

High-Pressure Reactions

- Pilot units for continuous reactions
- Stirred high pressure high temperature reactors
- Berty type reactor (magnetic stirrer; catalyst basket)
- Fixed bed tube reactors
- Tube reactor with static mixing elements
- Slurry and recirculation reactors



High-pressure pilot unit for ethynylation reactions (300 bar, 200 °C, 30 kg/h NH₃/C₂H₂, 2 x 0.8 litre fixed bed reactors, fluid cyclone separator 2 litre).



Advantages of reactions in or with supercritical Fluids

- high selectivity
- enhanced conversion rates
- smaller reactors
- homogeneous reactions because of unlimited solubility of the reactants
- precipitation of product from the reaction mixture as the reaction proceeds
- higher catalytic activity

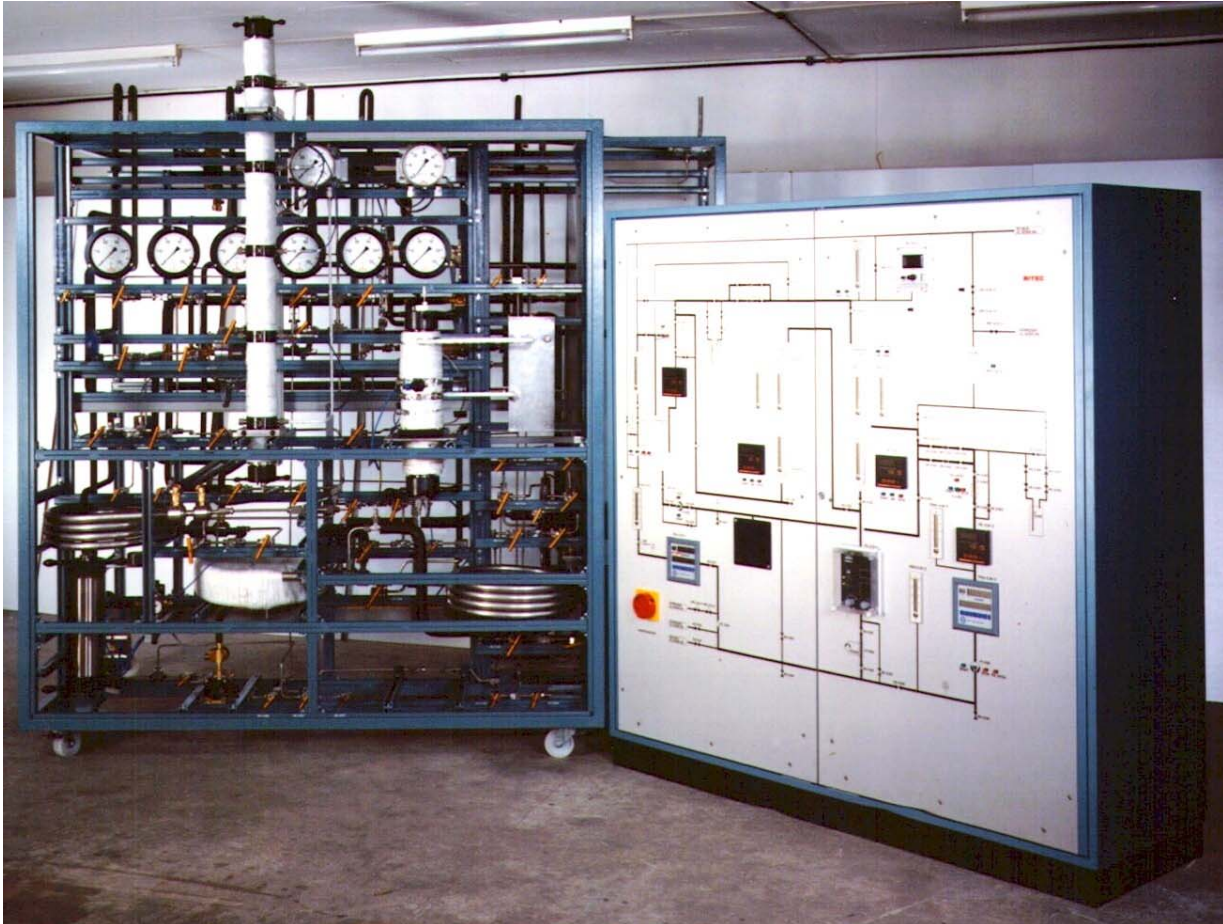
Investigated types of high-pressure reactions

- Hydrogenations
- Polymerisations
- Isomerisations
- Oxidations
- Catalytic reactions
- Enzymatic reactions
- Synthesis reactions
- Hydrolysis



Examples of SITEC pilot units

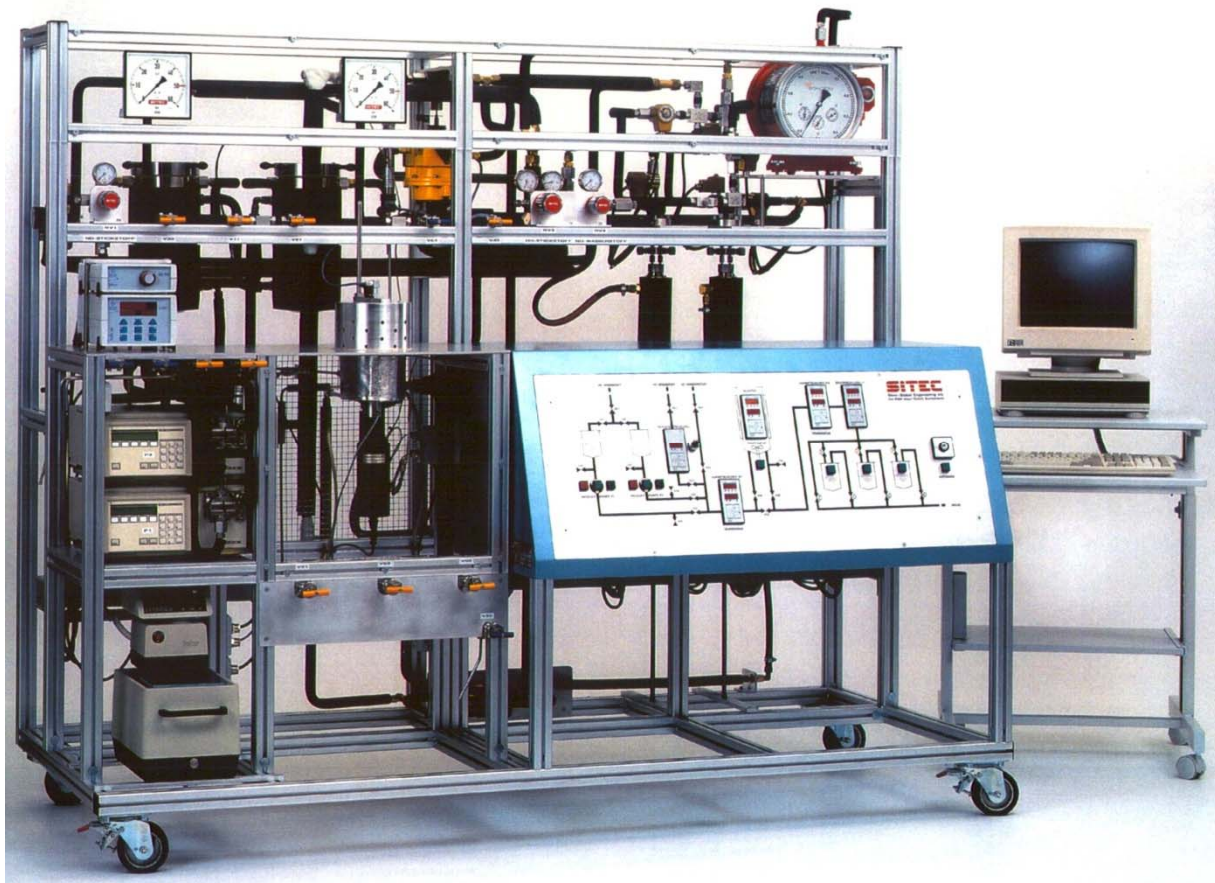
Catalytic synthesis reaction



High-pressure reaction pilot unit for continuous catalytic synthesis reactions with the following features:

- Reaction conditions 300 bar, 250 °C
- External recirculation of liquid and gas phase
- Measurement of recycle mass flows
- Continuous tapping of product
- Automatic compensation of educt losses
- Ex-proof design
- Several exchangeable reactor types, like slurry reactor, recirculation reactor and down flow column reactor

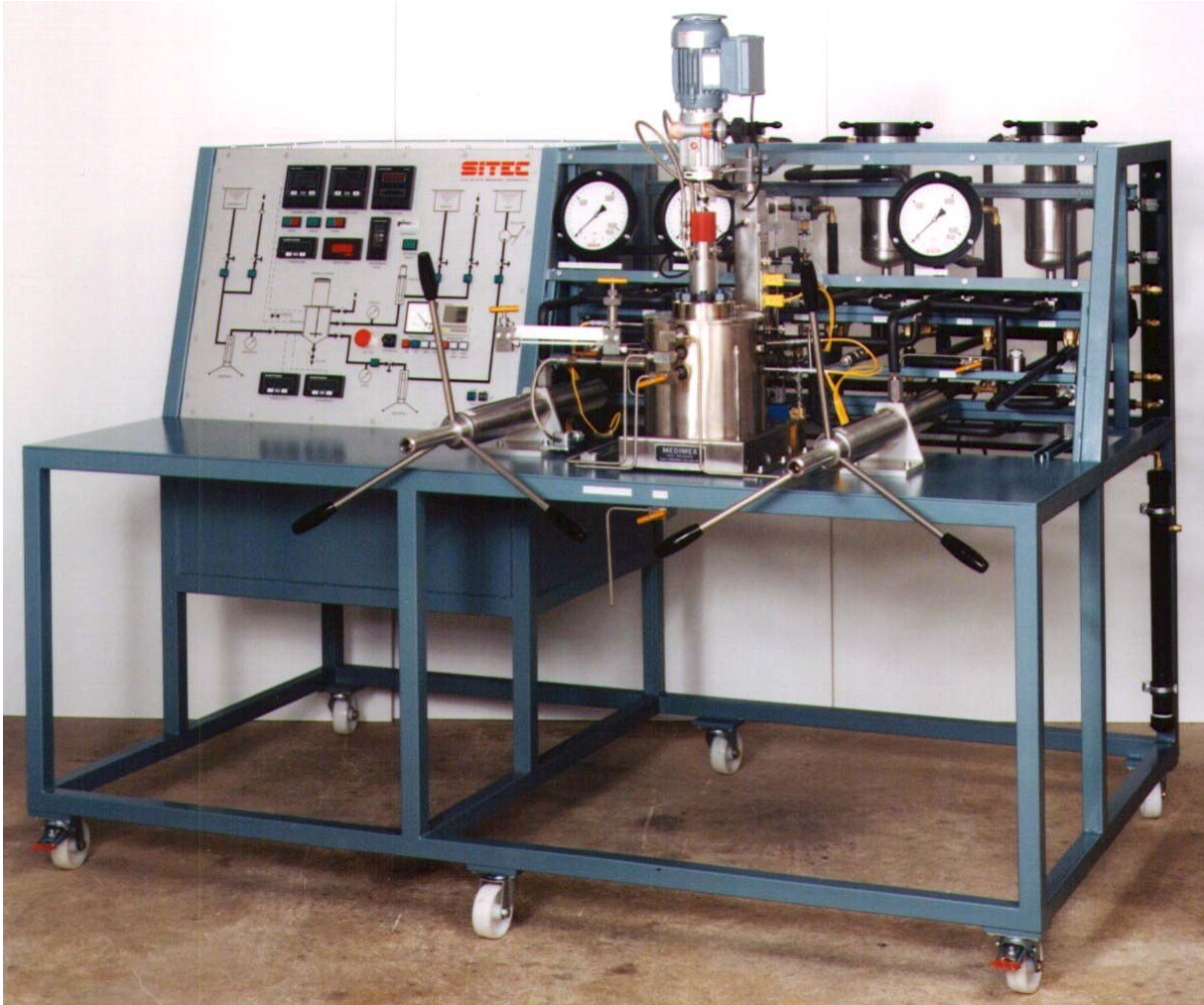
Reaction system with Bertz type reactor



High-pressure reaction pilot unit for catalytic reactions with the following features:

- Reaction conditions 40 bar, 450 °C
- 2 gas supplies and 1 liquid supply (HPLC pump)
- Bertz type reactor (volume 120 ml) with magnetic stirrer and catalyst basket
- Time controlled product collecting system
- Data acquisition system for on-line visualisation and data recording

Supercritical water oxidation (SCWO)



High-pressure reaction pilot unit for the investigation of supercritical water oxidation reactions (SCWO) with model substances. The main features are:

- max. reaction conditions 1000 bar / 700 °C
- Stirred high pressure high temperature reactor with water cooled magnetic drive
- Windows (optical width 6 mm) for the observation of the reaction volume
- Continuous metering of educts without any pulsations

Questionnaire for high-pressure reaction unit

Reaction pressure max.: 300 bar 500 bar 700 bar

Reaction temperature max.: 80°C 120°C 150°C 200°C
 450°C

Reactor type: Fixed bed tube reactor
 Reactor vessel with catalyst insert
 Berty reactor

Reactor capacity: 100 ml with 60 ml catalyst basket
 200 ml with 120 ml catalyst basket

Gas supplies:

gas name	gas capacity	pressure generation required
	NI/h	<input type="checkbox"/> Yes <input type="checkbox"/> No
	NI/h	<input type="checkbox"/> Yes <input type="checkbox"/> No
	NI/h	<input type="checkbox"/> Yes <input type="checkbox"/> No
	NI/h	<input type="checkbox"/> Yes <input type="checkbox"/> No

Liquid supplies:

liquid name	capacity	capacity of supply tank	options
	l/h	litre	<input type="checkbox"/> heating up to°C <input type="checkbox"/> stirrer
	l/h	litre	<input type="checkbox"/> heating up to°C <input type="checkbox"/> stirrer
	l/h	litre	<input type="checkbox"/> heating up to°C <input type="checkbox"/> stirrer
	l/h	litre	<input type="checkbox"/> heating up to°C <input type="checkbox"/> stirrer

Options:

- Mass-Flowmeter for all liquids
 all gases
 Data acquisition system by PC
 PLC control with integrated batch documentation



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Contact Details

Last name:

First name:

Title/gender:

Company:

Department:

Street:

P.O. Box:

Zip code:

Town/city:

Country:

Phone:

Fax:

E-mail:

www.

Please fill in this form and return it to SITEC-Sieber Engineering AG.



Data acquisition and online visualisation

As a useful addition to the SITEC high-pressure pilot units, we are able to offer you a simple and also a very flexible data acquisition program. This program allows to visualise your process data online during the experiments and to save it on your hard disk for a later interpretation.

The data acquisition and visualisation program will be completely integrated in your high pressure pilot unit and is configured for a specific application. It is also possible to upgrade an existing high pressure pilot unit, but with a bigger expenditure.

Based on the SCADA Software SpecView from EUROTHERM (see overview hereafter) SITEC provides several windows specifically programmed for a certain application.

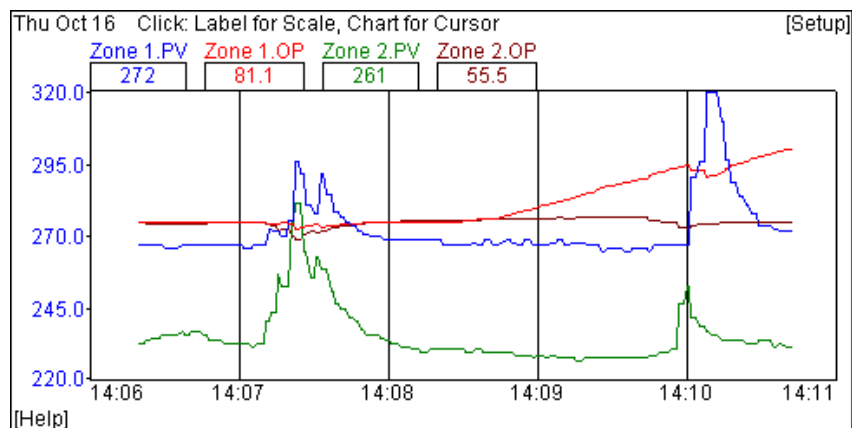
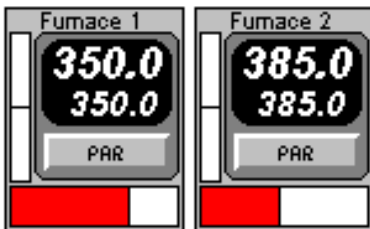
One window shows all the controller symbols and allows set-point adjustment or also alteration of control parameters. In addition, all monitoring signals are shown. On an additional screens all the data are graphically and digitally displayed.

All the data are automatically stored always the data acquisition program is started. On request a certain section (time interval) can be extracted and exported to Microsoft Excel.

The full development package of SpecView which is also supplied allows to change an existing or to create a new user interface using easy to handle “drag and drop” methods. On request, we will gladly send you a more detailed description of this development package.

The communication PC <-> Pilot Unit is made via USB. The controllers are interconnected by a RS485 interface.

The system requirements for the installation of SpecView: Windows PC with Windows 95, 98, Me, NT, 2000, XP or 2003 Server operating system, 64MB RAM minimum (128MB recommended), USB interface.



CONNECT

to Control and Measuring Instruments

Simple Display and Logging Applications setup in minutes!

Auto-Detection of Connected Instruments

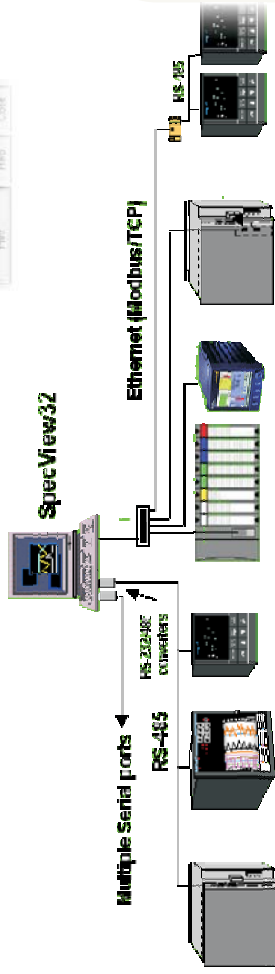
Pre-built Instrument View Database
Over 1000 instruments - no tags to define!
Access all instrument parameters

Concurrent Connections
RS232/RS485 (up to 40 ports)
TCP/IP, connect any RS485 instrument via Ethernet
OPC

Temperature
Pressure
Flow
Level
Vacuum
Speed
Status
Power

Controls
Systems
Meters
Indicators
Remote I/O
Data Acquisition
PLCs

RS232 / RS485
Ethernet
Internet
OPC
Radio



SpecView is unique. Many of my customers configure the program unaided. Some choose to have some assistance and for those that want a turn-key installation SpecView gives me the tools I need.

Rick Sabo, AQI Engineering

RECORD

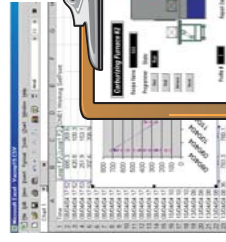
Data Management

Logging

Record any item
By time or event

User Variables

Batch data, comments etc
Integrate test data



Trends

Unlimited pens
Unlimited charts
Multiple time axes
Automatic printing

Reports

Log reports for spreadsheet analysis
Batch "Clipboard" report
Automatic process / shift reports

Batch Records

Find data quickly and easily
Multiple parallel batches

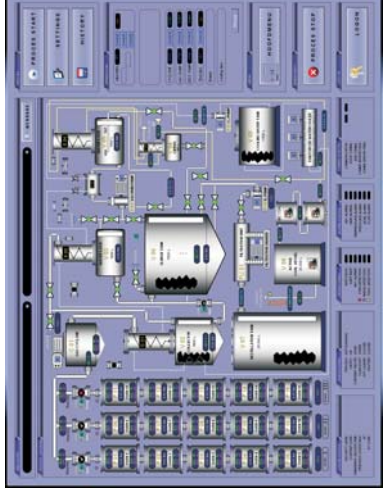
Batch/Tag / Code	Batch Number	Start	Stop	Duration
ABC Heatex 10mm #5 Pns	18-403-24	18-46:04	18-46:04	21:00:22
PLW 7555 Support	18-461:07	18-46:07	18-46:07	Running
DR Raising 25cm Log#218	09-46:21	09-46:20	09-46:20	15:02:49
Loadhead 55027 1st Brackets (2 items)	05:50:14	05:51:44	05:51:44	05:01:00
Loadhead 55027 2nd Brackets	11:22:00	11:22:00	11:22:00	Running

OPERATE

Operator Interface (HMI)

Create easy to use HMI
Unambiguous screens ensure error free operation

Visualize your process at a glance



Passwords

Multiple password levels
Restrict access to specified items
Record user login

Events & Alarms

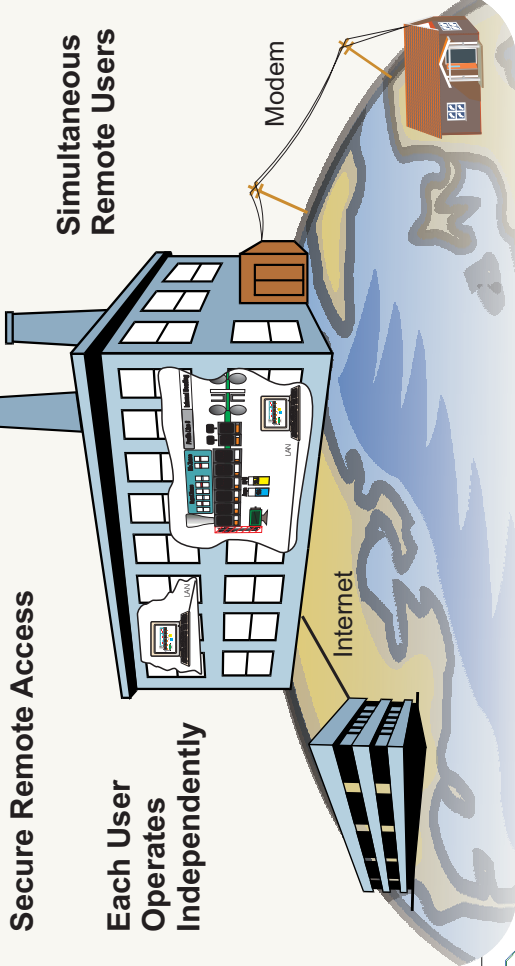
All operator actions recorded
Pop-up alarm window
Remote notification: pager / E-mail / SMS

Recipes

Multiple recipe screens
Process snapshot
Flexibility:
Full Access: select / review / edit / send
Read-Only: select / review / send
Single button send
Bar code recipe selection

Run	Temp	Flow	Pressure	Level	Speed	Status	Power
1	Ramp	100.0	450.0	0.1	On	Off	Off
2	Ramp	1400.0	450.0	1.1	On	Off	Off
3	Soak	1750.0	5.0	1.1	On	Off	Off
4	Ramp	1750.0	500.0	0.9	On	Off	Off
5	Soak	1650.0	2.0	0.9	On	Off	Off
6	Ramp	1650.0	1500.0	0.1	On	Off	Off
7	Soak	100.0	0.5	0.1	On	Off	Off
8	Soak	0.0	0.0	0.0	Off	Off	Off

Simultaneous Remote Users



Secure Remote Access

Each User Operates Independently

Loy Instrument, Inc. has installed close to one hundred copies of SpecView. I have found that SpecView is unmatched by anything else on the market. Its versatility has allowed us to use it in everything from straight data logging to full scale SCADA systems. For the money, no other software on the market can touch it.

Mark McDaniel, Loy Instrument Inc.

ANALYSE

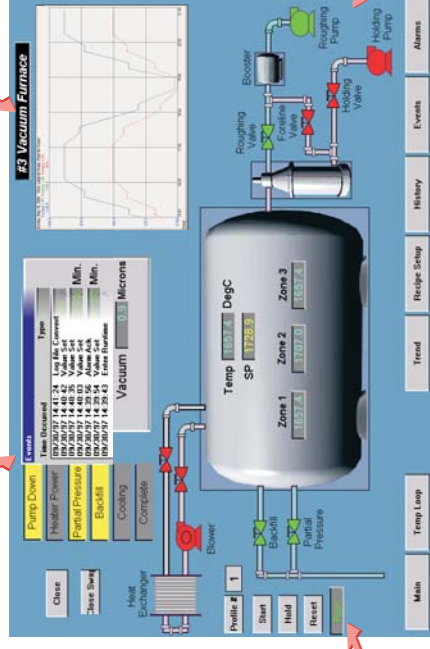
Explore and Troubleshoot

Integrate

Test measurements
Operator comments
Peripheral data

Event Window

What did the operator do?
...and when?



Visual Feedback

"I wish I had been standing here when..."
"Did the purge valve open correctly?"

Performance

How many parts?
Percentage downtime
Correlate run-to-run data

Historical Replay

'Video' replay of whole screen
Review your process in 'Fast Forward'

I received SpecView as a CD and manual. In a short time I had a configured and an operator provide both data logging and an operator interface to a number of different control devices. I had no previous experience with this kind of software. SpecView made it easy.

Lisa Reep, Corning

Process control with integrated batch documentation

This control allows you to master your processes by combining display, regulation, control and even batch documentation – all in one.

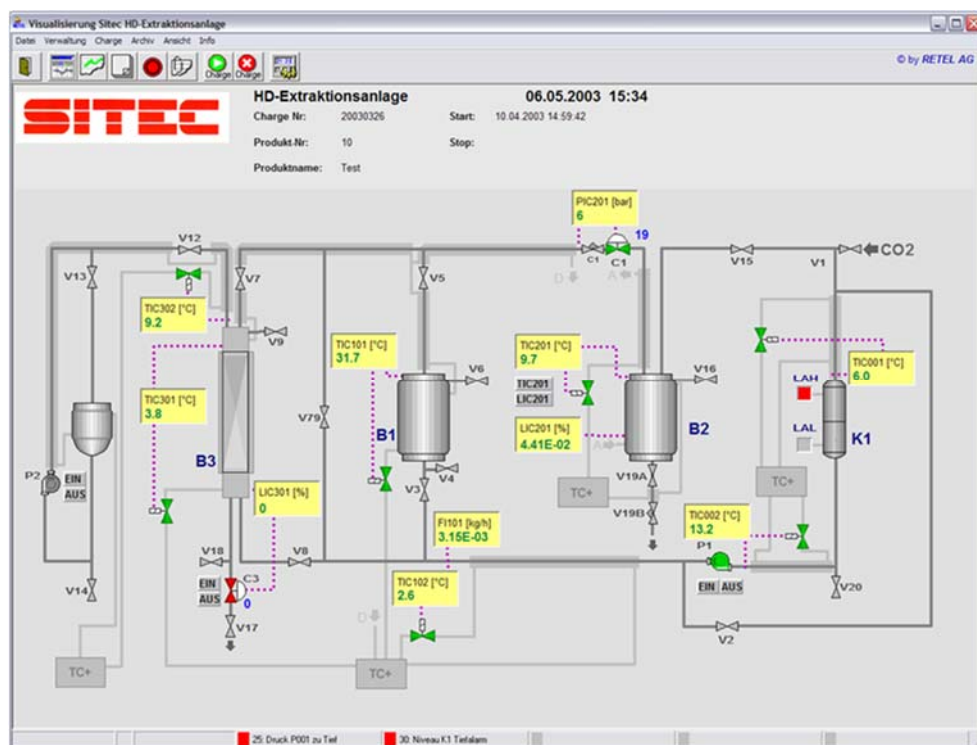
Advantages:

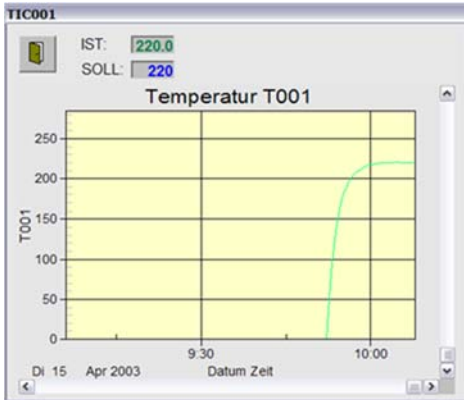
- complete batch documentation
- trend display of process flow
- dynamic overview of the installation
- easy input of nominal values
- exportable into standard formats
- protocols and diagrams accessible over network

The user-friendliness of the system operation is achieved by clearly arranged displays. This control system includes functions which otherwise are integrated in process control systems only.

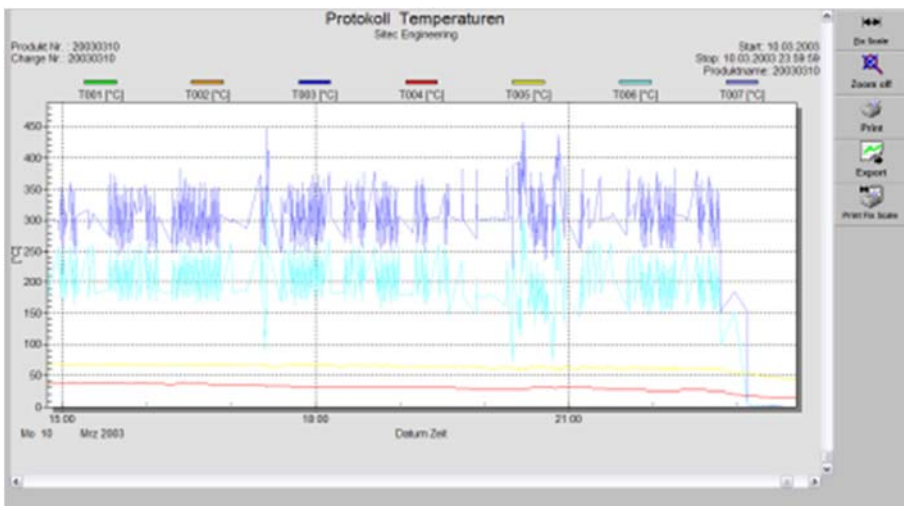
The control system allows manual and – as an option – automatic control of the installation. All process parameters can be displayed.

The data of the current batch as well as the system overview is displayed on the main window. The operator can control the process over the display picture.





The automatic control circuits have special display windows with integrated diagrams and nominal value input.



Important process parameters are shown in a trend display. The trend display has a zoom and Fix Scale function and can be printed or exported into bmp, wmf, or jpg graphic formats.



With the help of the integrated logging program the process can be documented completely. All protocols are exportable in pdf, html, or txt formats.

- data protocol
- error protocol
- event protocol
- comment protocol

The batches recorded can be retrieved from the archive. All protocols and diagrams can be exported and re-printed as desired.



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SITEC
High-Pressure Technology

Reference list for pilot plants

Rhône Poulenc, France	Chemical
University of Delft, Holland	Process engineering
University Wageningen, Holland	Agricultural research
BASF Ludwigshafen, Germany	Chemical
Salzgitter, Germany	Chemical
Hüls Chemie, Germany	Chemical
ENI, Italy	Petrochemical
Givaudan, Switzerland	Flavours and fragrances
Research Centre Karlsruhe	Environmental
Reemtsma, Hamburg, Germany	Tobacco
CNRS, France	Food research
TUBITAK, Turkey	Food research
SASOL, South Africa	Waxes
DEGUSSA-SKW, Trostberg, Germany	Hops, spices
Guinness, Ireland	Brewery research
English Hop Products, Great Britain	Hops
Fraunhofer Institute Pfinzthal, Germany	Process engineering
University of Bremerhaven, Germany	Food research
Novartis, Switzerland	Chemical
Firmenich, Switzerland	Flavours and fragrances
Haarmann & Reimer, Germany	Flavours and fragrances
University of Messina, Italy	Chemical engineering
MERCK, Germany	Chemical
University of Bari, Italy	Research
LIPI, Indonesia	Natural products
F.Hoffmann-La Roche, Switzerland	Reactions
University of Tübingen, Germany	Pharmaceutical research
National Technical University of Athens, Greece	Research
Inst. for "Nichtklassische Chemie", Leipzig, Germany	Research
University of Halle-Wittenberg, Germany	Research
Janssen Pharmaceutica, Beerse, Belgium	Drug delivery research
MAINELAB, Angers, France	Drug delivery research
Semnan University, Semnan, Iran	Research
JSC "Interbridge", Moscow, Russia	Research
Ecole des Mines d'Albi, Albi, France	Research
KRAFT Foods, UK	Coffee
Hochschule Niederrhein, Germany	Research
Solvay Solexis, Italy	Research (polymers)
EPFL, Switzerland	Research
University of Alicante, Spain	Research
King Fahd University of Petroleum, Saudi Arabia	Research
Inst. Nawozow Sztucznych Pulawy, Poland	Research
TU Bergakademie Freiberg, Germany	Research
3M, Seefeld, Germany	Research
FAPEX, Salvador de Bahia, Brazil	Research
University of Copenhagen, Frederiksberg, Denmark	Research
University Duisburg-Essen, Essen, Germany	Research
C. Illies, Hamburg, Germany (for China)	Research
AiFame GmbH, Wald-Schönengrund, Switzerland	Natural products

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Additional units in following countries:

Denmark
Turkey
Belgium
Italy
Canada
Greece
Spain
Brazil

Germany
Holland
Switzerland
India
Bulgaria
Iran
Saudi Arabia
China

South Africa
France
Great Britain
Ireland
Indonesia
Russia
Poland

Activities:

Flavours and Fragrances
Biotechnology
Chemical Industry
Coal Industry

Food Industry
Pharmaceutical Industry
Oil/Gas Industry



Chemical Reactions in Supercritical Fluids

One very interesting and, as yet, not fully investigated area of supercritical fluid extraction technology is the use of a supercritical solvent as a reaction medium in which the solvent either actively participates in the reaction or functions solely as the solvent medium for the reactants, catalysts, and products. With an SCF medium it may be possible to increase the selectivity of a reaction while maintaining high conversions, to dissolve reactants and catalyst in a single fluid phase and carry out the reaction homogeneously, and to capitalize on the solvent characteristics of the supercritical fluid to separate the product species from the reactants, catalyst, and unwanted by-products. Reaction rates may also be enhanced while the process is operating in the mixture critical region as a result of the potentially favorable effect of applied hydrostatic pressure. They also may be enhanced because the highly negative partial molar volumes of the product species, which can occur with dilute reaction mixtures operating near the critical point of the pure SCF solvent.

To take full advantage of an SCF reaction medium it is necessary to be cognizant of the phase behavior exhibited by the reaction mixture at high pressures. For instance, it has been shown that some of the kinetic studies reported in the literature on the high-pressure polymerization of ethylene are of little value, since the reaction-rate data were analyzed according to the assumption that the reaction was operated homogeneously when in fact two phases were present (Ehrlich and Mortimer, 1970). It should be evident after one has read chapter 3 that various types of phase behavior are possible with SCF reaction mixtures. Careful experimentation is therefore necessary when performing high-pressure reaction studies.

An example of investigating the phase behavior of a system before doing reaction studies is given in a patent describing a hydrocarbon isomerization process (Leder, Kramer, and Solomon, 1976). In this instance, the reacting mixture, consisting of a hydrocarbon feed, such as *n*-hexane, a metal halide catalyst, a hydrogen-halide solvent, such as HCl, and hydrogen, exhibits type-I phase behavior. A schematic *P-T* diagram for this mixture is shown in figure 11.1. Kramer and Leder recommend operating the reaction at *P-T* conditions

SUPERCritical FLUID EXTRACTION
Principles and Practice

M. McHugh
V. Krukonis

Butterworths 1986

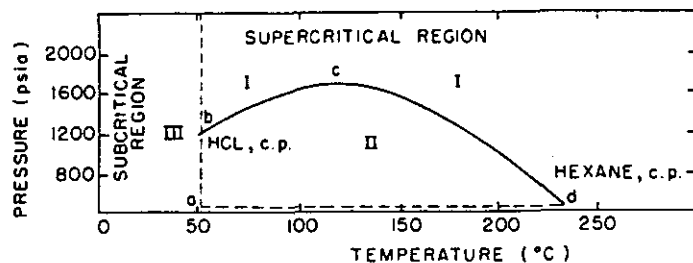


Figure 11.1 Schematic P - T diagram of the reacting mixture in the hydrocarbon-isomerization process proposed by Leder, Kramer, and Solomon (1976).

within region II bounded by the points $abcd$ shown in figure 11.1. Even though this is not strictly a supercritical fluid reaction, since it is run in the near-critical liquid region, it does provide an example of a case in which the researchers first determine the critical-mixture behavior of the reactants (see figure 11.2) and then proceed with the reaction studies in a well-defined region of the phase diagram.

As a reaction proceeds the resultant product species, if it contains a different functional group as compared with the reactant, may induce the reactant-product-SCF mixture to split into multiple phases near the critical point of the SCF. The work of Francis (1954), Dandge, Heller, and Wilson

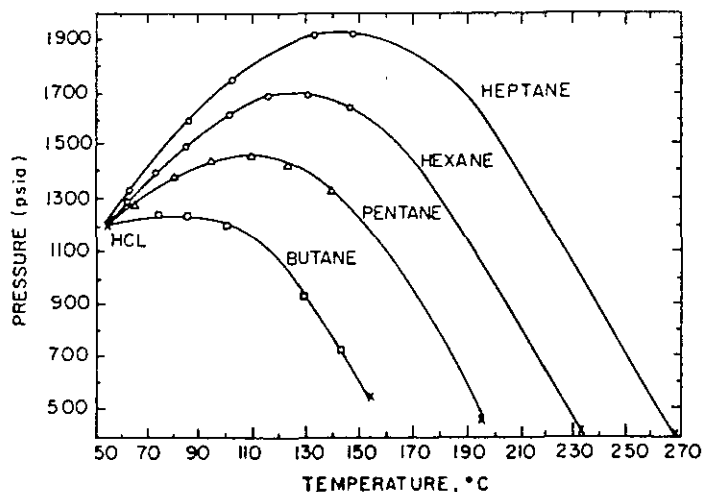


Figure 11.2 Critical-mixture behavior for various hydrocarbon-HCl mixtures (Leder, Kramer, and Solomon, 1976).

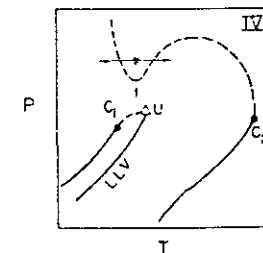
(1985), and Stahl and co-workers (Stahl and Quirin, 1983; Stahl et al., 1980) should be consulted for information on the types of functional groups that affect the miscibility behavior of solute-SCF mixtures. Since it was shown in chapter 3 that binary mixtures tend to exhibit multiphase LLV behavior as the differences in the molecular weights of the mixture components increase (Rowlinson and Swinton, 1982), it is reasonable to assume that a reacting mixture would also exhibit multiple phases if the product species were quite large relative to the SCF solvent.

It may be possible to design novel reaction/separation schemes using the information given in chapter 3 on the five basic types of phase behavior that can occur for binary mixtures at high pressures. For instance, type-IV phase behavior suggests a number of interesting reaction/separation scenarios. If one assumed that the reactant-product-SCF mixture exhibited type-IV behavior, it would be possible to run the reaction homogeneously at the temperature and pressure indicated by the asterisk in figure 11.3. Product recovery could be facilitated by splitting the reaction mixture into two phases when the critical-mixture curve is crossed, by either isothermally reducing the pressure or by isobarically increasing or decreasing the temperature. The reaction mixture could thus be cycled between a single-phase reaction step and a two-phase recovery step.

As mentioned previously, it may be possible to precipitate the product from the reaction mixture as the reaction proceeds. In this manner, unwanted side-reactions may be avoided if the product species is immediately removed from the reacting system as it precipitates from solution. Alexander and Paulaitis (1984) describe such a reaction/separation scenario for the Diels-Alder reaction of isoprene with maleic anhydride in supercritical CO_2 . They find that the product precipitates as a solid from the reaction mixture as the reaction proceeds. In this case, the reaction is run at fairly low concentrations of reactants in supercritical CO_2 near the critical point of pure CO_2 .

As also mentioned earlier, reaction rates may be improved if the reaction is run in the mixture critical region. A rate enhancement can potentially occur as a result of applied hydrostatic pressure and as a result of the unusual partial molar volume behavior of a heavy solute solubilized in a supercritical solvent. Numerous authors have used transition-state analysis (Laidler, 1965; Eckert,

Figure 11.3 P - T diagram for a type-IV binary mixture.



1972; Ehrlich, 1971) to explain the rate enhancement that can occur at high pressures. For a bimolecular reaction, a chemical equilibrium is assumed to exist between the reactants A and B and the transition state M^\ddagger :



The variation of the reaction-rate constant k with pressure is given by

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT}, \quad (11.2)$$

where ΔV^\ddagger , the volume of activation, is the difference in the partial molar volumes of the activated complex and the reactants and is given by

$$\Delta V^\ddagger = \bar{V}_M - \bar{V}_A - \bar{V}_B. \quad (11.3)$$

As shown in equation 11.2, a reaction with a positive activation volume is hindered by pressure, while one with a negative activation volume is enhanced by pressure. (As noted by Eckert (1972), equation 11.2 is applicable only if the reaction rate is expressed in terms of mole fractions not concentrations. Otherwise a second term is needed which accounts for the compressibility of the reaction mixture.)

Let us consider the application of transition-state analysis to interpret the work of Ehrlich and co-workers on the reaction behavior of ethylene polymerization in supercritical ethylene (Ehrlich, 1971). Ehrlich presents experimental data on the polymerization of ethylene at 130°C and 30,000 psia. At these conditions supercritical ethylene can solubilize approximately 5 wt-% to 10 wt-% high-molecular-weight polyethylene, which is produced during the reaction. Normally, the conversions are kept to less than 10%, and, therefore, from independent phase-behavior studies (Ehrlich, 1965), it is concluded that the reacting supercritical ethylene-polyethylene mixture is near a mixture critical point. Ehrlich argues that the partial molar volume of M^\ddagger , which has volumetric properties similar to the product polymer, can have a very large negative value in supercritical ethylene. It is well known that very large, negative partial molar volumes can exist for mixtures in which the solute is in dilute concentrations and the solvent is very close to its critical conditions or the mixture is close to the mixture critical point (Eckert et al., 1983; Chappellear and Elgin, 1961; Ehrlich and Wu, 1973). For example, consider the partial-molar-volume behavior of vinyl chloride solubilized in supercritical ethylene, shown in figure 11.4 (Ehrlich and Fariss, 1969). Using equation 11.2 and assuming that the absolute value of \bar{V}_M is much greater than the partial molar volume of ethylene, one would conclude that there should be a large rate enhancement occurring near the mixture critical point of the ethylene-polyethylene system. Ehrlich uses transition-state analysis to explain the large pressure effect on the polymerization rate as the pressure is dropped toward the mixture

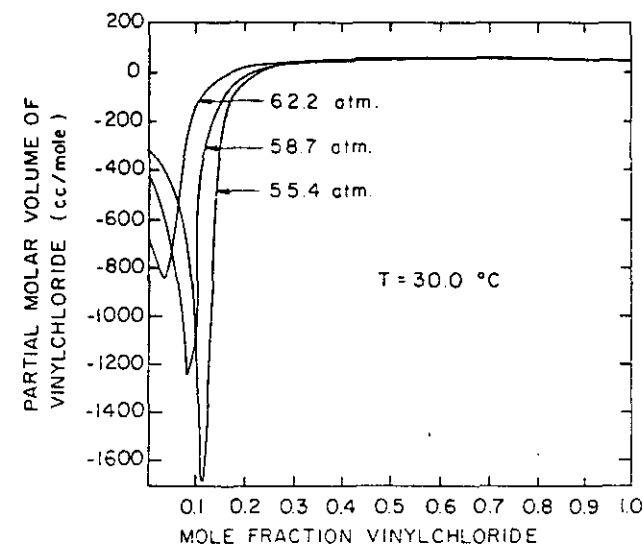


Figure 11.4 Calculated partial-molar-volume behavior of vinyl chloride solubilized in supercritical ethylene (Ehrlich and Fariss, 1969).

critical value, the small pressure effect on the polymerization rate when crystalline polymer is formed and falls out of solution, and the very high anomalous activation energy for polymerization at a temperature of 100°–130°C (the so-called critical polymerization boundary). However, in more recent work Ehrlich and co-workers find that the anomalous activation energy for ethylene polymerization in supercritical ethylene may be attributed to the presence of dissolved oxygen, which can be both a free-radical inhibitor in the subcritical liquid-gas region and a free-radical initiator in the supercritical region (Takahashi and Ehrlich, 1982; Ehrlich and Pittilo, 1960). Without the presence of dissolved oxygen in the system, the polymerization rates are very slow. Hence, the rate enhancements suggested by transition-state analysis are quite small in this instance.

Simmons and Mason (1972) employ transition-state analysis with an equation of state (EOS) (i.e., Redlich-Kwong and the virial equation) in an attempt to derive an expression for the pressure dependence of the dimerization-rate constant of chlorotrifluoroethylene ($T_c = 105.7^\circ\text{C}$, $P_c = 40.1$ atm). They attempt to predict the volumetric properties of the reactants by fitting experimental rate data. They can obtain the thermodynamic properties, such as the fugacity coefficient and partial molar volume, of the activated complex. The predicted fugacity coefficient of the activated complex exhibits the same trends as that of a normal molecular species. Also, quite interestingly, the partial molar volume of the activated complex, \bar{V}_M , decreases sharply near the critical

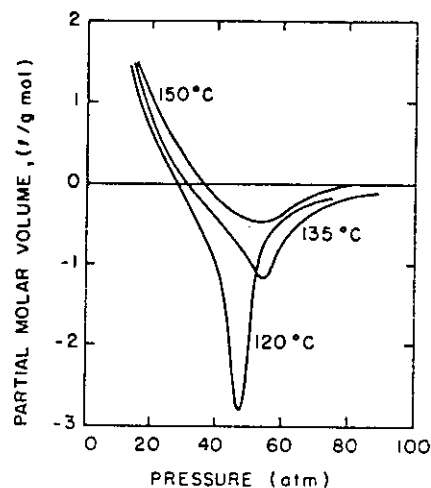


Figure 11.5 Partial-molar-volume behavior of the activated complex formed in the dimerization of chlorotrifluoroethylene in its critical region (Simmons and Mason, 1972).

point of the dilute reaction mixture (see figure 11.5). On the basis of transition-state analysis one might expect enhanced reaction rates at conditions very near the critical point of the pure chlorotrifluoroethylene. However, the observed rate enhancement is only 30% for pressures up to 100 atm. Unfortunately, the Redlich-Kwong EOS does not correlate the experimental data within 30%. Hence, more rate data are needed at higher pressures to better ascertain the pressure enhancement and to provide a more stringent test of the EOS.

For all practical purposes the large rate enhancements that occur as a result of large solute partial molar volumes are limited to the dilute-concentration region as shown in figure 11.4 and implied in figure 11.5. Although an enhancement of the reaction rate can occur as a result of hydrostatic pressure alone, excessively high pressures (i.e., greater than 1,000 atm) are needed for pressure to have any appreciable effect (Eckert, 1972).

HIGH-TEMPERATURE REACTIONS

It may be possible to use an SCF reaction medium to lower the operating temperature of pyrolysis reactions. The carbon formation that occurs at the high temperatures normally encountered in pyrolysis reactions can therefore be minimized. Improved yields, selectivities, and product separation have been attained in an SCF reaction medium, as compared with conventional pyrolysis methods.

Köll and Metzger (1978) report on the use of supercritical acetone as the reaction medium for the thermal degradation of cellulose and chitin. Since the pyrolysis of these polysaccharides occurs at such high temperatures, it is necessary to remove the primary products from the reaction zone as soon as they are formed to avoid degradation of the products into coke. The high

operating temperature also adversely affects both yield and product distribution. It is possible to reduce the carbon formation by carrying out the pyrolysis under vacuum, but the reaction rate is also reduced because of the poor heat transfer to the reactants.

As an alternative pyrolysis technique, Köll and Metzger react the cellulose in the presence of supercritical acetone ($T_c = 235.7^\circ\text{C}$, $P_c = 47.0$ atm), using a flow reactor. The reactor, operated isobarically at 250 atm, is temperature programmed from 150°C to 290°C. At SCF conditions, 98% extraction of the initial cellulose is achieved. The yield of glucosan, which is 38.8%, compares favorably with the 28.1% yield obtained with vacuum pyrolysis. Interestingly, the cellulose residue has the same crystallinity as the starting cellulose even after 50% degradation. Thus, the use of supercritical acetone as a reaction medium in the thermal degradation of cellulose results in an appreciable amount of extraction, less carbon formation, and better yield at temperatures lower than those used for conventional pyrolysis.

While doing their cellulose and chitin studies Köll and Metzger found condensation products of acetone (such as diacetone alcohol and mesityl oxide) that were apparently formed by a thermally induced aldol condensation (Köll and Metzger, 1978). This is an interesting finding since pyrolysis reactions are expected to dominate at these high temperatures. Metzger and co-workers (1983) initiated a program to investigate systematically thermal intermolecular reactions at high temperatures ($\sim 500^\circ\text{C}$) and high pressures (~ 500 atm) using a flow reactor with residence times of 1–10 minutes. It is assumed that at such high temperatures and pressures the reacting mixture is a single supercritical fluid. The researchers find that alkanes are added to alkenes (e.g., *n*-alkenes, acrylonitrile, methyl acrylate, methyl vinyl ketone), to 1,3-dienes (e.g., 1,3-cyclohexadiene), and to alkynes (acetylene). Thus, functional groups are added to hydrocarbons at supercritical conditions. The reactant mixture typically consists of an alkane-to-alkene feed in the ratio of 20:100. For example, when cyclohexane ($T_c = 280.3^\circ\text{C}$, $P_c = 40.4$ atm) is the representative alkane and methyl acrylate ($T_c = 263^\circ\text{C}$, $P_c = 42$ atm) is the representative alkene, the yield at 500°C (based on methyl acrylate) increases significantly with pressure up to 100 atm and thereafter remains essentially constant. The increase in yield is explained by the increase of density of the reacting mixture with pressure. At higher densities the intermolecular reaction proceeds at a much higher rate.

Other reactions studied by these authors include the thermal dimerization of methyl acrylate and the reaction of benzene with certain alkynes in a Diels-Alder reaction. Supercritical extraction in coal processing may also be classified under this scheme. However, this subject is reviewed adequately elsewhere (Williams, 1981) and, hence, is not included in this chapter.

HETEROGENEOUS CATALYSIS

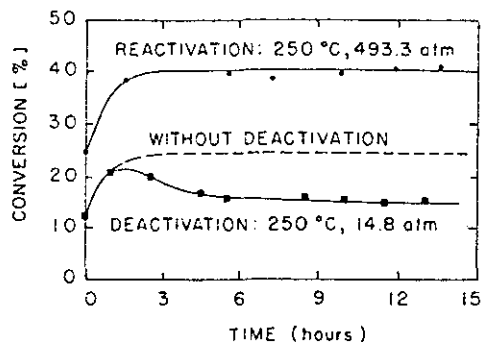
For certain heterogeneous catalytic reactions the catalyst activity can be renewed by adjusting the pressure and temperature so that the reacting medium

is in the supercritical state. The activity of the catalyst can be periodically regenerated by treatment with an SCF solvent or, in fact, the reaction can be run at supercritical conditions, thus maintaining high levels of catalytic activity for longer periods of time.

Tiltscher, Wolf, and Schelchshorn (1984) describe the influence of an SCF reaction medium on the activity of a heterogeneous catalyst used in a high-pressure differential-recycle reactor to study the catalytic isomerization of 1-hexene ($T_c = 231^\circ\text{C}$, $P_c = 30.7$ atm) on $\sigma\text{-Al}_2\text{O}_3$ with 2-chlorohexane as a cocatalyst. In this isomerization reaction they produce 1-hexene, cis-2-hexene, trans-2-hexene, and trans-3-hexene. The authors demonstrate how an SCF reaction medium can be used to reactivate a catalyst that has been poisoned by three different methods.

If the isomerization reaction is carried out in the gaseous phase ($T = 250^\circ\text{C}$, $P = 14.8$ atm), the resulting conversion-versus-time curve is characteristic of a curve in which a deactivation process occurs in parallel with the reaction (figure 11.6). The deactivation of the catalyst is a result of the unwanted low-volatile oligomeric compounds ($\text{C}_{12}\text{-C}_{30}$) that accumulate on the catalyst surface and eventually cause coking. If the reaction mixture is isothermally compressed to 493.3 atm, the oligomers are stripped from the catalyst surface and eventually cause coking. Although the phase behavior of the reactant-product system is not reported by Tiltscher and co-workers, it seems safe to assume the following: (1) the isomerization products are so similar to 1-hexene that the critical temperature and critical pressure of the reactant-product(s) mixture is very close to that of pure 1-hexene; and (2) the small amount of chlorohexane present in the system does not significantly affect the pressures and temperatures needed to obtain a single, fluid-phase mixture. Therefore, a pressure of 493.3 atm is more than sufficient to ensure that the reaction mixture plus the stripped oligomers is indeed a single fluid phase. If an elevated operating pressure is maintained at this high pressure level, a twofold increase in the overall isomerization rate and about a 30% increase in the cis-/trans-2-hexene ratio is observed (Tiltscher, Wolf, and Schelchshorn, 1984). At SCF conditions the catalyst activity is maintained at precoking levels even after twelve hours

Figure 11.6 Effect of unwanted oligomeric by-products formed during the catalytic isomerization of 1-hexene (Tiltscher, Wolf, and Schelchshorn, 1981).



of reaction time, as noted from the upper curve of figure 11.6. Not surprisingly, the authors also conclude that higher pressures are needed to enhance reactivation rates as the volatility of the oligomeric coking compounds decrease.

In another test the authors deactivate the catalyst by introducing a small amount of a finely dispersed catalyst-fouling substance (MoS_2) into the reactor under liquid-phase reaction conditions ($T = 220^\circ\text{C}$, $P = 493.3$ atm). In this instance the conversion-time curve is again characteristic of a reaction accompanied by catalyst deactivation (figure 11.7). If the reaction mixture is isobarically heated to 240°C , it becomes supercritical and eventually the catalyst activity is restored. Although it is not explicitly stated by the authors of this work, presumably the trace amounts of MoS_2 are solubilized by the reacting mixture.

In the final deactivation mode reported by the authors, the active acidic sites of the catalyst are poisoned ($T = 145^\circ\text{C}$, $P = 49.3$ atm) by continuous addition of a very dilute solution of pyridine to the reacting mixture over a period of twelve hours (see figure 11.8). The catalyst can be reactivated by heating and compressing the reaction mixture to conditions well within the mixture critical region ($T = 250^\circ\text{C}$, $P = 493.3$ atm). Tiltscher and co-workers report that the catalyst poison is precipitated from the product solution as

Figure 11.7 Effect of MoS_2 on the catalyst used for the isomerization of 1-hexene (Tiltscher, Wolf, and Schelchshorn, 1981).

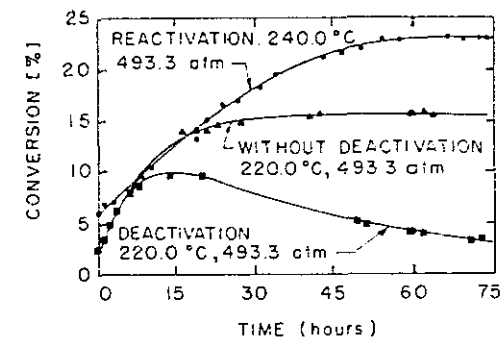
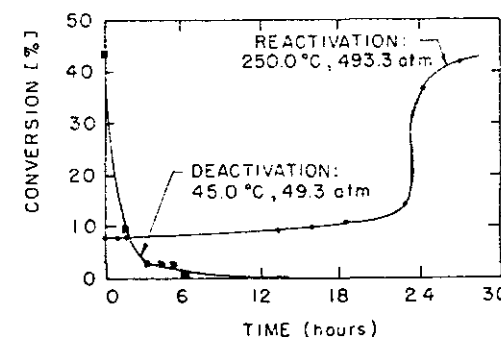


Figure 11.8 Effect of pyridine on the catalyst used for the isomerization of 1-hexene (Tiltscher, Wolf, and Schelchshorn, 1981).



pyridinium chloride. Presumably only a very small amount of pyridinium chloride is needed to deactivate the catalyst since supercritical hexene probably would not be able to solubilize much of this salt. It is surprising however that supercritical hexene can overcome the acid-base interactions that are occurring on the catalyst surface and, hence, remove the pyridinium chloride.

VISCOSITY EFFECTS

It is well known that solvent viscosity can have an effect on the product distribution for certain reactions (Saltiel and Charlton, 1980). The effect of solvent viscosity can be studied with an SCF reaction medium since a wide range of viscosities can be studied with a single SCF solvent if the system is operated in the vicinity of the critical point of the solvent (see figure 1.6).

Squires, Venier, and Aida (1983) describe an experimental technique they use to study the effect of solvent viscosity on the cis/trans ratio of stilbene irradiated in supercritical CO₂. They use a dynamic-flow technique similar to that described in chapter 4. In their system trans-stilbene is coated onto glass beads, which are then packed into a high-pressure column. Supercritical CO₂ flows through the column and solubilizes some of the trans-stilbene. The CO₂-stilbene phase is continuously irradiated with ultraviolet light as it flows through a quartz photoreactor at a fixed temperature and pressure. As the solvent viscosity increases, the photoisomerization of the cis isomer is inhibited while that of the trans isomer is facilitated. We should expect to see the cis/trans ratio of stilbene vary as the density of CO₂ varies. This viscosity effect is clearly shown in figure 11.9. While there is a small effect of pressure on the cis/trans ratio when the photoisomerization is run in near-critical liquid CO₂, the pressure effect is exacerbated in supercritical CO₂. This large pressure effect is highly correlated to the changes in CO₂ viscosity at 40°C near the critical pressure of CO₂ (i.e., compare figures 11.9 and 1.6).

Since the cis and trans structures exhibit different solubility levels in supercritical CO₂, it may be possible readily to separate the reaction mixture.

REACTION/SEPARATION SCHEMES

Supercritical fluid solvents can be employed as solvent media in chemically reacting mixtures, especially where it is difficult or prohibitively expensive to separate the desired species from a reaction-product mixture by conventional techniques such as distillation. It may be fruitful to consider using an SCF reaction medium in which the product can be more easily recovered from solution. For certain reactions using an SCF reaction medium can also improve the product selectivity without adversely affecting total conversion.

In a recent patent Kramer and Leder (1975) describe an SCF reaction scheme for isomerizing short-chain paraffinic hydrocarbons (4–12 carbon atoms). The reaction medium consists of CO₂, HBr, or HCl (as a promoter), a paraffinic hydrocarbon, and a Lewis acid catalyst (e.g., AlBr₃, AlCl₃, BF₃).

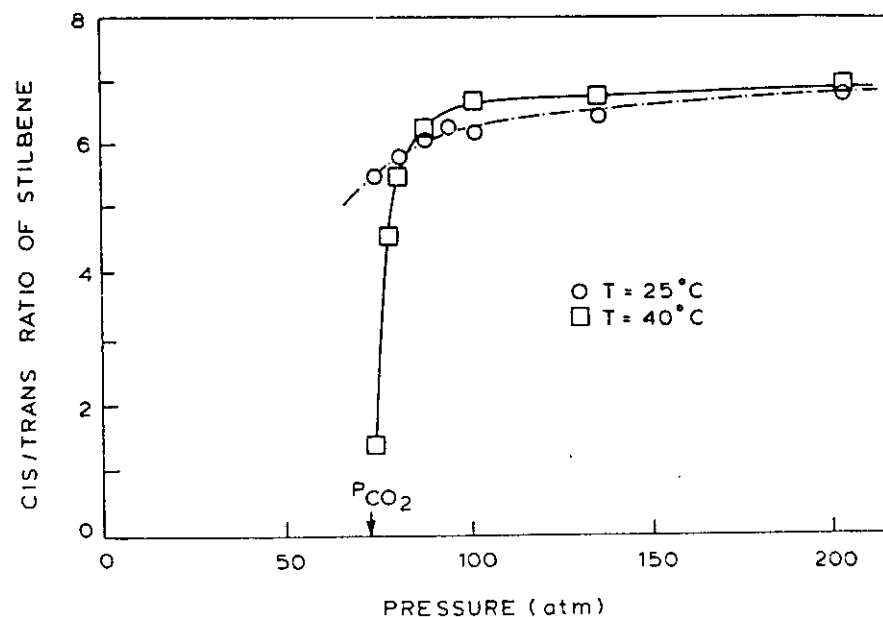


Figure 11.9 Transient-product distribution of the cis/trans isomer obtained when stilbene is irradiated in supercritical carbon dioxide at 40°C and 136 atm (Squires, Venier, and Aida, 1983).

An SCF reaction scheme offers several advantages as compared with a conventional subcritical-liquid CO₂ isomerization process. One obvious advantage is that hydrogen can be more easily dissolved in the SCF reaction phase as compared with a liquid reaction phase. The presence of hydrogen facilitates isomerization as opposed to cracking reactions and thus improves the selectivity of the reaction while not adversely affecting the conversion level.

As mentioned in chapter 10, SCF processing has been applied to the treatment of wastewater streams. In a very recent patent, Modell (1982) describes an efficient processing method for oxidizing the organic materials present in wastewater using supercritical water ($T_c = 374^\circ\text{C}$, $P_c = 217.6$ atm). The reaction is performed in a single fluid phase at supercritical conditions. For the purpose of minimizing the energy requirements for the process, the heat generated in the reaction is efficiently transferred to the reactor feed stream. An important advantage of the SCF reaction scheme over conventional processing is that virtually total oxidation of the organics can be realized with higher reaction rates. Since the reaction mixture is completely miscible in the mixture critical region, stoichiometric amounts of oxygen are easily added to the system for total oxidation of the organics.

In this process inorganic salts, which are virtually insoluble in supercritical water (1 ppb to 100 ppm in the temperature range of 450–500°C), are easily

precipitated from solution and readily removed from the system. As a consequence, the outlet water from the reactor is free of inorganic salts, thus eliminating the need for purifying reactor feedwater from sources such as brine and seawater. In addition, the heat liberated during the oxidation of the organics can be recovered in the form of superheated, supercritical steam without the need for heat-transfer equipment.

Another recent patent describes a multistep process for the production of ethylene glycol in near-critical or supercritical CO_2 (Bhise, 1983). In this instance CO_2 is first used as a solvent and then used as a reactant. Normally, ethylene oxide is produced by the vapor-phase oxidation of ethylene with molecular oxygen over a supported silver catalyst. In conventional ethylene-glycol processing, an effluent stream containing the ethylene oxide is scrubbed with water to recover the ethylene oxide. The ethylene oxide is then recovered for hydrolysis to ethylene glycol.

A schematic diagram of the SCF reaction/separation process is shown in figure 11.10 (Bhise, 1983). An ethylene oxide-rich CO_2 phase is obtained when

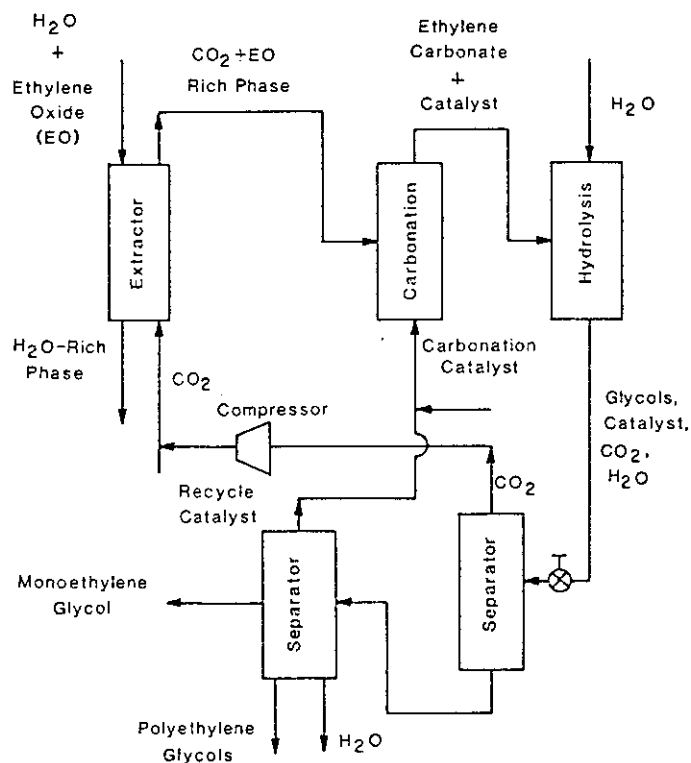


Figure 11.10 Proposed SCF reaction/separation process for producing ethylene glycol (Bhise, 1983).

the aqueous solution is mixed with near-critical or supercritical CO_2 at temperatures up to 100°C and pressures ranging to 300 atm. The ethylene oxide- CO_2 phase, which leaves from the top of the extractor (or from the bottom if the CO_2 is too dense), is then contacted with a carbonation catalyst (e.g., organic quaternary ammonium halides) and reacted to form a catalyst-ethylene carbonate- CO_2 stream. The catalyst-ethylene carbonate- CO_2 stream is then delivered to another reactor and hydrolyzed to form ethylene glycol and CO_2 . In this process the carbonation catalyst also catalyzes the hydrolysis reaction. In the final steps of the process the CO_2 is flashed from the ethylene glycol stream and recycled to the extractor. The ethylene glycol and the catalyst are then recovered.

Direct hydrolysis of the ethylene oxide-water stream tends to produce more of the higher glycols, such as diethylene glycol, as compared with the SCF reaction/separation scheme.

ENHANCED REACTION RATES AND SELECTIVITIES

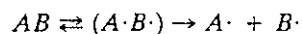
Certain chemical reactions, such as free-radical, vinyl-polymerization reactions, can exhibit enhanced reaction rates with different selectivities when the reaction occurs homogeneously in the mixture critical region as compared with heterogeneously in the subcritical gas-liquid region. Hence, it is possible to control the extent of reaction by isothermally adjusting the system pressure such that either the reaction proceeds rapidly when the reaction mixture exists as a single homogeneous supercritical mixture or the reaction slows considerably when the mixture exists as a heterogeneous gas-liquid mixture in the subcritical region.

In a very early study Patat (1945) investigated the hydrolysis of aniline to phenol in a water-based acidic solution in near-critical and supercritical water ($T_c = 374.2^\circ\text{C}$, $P_c = 217.6$ atm). Phosphoric acid and its salts are used as the catalyst for this reaction. The reaction proceeds extremely slowly under normal conditions and reaches equilibrium at low conversion levels. For these reasons, Patat chooses to study the reaction in supercritical water to temperatures of 450°C and to pressures of 700 atm in a flow reactor. He finds that the reaction follows known, regular kinetics in the entire temperature and pressure space studied and the activation energy of the hydrolysis (approximately 40 kcal/g-mol) is the same in the supercritical as well as in the subcritical water. He suggests that the reaction is catalyzed by hydrogen ions formed from dissolution of phosphoric acid in supercritical steam. Very small amounts of phosphoric acid and the salts of the phosphoric acid are dissolved in the supercritical steam and are split into ions. Patat lists several dissolution constants for primary ammonium phosphates in supercritical steam. In this instance, the reaction performance is improved when the reaction is operated homogeneously in the mixture critical region and, thus, in intimate contact between the reactants and the catalyst.

Using a batch reactor Blyumberg, Maizus, and Emanuel (1965) studied the oxidation of *n*-butane at conditions near the critical point of butane ($T_c = 152.1^\circ\text{C}$, $P_c = 37.5$ atm). Both liquid-phase and SCF-phase oxidations are studied. In this reaction butane hydroperoxide is first formed via a free-radical chain mechanism and then broken down into products.

With the liquid-phase oxidation a long induction period is observed, whereas the SCF-phase oxidation has much shorter induction times. Also, the liquid-phase oxidation products are predominantly acetic acid and methyl ethyl ketone, whereas the SCF-phase oxidation products are formaldehyde, acetaldehyde, methyl, ethyl, and propyl alcohols, and formic acid. The authors offer no explanation for the differences in product spectrum or induction periods for the reactions.

Subramaniam and McHugh (n.d.) suggest that the increased reaction rates in the SCF phase may be associated with the more efficient production of free-radical pairs. When initiator molecule *AB* dissociates to form a geminate radical pair ($A\cdot B\cdot$) it may either diffuse apart to form a free-radical pair or may recombine before it can diffuse apart in the so-called cage effect (Eckert, 1972):



Since the resistance to diffusion will be lower in the mixture critical region than that in the liquid phase it is expected that the ($A\cdot B\cdot$) radical pair should more readily diffuse apart in the critical region. Although applied hydrostatic pressure favors the recombination of ($A\cdot B\cdot$) to form *AB*, it seems reasonable to assume that the rate of diffusion dominates the pressure effect as long as the system pressure is maintained below approximately 1,000 atm. Therefore, the formation of free radicals should be facilitated in the SCF phase, as compared with the liquid phase, and shorter reaction times are to be expected.

The difference in product spectrum obtained from a system operating in the SCF phase as compared with the liquid phase is probably a function of the types of free radicals that are formed in each phase. In the SCF phase, the butane-derived free radicals have a higher probability of further decomposing into methyl radicals rather than terminating the reaction by recombining since the reaction temperature is greater in the SCF phase as compared to the liquid phase. If the methyl radicals undergo further oxidation, a broad spectrum of products will be obtained (Winkler and Hearne, 1961).

In a similar process Baumgartner (1983) describes a process for enhancing tertiary-butyl-hydroperoxide (TBHP) formation by reacting isobutane ($T_c = 142^\circ\text{C}$, $P_c = 37.0$ atm) with oxygen in a dense-phase reaction mixture. In previous studies, Winkler and Hearne (1958, 1961) show that the catalytic oxidation of isobutane in the vapor phase produces significant amounts of tertiary butyl alcohol and minor amounts of other oxidation products such as acids, aldehydes, ketones, and other alcohols, in addition to the desired TBHP. They also demonstrate that reacting isobutane with molecular oxygen nonca-

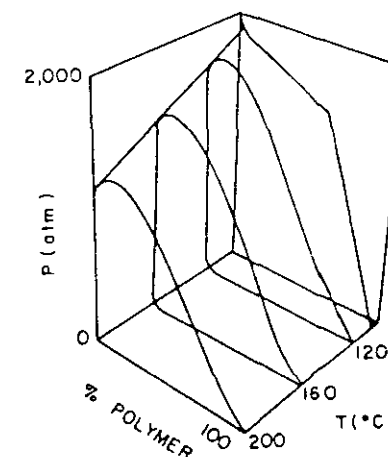
talytically in the liquid phase of a two-phase liquid-gas mixture at 100–150°C and at 28.2 atm produces reaction products consisting of TBHP and tertiary alcohol. However, this liquid-gas phase reaction suffers from very low reaction rates and a low selectivity for TBHP. The occurrence of a broader spectrum of products in the gas-phase oxidation of isobutane, as compared with its liquid-phase oxidation, is consistent with the observations of Blyumberg, Maizus, and Emanuel (1965) in the case of the oxidation of *n*-butane.

In the work of Baumgartner, isobutane is oxidized at conditions significantly higher than the T_c and P_c of isobutane and also above the critical pressure of the reaction mixture. The reactor operating variables must be carefully optimized and controlled to attain enhanced TBHP selectivities. Also, as with the case of *n*-butane oxidation, enhanced TBHP formation is observed when the reaction is run homogeneously in the dense phase as compared with the corresponding formation obtained when the reaction is run in the liquid phase (Baumgartner, 1983).

Within the last two decades Ehrlich and co-workers have compiled a comprehensive picture of the free-radical polymerization of ethylene in supercritical fluid ethylene ($T_c = 9.3^\circ\text{C}$, $P_c = 49.7$ atm) (Ehrlich and Mortimer, 1970; Takahashi and Ehrlich, 1982; Ehrlich and Pittilo, 1960; Ehrlich and Kurpen, 1963; Ehrlich, 1965; Takahashi, 1980).

As noted in chapter 6, early chromatography work showed that polymers, especially polystyrene, can be fractionated with a supercritical fluid mobile phase (Jentoft and Gouw, 1969, 1970). Ehrlich and Graham (1960) also found that polyethylene is soluble in supercritical propane when the pressure is increased above 500 atm. Knowledge of this solubility behavior is extremely important since it has a direct bearing on the interpretation of reaction-time data. Ehrlich has done a comprehensive study on the phase behavior of polyethylene-ethylene mixtures at high pressures. The results from his phase-behavior studies are shown in figure 11.11 as a schematic *P-T-x* diagram for

Figure 11.11 Schematic *P-T-x* diagram of the ethylene-polyethylene system (Ehrlich and Mortimer, 1970).



the polyethylene-ethylene system. Notice that the two-phase liquid-vapor region for polymer-solvent systems persists to very high pressures. Ehrlich and Mortimer (1970) conclude that kinetic studies reported in the literature on ethylene polymerization are often of little value since the authors of the studies are unaware of the phase behavior involved with SCF systems at moderate or high pressures. Many times polyethylene polymerization studies reported in the literature are performed on systems that are thermodynamically underdetermined because of the number of phases present and the number of constituents in the system.

In a 1946 patent Kruse and Lawrence (1946) describe an SCF reaction process for making ethylene polymers. Ethylene is reacted in the presence of a catalyst at temperatures between 40°C and 400°C and at pressures from 800 to 4,000 atm. The polymer is then recovered using a stepwise reduction in pressure with the objective of reducing compression costs. The authors note in this very early patent that appreciable quantities of the polymer are still solubilized in the supercritical fluid phase at pressures as low as 150 atm. This solubility behavior suggests that the product polymer can be precipitated from solution essentially free of lower-molecular-weight oligomers, residual monomer, and catalyst.

In a patent entitled "Supercritical Polymerization of Olefins," Cottle (1966) describes a process for reacting and separating polymers made from olefins. In this case propylene is reacted to polypropylene in a process using a catalyst and operating at conditions above the critical temperature and pressure for propylene ($T_c = 91.9^\circ\text{C}$, $P_c = 45.0$ atm). At the end of the reaction the system pressure is reduced to precipitate the crystalline polypropylene from solution while leaving the noncrystalline fraction solubilized in the propylene-rich phase. This fractionation behavior is another example of the effect of polymer tacticity on solubility level. In this process the supercritical fluid is used as both a reactant and a solvent, as in the ethylene polymerization processes previously described. Also, the example listed in this patent implies that the catalyst is soluble in the SCF phase, thus allowing for all the advantages of homogeneous reaction conditions.

It is clear from the several examples cited in this chapter that supercritical fluids can be advantageously used as reaction media. The field of reactions in supercritical fluids has, as yet, not been fully investigated. Isomerization reactions and free-radical oxidations of hydrocarbons are just two examples of the types of reactions that merit further study. There are still many unanswered questions in this area. How do near-critical or supercritical conditions affect the rates and paths of chemical reactions? How is the phase behavior of the initial reactants affected by product formation? Is it possible to exploit the above results to devise efficient reaction/separation schemes? These questions pose considerable experimental and theoretical challenges.

Most of the studies reported in this chapter fail to include the phase behavior of the reacting mixture. Since multiple phases can occur in the mixture critical region, reaction studies need to be complemented with phase-behavior

studies so that we may gain an understanding of the fundamentals of the thermodynamics and kinetics of chemical reactions in solution. As described in chapter 5, a simple, cubic equation of state (EOS) can be used to extend and complement the phase-behavior studies. The location of phase-border curves in P - T space can be determined with an equation of state. Also, an EOS can be used with transition-state theory to correlate the pressure dependence of the reaction-rate constant when the pressure effect is large (i.e., at relatively high pressures).

The advantages of using a supercritical fluid reaction medium are that it may be possible to run the reaction in a single, homogeneous phase, thus eliminating interphase mass-transfer limitations, and labile reaction products may be more readily isolated from the reaction mixture by adjusting the pressure or temperature to induce a phase split, thus avoiding unwanted side-reactions. To a lesser degree, reaction rates may be advantageously enhanced by running the reaction in the dilute-mixture region at conditions close to the critical point of the pure supercritical fluid. However, the rate enhancement does not appear to be extremely large and it is restricted to the dilute-mixture region.