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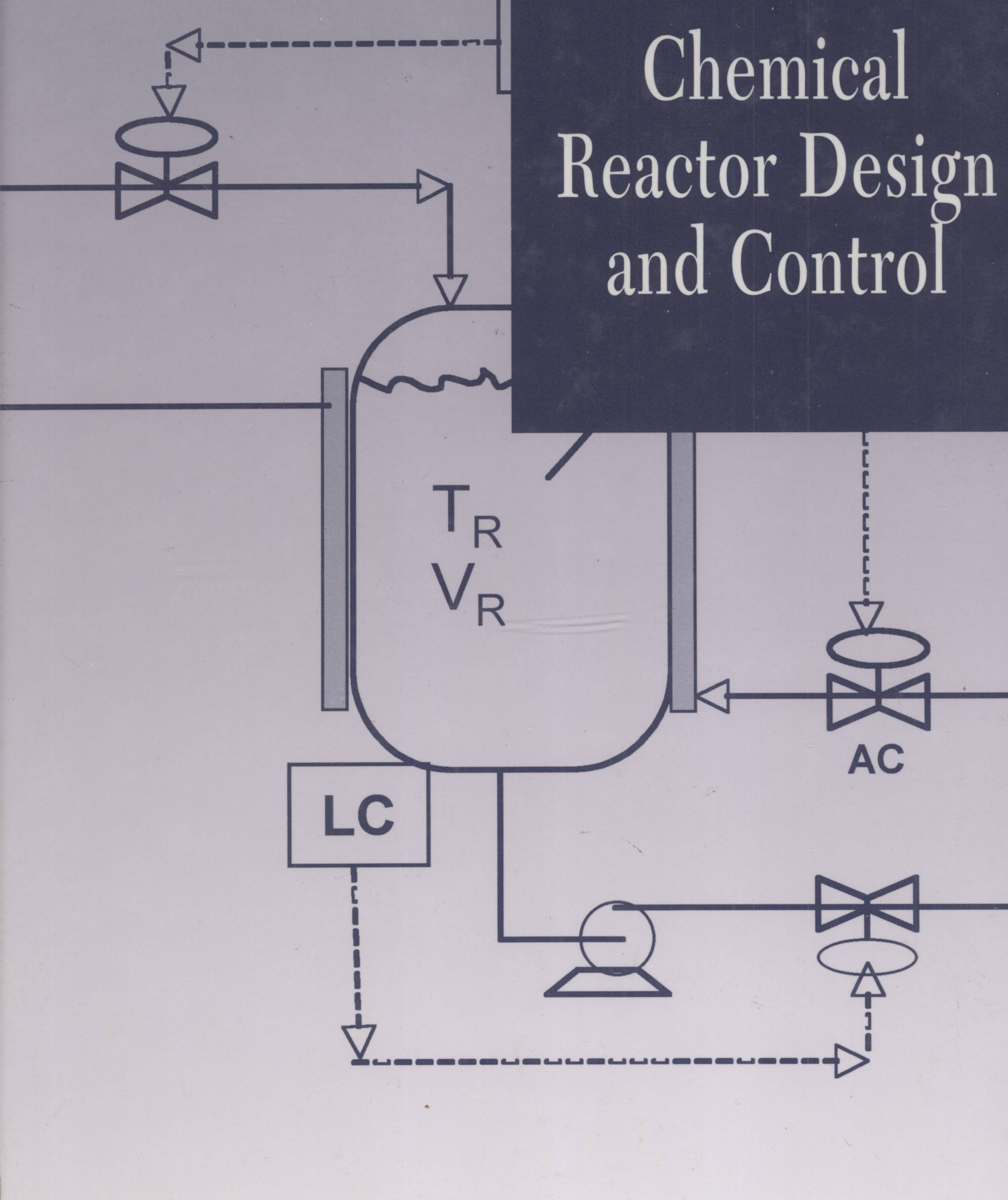

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CHEMICAL REACTOR DESIGN AND CONTROL

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PREFACE

Chemical reactors are unquestionably the most vital parts of many chemical, biochemical, polymer, and petroleum processes because they transform raw materials into valuable chemicals. A vast variety of useful and essential products are generated via reactions that convert reactants into products. Much of modern society is based on the safe, economic, and consistent operation of chemical reactors.

In the petroleum industry, for example, a significant fraction of our transportation fuel (gasoline, diesel, and jet fuel) is produced within process units of a petroleum refinery that involve reactions. Reforming reactions are used to convert cyclical saturated naphthenes into aromatics, which have higher octane numbers. Light C4 hydrocarbons are alkylated to form high-octane C8 material for blending into gasoline. Heavy (longer-chain) hydrocarbons are converted by catalytic or thermal cracking into lighter (shorter-chain) components that can be used to produce all kinds of products. The unsaturated olefins that are used in many polymerization processes (ethylene and propylene) are generated in these reactors. The polluting sulfur components in many petroleum products are removed by reacting them with hydrogen.

The chemical and materials industries use reactors in almost all plants to convert basic raw materials into products. Many of the materials that are used for clothing, housing, automobiles, appliances, construction, electronics, and healthcare come from processes that utilize reactors. Reactors are important even in the food and beverage industries, where farm products are processed. The production of ammonia fertilizer to grow our food uses chemical reactors that consume hydrogen and nitrogen. The pesticides and herbicides we use on crop fields and orchards aid in the advances of modern agriculture. Some of the drugs that form the basis of modern medicine are produced by fermentation reactors. It should be clear in any reasonable analysis that our modern society, for better or worse, makes extensive use of chemical reactors.

Many types of reactions exist. This results in chemical reactors with a wide variety of configurations, operating conditions, and sizes. We encounter reactions that occur in solely the liquid or the vapor phase. Many reactions require catalysts (homogeneous if the catalyst is the same phase as the reactants or heterogeneous if the catalyst has a different phase). Catalysts and the thermodynamic properties of reactants and products can lead to multiphase reactors (some of which can involve vapor, multiple liquids, and solid phases). Reactions can be exothermic (producing heat) or endothermic (absorbing heat). An example of the first is the nitration of toluene to form TNT. A very important example of the second is steam–methane reforming to produce synthesis gas.

Reactors can operate at low temperature (e.g., C4 sulfuric acid alkylation reactors run at 10°C) and at high temperatures (hydrodealkylation of toluene reactors run at 600°C). Some reactors operate in a batch or fed-batch mode, others in a continuous mode, and still others in a periodic mode. Beer fermentation is conducted in batch reactors. Ammonia is produced in a continuous vapor-phase reactor with a solid "promoted" iron catalyst.

The three classical generic chemical reactors are the batch reactor, the continuous stirred-tank reactor (CSTR), and the plug flow tubular reactor (PFR). Each of these reactor types has its own unique characteristics, advantages, and disadvantages. As the name implies, the *batch reactor* is a vessel in which the reactants are initially charged and the reactions proceed with time. During parts of the batch cycle, the reactor contents can be heated or cooled to achieve some desired temperature–time trajectory. If some of the reactant is fed into the vessel during the batch cycle, it is called a "fed-batch reactor." Emulsion polymerization is an important example. The reactions conducted in batch reactors are almost always liquid-phase and typically involve slow reactions that would require large residence times (large vessels) if operated continuously. Batch reactors are also used for small-volume products in which there is little economic incentive to go to continuous operation. In some systems batch reactors can provide final product properties that cannot be achieved in continuous reactors, such as molecular weight distribution or viscosity. Higher conversion can be achieved by increasing batch time. Perfect mixing of the liquid in the reactor is usually assumed, so the modeling of a batch reactor involves ordinary differential equations. The control of a batch reactor is a "servo" problem, in which the temperature and/or concentration profiles follow some desired trajectory with time.

The CSTR reactor is usually used for liquid-phase or multiphase reactions that have fairly high reaction rates. Reactant streams are continuously fed into the vessel, and product streams are withdrawn. Cooling or heating is achieved by a number of different mechanisms. The two most common involve the use of a jacket surrounding the vessel or an internal coil. If high conversion is required, a single CSTR must be quite large unless reaction rates are very fast. Therefore, several CSTRs in series are sometimes used to reduce total reactor volume for a given conversion. Perfect mixing of the liquid in the reactor is usually assumed, so the modeling of a CSTR involves ordinary differential equations. The control of a CSTR or a series of CSTRs is often a "regulator" problem, in which the temperature(s) and/or concentration(s) are held at the desired values in the face of disturbances. Of course, some continuous processes produce different grades of products at different times, so the transition from one mode of operation to another is a servo problem.

The PFR tubular reactor is used for both liquid and gas phases. The reactor is a long vessel with feed entering at one end and product leaving at the other end. In some applications the vessel is packed with a solid catalyst. Some tubular reactors run adiabatically (i.e., with no heat transferred externally down the length of the vessel). The heat generated or consumed by the reaction increases or decreases the temperature of the process material as it flows down the reactor. If the reaction is exothermic, the adiabatic temperature rise may produce an exit temperature that exceeds some safety limitation. It may also yield a low reaction equilibrium constant that limits conversion. If the reaction is endothermic, the adiabatic temperature change may produce reactor temperatures so low that the resulting small chemical reaction rate limits conversion.

In these cases, some type of heat transfer to or from the reactor vessel may be required. The reactor vessel can be constructed like a tube-in-shell heat exchanger. The process fluid flows inside the tubes, which may contain catalyst, and the heating/cooling medium is on the shell side. Variables in a PFR change with both axial position and time, so the modeling of a tubular reactor involves partial differential equations. The control of a PFR can be quite challenging because of the distributed nature of the process (i.e., changes in temperature and composition variables with length and sometime radial position). Tubular reactor control is usually a regulator problem, but grade transitions can lead to servo problems in some processes.

The area of reactor design has been widely studied, and there are many excellent textbooks that cover this subject. Most of the emphasis in these books is on steady-state operation. Dynamics are also considered, but mostly from the mathematical standpoint (openloop instability, multiple steady states, and bifurcation analysis). The subject of developing effective stable closedloop control systems for chemical reactors is treated only very lightly in these textbooks. The important practical issues involved in providing reactor control systems that achieve safe, economic, and consistent operation of these complex units are seldom understood by both students and practicing chemical engineers.

The safety issue is an overriding concern in reactor design and control. The US Chemical Safety Board (CSB) published a report in 2002 in which they listed 167 serious incidents involving uncontrolled chemical reactivity between 1980 and 2001. There were 108 fatalities as a result of 48 of these incidents. The CSB has a number of reports on these and more recent incidents that should be required reading for anyone involved in reactor design and control. In 2003 the American Institute of Chemical Engineers published *Essential Practices for Managing Chemical Reactivity Hazard*, which is well worth reading.

There are hundreds of papers dealing with the control of a wide variety of chemical reactors. However, there is no textbook that pulls the scattered material together in a cohesive way. One major reason for this is the very wide variety in types of chemistry and products, which results in a vast number of different chemical reactor configurations. It would be impossible to discuss the control of the myriad of reactor types found in the entire spectrum of industry. This book attempts to discuss the design and control of some of the more important generic chemical reactors.

The development of stable and practical reactors and effective control systems for the three types of classical reactors are covered. Notice that "reactors" are included, not just control schemes. Underlying the material and approaches in this book is my basic philosophy (theology) that the design of the process and the process equipment has a much greater effect on the successful control of a reactor than do the controllers that are hung on the process or the algorithms that are used in these controllers. This does not imply that the use of models is unimportant in reactor control, since in a number of important cases they are essential for achieving the desired product properties.

The basic message is that the essential problem in reactor control is temperature control. Temperature is a dominant variable and must be effectively controlled to achieve the desired compositions, conversions, and yields in the safe, economic, and consistent operation of chemical reactors. In many types of reactors, this is achieved by providing plenty of heat transfer area and cooling or heating medium so that dynamic disturbances can be handled. Once temperature control has been achieved, providing base-level stable operation, additional objectives for the control system can be specified. These can be physical property specifications (density, viscosity, molecular weight distribution, etc.) or economic objectives (conversion, yield, selectivity, etc.).

The scope of this book, like that of all books, is limited by the experience of the author. It would be impossible to discuss all possible types of chemical reactors and presumptuous to include material on reactors with which I have little or no familiarity. Despite its limitations, I hope the readers find this book interesting and useful in providing some guidance for handling the challenging and very vital problems of chemical reactor control.

The many helpful comments and suggestions of Michael L. Luyben are gratefully acknowledged.

WILLIAM L. LUYBEN

CONTENTS

CHAPTER 1

REACTOR BASICS

In this chapter we first review some of the basics of chemical equilibrium and reaction kinetics. We need to understand clearly the fundamentals about chemical reaction rates and chemical equilibrium, particularly the effects of temperature on rate and equilibrium for different types of reactions. Reactions are generally catagorized as exothermic (releasing energy) or endothermic (requiring energy), as reversible (balance of reactants and products) or irreversible (proceeding completely to products), and as homogeneous (single-phase) or heterogeneous (multiphase).

One major emphasis in this book is the focus of reactor design on the control of temperature, simply because temperature plays such a dominant role in reactor operation. However, in many reactors the control of other variables is the ultimate objective or determines the economic viability of the process. Some examples of these other properties include reactant or product compositions, particle size, viscosity, and molecular weight distribution. These issues are discussed and studied in subsequent chapters.

Many polymer reactions, for example, are highly exothermic, so the temperature control concepts outlined in this book must be applied. At the same time, controlling just the temperature in a polymer reactor may not adequately satisfy the economic objectives of the plant, since many of the desired polymer product properties (molecular weight, composition, etc.) are created within the polymerization reactor. These key properties must be controlled using other process parameters (i.e. vessel pressure in a polycondensation reactor or chain transfer agent composition in a free-radical polymerization reactor).

Many agricultural chemicals (pesticides, fungicides, etc.), for another example, are generated in a series of often complex batch or semibatch reaction and separation steps. The efficacy of the chemical often depends on its ultimate purity. Operation and control of the reactor to minimize the formation of undesirable and hard-to-separate byproducts

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