perspective. Other light-scattering interactions besides Raman can be used for surface diagnostics, just as they are used for the gas phase. Nonlinear interactions are being developed, including coherent anti-Stokes Raman spectroscopy (CARS) and the potentially more powerful second-order effects (Heinz, Tom, and Shen 1983). These occur only at surfaces and may be able to provide information about the very top layers of a solid, the most important layers for surface science. It is likely that the same rule that applies to gases will apply here, however--that the simplest techniques that can make the measurement should be used. Therefore, the measurements that can presently be made with Raman should be done even if more sophisticated techniques are developed.

2.2 TRIBOLOGY

Tribology is the study of friction, lubrication, and wear. Tribology generally supports other technologies rather than directly producing or affecting industrial products or output itself. Perhaps because of this, and the resulting difficulty of assessing its quantitative importance, tribology research has historically been underfunded. Much of the research has been government-sponsored in universities and laboratories, with a great deal of important work performed in England and Japan. Private research efforts are limited because the benefits from the work are typically spread across so many technologies and sectors that it is difficult for a company to derive full profits from those benefits.

2.2.1 In-Situ Monitoring

There are many promising research topics in the field of tribology. Perhaps the most critical need, however, is for results that can help guide engineers in selecting and maintaining tribological systems, particularly new systems that do not have operating histories. Ideally, such guidance would include verified models that could predict both the optimum time to change components (bearings, oil, etc.) and imminent failure. This goal is illusive because of the difficulty in relating factors that can be easily monitored (e.g., the lubricant) to changes in the materials undergoing wear over time.

To understand the mechanisms of wear and develop a data base sufficient for developing predictive models, experiments must be conducted both in-situ and in real time. Through control of system parameters and monitoring of the surfaces and the lubricant, changes can be noted and, at intervals, samples can be pulled out and examined in detail. In this way, complete processes that occur during wear can be studied and the breakdown and failure mechanisms modeled.

This in-situ examination of processes has never been effected,^(a) as it is dependent on both Raman and other technologies that are relatively recent developments. A significant effort has been underway to understand wear phenomena, because of the large costs from the maintenance, replacement, downtime, and energy utilization involved in tribological components of industrial applications. These studies focus on individual components of tribology, such as the lubricant, the bearing, or the mechanical engineering. Good data and models have been developed in each of these separate areas. However, a tribological system involves the synergistic interaction of all of the components of the system. Predictive models must take into account surface chemistry changes and modifications to the lubricants as they occur. This can only be done by monitoring surface and lubricant chemistry in-situ and in real time. Raman measurements of this sort would produce data that would help determine the initiating failure mechanisms. This knowledge, incorporated in predictive models, could be used to ascertain appropriate maintenance schedules, to minimize downtime, and to develop systems to maximize energy savings.

Surface Raman measurements are the crucial component of this new approach to tribology research, and will certainly impose restrictions on the systems that can be studied. The ability to do detailed characterizations of material surfaces and near-surface regions is also vital, and other advancements in this area (e.g., the methods listed in Table 2.1) must be utilized as well. Combining several types of measurements involves unique experimental capabilities. No specific suggestions of systems to examine will be made here, as development

(a) Discussion with M. T. Thomas, surface science researcher at PNL, May 1, 1984.

of these ideas is just beginning at PNL. It appears, however, that the in-situ, time-resolved measurements that surface Raman can provide may be the key to successful modeling of tribological systems.

2.2.2 Impacts

The impact of such advancements cannot readily be calculated. It has been broadly estimated that 1.3% of U.S. energy consumption can be saved through overall reduction of friction and wear in U.S. industry (Jost 1975). Perhaps 10% of this is due to reduced energy cost of replacement parts. More detailed estimates recently prepared for DOE by PNL indicate that although direct energy savings are probably considerably smaller than Jost's estimates, significant savings in replacement parts have been achieved, as well as productivity gains from reduced downtime.^(a) In-situ research will also provide information that may result in major improvements in the efficiency of specific tribological processes. The steel and utility industries are two areas where such breakthroughs might have significant impact. Reducing the energy used in metal-forming operations in the steel industry by 25% would save 0.3 quads of energy, or 0.04% of U.S. consumption. Steam turbines, which are used for over 80% of U.S. electricity production, might, save 0.19% of U.S. consumption (Hopp et al. 1981) through improving bearing and seal and tip clearance by 25%.

Savings of this breakthrough type can be added to those resulting from general industrial wear control. Equally important, yet unquantified, are the savings due to proper maintenance, which also provides an obvious energy benefit and an overall increase in productivity. This type of gain may be the strongest incentive for in-situ tribological research, as it is readily appreciated by industry.

2.3 CATALYSIS

A catalyst can be broadly defined as a substance that augments the rate of a chemical reaction without becoming consumed or altering the final thermodynamic equilibrium for the reaction. Catalysts are indispensable components

(a) Imhoff, C. H., et al. 1984. (Draft). A Review of Tribological Sinks in Six Major Industries. Pacific Northwest Laboratory, Richland, Washington.

of most chemical reactions--80% of all chemicals rely on catalysts during their synthesis (Pearce and Patterson 1981). The impact of a particular catalyst will depend not only on its properties but also on how well it is used--on the process design, environmental impact and choice of raw material. However, catalysis will only be viewed on a molecular level here, in the context of surface science. This new, scientific level of catalysis research is the appropriate aspect for government research. Companies have substantial incentive to develop processes and optimize existing catalysts. But for truly significant improvements, understanding is the key--and adventurous fundamental research is required.

Catalysts can be divided into two general groups, homogeneous and heterogeneous, depending on whether or not the reactants and products have the same phase as the catalyst. Homogeneous catalysts are necessary for 15% to 20% of chemicals production (Science 1983). Their main benefit is high product selectivity (ability to select the desired reaction from among many possible reactions). In addition, they are often relatively well understood, because the chemically active complexes they form are essentially all the same. Heterogeneous catalysts, which are usually implanted on a surface, have fewer atoms involved in the chemistry; however, there are several catalytically active environments, which are therefore poorly documented. The primary drawback to the homogeneous approach is the need to separate the often expensive catalyst from the reaction products, which can be quite difficult. One recent alternative has been to make homogeneous catalysts heterogeneous by bonding them to an inert substrate.

Catalysts have historically been discovered by experimental screening of large numbers of candidates. Only recently has catalysis become more of a science than an art, aided by new tools and computational abilities. A very important element in this change is the ability to watch a chemical reaction occur and resolve its progress over time. This must be accomplished without changing the reaction, an obvious impossibility if samples must be extracted and subjected to detailed tests. However, Raman measurements have this capability, and can be applied to both homogeneous and heterogeneous catalysts.

Because Raman gives information about molecular bonding and phases, it will be singularly useful in this area, despite the general difficulty of the measurements.

Because catalysis is an immense field, no specific reactions are suggested as candidates for Raman work. A recent publication (Chemical and Engineering News 1984) outlined the major research needs in catalysis. These have been used to develop the following short discussions on important research topics: studies of intermediates in catalyzed reactions, studies of a wide variety of important surface effects, work on carbon and combustion catalysis, work on catalyst deactivation (poisoning), and a small selection of innovative, but very basic, research ideas. Most of the topics are related to heterogeneous rather than homogeneous catalysis; however, there is no intrinsic impediment to using Raman methods in homogeneous systems, provided the systems are not too optically dense.

2.3.1 Chemical Intermediates

Raman measurements are an excellent means of gaining knowledge about intermediate species and reaction pathways because they can provide in-situ and time-resolved information. The residence times of intermediates chemisorbed on catalytic surfaces need to be measured. If the residence times can be shortened, the catalyst efficiency can be improved, resulting in higher process output rates or permitting use of a less-expensive catalyst. Examining the intermediate species to find their molecular structures and oxidation states is also very important. Such study could help discover which arrangements provide the highest possible selectivity, thus increasing the yield of desired products.

2.3.2 Surfaces

The chemistry at surfaces is dramatically different from that of the same reactants in solution or in a gas phase, because of the unsatisfied bonding capability of the atoms at the surface. Raman can help scientists "see" what molecular structures are on the surface, and that awareness can then be related

to the extensive knowledge of reactions in conventional settings. The technique probably will not match the power of methods now available for solid/vacuum interfaces, but it can contribute in the far more prevalent situation of solid/liquid interfaces. Some more specific topics of interest can be noted, as well. For example, probe laser beams can be focused to their diffraction limit so that good spatial resolution can be achieved. This technique might be used to study migration of chemisorbed species on surfaces (and the role of such migration in catalysis), or, more plausibly, simply to identify and characterize active sites. Light-absorbing dyes useful in photocatalysis (as well as in Raman experiments) could be investigated as well, along with their bonding to semiconductor surfaces. Finally, many questions about cathode reactions in electrocatalysis (as in fuel cells) also could be pursued.

2.3.3 Carbon and Combustion Catalysis

Because fossil fuels are pre-eminent in our energy economy, applications of catalysis to carbon conversion and combustion are extremely important. Catalysts are being developed for various fuel conversions. Perhaps the most desirable catalysts would selectively convert coal to specific desired end products. Such catalysts would probably be homogeneous, but Raman methods could nonetheless be useful. Raman can even be used to examine individual coal particles (with a microprobe) if necessary (Rosasco and Etz 1977). The burning of conventional or alternate fuels is also a target area for improved efficiency, as the voluminous combustion research literature demonstrates. Surface-catalyzed combustion is a good area for study; catalysis is already applied in wood stoves. The combustion process is poorly understood even without the addition of catalysis, but surface Raman and combustion diagnostics might provide important information on the profitable application of catalysis to combustion systems.

2.3.4 Deactivation

Deactivation of the catalyst is an important concern in combustion catalysis and most other heterogeneous catalysis. The mechanisms of this phenomenon, and therefore its avoidance, are generally unknown. Certain compounds, e.g., nickel and vanadium compounds (Chemical and Engineering News 1984), are known to cause deactivation by changing selectivities; alleviation

or mitigation of this occurrence would be tremendously important. Sulfur and nitrogen cause deactivation on other occasions; these mechanisms also need examination. Although Raman methods cannot detect metals, many of the suspect compounds can probably be measured; vanadates, for example, have been examined in various experiments for other reasons (Hamilton 1984).

2.3.5 Innovative Catalysts

Some new areas of catalysis research might benefit from Raman measurements, although Raman will hardly provide all the answers. One interesting question is whether the oxidative fixation of nitrogen (to make fertilizers, for instance) can be catalyzed. Fertilizer production presently consumes tremendous amounts of fossil fuel. A second, new area is electrocatalysis, where principles to guide catalyst development are unknown. A third, photocatalysis (light-assisted reactions), is similar; a familiar (though incompletely understood) example is photosynthesis. Biology also provides another budding area of research, in catalysis of artificial enzymes. Enzymes are very large molecules that appear to catalyze reactions as a function of their shape rather than just their chemistry. The molecular bond information that Raman provides may be useful here, although measurement difficulties may outweigh the benefits.

2.3.6 Impacts

As the topics outlined above demonstrate, the implementation of Raman techniques could be very important to fundamental catalyst research. The catalyst research is, in turn, important in meeting industry and U.S. goals. The chemicals industry needs to develop feedstock flexibility and increased energy and process efficiency. The U.S. needs to maintain supplies of domestic fuel and raw materials. Energy savings, which are difficult to evaluate for catalysis improvements in any general sense, are thus not the only benefit of research. PNL is presently studying the energy impacts of certain developments in catalysis, but results are not yet available. Dollar savings will clearly be significant, as perhaps 20% (Chemical and Engineering News 1984) of the GNP is produced through the use of catalysts. In the chemical industry alone, energy savings might easily amount to one quad per year (Hopp et al. 1981). Additional savings would accrue from the petroleum industry, which uses 60% of

all the catalysts produced, and from using catalysis for emissions control in a variety of industries (Hopp et al. 1981).

2.4 CORROSION AND FOULING

Surfaces in many types of energy conversion equipment are degraded by corrosion, fouling, slagging or erosion. Generally the components for such systems have been designed primarily on the basis of mechanical properties. In practice, however, component life is often controlled by the rate of environmental attack, particularly if high temperatures are involved (Stearns, Kohl, and Rosner 1983). Contributing factors are combustion products and certain impurities contained in the fluid stream. Component performance is often degraded considerably as well. These environmental problems can be expected to intensify in the future, because of continuing attempts to obtain higher efficiencies by using higher temperatures and pressures, and because of burning "dirty" fuels with higher levels of impurities (such as coal).

The examination of corrosion and fouling can be divided into two categories, each of which can benefit from the applications of Raman and other diagnostics. The first category includes processes leading to corrosive deposits in combustion systems. The second covers a wide variety of corrosion and fouling mechanisms that occur in noncombustion heat transfer systems. There are significant possibilities for using Raman techniques in corrosion and fouling studies. In-situ measurements are required for finding data concerning chemical reactions (species concentrations and rates). In-situ measurement may not be necessary in some cases, but Raman microprobes and other advanced techniques are still very important. There is often simply not enough existing knowledge to determine the necessity of in-situ work.

2.4.1 Combustion System Processes

Environmental attack in combustion systems involves synergistic combinations of high temperatures, air and fuel combustion products, and impurities that enter the system in the fuel or air. Impurities are a key factor controlling this attack (Stearns, Kohl, and Rosner 1983). For fuels with essentially no impurities (e.g., natural gas) attack is usually only simple oxidation, which seldom threatens modern alloys. Certain impurities, however, notably

alkali sulfates (from coals), can produce accelerated and even catastrophic attack. Beyond simple oxidation and degradation modes involving erosion (which is not discussed here) most accelerated attack involves some sort of material deposited on the surface. The material might be benign or act as a corrosive agent. The nature of deposits, the rate of deposition, and the chemistry that subsequently occurs are fundamental aspects of the environmental attack problem. All three can be studied in various ways with laser diagnostics, particularly with Raman techniques.

Combustion Chemistry of Impurities

Studies of combustion chemistry have been the primary reasons for the development of laser diagnostics. Studying combustion chemistry is so difficult that even the chemistry of clean flames is poorly understood, let alone the chemistry of various impurities. Laboratory flames seeded with various metal salts and inorganic compounds have received considerable attention, with and without the help of lasers. Some degree of understanding is developing, although little effort has been exerted in the study of specific seeding compositions relevant to environmental attack (Stearns, Kohl, and Rosner 1983).

However, a better understanding of clean flame chemistry is apparently not mandatory for impurity work to be successful, as provided by some very effective work on sulfur chemistry (Muller et al. 1979). Because of the tremendous impact of environmental attacks on combustion systems, such work is probably just as important as the most fundamental flame work. Unfortunately, the application of laser diagnostics in this area may have to wait, because concentrations are rather low for Raman methods, and laser-induced fluorescence (LIF) can as yet only be used on the simplest molecules (e.g., diatomic). Advanced, more sensitive methods being developed at Sandia, Los Alamos National Laboratories, and elsewhere may provide an approach, although their complexity makes their practical application less likely.

Deposition

The importance of deposition has been recognized for many years, but the increasing interest in using coal, coal-derived products, and impure liquid fuels has given it new emphasis. Deposition of alkali sulfates, for instance,

is a dynamic field of study (Rosner 1983). Deposition can be divided into two distinct phenomena: transport of species to the surface and the adhesion of those species. Because the various transport and adhesive mechanisms depend on the physical characteristics of the depositing species (e.g., size, stickiness, and shape), deposit formation is highly dependent on the chemical properties of the relevant species and surface (France et al. 1984).

Laser particle-sizing techniques could therefore be applied to help quantify the study of deposition, although the accuracy might be questionable because the particles would be far from perfect. Temperature is crucial to determining particle properties--their stickiness and composition, for example--and it could be measured with Raman. Thus it appears that laser diagnostics could provide important data about depositing species and perhaps could clarify how dependent relevant species properties are on their time/temperature/pressure histories.

Adhesion and Retention

In order to form a deposit, particles must be retained on the surface. Several basic removal mechanism modes may be involved, including aerodynamic lift, erosion, and elastic rebound. A variety of physical forces can cause particles to stick; Van der Waals forces, surface tension, chemical bonding, sintering, and ash adhesion are all important (France et al. 1984). Though deposition rates can be measured quite simply, understanding the role of these mechanisms in various circumstances requires precise knowledge of temperature and chemistry conditions over time at the surface and in the near-surface gas.

Here surface Raman can have significant impact. The need for time- and space-resolved chemical and temperature information is clear, and apparently such information is unobtainable through any other (nonoptical) technique (Sheshadri and Rosner 1984). A recent review (Marnier and Henslee 1984) notes, however, that there has been little optical work of any sort.

Deposition Control

Current methods for deposition control are not based on close knowledge of deposition processes, although controls could be more effectively applied if better process knowledge existed. Specifications used to control ash levels in

fuels could be more exactly based on firing conditions, as could fuel treatments used to remove contaminants. New surface arrangements designed to limit deposition could be made more effective, as could efforts to reduce surface temperatures in order to weaken adhesion mechanisms. The interdependencies of these mechanisms, once understood and modeled, could be used in conjunction with better combustion control to mitigate deposition quite effectively.

Corrosion

Corrosion can be viewed as the effective degradation or removal of material from a surface caused by chemical reaction with the environment. It occurs in solid, liquid, or gas phases. Solid-phase corrosion is generally very slow, and gas-phase oxidation is often not a problem, at least not with modern alloys. Liquid-phase attack, however, is extremely troublesome (France et al. 1984). Corrosion "windows" can be established for each corrosive agent between its melting and boiling points. Thus, metal temperatures and fuel impurities are the two key factors in high-temperature component attack. The first step in such an attack is deposition of the liquid. The alkali sulfates mentioned earlier have many compounds that are liquid in relevant temperature ranges; this characteristic and their relatively high concentrations make them the primary coal-derived corrosive agents. Many other agents are present for deposit formation, however, including vanadium salts often found in oils. Thus, deposition and corrosion act together, often with additional help from erosion, to attack surfaces.

Initiation

The process of corrosion, especially hot corrosion at very high temperatures (as in gas turbines), involves an initiation stage, when corrosion is slow, and a propagation stage, when it is very fast. During the initiation stage, the surface is being fundamentally altered, making it susceptible to rapid attack. Surface Raman is an excellent tool for studying this stage, as it can follow the microscopic chemistry occurring at the surface. An important example is work tracing the effect of vanadates on stabilized zirconium-oxide turbine blade coatings (Hamilton 1984). Recent results show exactly how the phase stability of the coating is broken down by the vanadate over time. Substantial preliminary work has also been completed on oxides that form on

steels and on oxides used as protective coatings (Farrow, Mattern and Nagelberg 1980; Benner and Nagelberg 1981; Farrow and Nagelberg 1980; Tjong 1983). Discovering what occurs during this initiation stage is vital to solving many potentially catastrophic corrosion problems, and the time-resolved species and temperature measurement capabilities of surface Raman make it a powerful tool in the solution effort. The early stages of lower-temperature deposition corrosion processes are also research areas amenable to Raman measurements.

Corrosion Control

Corrosion control involves the same basic methods as those for deposition control, with the addition of corrosion-resistant alloys and coatings (France et al. 1984). This similarity is due to the dependency of corrosion on the deposition of corrosive agents. Surface diagnostics will be tremendously useful in the development of new coatings and alloys through the intimate knowledge they can provide of corrosion initiation mechanisms. Once more, however, the success of such efforts will involve integrating other surface-sensitive instruments to gain complementary atomic data along with Raman's in-situ chemical information.

2.4.2 Heat Transfer System Processes

As noted in the previous section, the occurrence of oxidation without deposition is seldom a problem with high-quality materials. It can be serious on iron or carbon steel surfaces, however, and surface Raman methods are a good choice for examining the development of the oxides. Deposition is much more of an unknown, and is more difficult to measure. Discussion here, therefore, centers on several different kinds of fouling. Recent reviews (Epstein 1978) have developed six categories for fouling, several of which frequently coexist: scaling, particulate fouling, chemical-reaction fouling, corrosion fouling, biofouling and freezing-fouling. The latter two categories are not covered here, as they are probably unsuited to Raman studies.

A general point about the need for better measurement of fouling phenomena should be made before individual categories are discussed. Fouling is currently monitored, in experiments as well as in practice, by several methods: measuring changes in heat transfer rates, testing the fluid composition, using

radioactive tracers, checking for pressure drop changes, performing visual examinations, or conducting electrolytic or chemical tests. These methods cannot provide information about many possible deposition phenomena. An example (usually treated separately from deposition) is re-entrainment. There is, of course, a conceptual problem of how a particle can actually be deposited if it can re-entrain. The answer probably lies in the intermittency of re-entrainment due to random turbulent bursts. Only very recent models, of the few that have been developed for re-entrainment of foulants, take notice of turbulence, for the necessary data are virtually nonexistent. Standard monitoring methods do not give such data. The need for localized measurements is also obvious in another dilemma based on velocity--that fouling decreases as velocity increases. The answer might seem obvious, but it is complicated when fouling is dependent on local temperature gradients (e.g., thermophoresis), because velocity changes temperatures as well. Fouling is often highly dependent on oxygen concentration, and further complications are created by the effects of velocity and temperature on oxygen transfer. Detailed measurements are clearly needed to resolve such difficulties.

Scaling

Scaling is the precipitation of inverse solubility salts onto heated transfer surfaces; it is most severe under boiling conditions. It generally involves a delay time for initial nucleation of the foulant. This phase change can possibly be watched in some cases by Raman methods. The change depends very closely on the degree of supersaturation of the solution, and is therefore dependent on concentration and temperature simultaneously. These quantities also can be measured by Raman techniques. The effects of other factors that are apparently important, like surface roughness and air bubbles, can also be examined.

Present techniques to prevent scale include using additives to decrease the material available to form scale and reducing nucleation sites on the surface. Both methods can probably be investigated in-situ with Raman techniques.

Particulate Fouling

Particulate fouling is the accumulation on a heat transfer surface of particles originally suspended in a fluid. The fluid mechanics of the problem have long been studied but must still be treated by semi-empirical methods. Other research efforts focus on the surface forces involved, despite the drawback that these forces only apply until the surface has received its first thin layer of deposit. Electrophoresis and thermophoresis--the motion of particles under the influence of electric fields and thermal gradients, respectively--are also involved in particulate fouling.

The uses of laser diagnostics in this area are similar to those described in the section on combustion deposition. Particle measurements of limited accuracy are possible. Particle properties, which are especially useful in determining whether a particle will adhere to the surface or re-entrain, may also be determined by combinations of temperature, concentration and perhaps microscopic measurements.

Chemical Reaction Fouling

Chemical reaction fouling deposits are formed by chemical reactions at the heat transfer surface in which the surface itself is not a reactant. The study of this type of fouling is excellent for surface Raman investigation if the deposits are not chemically complex; unfortunately, major examples of such fouling are polymerization, and the cracking and coking of hydrocarbons. The reactions are often catalyzed by sulfur or metallic compounds present in only trace compositions. Prevention generally involves avoiding feed stream contact with air or oxygen and careful removal of sulfur. Chemical understanding of this phenomenon is definitely needed; it is not clear, however, whether effective Raman measurement schemes could be developed.

Corrosion Fouling

In corrosion fouling, the heat transfer surface itself reacts to produce corrosion products. These products foul the surface and may foster the attachment of other fouling materials. A great deal of research has been done on corrosion metal loss, but little of it has examined how corrosion promotes fouling. Corrosion is stimulated by saline fluids and high oxygen content (in

water). Temperature is important because of the electrochemical nature of corrosion, and the oxygen transport is also significant. Because corrosion control generally involves inhibitors that may actually promote fouling (Epstein 1978), an integrated research approach is clearly needed. This could be provided by in-situ measurement, at some cost in complexity. For instance, Raman is a good corrosion probe, particularly for the initial stages (Thibeau et al. 1980).

2.4.3 Impacts

Environmental attack in combustion and heat transfer systems is a topic that defies generalization. The effects of corrosion and fouling on energy consumption cannot really be calculated, for two reasons. First, systems that generally suffer environmental attack are designed to meet performance specifications after they are fouled. They may be oversized by as much as 30%. Thus, the present systems are not representative of the systems that could be designed if fouling were well understood, and the energy impact is therefore unknown.

The impact of corrosion and fouling is best evaluated in terms of economics. This allows many highly significant nonenergy impacts to be assessed in understandable terms. There is no doubt that fouling and corrosion are expensive. In industrial nations they may siphon off 3% to 4% of the gross national product (Lister 1979). The costs can be placed in four categories: 1) capital costs due to oversizing and related installation costs; 2) costs for additional fuel due to extra pumping requirements, lower efficiency, and losses from heat exchangers, which are increasing rapidly as prices climb and more waste heat is recovered; 3) maintenance costs, which include substantial expenditures for chemicals and additives used to defend against the environmental attack; and 4) costs for downtime due to corrosion and fouling.

Various studies have illustrated the magnitude of these costs. A British researcher (Pritchard 1979) surveyed industrial fouling in that country and concluded that yearly expenditures in 1977 were (converted to dollars) \$300 million on capital costs, \$180 million on fuel, \$240 million on maintenance, and \$150-300 million on downtime. After obtaining a rough total of \$900 million, he consulted with British industrialists and others who told him that

it probably should actually be \$1.5 billion per year. Roughly extrapolated to the American economy and current dollars, this is about \$13 billion per year. An American analyst studying corrosion and fouling in the power industry (Lister 1979), noted that the power industry accounted for about 9% of the total U.S. expenditure on fouling and corrosion, or \$1.2 billion. He also observed that half of all power industry maintenance costs were due to such environmental attack.

More detailed studies of costs can probably indicate important areas for improvements. A detailed study by Exxon of four major processes in a typical petroleum refinery showed that \$428 million in fuel costs, \$872 million in downtime and other lost capacity, and \$15.4 million in maintenance were accrued in one year in the U.S. refining industry (Van Nostrand et al. 1979). Most of the cost could be attributed to crude oil distillation. Refiners are aware of this and have pursued engineering solutions for many years. It appears, however, that more complete understanding is necessary.

3.0 FLUIDIZATION

Fluidization involves the suspension of particles in a flow of liquid or gas. Fluidized beds provide excellent mixing of solids and effective transport between the fluid and solid phases. In the past two decades, fluidization technology and fluidized-bed reactor operations have been widely applied throughout the process industries. The technology has been used, not only in the chemical and petroleum industries, but also in the coal combustion and conversion industry, in metal extraction and processing, in environmental and drying applications, and in other fields requiring techniques for handling solids. These applications have been derived largely from research and development on commercial and semi-commercial fluidized beds. Perhaps the best known and most important applications, from an energy conversion standpoint, are the fluidized-bed catalytic crackers used in the petroleum refining industry and the fluidized-bed combustors used in the coal and solid fuels conversion industry.

Despite fluidization's extensive application, designing fluidized reactors is not possible without resorting to wholesale empiricism and trial-and-error methods. For a new, large system this is an expensive proposition. Although fluidization has been the focus of a tremendous amount of productive work in the past few decades, design and scale-up of commercial units from bench scale data continually highlight shortcomings in understanding. In both combustors and reactors, correlations probably do not account for important physical phenomena that become critical in large-scale operations. In this sense the difficulties are similar to those for conventional coal combustion research. But because they include non-reacting situations as well as combustion and other reactions, fluidized beds comprise a more generic research area. Basic physical problems related to the hydrodynamics of solids and fluids are present in fluidized beds, even before the problems of multi-phase reaction chemistry come into play.

Another complicating factor involves the different modes of fluidization, from aggregative bubbling and mixing to highly dilute, turbulent, high-velocity flow with very fine particles. The latter is called "fast fluidization."

Different modes suit various applications. There is a trend toward fast fluidization, at least for combustion applications, which will be discussed shortly. First, however, several basic aspects of fluidized beds with immediate appeal for laser diagnostics study are examined. Then the needs of promising concepts such as fast fluidization and pressurized beds are discussed.

3.1 FREEBOARD REACTIONS, ENTRAINMENT, AND ELUTRIATION

The freeboard is the region above a fluidized bed that is primarily fluid. It contains fast-moving particles, spewed up by the bed, that may be carried along with a fluid flow (entrained) and, if fast or light enough, may leave the reactor altogether (be elutriated). Although the freeboard's interactions with the bed itself are important, they are generally ignored in modeling efforts (Levy and Lockwood 1983). The heterogeneous (two-phase) and fluid phase reactions occurring in the freeboard are also significant (DeLasa and Grace 1979). Finally, elutriation and its effects on system efficiency can be very important indeed. Loss of carbon from fluidized-bed combustors via elutriation is the primary cause of carbon conversion inefficiency, even when expensive cyclone systems are used to remove carbon and other particulates (Arena, D'Amore, and Massimilla 1983). Carryover of catalysts requires expensive collection mechanisms in a variety of fluidized reactor applications. Elutriation correlations are poor at present (Wen and Chen 1982; Matsen 1979; George and Grace 1981). Freeboard flows and reactions are candidates for characterization using laser diagnostics, since the solids are generally dilute enough to permit optical probing. The large-scale turbulence involved can bend the laser light, however, making many types of measurements difficult.

One important prospect for diagnostics work is the examination of gas and fluid velocities in the freeboard with the use of laser Doppler anemometry (LDA). Only detailed information about local gas and particle velocity fields can give sufficient insight into the anomalies of the elutriation phenomenon. Preliminary efforts (Levy and Lockwood 1983) have demonstrated the technique. Early results have shown that because of the high turbulence from bubble

eruptions in the bed and high gas velocities near the wall, simple calculations based on time-averaged flow velocities and uniformity between regions of the bed are highly inaccurate.

Diagnostics generally serve best when used to develop and validate models, and in this application there is an important opportunity to do just that. For combustion freeboards, for example, conventional pulverized coal models might be adapted, with special considerations for the extra turbulence and the boundary condition at the bed. Because of the different modes of fluidization mentioned above, there is a tremendous amount of work available in this area. In addition to the work conducted by Levy and Lockwood (based at Israel's Technion and at Imperial College, respectively), related cold-flow work has begun at Stanford (Kale and Eaton 1984) on the effects of various design choices (such as diffuser shape and bed height) on flow in fluidized bed freeboards. If properly planned, such work could be both exceedingly useful and generic in application.

Scientists at Sandia National Laboratories in Livermore have suggested that freeboard reactions can be studied with combustion diagnostics such as CARS (Hardesty 1984). This, too, is an interesting opportunity within the field of fluidized-bed combustion. Such an effort would not be complete without companion in-bed work, however, requiring probes and perhaps X-ray tomography, and certainly a very sophisticated experimental apparatus.

There are possibilities for other work related to freeboard flows. For instance, the particles that are elutriated must be collected by cyclones for recycling. The carbon loss figures discussed earlier (with reference to combustion) assume the presence of typical current cyclones. Cyclones are widely applied in a tremendous range of sizes, and are critical components in fluidized systems. Better understanding of freeboard mechanics and elutriation should produce new fluidized-bed designs that reduce cyclone loads. In addition, the measurement methodology for particle and gas velocity developed for the freeboard could be used to investigate the details of cyclone flow--and perhaps improve cyclone performance as well.

A second research possibility would involve detailing the flow around heat exchange tubes in the freeboard in order to properly model the effect of

particle impingement and flow fluctuations on freeboard heat transfer. While such heat transfer is of smaller magnitude (in combustion) than in-bed heat transfer, it is important in reactor control for both combustion and noncombustion applications (Biyikli, Tuzla, and Chen 1983; George and Grace 1982). The in-bed heat transfer and other in-bed diagnostic possibilities are discussed below.

3.2 BED HEAT TRANSFER AND MIXING

In-bed laser diagnostics are not feasible in practical fluidized-bed reactors or in realistic models of these reactors (except with the use of probes). It is worthwhile to examine important bed processes, however, to see whether measurements to help clarify them might be made on some special apparatus. One of the primary sources of information about bed properties has been high-speed movies of thin (two-dimensional) beds. These have provided only a simple base of information.

Current wisdom on in-bed heat transfers, both between particles and fluid and between the fluid and tubes or walls, is that they depend on interstitial turbulence and fluid properties and mass transport across particle boundary layers. Macroscopic measurements indicate that a change in gas velocity most directly affects heat transfer (of all the independent variables). The effects of particle shape and size are largely unknown. Work at the Aerospace Corporation (Bernard, Wang, and Lee 1981) has shown that LDA measurements in a fluidized bed of transparent particles are possible when the fluid used is a liquid index-matched to the (glass) particles. Early measurements showed that in-bed turbulence was essentially isotropic (independent of direction), at least for the cold flows tested. A more sophisticated approach might provide enough details of particle flows and their dependencies on particle size and shape distributions to formulate a good detailed model, at least for solid-liquid fluidization. LDA work has been done in a fluidized bed using probes.^(a) Although probes have been noted to thoroughly disrupt many types of fluidized beds, such work might also provide data on in-bed mixing.

(a) A. Boiarski, Battelle Columbus Laboratories.

Information on solids mixing in fluidized beds is insufficient for many applications. Such information is especially important for fast fluidized beds in combustion applications. Digital image processing may provide a suitable extension of the classic method of high-speed movies and painstaking hand measurements. Other completely different methodologies are possible as well.

One of the major advantages of fluidized-bed combustion, as well as a major source of engineering design difficulty, is the use of additional limestone or dolomite as an extra solid in a fluidized bed. Through complex reaction mechanisms that are poorly understood, sulfur in the fuel can combine with lime in solid form, thus eliminating a major source of sulfur dioxide (and acid rain) in the atmosphere. The details of the reaction, its rate, and the effects of various design parameters, if known, would result in more effective and cheaper control of a major pollutant. Other applications of lime as a sulfur sorbent would be aided as well. Background work using Raman microscopy is currently proceeding at Battelle Columbus Laboratories. Eventually, LIF can probably provide the fundamental chemical data that are needed.

Perhaps the most important point in this discussion is that fluidized bed measurements need not be made in an actual operating reactor to provide critical and ground-breaking new information. Indeed, even when this is possible, as in freeboard measurements, there is a strong argument for doing substantial work with laser diagnostics in a simple lab situation first. Insight can be developed gradually by isolating the poorly understood facets (such as those suitable for laser diagnostics discussed in this report) of the fluidization process and probing each facet with care and diligence.

3.3 TRENDS: FAST FLUIDIZATION AND PRESSURIZED FLUIDIZATION

The fluidized beds of the future will not all be based on the standard bubbling bed developed by the chemical industry several decades ago. Some will depend on fast fluidization, a technique in which fine particulates and high gas velocities are used to form an entrained but dense suspension. The probable applications are in combustion, catalytic cracking, and coal gasification. A further refinement is to operate a bed at high pressure, a technique that has received the most attention in combustion applications because of its

enhancement of heat transfer and the possibilities it creates for combined power generation cycles. These developments may have an influence on research strategies, including those based on laser diagnostic efforts. These potential impacts are discussed below.

Fast fluidized beds appear to retain all the qualities that first brought bubbling beds into use (Yerushalmi and Squires 1977): temperatures are basically uniform throughout a bed, newly introduced solid or fluid is very rapidly brought to bed temperature, and heat transfer to walls and immersed surfaces is extremely high. However, the fast beds have additional qualities with considerable bearing on many applications. They have much higher processing rates, so smaller, less-expensive reactors are possible. Contact between gas and solid appears to be far more thorough than in an ordinary bed. Cohesive (sticky) solids probably can be handled more easily in a fast bed. A simpler particulate flow condition, called "plugflow," might be attainable in a fast bed, with concomitant process and control advantages. Finally, initial experience has shown that fast beds may well be easier to scale up than bubbling beds.

These advantages seem to indicate that fast beds will be a viable option in the future, particularly for combustion reactors. The high velocities do cause extensive elutriation and a need for recirculating particles. The highly turbulent flow and fine particles make fluidization phenomena exceedingly difficult to understand. This environment may be probed successfully with LDA, especially since fast or turbulent fluidization can be obtained for various combinations of particle size, loading, and gas velocity. Very little data have been reported on mass transfer, heat transfer, or chemical reaction in such beds. The proper approach with laser diagnostics would be to examine generic phenomena as described above; freeboard work with LDA is the obvious starting point, but fast fluidization offers a variety of opportunities.

Pressurized fluidization is generally thought of for combustion, although chemical processes often operate at high pressures as well, particularly those for methanation of high-quality synthetic gas. Few data are available on high-pressure fluidization, particularly in realistically sized units. Even cold flow data are sparse. Heat transfer is significantly enhanced, as would be

expected from elementary theory. High pressure may not affect basic bed characteristics like bed expansion and bed density, but operation is smoother, and therefore easier to control, than in atmospheric-pressure beds (Canada and McLaughlin 1978). Finally, bed entrainment increases significantly at high pressures. It may be even more of a problem than in atmospheric beds because of the need for such items as high-pressure cyclones; this is unclear from present references. Data on entrainment might be obtainable from laser diagnostic study, although the beds require windows because of their pressurization that can severely affect optical measurement.

3.4 IMPACTS

Perhaps the clearest illustration of the influence of fluidization technology on the energy scene is provided by fluidized bed boilers (FBB). Since 1980, FBBs have captured a rapidly increasing percentage of the coal-fired boiler market, growing from 5% in 1980 to 20% in 1981 (Schroppe and Gamble 1982). Although the technology is still being refined and its physical mechanisms are only poorly understood, the attractive features of FBB have persuaded many buyers. FBB units have several advantages over conventionally-fired units (Siman-Tov and Jones 1980):

- no need for flue gas scrubbers
- reduced NO_x emissions
- ability to burn many fuels, including all ranks of coal
- reduced steam tube heat transfer area, due to high heat transfer
- little ash agglomeration or slagging, due to lower operating temperatures
- no need for coal pulverizing systems
- generation of dry, easily handled, solid waste rather than wet desulfurization sludge.

Industrial boilers consumed over 50 million short tons of coal in 1980, or about 1.3 quads of energy. FBB technology is expected eventually to be a mainstay of the utility industry as well, according to published Electric Power

Research Institute predictions (Yeager 1982). In both sectors, FBBs are energy efficient and are a very effective multi-fuel device. The tremendous potential efficiencies of pressurized FBBs (40.6%) (Davidson et al. 1983) are a more distant enticement. Better understanding of the basic principles of fluidization would certainly be helpful in optimizing these savings. The Fossil Energy Division of DOE is actively working on pressurized beds at present for precisely these reasons.

A second major application of fluidization is in fluidized-bed catalytic crackers in the petroleum industry. They are present in almost every U.S. refinery; hence, they are a mainstay of an industry that is the second largest energy-consuming industrial process. A rough estimate of energy consumption within the refining process, based on 1980 U.S. oil consumption data, is 0.44 quads, of which 1/4 or 0.11 quads are not recovered for use in subsequent processes. More efficient crackers would be smaller and cheaper to build, and would require less heat, electricity, and maintenance. These advantages are certainly realized by the industry, but the basic research necessary has not been performed because of its long-term nature--and the fact that the results would benefit the competition as well.

Fluidized beds are also used in other applications, many of which are not as firmly established as the two major examples given here. These drying, mixing, and other applications for solids transport could have significant effects on many industrial processes by decreasing costs and increasing energy efficiency and productivity. Such generic technologies are exceedingly valuable, once understood, although impacts are hard to determine at this stage.

4.0 CAVITATION

Cavitation is generally defined as the formation of the vapor phase in a liquid by lowering its hydrodynamic pressure. Cavitation is a design consideration for a wide variety of devices that handle liquids. It affects the performance of these devices in a number of ways--increased drag on ships, thrust limitations on propulsion systems, decreased power output and efficiency of turbines, and head and efficiency drop in pumps, to name a few. Cavitation can cause noise and vibration in valves and turbomachinery, and introduces the possibility of erosion as well. This erosion can occasionally induce disastrous failures very quickly; more often it involves a gradual but significant performance decline. In certain situations, cavitation can even be useful--ultrasonic cavitation cleans false teeth, for instance (Arndt 1981). Cavitation is generally a very pervasive problem in energy systems, and is currently thought to be more complicated than was believed 20 years ago.

Cavitation directly involves two major fields: fluid mechanics of the liquid flow, and acoustics of the shock and sound wave emission of the rapid bubble growth and collapse. It is this shock that can cause damage to flow machinery. The exact damage mechanisms are poorly understood, however, and involve still other fields, such as materials science and surface science. Cavitation can be detected by the loss of performance it may eventually cause, by its acoustic emission, and by optical methods. Laser holographic techniques have proved to be especially useful in experimental studies because of their resolution in three dimensions and their great recording speed (Ebeling 1978; Deason and Fincke 1981). Cavitation erosion, the mechanism by which cavitation damage is actually inflicted, is not discussed here because erosion is not currently measurable with laser diagnostics. Erosion itself is often classed as a tribological problem.

Lasers can actually be used to induce cavitation by focusing the beam into the bulk of the liquid (Lauterborn and Vogel 1984). The laser power, when focused, can trigger localized breakdown of the liquid, and the resulting plasma quickly forms a bubble. Such laser-induced bubbles can be formed free of mechanical disturbances at a precise point in the liquid and can be very

useful for studying bubble dynamics and other cavitation-related phenomena. Discussion here will center on more conventional laser diagnostics, however. Most of the topics here derive from a recent review paper on fluid mechanical aspects of cavitation (Arndt 1981).

From an engineering-design standpoint there are two basic questions to be answered about cavitation: Will it occur? If it does, will the design still function acceptably? Often, system or economic considerations force operation with cavitation; it is then necessary to understand the effects of cavitation on normal operating loads. Experimentation must still be heavily relied upon in developing fluid machinery. Because fluid machinery is often large and involves a variety of fluids, complete modeling must include factors related to scale-up, as well as extrapolation to fluids besides water, in which tests are easiest to carry out. The equipment cannot be tested for its full lifetime in all possible operating conditions, however, so in order to predict cavitation inception or performance, the physics of the phenomenon must be sufficiently well understood to model it properly. Lifetimes and maintenance schedules must at least be estimated. Several factors influencing cavitation inception are discussed below in the context of using laser diagnostics to provide high-quality data.

4.1 CAVITATION SCALING

Basic cavitation scaling laws use the cavitation index, a simple relation involving fluid velocity, density, pressure, and vapor pressure. Using this index depends on the assumption of an inviscid fluid and of cavitation occurring when the pressure in the flow field equals the vapor pressure at the bulk temperature. Granted these assumptions, the cavitation index is the primary scaling factor for cavitation inception and all other hydrodynamic parameters involving cavitating flow. This simple scaling has severe limitations, however. Most experimental data on cavitation are based on laboratory data covering a narrow range of independent variables. Thus, few data are available for judging the correlation between a laboratory version of a particular piece of flow machinery and the full-scale version.

The many ways in which simple cavitation index scaling can be wrong are barely delineated, far less understood. Several areas of variance that can be studied with laser diagnostics are outlined in the next few paragraphs. The limited range of experimental data available might also be addressed with diagnostics. Innovative transparent modeling fluids could be used instead of water in a few selected experiments to broaden the data base. Optical methods can work quite well in such fluids, as they are not dependent on its transport properties (as are hot wire probes, for example) to make a measurement.

4.2 VISCOUS EFFECTS

Boundary layer development and the phenomena of separation and transition can have a marked effect on cavitation. Furthermore, as they violate the cavitation index assumption of a perfect fluid, they represent a complicating factor in cavitation prediction. They have only been studied in detail in the past ten years, however. These very sensitive areas in the fluid flow are difficult to characterize even in stable wind tunnels, much less under cavitation conditions. The flow perturbations induced by probes may distort cavitation results, thus this area may require LDA and holographic study. Vortical motion, another viscous effect (for the purposes of this report), is common in many kinds of fluid machinery, including propellers, pump clearance passages, and secondary flows in corners. The pressure field in a vortex is highly variable; cavitation often occurs in the smallest vortices. Probe measurements and other stream disturbances can severely affect such vortices, so sophisticated measurement methods like LDA are probably necessary for detailed study of this phenomenon.

4.3 CAVITATION AND TURBULENCE

Turbulence is highly non-ideal flow; like boundary layer and vortical flows it is not tractable under current simple scaling laws. Laboratory estimates do not currently provide reasonable estimates of critical cavitation indices in fluid machinery operating under turbulent conditions. Indeed, because of the wide pressure excursions of turbulent flow, there is at present no limit on the index beyond which cavitation can be clearly ruled out. There

may even be feedback mechanisms between turbulence and cavitation, wherein the turbulence produces a burst of localized cavitation that increases the turbulence of the main flow, thereby exacerbating the cavitation. Almost nothing is known about such interactions, however, and very little data exist on turbulent pressure fields. These interactions are obvious (though very difficult) candidates for diagnostic measurement. This topic is examined in greater detail in a forthcoming PNL report on turbulence and its effects on energy conservation.

4.4 DISSOLVED-GAS EFFECTS

Free or dissociated gas has a documented effect on cavitation inception, but its effect on cavitating loads has received little attention in the literature. The effect depends on the change in acoustic properties of the liquid by the dissolved gas, as well as the effects of varying cavitation inception. It has complicated many experiments designed to illuminate other matters. Inventive approaches to this problem are necessary. Use of the species identification capability of laser diagnostics may be such an approach, although the complexity must be carefully weighed against the probability of success.

4.5 CAVITATION NUCLEI

A major aspect of cavitation that has not been discussed up to this point is its dependence on the presence of small bubbles or nuclei. It is around such nuclei that bubbles explosively grow (and then shrink) as a result of changes in local pressure. The presence of these nuclei, imbedded in the flow or crevices at boundary surfaces, is a major factor in cavitation inception under all circumstances. Understanding the relationships between nuclei availability and make-up and complex flows is extremely difficult. Even the sources of nuclei in various flows are not agreed upon. Very little has been done to investigate many related questions, such as the influence of nucleus size distribution on cavitation. If the nuclei are bubbles, this question could be very important because of the dependence of bubble surface tension (which restrain a bubble's growth) on bubble size. Laser methods, including holography and light-scattering approaches, are being applied to this problem

(Katz and Acosta 1982). It is yet another area of cavitation research in which laser diagnostic techniques are becoming invaluable.

4.6 IMPACTS

Cavitation is a difficult and highly experiment-based field, and research in it is therefore expensive. The impacts of such work are essentially unknown, however, because of the diversity of cavitation applications and cavitation's role as both a design and operational constraint on system performance. Most work in the area is funded by the military, in terms of specific applications (naval), or from pure-science sources like the National Science Foundation. Neither group has shown interest in determining the overall impact of such work.

Based on the personal experience of R. E. A. Arndt, a noted researcher in the field,^(a) cavitation impact is considered to be quite significant in dollar terms--hundreds of millions of dollars per year worldwide. Most evident are occasional catastrophic failures, such as the loss of a large water turbine or tunnel spillway. These and other, less obvious failures can have considerable direct (use) and indirect (equipment replacement) energy consequences.

Other impacts may be more important to energy conservation, however. It has been noted that cold water experiments used to make cavitation tests are generally conservative (except when such factors as viscous effects come strongly into play) with respect to applications. This means that many flow devices must be designed to be suboptimal because of the lack of knowledge of relationships between working fluids. For the same reason, many installations are specified and operated in an unduly conservative manner. Yet, on occasion, all of the extra conservatism is still insufficient because of factors such as turbulence or dissolved gases. Because of the generic nature of cavitation phenomena, the design and operating conservatisms proliferate, and their quantification would require considerable research. For example, four million

(a) R. E. A. Arndt, St. Anthony Falls Hydraulic Laboratory, University of Minnesota, Minneapolis. May 4, 1984, telephone conversation with the author at Pacific Northwest Laboratory, Richland, Washington.

pumps were shipped in 1982, valued at almost \$2 billion (Current Industrial Reports 1982). Cavitation played a role in the design and installation of many of these pumps (either in the flow being pumped or in the pump bearings), and without question, compromises were made with insufficient knowledge of the phenomenon. The energy impact of those decisions will require further study.

5.0 INDUSTRIAL PROCESSES AND ENERGY CONVERSION

Laser diagnostics can be used for developing new and more efficient processes. The combustion diagnostics work generally involves special types of processes that will be described here as energy conversions. The other research areas discussed up to this point are also aimed at improved industrial process efficiencies through basic studies of tribology, corrosion and fouling, catalysis, fluidization, and cavitation. More specific work, perhaps even the use of laser diagnostics in industry, is also possible. The complexity and frailty of many laser diagnostics clearly make them poor candidates for immediate use as sensors for industrial process streams, although their potential in future control systems cannot be totally ignored. Simplified diagnostics based on today's more complex versions, particularly when implemented as probes, may be very useful. However, the middle ground between basic research and everyday industrial use probably has the most potential. It involves improvements to existing systems for energy conversion and use in research on new industrial processes.

This chapter contains an overview of some important energy conversion systems and noncombustion process development possibilities, as well as a discussion of the role of diagnostics as industrial controls. The important systems are outlined before a more general discussion on industrial process and sensor development because these systems are so prevalent in our fossil-fuel-based energy economy. Since industrial application is the ultimate goal of the development of any energy-conserving technology, this chapter, in a sense, summarizes many of the points made in the earlier portions of this report.

5.1 DIAGNOSTICS FOR ENERGY CONVERSION EQUIPMENT

This report (and the long-term focus of conservation research) centers largely on the need for increased understanding of fundamental processes. There are some major types of conversion equipment, however, which are of tremendous importance. It is worthwhile to briefly examine some fundamental

research needs of these technologies that might be addressed with laser diagnostics. Boilers, turbines and heat exchangers will be discussed. Because of the widespread use of these technologies, they receive considerable research attention, so projects must either be of a fundamental nature or be closely specified to produce new and important information.

5.1.1 Boilers

Flows, combustion, and environmental attack are important problems in boilers that can be studied with laser diagnostics. An important aspect of all the areas is the impact of alternative fuels on boiler design and performance. Laser diagnostic work on combustion and flow problems is apparently progressing well, although it generally (with the exception of CARS) seems best suited to a fundamental level of research. This level includes flame studies and work on coal particle sizing and devolatilization. Because of steering problems with laser beams in larger-scale measurements, the shift to work actually describing boilers will be a major step, requiring a huge apparatus and probes. Cooperative work with industry, perhaps with utilities, would probably be most suitable. Programs in the Fossil Energy Division of DOE, largely on coal conversion, are presently the leaders in this area. There is considerable interest on the part of various application-minded researchers, but there is some question about whether the basics are sufficiently well understood to merit a large effort.

Corrosion and slagging (deposition of melted ash) were discussed earlier in this report. If accompanying combustion conditions can be sufficiently well characterized, boiler-related environmental attack is a good area for research. One way to minimize such attack problems is to use a fluidized bed. Fluidized-bed combustion has the added advantage of multi-fuel capability.

5.1.2 Turbines

There are two very important classes of turbines in use today: combustion turbines and steam turbines. Each class has a number of large, highly skilled research establishments involved in its development and production. Federal research in these areas must definitely retain a basic, process-oriented approach. Combustion turbines, in moving to lower-quality fuels, suffer

tremendously from corrosion, deposition, and erosion. The earlier discussion on the use of surface Raman and other diagnostic techniques in combustion systems is relevant to these problems. Steam turbines have not yet been discussed; but they are certainly very important, as they turn the majority of this country's electric generators. One important problem related to such turbines is the nonequilibrium condensation of water droplets from the steam. Not only does it adversely affect turbine performance, but it cannot be measured by standard methods. Recently, laser Raman methods have been used to make local temperature measurements in such situations (Anastasia et al. 1982). Finally, the importance of understanding the complex flows inside both types of turbines must not be ignored. LDA and holographic methods are slowly being implemented by major turbine developers to study flow and fluid-structure (blade vibration) interactions. Many of the most difficult questions are related to turbulence, which is one of the primary targets for LDA and other diagnostics work in many fields.

5.1.3 Heat Exchangers

Heat exchanger research needs focus on the development of enhanced designs and their implementation in systems, and on fouling and other performance degradation mechanisms. Both depend in part on details of the flow in the heat exchanger, which is seldom thoroughly studied. LDA work may provide insights in important situations, but such measurements are of limited value unless the transport processes that are occurring are sufficiently well understood to make the data useful. Fouling and corrosion processes have been thoroughly discussed earlier in this report. Enhancement processes have a variety of mechanisms, so work must be carefully focused. Although basic processes should be the target of heat exchanger research on energy conservation improvements, the processes examined should be based on problems as they occur in the field. Heat exchangers are subject to such a variety of conditions in the field that no exchanger can be built to work in perpetual perfection. Attention must focus on heat exchangers as part of energy systems.

5.2 PROCESS DEVELOPMENT

Laser diagnostics will--and to some extent already do--have a significant impact on the development of new or improved industrial processes. The impact of laser diagnostics in combustion research is certainly an example, for combustion is our most ubiquitous industrial process. Until recently, combustion diagnostics have primarily treated fundamental problems, and certainly a great deal of time has been spent in perfecting the methods. Recent progress has been considerable, however, most particularly with CARS systems. Work has been impeded by the difficulty of the subject, the lack of experience with these systems, and the relatively low-tech nature of practical combustors. Work on new combustion processes is briefly outlined below, and a discussion follows on new areas of interest, such as plasma and chemical vapor deposition (CVD) processes.

5.2.1 Combustion Processes

Combustion processes, for which the laser diagnostics were originally developed, are being studied and improved by current diagnostics work. The future for such work is bright. Certain aspects of combustion work (e.g., fluidized beds, fouling, boilers, and gas turbines) have already been described in this report. In general, advanced combustion processes can be expected to undergo greater tailoring of their fluid mechanics, for better mixing and more effective reactions, and they may also involve unsteady operation (like pulse combustors). Because of the capabilities of diagnostics in detailing such processes, the diagnostics are a critical part of the development process. Problems for diagnostics use arise when systems get dirty and optically dense as fuel quality degrades. Continuing research on laser and nonlinear optics will attempt to provide answers. Another equally important problem concerns the move from pure research to application. As discussed earlier, the technical sophistication required for effective diagnostics use is tremendous. Industrial users must be technically sophisticated to have any chance of getting results. This fact will heavily influence which combustion systems can most effectively be improved upon, and will therefore affect applied research decisions.

5.2.2 Plasma Processes

A flame is a weak plasma that is undergoing a variety of chemical reactions. Both chemical and plasma processes can be investigated for possible use of laser diagnostics techniques. Plasmas can be divided into two categories--low and high temperature--which have different uses. Diagnostics have been used in each category, though mostly in high-temperature applications such as magnetohydrodynamic (MHD) channels. Schlieren, LDA, and even absorption measurements have been made, but the more complex techniques have not been applied and may not work. Interest in the area is quite high, however. Although plasma processes require significant amounts of electricity--and thus to some degree depend on the availability of low-cost electricity --they have significant benefits for some industries. High-temperature plasmas used for metals reduction, for instance, can produce high-quality steels and steel alloys with excellent productivity rates and close control of composition and material properties (Ettlinger, Nainan, and Ouellette 1979).

Low-temperature plasmas have a far wider variety of uses than the high-temperature variety, but they lack direct, significant energy impact. Some, however, are very important (and poorly understood) technologies (Ouellette and Barbier 1978). For example, various steps in silicon chip production involve plasmas. Such processes, still art rather than science, are attracting detailed study (which may involve diagnostics) for the first time. They are part of a class of plasma processes that have considerable capabilities in surface modification. The push for understanding is not based on energy considerations, however, nor should it be. The chip producers simply need a better understanding of their techniques. Electronics-based interest has similarly driven applications of laser diagnostics in chemical vapor deposition (CVD) on silicon (Breiland 1984). Although CVD certainly has energy-saving applications (in high-temperature coatings), CVD, like computer chips, is not a direct target for energy conservation.

CVD is actually a chemical interaction, and chemical reactions are another huge branch of interesting industrial processes. Specific targets for diagnostics are not readily distinguished, however. Some topics are already discussed in this report under the headings of flow, fouling, and corrosion. Innovative

processes, or to be more accurate, innovations in existing processes, occur constantly through efforts to lower operating costs without incurring huge capital costs. Complete new systems are also occasionally developed. If process control systems and the processes were designed at the same time to complement each other and maximize performance, some current diagnostic techniques might even be included. Certainly there are applications for laser diagnostic techniques within process development laboratories.

5.3 CONTROLS

In the previous section, the possibility was noted of designing an industrial system from scratch in order to use a laser diagnostic tool as part of its control structure. It may also be possible to apply diagnostic controls to existing processes, although new formats for the diagnostics (e.g., probes) will probably be required. The ability to apply techniques of automatic control to improve an energy system's performance is critically dependent on measurements of process or system variables. It requires, in addition, an adequately detailed, dynamic model of the system to be controlled. Such dynamic modeling and its interrelationships with laser diagnostics were discussed earlier in this report. This section focuses on measurement needs in current energy systems, and the possible use of laser diagnostic technologies for sensors. That use may involve implementing diagnostics through probes, which are also discussed here.

It is important to note at this point that perhaps 90% of industrial energy use comes from fossil fuels; thus, the most important sensor needs, in terms of energy impact, are generally related to combustion. Only in the last ten years or so have measurement and control been considered integral to methods for conserving and improving the utilization of energy. Effective sensors that have been installed in energy-intensive processes have already resulted in tremendous savings. For example, on-line gas chromatographs in distillation columns in the petroleum refining industry have resulted in energy savings of 10% to 20% (ESCOE 1980).

5.3.1 Sensor Requirements

The need for control system sensors focuses on real time, on-line devices that are reliable, of adequate accuracy, and not prohibitively expensive. They should measure pressure, temperature, and mass flow rates. For combustion systems, they should measure pollutant species in exhausts and concentrations of other, in-flame species that indicate flame quality. It is clear that laser diagnostics do not fulfill all these requirements, particularly the cost limitations--indeed, they were never meant to do so. Control system sensors in current generations of energy systems are, in energy terms, performing a "housecleaning" function; for instance, they may optimize performance of individual burners within a boiler or furnace.

This type of operation does not seem likely for current diagnostics, since they require constant attention to their lasers, detectors and other components. The simpler diagnostic techniques (e.g., flow visualization) do not provide "on-line" output, and the more complex methods use equipment that is notorious for its balkiness even in very carefully planned environments. United Technologies is presently working on the second generation of a hardened CARS system, which has the laser packed into a box cooled with liquid nitrogen and the scattered light safely carried away by fiber optics to provide a portable measurement capability.^(a) Further developments in this area, while expensive, have considerable potential.

5.3.2 Probes and Fiber Optics

Recently there has been a variety of reports from researchers making diagnostic measurements using small probes. Some possibilities for probes have been discussed earlier in this report. Their use in applied research has great potential, for many industrial flows are not transparent, uniform, or stable enough to be probed over long distances with a laser beam. Fluidized beds are an example; beams cannot traverse in-bed flow, but local measurements can be made with a probe that carries the laser beams and collects the scattered light

(a) A. Eckbreth, United Technologies, March 7, 1984.

through fiber optics. Fiber optics developments (driven by communications research) have great implications for laser diagnostics (Milanovich and Hirschfeld 1983).

Use of probes as sensors in industrial control systems is still an idea for the future. A tremendous amount of signal processing (e.g., of spectra) would be required before useful output (e.g., concentration of CO) could be found. A sensor using absorption, perhaps the simplest species-specific approach, could be conceivable. Variants have been considered for stack gas monitoring, at least. Above all, any such application must be decently reliable and accurate--current CO and O₂ stack monitors used for boiler control can produce rather dangerous operating conditions if they malfunction (Presser and Semerjian 1983).

One type of optical probe that should be useful for industry is Ray Dils' high-accuracy, high-frequency-response fiber optic temperature probe (Oils and Tichenor 1984). It fills a sensing need, being at the same time capable of superior performance and quite bomb-proof. It is not a spectroscopic tool, but instead relies on long-established relationships between radiation from a black-body cavity and temperature. It is simple enough to perform in industrial control systems, where laser diagnostics are not.

It should not be concluded, at this point, that current diagnostics completely lack benefits in filling sensor needs. Their principles of operation may, in the future, be applied to simple devices designed to operate reliably as sensors. Moreover, even if spectroscopy proves to be too difficult to automate, the knowledge gained by diagnostics is still applicable to the other side of the automatic controls equation--the dynamic model of the process that is necessary to interpret information from sensors and make control decisions. This interrelationship with models, discussed early in the report, is perhaps the most important point to be made about laser diagnostics. As tools, they are uniquely adapted to developing and verifying dynamic models of processes and are so closely tied to modeling that their benefits are far fewer when used for other purposes.

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