PART 2

ADVANCES IN SUPPORTING DISCIPLINES

INTRODUCTION TO PART 2

In Part 1 of this study, the key developments in catalysis that have taken place in the last decade were discussed and reviewed in terms of their impact on the problems of catalytic coal conversion. Included in this discussion were six broad areas: multimetallic catalysis; effects of catalyst-support interactions, particle size and surface morphology on the behavior and properties of catalysts; catalyst characterization; catalyst preparation; effects of poisoning and regeneration; and a discussion of the reaction mechanisms of importance to catalytic coal conversion.

Part 2 of this study reviews a number of supporting disciplines which are likely to impact on the catalytic areas discussed in Part 1. The discussion has been divided into four general subjects: engineering, including testing procedures and reactor types; inorganic chemistry, discussing primarily the properties of a number of important classes of compounds; materials science, which covers several topics including new supports, sintering phenomena and a number of novel materials developed by materials science laboratories; and finally, surface science which concentrates on newly developed techniques for materials analysis and characterization. The impact of these areas on coal conversion in general is highlighted in each of these sections. Specific application to a number of coal processes will be discussed in Part 3.

I. REACTOR ENGINEERING AND CATALYST TESTING

A. INTRODUCTION

The major developments in reactor engineering and catalyst testing can be adequately divided into four areas. The first is the concept and hardware of continuous stirred tank reactors (CSTR). This form of test reactor provides an experimental method to study the kinetics of a catalytic process at high conversion while minimizing concentration and temperature gradients. The CSTR reactor will be discussed in more detail in the review of catalyst test reactors to follow and its use in three phase catalytic coal conversion processes described in subsequent sections. Second would be the development of a clear understanding of the effects of internal and external[a] concentration and temperature gradients on reactivity and selectivity. This area has been extensively treated by Satterfield and Sherwood (1) and Peterson (2), and has been reviewed more recently by Carberry (3). Criteria have been developed to define the conditions at which mass and heat transfer limitations become important in a variety of catalytic systems, and these will be reviewed in Section 3. Data handling and model discrimination has proceeded at a very rapid pace for both the mathematical treatment of complex reacting systems and the application of such techniques to specific systems. The reader is directed to reviews by Forment (4) and Weekman (5) in which a variety of approaches are described and application to a number of specific systems are considered. Also, the treatment of complicated reaction schemes has been considered extensively by Lapidus (6).

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[a] Internal - within the catalyst particle or pellet
External - between the surface of the catalyst pellet and the bulk fluid.

A number of reactor types have been used over the years to study catalytic processes. Some of these reactors operate in regimes quite far removed from the conditions at which the catalyst would operate in an industrial process. Consider, for instance, a catalytic packed bed reactor. It can be operated differentially or as an integral reactor. The differential reactor, a widely used type of laboratory test reactor, operates at very low conversion levels, thus maintaining nearly constant reactant composition through the catalyst bed. Since the reactant stream composition is well defined and mass and heat transfer limitations may be minimized by keeping the rate of reaction as low as possible, such reactors supply accurate kinetic quantities such as reaction rates, reaction orders, activation energy, etc. However, to model accurately a high conversion catalytic process, a large number of measurements would be required. Effects such as product inhibition would have to be accounted for. An integral reactor better simulates the real catalytic process. It operates at high conversion levels, with the reactant composition changing throughout the catalyst bed. However, because the reactant stream composition is not constant throughout the bed, well defined kinetic parameters are difficult to obtain. Such reactors are also prone to mass and heat transfer problems, both locally and throughout the reactor.

Each type of laboratory test reactor is best suited to give certain types of information. The usefulness and applicability of test data is dependent on the skill shown in choosing a test reactor as well as in the design of the test. A number of authors have discussed this problem. In particular, Weekman (7) and Difford and Spencer (8) and Carberry (3, 9) give a detailed listing of the advantages and disadvantages of each reactor type and comment on their usefulness in each stage of catalyst development.

In the present section, a brief review of the major types of catalyst test reactors will be given, with emphasis on their advantages and applicability. Specific testing systems that have particular relevance to coal conversion will then be discussed in more detail.

B. GENERAL REVIEW OF TEST REACTORS

1. DESCRIPTION OF REACTOR TYPES

Catalytic reactors can be classified on the basis of a number of parameters that define the ideal limit of reactor operation important for proper measurement of reaction rates (10). In general, industrial reactors approach these limits more or less closely. As collected in Table I-1, the exchange of mass by the reactor with the surrounding at the limit of zero exchange defines a batch reactor, while at the other limit specifies a flow reactor. Similarly, the total absence of the exchange of heat defines an adiabatic reactor while complete equilibration of the reactor with the surroundings makes the reactor isothermal. Other parameters specify mechanical variables such as pressure and volume, residence time and space time behavior all of which are important in defining the operation of a catalytic reactor.

In laboratory catalyst testing, a simplified classification system modeled on the reactors in common use is that presented in Table I-2. The major categories are integral, differential and pulsed microreactor where the operational parameter of reactant conversion is used to classify reactors. Sub-categories are the experimental embodiments of these categories. Each of these reactor types will be discussed and rated in terms of applicability in obtaining test data for a variety of uses such as catalyst selection, kinetic information, reactor design and process optimization.

TABLE I-1

LIMITING CONDITIONS OF REACTOR OPERATION[a]

CLASSIFICATION PARAMETER	LIMITING CONDITIONS
Exchange of Mass	Batch ⟷ Flow
Exchange of Heat	Isothermal ⟷ Adiabatic
Mechanical Variables	Constant Volume ⟷ Constant Pressure
Residence Time	Unique ⟷ Exponential Distribution
Space-Time Behavior	Transient ⟷ Stationary

(a) From ref. (10)

TABLE I-2

CONDENSED SUMMARY OF CATALYST TEST REACTORS AND THEIR PRIMARY AREAS OF APPLICATION

Reactor	Catalyst Selecion (Screening)			Kinetic Information	Reactor Design	Process Optimization
	Activity	Selectivity	Life			
Integral -Plug Flow						
Adiabatic	●	●	●		*	*
Isothermal	●	●	●	●	●	●
Integral - Gradientless						
Well Stirred Continuous (CSTR)	●	●	●	●	●	●
Differential						
Single Pass	●	●	●	●	●	
Batch Recycle	●	●		●	●	
Pulsed Micro	●	●				

● Generally applicable

* Applicable only in specific instances

a. Integral Reactors

The first category considered is integral plug flow reactors, which are operated at high conversion with the reactant composition changing along the catalyst bed. They can be divided into two groups, isothermal in which the temperature is constant throughout the catalyst bed and adiabatic where the reaction heat raises or lowers the reactor temperature. Thus, in contrast to the adiabatic reactor, the catalyst temperature in the isothermal reactor is well defined and controlled. It is therefore more suited for certain applications, in particular for the determination of kinetic information. On the other hand, either type of integral reactor can be used in catalyst selection since this is a comparative process in which one catalyst is rated against another. The value of the comparative data or its discriminating nature will depend on the test and the parameters measured. Typical schemes of measurement are:

i. Temperature of 50% conversion (or other conversion value) with space velocity, reactor geometry, and catalyst geometry maintained constant.

ii. Light-off temperature for an exothermic reaction, which is a variation of (i) and represents the temperature at which the reaction rate is sufficiently fast that the rate of heat release becomes larger than the rate of heat removal and the reactor temperature jumps to a high steady-state value.

iii. Conversion at a given temperature with space velocity, reactor geometry, etc. constant.

iv. Rate parameters obtained by assuming analytical rate expression and fitting the reactor data.

Only the procedure in (iv), in which a kinetic model for the reaction and reactor is assumed, is the data in the form of kinetic parameters related to the reactions occurring. The accuracy of the kinetic data is only as good as the assumed reaction model and the simplifications employed. This is a fine art and the reader is directed to the work of Froment (4) and Lapidus (6) among others.

In the use of integral plug flow reactors to screen catalysts, the best choice would be a reactor system closely resembling the "in use" process reactor with respect to flow properties (Reynolds number), catalyst particle size and pore size, space velocity, and reactant stream composition. As an extreme example of this, the best procedure for testing automotive pollution control catalysts, and one that has found widespread use, is an adiabatic integral reactor under conditions closely simulating those encountered in actual vehicle use (11).

A second point that should be emphasized when discussing integral reactors is that not all reactions of interest proceed to 100% conversion as a result of the thermodynamic control. The equilibrium under reaction conditions may be equivalent to only 1% conversion as in ammonia synthesis at atmospheric pressure or 20% for methane synthesis from H_2 and CO at high temperature, 700°C.

The gradientless integral reactor is defined as integral due to the high conversion of reactants across the reactor. The gradientless condition is obtained by, in effect, operating the catalyst differentially using low reaction rates and very high stirring rates. As illustrated schematically in Figure I-1, the reactant flows into a well stirred tank in which the fluid phase is uniform due to a high rate of mixing. Reactant conversion as the fluid passes over the catalyst is small minimizing heat and mass transfer gradients while the overall conversion

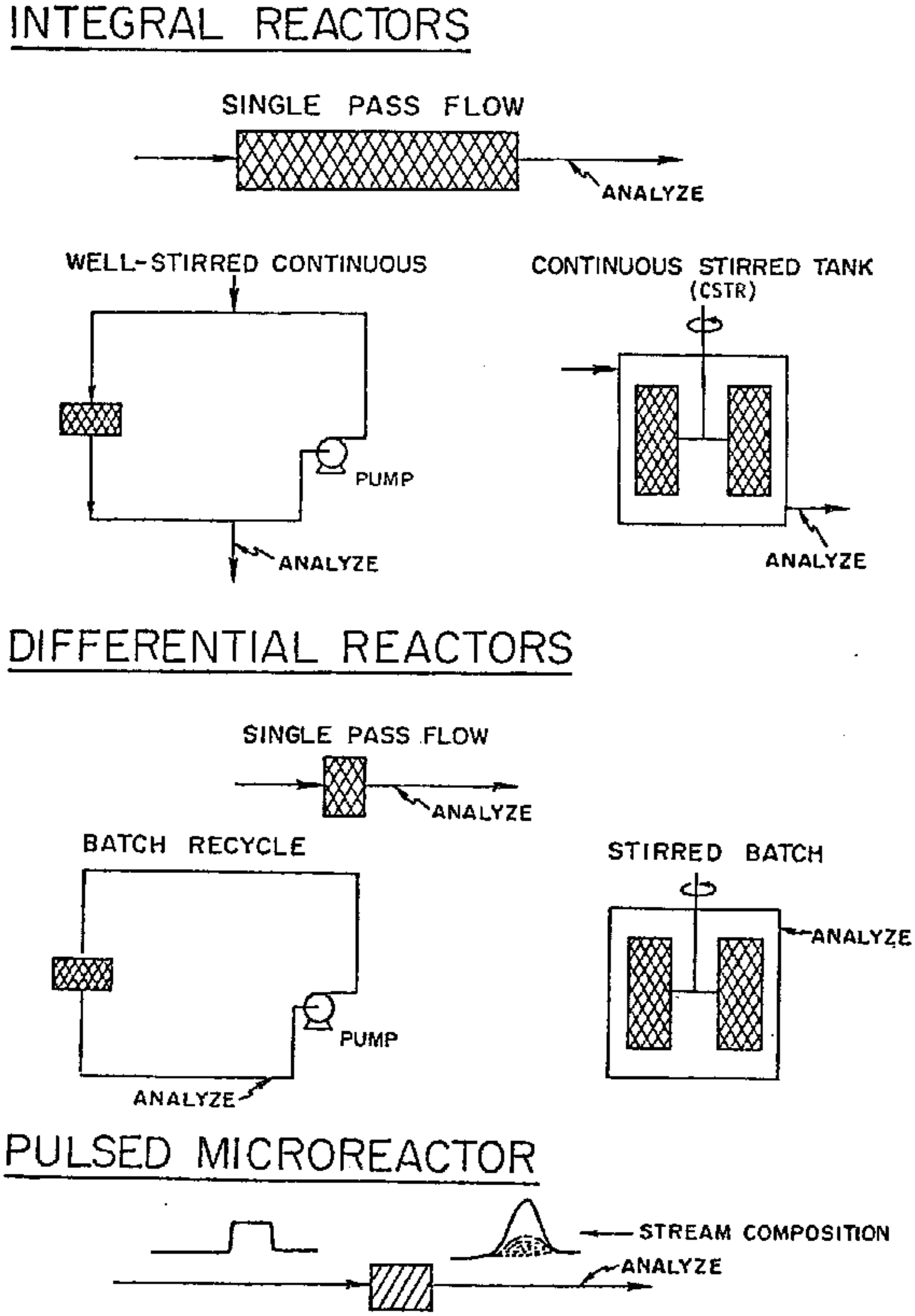

FIGURE I-1. GENERAL REACTOR TYPES

in the tank may be quite high.

The well-stirred continuous reactor can consist of a separate catalyst container and pump connected by an appropriate loop. More recently, these reactors have been modified into a single unit with the catalyst mounted on a rotating paddle, as first described by Carberry (12), or the catalyst stationary and the gas circulated thorugh the catalyst bed by an impeller, after Berty (13). To qualify as a CSTR reactor, i.e. to have perfect mixing of the gas contained in the system volume, a recycle ratio (ratio of volumetric flow over the catalyst to the flow rate of reactant into the system) greater than 25 is required (12). Values of 20 (13) to 60 (14) are common. A number of test procedures have been used to determine if sufficient mixing, and therefore gradientless operation, has been achieved (15, 16, 17).

Carberry, et al. (16), Berty (13), Brisk, et al. (17), and Bennett (15) discuss the detailed design, construction, and use of several types of CSTR reactors.

b. Differential Reactors

Differential reactors operate with a very low conversion of the reactants during passage through the catalyst bed. Since the conversion is very small, the reactant composition in the catalyst bed is assumed to be the average of the composition into and out of the reactor. Because of high flow rates, diffusion and heat transfer are also generally fast enough to prevent concentration gradients and temperature gradients from developing in the boundary layer surrounding the catalyst particles.

The various types of differential reactors are shown schematically in Figure I-1. The single pass differential reactor is a once through flow reactor in which the reactant stream passes over the catalyst and the effluent is analyzed. Sinfelt has described the use of this reactor and its applications, especially for systems in which the catalyst activity deteriorates with time (18). The differential batch recycle reactor has a reactant stream which is contained in a loop and is continuously passed over the catalyst at a constant flow rate. The conversion per pass is differential, but the reaction products build up and the reactants are depleted with time. The recirculating stream is periodically sampled and the change of overall conversion with time yields the reaction rate at any time or conversion. Like the CSTR reactor discussed earlier, the differential batch recycle reactor can consist of separate catalyst container and pump, or can be combined in a single unit. The designs of Carberry (12) and Berty (13) are quite useful in this application as well.

At this point, some comments are useful on the differences between the reactors discussed here. The very small conversion necessitated by differential operation may make the analysis difficult in the case of the single pass reactor. However, present day analytical techniques and instrumentation remove this as a major drawback. Most hydrocarbon reactions can be easily studied with capillary column gas-liquid chromatography and flame ionization detectors at extremely low concentrations. In the batch recycle reactor, each pass over the catalyst increases the total conversion in the system volume making the analysis easier. As long as the conversion per pass is small, the reactor operation remains differential. Rates at high conversion can be obtained from the batch recycle reactor, but this is transient data of conversion versus time. The CSTR is perferred because it provides stationary-state rates at high conversions and differential conditions. Versions of the Berty and Carberry reactor are produced commercially and are readily available (13).

c. Pulsed Microreactors

This is the last reactor type in Table I-1. In this technique the reactants are injected as a pulse into a carrier gas stream continually flowing over the catalyst. The carrier gas stream then passes into a gas chromatograph for analysis. The conversion of the pulse may be small or large, but in both cases the reactant concentration over the catalyst bed is poorly defined due to mixing with the carrier gas, and reactant pulse broadening. For certain narrow conditions, such as first order kinetics, reaction rate constants can be obtained from a pulsed reaction (19). In most other cases, adequate theoretical treatment of the system has been difficult. Thus, while pulsed microreactors are not suitable for generating kinetic parameters, they have a lot of merit for catalyst screening because of speed and flexibility.

2. APPLICABILITY OF TEST REACTORS

All reactors in Table I-2 are capable of screening catalysts for relative activity. The measurement may be a quantity of limited usefulness such as light-off temperature or 50% conversion temperature in the case of the adiabatic reactor, or it may be an actual rate constant at a given temperature in the case of the differential reactors. The single pass, batch recycle, and pulsed microreactors are capable of giving initial rates, that is, reaction rates on the catalyst as prepared and characterized, but before the reaction has significantly contaminated or altered the active surface. The other reactors obtain the activity measurement at some later time, and may more closely correspond to a steady-state catalytic activity. An initial activity or reaction rate is desired when the main interest is the determination of reaction mechanism or reaction rates on a well defined surface. Steady-state catalytic activity would include the phenomena of catalyst deactivation and poisoning, and will be considered under catalyst life testing. An example is catalytic hydrodesulfurization where it is observed that catalytic activity decreases rapidly with time and reaches a pseudo steady-state where the activity decreases more slowly.

When the reactant can undergo reaction to produce two or more products, only one of which is desired, then selectivity (defined as the ratio (or percent) of desired product to total products) is an important parameter. As in the case of activity, selectivity measurements can be done on a comparative basis. However, process parameters such as temperature, pressure, or residence time can affect the reaction to each product differently. Therefore, the catalyst test conditions become important, and those closest to the practical process are best to simulate the selectivity that might be obtained in use.

In the case of catalyst life testing, the necessity to be near operating conditions becomes even more important. Without a great deal of prior experience it would be difficult to assess the effect of unusual reactant concentration or low reactor temperature in extending or shortening catalyst life. Although most process reactors do not operate differentially, the single pass differential reactor (20) and the CSTR reactor (14) can be used in some cases to follow realistically catalyst activity with use. The batch recycle and pulsed microreactor are inherently poor in testing catalyst life since their operation deviates so drastically from steady-state processes.

To obtain kinetic information on a catalytic process requires knowledge of the gas composition and temperature at the catalytic surface. This effectively eliminates the adiabatic integral reactor and the pulsed microreactor in most cases. The other reactors are applicable to a varying extent, the isothermal integral reactor through a model fitting procedure and the differential reactors directly. It should be emphasized that kinetic information is widely useful not only in basic studies of reaction mechanism and catalytic activity of well characterized catalytic surfaces, but can be invaluable in reactor design and process optimization. Such basic kinetic data can greatly simplify the effort required in developing a process model and also reduces the amount of data required to adequately describe a process. Other reactors can supply useful reactor design data with the only criterion being that the test in some manner simulates the actual process. In many cases the data is used in conjunction with a model of the catalytic process.

In process optimization, which can be considered a last fine-tuning step in overall process development and reactor design, it is generally necessary to simulate the process reactor as closely as possible. Tests are run on a process development unit (PDU) which is a bench scale simulation of the actual process. In this reactor the interaction of variables such as throughput, reactor length, and operating temperature with selectivity and conversion can be studied with the object to maximize yield of the desired product. Of course, economic questions such as capital investment costs and feed costs enter at this point, limiting reactor size or placing a lower limit on space velocity. Smith and Carberry (21, 22) describe a detailed procedure for modeling a reaction and optimizing process variables to maximize the yield of product. The procedure was applied to both fixed-bed (21) and tube-wall (22) reactors for the oxidation of naphthalene, but the approach should be applicable to most reactions. As an example of the type of data obtained in this analysis is that the fixed-bed reactor was diffusion limited in the catalyst pellet while the tube-wall reactor is heat transfer limited at the reactor wall.

Such observations suggest routes to further optimize the process by changes in the catalyst or reactor construction, respectively.

3. TESTS FOR KINETIC CONTROL

Before concluding this general discussion of catalytic test reactors, some mention should be made of the importance of transport limitations. A number of properties may differ between catalysts in addition to changes in the active component or its surface area so that comparative testing of catalysts may reflect changes in transport properties rather than changes in catalytic activity. Thus, in a series of catalysts, catalyst particle size, pore size, thermal conductivity, and location of the catalytically active material may change. Even when efforts are made to retain the same catalyst base, thus maintaining particle and pore size, the distribution of the active component in the catalyst particle may vary, making more or less of it accessible to the reaction. It is also possible that the reaction conditions are such that the rate is controlled by transport properties and not the catalyst activity so that the results are not just modified, but erroneous. These problems have been considered in some detail, and a number of theoretical and experimental test procedures exist to probe for transport or thermal limitaitons in catalytic systems. Transport within catalyst particles has been treated extensively by Petersen (23) and Satterfield and Sherwood (24). Mears (25) recently reviewed the field, discussing transport limitations in the reactor as well as in the catalyst. A common empirical test for external mass and heat transfer involves varying the flow rate at constant space velocity and noting changes in conversion. However, Chambers and Boudart (26) showed this test is not sensitive at low Reynolds numbers, and does not check for transport limitation within the particle. The latter phenomena can be checked by the test described by Koros and Nowak (27) where the number of catalytic sites per unit volume of catalyst is changed. This particular experimental procedure can test for diffusion of heat and mass to the surface of the catalyst particle as well as within the particle. The development of hot spots during an exothermic reaction has been treated extensively by Luss (28).

C. ANALYSIS OF SELECTED REACTOR SYSTEMS

All of the systems discussed above consisted of a solid catalyst with the reactant, generally a gas, flowing through the reactor containing the catalyst. The operation of such a system is well understood. Many of the reactions associated with coal conversion unfortunately do not fit into this simple category. This is clearly the case for reactions where solid or even partially liquified coal is to be catalytically treated to increase the hydrogen to carbon ratio or selectively remove the sulfur. Such a system would include a solid reactant phase in the catalytic reactor. Even the hydrogen - carbon monoxide reaction may be complicated by the introduction of a liquid phase as a heat transfer medium to control catalyst temperature. In multi-phase systems such as (a) a liquid reactant and a solid catalyst, (b) liquid plus solid reactants and a solid catalyst, or (c) a solid reactant and a solid catalyst, either with or without gaseous reactants, the system is much more complicated and less well understood. Few laboratory scale test reactors are in wide use. Yet, these systems are important in hydrodesulfurization, coal liquefaction, and coal gasification.

The remainder of this section will cover five specific systems considered important because of the current necessity to study three phase catalytic processes as found in coal liquefaction, or because they are important in other catalytic coal conversion processes. The systems chosen for detailed discussion are:

1. Batch three phase reactors. High pressure autoclave test units are the most commonly used type of three phase reactors. The advantages and disadvantages of autoclave testing will be discussed.
2. Flow three phase reactors. To obtain catalyst deactivation data requires a flow reactor capable of operation with three phase reactant systems.
3. Counter current liquid phase reactors. These reactors have been applied to highly exothermic synthesis reactions to control the catalyst temperature.
4. Supercritical state reactors. Operation of a reactor above the critical point of the solvent may offer unique advantages.
5. High pressure thermobalance. This particular technique makes possible a laboratory scale coal gasification reactor.

1. BATCH THREE PHASE REACTORS

In addition to a system where the only solid is the catalyst, the present discussion of three phase systems will include the presence of a solid reactant. In the context of the subject of this study, the specific processes that will be considered are hydrodesulfurization and hydrodenitrogenation of coal liquids and hydrogenation and hydrotreating of coal slurries. Coal liquefaction can be accomplished by 1) mixing the coal, solvent, and catalyst in the same reactor where H_2 gas hydrogenates the solvent and/or the coal, or 2) hydrogenating the coal with a hydrogen donor solvent in one reactor and catalytically rehydrogenating the solvent in a second reactor. Although all the basic reactor types discussed earlier are in theory applicable here, significant experimental difficulties are encountered in using a number of these reactor types for liquid or solid reactants. In the case of hydrodesulfurization, studies are greatly simplified by substituting a model compound such as thiophene (29, 30). The reactor then operates with gas phase reactants and a solid catalyst, and fits into the category of conventional catalyst test reactors discussed earlier. However, to adequately test all aspects of catalysis during coal liquefaction and hydrodesulfurization, including poisoning, deactivation of the catalyst by heavy metal fouling and coke formation, coal, or coal derived liquids must be used.

Because of the high pressures and temperatures involved, in the range of 1000 psig and 300°C, the most common laboratory procedure is to use a bomb autoclave as a batch reactor. The autoclave is loaded with the solid reactant, the solvent, and a catalyst. It is then filled with hydrogen and heated to reaction temperature. After being held for a specified time and cooled, the reaction products are analyzed.

The above procedure was used recently in a non-catalytic study of coal desulfurization and liquefaction (31). The work was done in a massive rocking bomb autoclave which, after loading, required almost two hours to heat to reaction temperature. The reactor was held at this temperature for fifteen minutes and then cooled. The long heating time made it impossible to obtain reaction rate data or to determine the effects of varying the reaction time. Such a test would not be very discriminating between catalysts since most reactions would be driven to equilibrium. Such a reaction can be said to run at very low space velocities.

A similar problem is encountered when the stirred tank reactor developed by Carberry (9) and Berty (13) are adapted to batch operation. In an extensive study of the solvent refining of a number of coals and the effect of solvent, temperature, and some catalysts, such a stirred autoclave was used (32). Again in this system the large thermal inertia made it difficult to heat the reactor to the required temperature in less than one or two hours.

A better system is that described by Curran, et al. (33). A high pressure batch autoclave is rapidly heated by immersing a low thermal inertia reactor in a heated sand batch, and cooled by submersing in water. The small volume reactor (30 cc) can be heated to 400°C in 2.5 minutes and cooled in 0.5 minutes, thus permitting the measurement of kinetic data. The reactor is efficiently mixed during reaction by shaking at a relatively high frequency, 40 Hz.

The low thermal inertia reactor was used by Curran, et al. (33) to study the kinetics of hydrogen transfer from a hydrogen donor solvent to a coal slurry. The products were analyzed for hydrogen content. The system could be used in a similar manner for catalytic studies. The high speed shaking would provide good mixing of the catalyst and solid plus liquid reactants. Such a test would be useful in the screening of catalysts for activity and selectivity. A simple measure of conversion such as hydrogen uptake would provide a measure of activity, while detailed analysis of the products would provide selectivity data.

Except for crude comparative activity measurements, a low thermal inertia reactor capable of being heated and cooled rapidly is required for kinetic or accurate catalyst activity measurements in a batch system. This requirement disappears when a flow or continuous experiment is performed.

Reactors capaple of such operation will be discussed in the following section.

2. FLOW THREE PHASE REACTOR

Instead of operating an autoclave as a batch system, a reactant flow into the reactor and a product stream leaving the reactor make the autoclave a flow or CSTR (continuous stirred tank) reactor. Such a system has greatly improved capabilities. However, they are not without cost. Instead of simply charging the system with a gas at high pressure and heating to reaction temperature, a feed system is needed to continuously pump a liquid and/or a slurry at high pressure into the reactor. Although equipment does exist to handle and pump slurries, the experimental complexity and system cost are greatly increased. Particular problems are encountered in storage of the slurry, plugging of the feed lines, and plugging of the reactor.

Flow reactors with a packed catalyst bed have been used to hydrogenate coal slurries with mixed results (34, 35, 36). A number of groups are currently developing continuous stirred tank reactors for use in coal processing studies. Weller and Bergantz are developing a Carberry type reactor to study the catalytic liquefaction of coal (37). The coal will be fed continuously as a slurry and product continuously removed for analysis. Similar systems are being developed by other groups (38), including continuous bench scale operation where the reactant slurry is fed to a catalyst contained in a rotating basket (39). This last unit is rather large, consisting of a one liter reactor with expected feed rate of one-half poun of coal per hour.

The data that can be obtained from such a reactor is substantial. For example, the reactor can be preheated with just catalyst, solvent, and gaseous reactant. Then, the solid reactant, as a slurry, is introduced and initial reaction rates can be obtained on fresh catalysts. As the reaction proceeds, catalyst deactivation data can be obtained directly. If a high stirring rate is used such that the reactor is well mixed and approximates a CSTR reactor, then data at a number of different conversion levels can be obtained and the effect of conversion level on selectivity can be measured. By contrast, such catalyst life testing and determination of changes in selectivity with deactivation and conversion level are impossible to obtain in a batch reactor.

One continuous system that provides maximum flexibility is the adaptation of the Carberry type reactor to three phase reactions. A commercial version of this reactor has been produced (13) and others are available with some modification of existing equipment. Most of these reactors are capable of operation at high pressures and temperature. Addition of a continuous reactant feed system and a product collection and analysis train makes the reactor complete for most catalyst studies. The high stirring rates that can be achieved insure well mixed conditions within the reactor and good contact between the catalyst and solid, liquid and gas reactants.

3. COUNTER-CURRENT LIQUID PHASE REACTORS

Several of the reactions important in fuel conversion, such as the synthesis of methane and hydrocarbons from CO and H_2, are highly exothermic. If the heat is not efficiently removed, the catalyst or the entire reactor may reach temperatures higher than is desirable. High temperatures could accelerate catalyst deactivation, thermally sinter the active component, and adversely affect product selectivity. A high reaction temperature could also make the reaction thermodynamically unfavorable, limiting maximum conversion and process efficiency.

Many of these problems are found in the synthesis of hydrocarbons from CO and H_2 where high concentrations of CO and H_2 are converted to hydrocarbon materials. The reaction occurs rapidly at 250°C or higher, but at temperatures near 400°C the equilibrium becomes unfavorable and the total conversion becomes equilibrium limited. Recent work has shown that the presence of a flow of liquid, counter-current to the flow of gaseous reactants, acts as a heat transfer medium with a high thermal conductivity and heat capacity (40). The liquid flows down the catalyst bed as in a trickle-bed reactor and the gas passes upward. Better temperature control and efficient heat removal should permit operation at higher conversion levels and greater throughput. The major problem is the reduced mass transfer of gaseous reactants through the liquid layer to the catalyst surface. Satterfield, et al. have analyzed the mass transfer properties of trickle-bed reactors, and found diffusion through the layer of liquid around the catalyst particle to be the limiting process(41). Work currently in progress at the University of Delaware is directed at modeling trickle flow and batch liquid-phase reactors (42). Counter-current reactors are also being studied for application to Fischer-Tropsch and methanation (40).

The counter-current reactors will become more important as processing of petroleum residuum and upgrading of coal liquids increases. A number of groups are currently investigating liquid processing in such fixed bed (43) and trickle flow reactors (44, 45).

4. SUPERCRITICAL-STATE REACTORS

An interesting concept in reactor engineering concerns reactions occuring in a medium above its critical point. Under supercritical conditions, the phase of a material cannot be described as a gas or as a liquid. A gas can be condensed by a reduction in temperature at constant pressure. A liquid can be vaporized by a reduction in pressure at constant temperature. The supercritical phase fits neither of these definitions and can best be described as fluid. Figure I-2 shows a typical pressure temperature (P-T) diagram for a pure material. Above the critical point, the liquid and gas phases become indistinguishable. The heat transfer properties of supercritical fluids are of particular interest since many coal conversion processes are highly exothermic. Unfortunately, the information is limited and comes mainly from the Russian literature (49-52). Table I-3 lists the critical properties of several materials of interest in coal chemistry.

Supercritical fluids have demonstrated their usefulness in the field of analytical chemistry because of their solvent properties. Because supercritical fluid densities approach those of liquids, intermolecular forces become important, giving the fluid the solvent capacity of a liquid. Dense gas chromatography has been used with CO_2 and NH_3 under supercritical conditions (53, 54). Using these carriers at temperatures of 40°C and 140°C, and pressures in the range of 1030-29,400 psi (2000 atm), polymers and biomolecules of molecular weight up to 400,000 have been made to migrate in a chromatographic column (53).

The solvent properties of supercritical fluids have also been used in coal extraction. Bartle, Martin, and Williams (55) used toluene to extract 17% of a low rank coal for chemical analysis. The conditions for this extraction were 350°C and 1450 psi. The compounds present in the extract lead the team to believe that the material was not degraded during removal from the coal. Furthermore, the small yields of gas and water (and the extraction of materials not recoverable from coal using higher temperatures and more severe conditions) lead to the conclusion that the extraction was mild. A further example of supercritical fluid coal extraction is given by Wise (56). Benzene at 300°C and 1750 psi extracted the carbonaceous

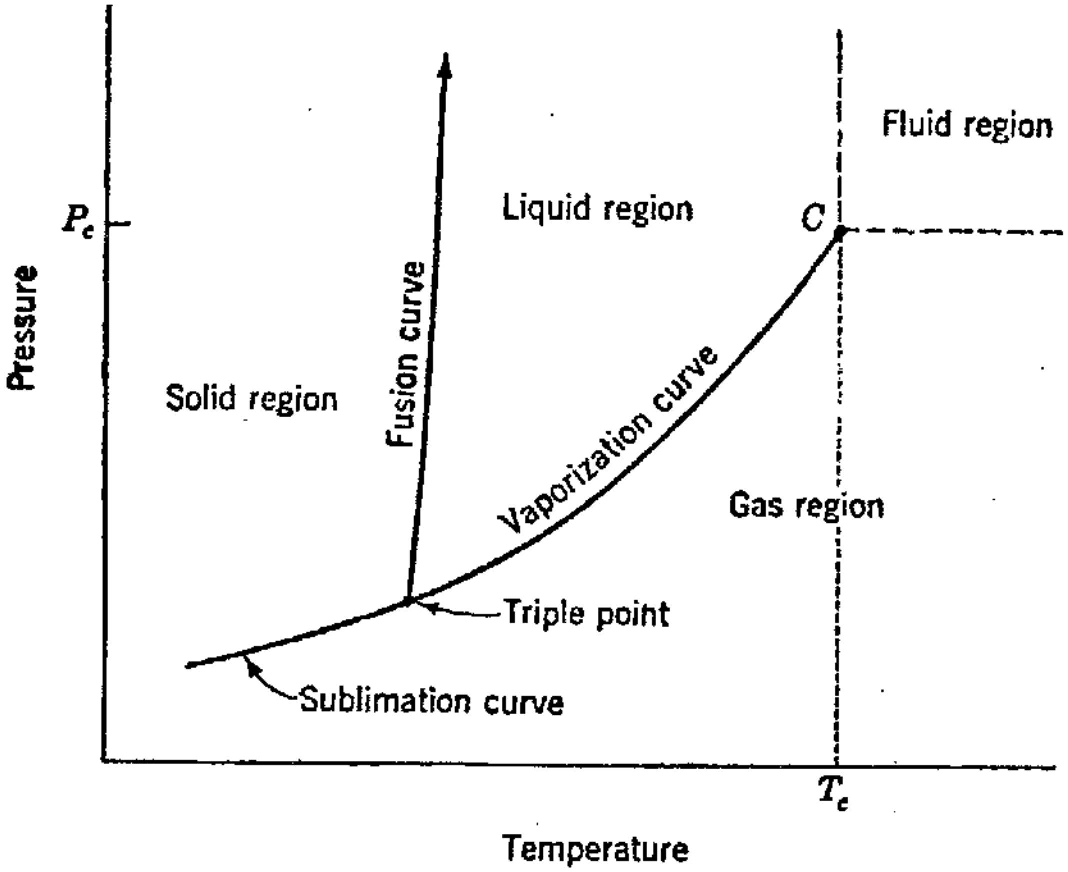

Figure 1-2. P-T Diagram For a Pure Material (Ref. 46).

TABLE I-3

CRITICAL PROPERTIES OF SELECTED COMPOUNDS

Compound	Reference	Tc(^oC)	Pc(psi)	Dc($^{gm}/_{cm^3}$)
Ammonia	47	132.4	2640	.235
Carbon Dioxide	47	31.1	1070	.460
n-Hexane	47	234.8	434	.234
Benzene	47	288.5	701	.304
Toluene	47	320.6	611	.292
Decalin, cis-	48	418	422	-
trans-	48	408	422	-

material from coal while leaving the mineral matter. Supercritical materials appear to have useful solvent properties for coal chemistry.

Supercritical fluids have also been used as a reaction medium in paraffin isomerization (57). C_4 to C_{12} hydrocarbons have been isomerized with a Lewis acid catalyst in a CO_2-hydrocarbon solvent at pressures from 1000 to 5000 psig and temperatures up to 200°C. Comparison of the supercritical CO_2 containing system with a normal hydrocarbon isomerization system showed a five fold increase in the ratio of isomerization to cracking. Under CO_2 hydrocarbon supercritical conditions, the Lewis acid catalyst may be chosen to be either miscible or immiscible in the reaction medium. If a miscible catalyst is selected, many of the advantages of a homogeneous isomerization are obtained. Hydrogen, for example, is easily dissolved in the supercritical mixture, while it is soluble only to a limited extent in the usual homogeneous reaction mixtures. In n-hexane isomerization, using an $AlBr_3$ catalyst and a supercritical CO_2 solvent, the isomerization-cracking ratio changed from 4 or 5:1 in the absence of hydrogen to 50:1 in the presence of hydrogen. This dramatic effect was due to the high H_2 solubility.

In summary, the properties of supercritical fluids that may be of use in catalysis are high solvating power, high heat capacity due to higher density, higher diffusivity, and higher heat transfer properties. However, there is some question as to the actual value of these properties in the supercritical state, especially heat transfer (49-52).

5. HIGH PRESSURE THERMOBALANCES

In the laboratory study of coal gasification, gaseous reactants can be flowed over coal and the appearance of reaction products such as the oxides of carbon or hydrocarbons can be monitored. An alternative is to follow the weight change in the coal sample as it is gasified. This technique is generally applicable to any solid or gas-solid reaction including decomposition, absorption, or adsorption. Monitoring the weight change of the solid reactant has the advantage of being a direct measure of reaction without the need for analysis of all possible products.

Otto and Shelef have recently reported work using an atmospheric pressure microbalance to study the catalytic gasification of several coals (58, 59). This group compared the gasification of pure graphite with coal and found little difference on a per unit surface area basis. The surface area was measured in situ before and after gasification by the microbalance. Prior incorporation of a catalyst into the coal permitted an assessment of the absolute magnitude of the catalytic effect and, as the work showed, the rapid loss of this effect.

The use of high pressures, above 20 atmospheres, makes possible the testing of reactions very near conditions found during gasification. A number of high pressure balances have been used including quartz spring balances (60) and sensitive electronic balances (61, 62, 63). A commercial version is also available (64).

D. CONCLUDING REMARKS

The testing of catalytic reactions requires a careful choice of reactor systems and test conditions. This is particularly important with complex processes such as encountered in coal conversion. The presence of three phase systems introduces parameters that are not properly accounted for with the usual laboratory reactors described at the beginning of this section. These reactors can, however, be used with model compounds, and important information can be obtained from such simplified systems. Certain tests such as catalyst life and deactivation, on the other hand, required the more complex three phase reactors. A number of these were discussed. The most commonly encountered reactors are batch autoclaves. In general, they are inadequate for testing coal, unless special care is taken to minimize heating and cooling time. This can be achieved with a low thermal inertia reactor. It permits accurate determination of catalyst activity and selectivity. For catalyst life and activity maintenance, on the other hand, a flow system is mandatory. Several designs were discussed. The application of these and the other reactors to specific coal conversion problems will be considered in more detail in Part 3.

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