Indo-German Workshop on High Pressure Technology-Engineering

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edited by
R.V. Chaudhari, H. Hofmann
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High Pressure Technology-Engineering

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HIGH PRESSURE TECHNOLOGY– ENGINEERING

EPILOGUE

High pressure technology and engineering has wide ranging applications in major chemical processes for the manufacture of basic commodity as well as speciality chemicals. Though many operations under high pressure are known, very few attempts were made to understand this subject in depth. This workshop enlightened on the various important developments in this area and the presentations followed by a panel discussions led to some important conclusions, which are summarized here.

The application of high pressure technology is growing rapidly leading to innovations in new processes and specially in areas like catalysis and separation technology (e.g. supercritical extraction). A combination of innovative catalytic chemistry and expertise in high pressure engineering is a need of future. The reaction engineering of high pressure reactions is complex and recent reports indicate careful considerations of kinetic pressure effect (volume of activation) and the significance of the changes in physicochemical parameters on mass and heat transfer parameters under high pressure. Specially, the effect of supercritical conditions on the kinetics and mass transfer properties can be very important. On this aspect, new data indicating advantages like increased rates is emerging in the literature, however, in-depth analysis of consequences of supercritical conditions need to be developed. The need for development of new technique for investigating reactions under high pressure conditions was emphasized. Further, methodology for predicting the system properties based on fundamental principles as well as their experimental determination need to
be developed.

The technology for high pressure equipment for chemical plants and particularly the mechanical design is considerably advanced, however, the current state of the understanding of the analysis of fatigue, creep and corrosion under high pressure is not very complete. The need for inspection of equipment and development of diagnostic tools for it was strongly emphasized.

Safety in high pressure technology would require more attention in future. Automation in laboratory scale experiments for pressure reactions is necessary. A detailed analysis of potential hazards is also very vital for the development of new generation technologies.

Further development on scale-up methodologies and reduction of the overall cost in the high pressure processes is also equally important. It was also concluded that the future developments in this area should be aimed at reducing the operating pressures in the chemical processes, which in turn will lead to more economical and intrinsically safer technologies.
Prof. M.M. Sharma, Prof. H. Hofmann, Prof. Y.T. Shah, Prof. H. Tiltscher

Prof. H. Hofmann, Prof. H. Tiltscher, Prof. G. Luft,
Prof. Y.T. Shah, Dr. R.V. Chaudhari
SOME PROBLEMS IN HIGH PRESSURE REACTION ENGINEERING

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Some Problems in High-Pressure Reaction Engineering

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I. INTRODUCTION

In the first decades of this century the production of chemical industry was extended from pharmaceuticals and dies to mass products like fertilizer, methanol, synthetic rubber, polymeres and fibers. In connection with this change also the way to perform chemical reactions has changed. Whereas in the last century chemical reactions have been forced with highly active reactants like strong acids or alkaline, in mass production physico-chemical factors became more important like catalysis, mass action by non-stoichometric feed and high reaction pressure. The variation of physico-chemical properties, equilibria etc. with pressure is a powerful tool to control homogeneous as well as heterogeneous reactions. Nevertheless the potential of high-pressure in its influence on the rate of chemical reactions seems not to have been analyzed in its admost in the past. Whereas e.g. the Arrhenius law for the temperature dependence of chemical reaction rate as well as the thermodynamic pressure effect is well known and used in practice to force chemical reactions, the so called kinetic pressure effect described by

\[ \frac{\partial \ln k}{\partial p} \bigg|_{T, RT} = \frac{-\Delta V''}{RT} \]  

with \( \Delta V'' \) as volume of activation is less known. As according to this effect the rate of a reaction can be accelerated or retarded by increasing pressure, significant changes of conversion and selectivity with pressure are possible [1]. The
influence of pressure on heterogeneous catalytic surface reactions is even more complex due to the interaction of transport, adsorption and chemical steps; also the deactivation of a catalyst can be strongly dependent on pressure (see Fig. 1).

Therefore it seems to be interesting to discuss some problems in heterogeneous catalytic reactions under higher pressure, we have studied in the past in our laboratory

* Catalyst deactivation and reactivation by a supercritical reaction mixture
* Rate factors in liquid phase high-pressure hydrogenation with suspended catalyst and
* Kinetic description of heterogeneous catalytic multicomponent-multireaction systems

II. CATALYST DEACTIVATION AND REGENERATION BY A SUPERCritical REACTION MIXTURE

Deactivation of catalysts is one of the important problems in catalytic reaction engineering. To estimate the time on stream a catalyst can be used economically, its deactivation kinetics must be known. Activity of a catalyst usually is defined [2] as the ratio of the reaction rate at time \( t \) to the respective rate at time \( t=0 \) (both at the same temperature \( T_{\text{ref}} \) and the same concentration \( c_{\text{ref}} \))

\[
a_j(t) = \frac{r_j(t)}{r_j(0)} \quad (2)
\]

Provided the kinetics of deactivation can be separated from the stationary kinetics of the respective reaction the activity of a catalyst as function of time on stream can be measured most
conveniently in a gradientless recylce reactor with temperature and concentration control. Due to the fact that density of fluids and therefore their solvent power changes dramatically near the critical point (Fig. 2) a special ability to dissolve higher molecular weight materials (polymers) may be expected under supercritical conditions. With the assumption of an incompressible solid of low vapor pressure, its solubility in a liquid phase can be described by

\[ y_2 = \frac{P_2^{\text{sat}}}{P} \exp \left( \frac{v_2^{\text{sat}} (P - P_2^{\text{sat}})}{RT} \right) \]  

(3)

with \( \psi_2^f \) as fugacity coefficient according to the Redlich-Kwong equation.

It is therefore an interesting question whether coke or coke-precursors deposited on the surface of the catalyst can be removed by a supercritical reaction mixture. To study this phenomena in detail we have selected the disproportionation of ethylbenzene catalysed by a zeolite [3].

Fig. 3 shows some estimated solubilities of condensed arenes (as model substances for precoke) in ethylbenzene (T_e =617 K, P_e = 36 bar) as function of pressure and (in the lower part) the influence of sublimation pressure and critical properties on solubility. Higher critical temperature and lower critical pressure increase the solubility. From the step change in solubility it can be expected that under supercritical conditions at least coke-precursor really could be removed from catalyst surface.

Fig. 4 shows a flow diagram of the equipment used for this study. It consists of an HPLC-pump to feed the reactants, an integral reactor which could be exchanged by a gradientless reactor, a pressure control, a gaschromatograph for the analysis of the reaction mixture and a condenser.
Preliminary experiments have shown that by shifting the reaction conditions into the supercritical range higher molecular material is dissolved by the reaction mixture. These products absorb light in the range of 400 - 600 nm. The intensity of this absorption was used as an easy measure for the "concentration of dissolved material", since the absorption was found to be proportional to the concentration of solid materials.

A normalized rate of removal $R_{ren}$ was defined as the amount of solid dissolved ($A$) times the ratio of throughput of regeneration liquid ($\dot{Q}$) to mass of catalyst in the reactor. If mass transfer between catalyst and fluid is a limiting step for the dissolution, the dependence of the rate of dissolution on concentration can only be studied in a gradientless reactor as there the mass transfer coefficient $k_a$ can be kept constant by a fixed recirculation rate. If the feed is sufficiently low one can also determine the solubility limit $c_{sol}$ of the solid as the measured concentration of dissolved material $c$ is (according to a material balance) given by

$$
1 = c_{sol} \frac{m_{feed}}{1 + \frac{m_{feed}}{k_a a_o m_{cat}}}
$$

Fig. 5a shows the experimentally determined normalized rate of removal $R_{ren}$ as function of time and operating pressure. In the experiment the catalyst was deactivated for 15 minutes under normal pressure at 570 K. At the end of this period pressure and temperature of ethylbenzene feed were shifted into the supercritical range (P=40 bar, T= 623 K). The figure shows a significant decrease of the rate of removal with time, obviously as with increasing time on stream (i.e. increasing deactivation) the formation of new coke decreased, whereas at the same time also the removal of remaining higher polyaromatics becomes more difficult. An analysis of the catalyst bed after 3 hours on
stream showed that with ethylbenzene, a complete removal of coke could not be achieved, as under supercritical conditions ethylbenzene also exhibits a stronger coke deposit in parallel to coke removal. To reduce the rate of coke formation in a second experiment supercritical benzene (with a lower critical temperature and lower tendency to form coke) was used for the regeneration. Fig. 5b shows that also with benzene the removal rate decreases with time, even faster at higher temperature. This indicates that obviously only freshly formed coke-precursor can be removed and coke already deposited on the catalyst surface for a longer period of time can hardly be redissolved. At the end of this experiment when temperature was set back to its original value no coke-concentration was measurable in the product stream.

To avoid catalyst deactivation during pressurizing of the reactor, experiments have been performed where the reactor was prepressurized with nitrogen to supercritical conditions before the ethylbenzene feed was started. Under this conditions the reaction mixture was capable of removing some solid even below the critical temperature and a much lower deactivation was observed. This suggests that coke-precursor was removed from the very beginning and that at the high turbulence in the gradientless reactor coke removal was not limited by external mass transfer. Fig. 6 shows the deposit of coke on the catalyst under different operating conditions after 3 hours; even at a slightly higher temperature with a pressure of 50 bars, less coke remained on the catalyst as under normal pressure.

To sum up it could be demonstrated that with a supercritical reaction mixture the activity of the catalyst could be preserved for a longer time on stream as coke-precursors formed are instantaneously dissolved by the supercritical reaction mixture, i.e. supercritical reaction conditions may save catalyst regeneration cost.

As higher temperatures speed up the coke formation rate and as
at the same time higher temperatures promote removal of coke-precursors (because of higher solubility and faster diffusion in catalyst pores) but with a different activation energy, it can be expected that an optimal temperature exists at which deactivation is significantly reduced whereas the desired reaction rate is still fairly high.

III. RATE FACTORS IN LIQUID PHASE HIGH-PRESSURE HYDROGENATION WITH SUSPENDED CATALYST

Catalytic liquid phase reactions with suspended catalyst are very common in chemical industry. In this case the effective rate of reaction depends not only on the chemical rate but also on the intensity of mixing. The mixing device on one hand has to provide a homogeneous suspension of the (usually small) catalyst particles of relatively high density, on the other hand it must provide a large enough gas-liquid interface to avoid a transport limitation of the gaseous reactant into the liquid. Therefore under stationary operating conditions one can derive the following overall rate expression for the formation or consumption of a reactant:

\[
R_i = \frac{1}{k_{Li}a} + \frac{1}{k_{ki}a_i} + \frac{(\text{adsorption term})}{(\text{kinetic term})(\text{potential term})} \quad (5)
\]

Dependent on the relative importance of each resistance term in the determinator of Eq. (5) the global rate of reaction is practically equal to the inverse of the largest.

To study the interaction of these different reaction steps the well known hydrogenation of glucose with Raney-nickel as catalyst to sorbitol has been used as model reaction [4]

\[
C_6H_{12}O_6 + H_2 \rightarrow C_6H_{14}O_6 \quad (6)
\]
In reality this reaction is much more complex as given by the above stoichiometry. Dependent on the pH-value of the aqueous solution the main reaction is accompanied by isomerization of glucose into fructose and a disproportionation into gluconic acid and mannitol as undesired side reactions (Fig. 7). Whereas the presence of some mannitol in the product is not important for the use of sorbitol in cosmetics, a substantial formation of gluconic acid has to be avoided by a high enough rate of hydrogenation and a well selected constant pH-value.

To find optimal conditions and to understand the influence of the different operating variables on the reaction rate experiments have been performed in an autoclave operated batchwise under constant hydrogen pressure equipped with a hollow self-suction stirrer with paddles (Fig. 8) to assure a homogeneous suspension of the catalyst particles as well as a good dispersion of the gas phase in the liquid [5]. The progress of the reaction was followed by the consumption of hydrogen (from a thermostated reservoir) as well as by HPLC-analysis of the liquid products. Fig. 9 shows that at a hydrogen pressure of 25 bars and 120°C, dependent on the activity of the catalyst used, the rate of glucose consumption is different, whereas at 140°C both catalysts seem to have the same activity, indicating that under this conditions the global rate of reaction is not limited by the chemical rate (i.e. catalyst activity) itself. For a hydrogen pressure of 50 bars (bottom) at 140°C as well as 120°C both catalysts seem to have the same activity, suggesting that now even at 120°C the overall rate is limited by a transport step.

In order to find the limiting transport step, experiments have been performed at different degrees of turbulence (i.e. at different speeds) and at increased chemical rates by doping the catalyst with magnesium. Fig. 10 shows that even with the double amount of doping material (see the 2 points on the top right of Fig. 10) the effective rate of reaction can not surpass a certain value limited by a transport step which is dependent on
the degree of turbulence in the liquid, whereas at the lowest
temperature obviously the chemical rate is limiting because of
its higher activation energy, making the overall rate
independent on stirrer speed. Supposing that the transport
resistance in the gas film at the gas-liquid interface can be
neglected as the gas phase consists of nearly pure hydrogen (the
vapor pressure of the aqueous glucose solution under this
conditions is less that 1/10 of the total pressure). Also the
hydrogen transport through the liquid film at the interface gas-
liquid cannot be rate limiting, as in this case the glucose
conversion under constant hydrogen pressure should have followed
a zero order rate law, whereas experimentally a quasi first
order has been found. Therefore it is obvious that the
transport limitation is located in the stagnant liquid film
surrounding the catalyst particles.

The independent observation that small amounts of ethanol added
to the solution (converting the originally coalescing system
into a non-coalescing system with a much higher gas-liquid
interface) did not change the rate of reaction also indicates
that mass transfer limitation must be located at the liquid-
solid interface.

Under the assumption that the hydrogenation is irreversible and
with the observation that the glucose consumption as well as the
sorbitol formation can be described sufficiently precise by a
first order rate law with respect to glucose concentration, the
hyperbolic rate expression given in Eq.(5) can be simplified to

\[
R_{\text{gl}} = \frac{C_{\text{gl}}}{1/k_s \ m \ a_s + 1/k_c(C_{n2}) m}
\]  
(6)

with a chemical rate constant \( k_c \) dependent on the hydrogen
pressure. Eq.(6) can be rewritten in dimensionless form as

\[
\frac{R_{\text{gl}}}{C_{\text{gl}}} = 1 + \frac{k_s \ a_s}{k_c(C_{n2})}
\]  
(7)
To check experimentally whether Eq.(7) is valid the volumetric mass transfer coefficient and its temperature dependence has been determined from the experiments with the highest temperature (i.e. the highest diffusion limitation) and with doped catalyst. Furthermore at the lowest temperature (80°C) where the overall rate is practically equal to the chemical rate (and with the known solubility of hydrogen in the aqueous solution) $k_0$ has been determined. In Fig. 11 the inverse value of an "acceleration factor" has been plotted as function of the ratio of a characteristic transport time to a characteristic reaction time. It can be seen that the experimental data follow very well Eq. (7), indicating that transport of glucose through the liquid film surrounding the catalyst particles is rate limiting at higher catalyst activity and higher temperature respectively.

From these results it can be concluded that for a high selectivity to sorbitol the glucose hydrogenation should be performed at a high hydrogen pressure as well as at the highest possible turbulence in the liquid-phase and with catalyst particles as small as possible. Additionally at the same time the pH-value should be kept in the range of 5 - 6 by a buffer to avoid as much as possible isomerization and disproportionation. Finally it could be of interest, that similar observations have been made for xylose hydrogenation into xylitol using a ruthenium catalyst on active carbon.

IV. KINETIC DESCRIPTION OF HETEROGENEOUS CATALYTIC MULTICOMPONENT-MULTIREACTION SYSTEMS

Heterogeneous catalytic multicomponent-multireaction systems are very common in hydrotreating of petroleum fractions as well as in cracking or polymerization. For the rational design of a respective catalytic reactor a sufficiently detailed description of the kinetics is needed. At present amongst chemical reaction engineers exists a certain discussion about the detail really
needed in modeling this systems. one group favors a very
detailed description down to the elementary reactions with the
argument that with present day digital computers even very
complex models can be solved in a reasonable time [6]. The other
group prefers a more or less severe lumping, arguing that one
of the golden rules in chemical reaction engineering is that
modeling should never be more sophisticated than needed for the
purpose to enable the chemical engineer to give a satisfying
answer in a limited period of time [7].

To study experimentally such a system the high-pressure
hydrodesulfurization of gas-oil on a commercially available
cobald-molybdenum catalyst has been used as a model reaction
[8]. Fig. 12 gives the schematic diagram of the experimental
equipment with a high pressure autoclave, a hydrogen supply and
devices for liquid and gas phase samples. The reactor pressure
was held constant by a pressure reducing valve; temperature was
controlled at 280-360°C. Both catalyst powder with a particle
size smaller than 60 nm as well as 3 x 3 mm and 5 x 5 mm
pellets, presulfided in an H2S-atmosphere have been used. Whereas
the powder was added directly to the oil the catalyst pellets
were fixed in a small basket serving simultaneously as stirrer.
The analysis was performed by GC equiped with a sulfur-sensitive
flame photometric detector (FDP) and a flame ionization
detector (FID). The FID-signal showed distinct peaks for the n-
alkanes between C11 and C28 whereas the FDP-signal gave the
distribution of the sulfur-components only (Fig. 13). The
chromatogram shows a variety of sulfur-components contained in
the gas-oil, which obviously are more or less reactive.

To get a better understanding of the reacting system the
concentrations of sulfur-components with different boiling
temperature were analyzed in the course of an experiment as
function of reaction time (Fig. 14). In this diagrams every
integrated peak from the sulfur-sensitive chromatogram is
represented by a single line, whose length corresponds to the
respective amount. (However not every peak really corresponds to
a single component; in most cases one peak represents several sulfur components having nearly the same boiling temperature).

Fig. 14 shows clearly the varying reactivity of the different "components". Low boiling components disappear appreciably faster than components with higher boiling temperature. On the basis of this results kinetic constants for each component could be defined under the assumption that for its consumption a first order power rate law can be assumed to hold. Fig. 15 shows the reactivity distribution of the different sulfur components expressed by their first order rate constant for the suspended catalyst as well as for the 5 x 5 mm catalyst pellets, determined for a temperature of 623 K. Fig. 16 shows that in relation to their reactivity the initial concentrations $c_n(0)$ of the different sulfur components has the shape of a distribution which interestingly seems to be much smaller for a catalyst pellet than for the catalyst powder.

On the basis of these facts a lumped kinetic model can be developed under the assumptions that

1. Each single component follows a first order rate law in desulfurization.
2. The rate constants can be considered to be a continuous function of the initial concentration distribution $f(k,0)$.
3. The overall reaction can be described by an n-th order model

From this assumptions, it follows that

$$c_n(t) = \int_{0}^{\infty} f(k,t) dk = \int_{0}^{\infty} f(k,0) \exp(-kt) dk = \frac{c_n(0)}{[(n-1)k_n tc_n(0)^{n-1}+1]^{1/(n-1)}}$$

The right hand side of this equation can be regarded as the Laplace transform of the left hand side for which from the appropriate mathematical tables the original function can be found [9]. Here a relation between $f(k,0)$ and the gamma function results:
\[
\begin{align*}
f(k,0) &= \frac{k^A C_n(0) B^p \exp(-kB)}{\Gamma(A+1)} \\
A &= \frac{2-n}{n-1} \\
P &= \frac{1}{n-1} \\
B &= \frac{1}{(n-1) k_n C_n(0)^{n-1}} \\
\end{align*}
\]

By comparing the coefficients, the distribution parameters of the gamma function can be determined as functions of the \(n\)-th order power rate law:

\[
\begin{align*}
A &= \frac{2-n}{n-1} \\
P &= \frac{1}{n-1} \\
B &= \frac{1}{(n-1) k_n C_n(0)^{n-1}} \\
\end{align*}
\]

Finally the following relations result:

\[
C_n(0) = \int_0^\infty f(k,0) dk 
\]

and

\[
C_n[(0), (k_a, k_n)] = \int k_n f(k,0) dk 
\]

The last equation provides the concentration in the bulk solution \((k=a, k=b)\) for the time \(t=0\). The application of the \(n\)-th order model to the experimental results showed that nearly all experiments could be described quite well by this model (see Fig. 17 for a pressure of 50 bars with catalyst powder and Fig. 18 for 5 x 5 mm pellets). In the first case the pseudo-order of the reaction is about 3, as in the second the pseudo-order of the reaction is about 2. The different symbols in this diagrams represent the experimental points whereas the full lines show the calculated curves with the optimal parameter values. The global description as consumption in gramm sulfur per litre oil
(the only value of interest) are well represented by the calculated curves. A statistical analysis shows that the parameter \( n \) is only weakly correlated with the two remaining model parameters. The reason that catalyst powder causes a much broader reactivity distribution than the pellets can be explained by some diffusion limitation in the catalyst pores which also reduces the pseudo-order of reaction down to 2.

The \( n \)-th order rate expression derived can be extended in a simple way to implement also the pressure dependence of the hydrodesulfurization:

\[
    r = k'_n \cdot c^n \cdot p^m
\]

This expression should be correct under the assumption that the surface concentration of hydrogen on the catalyst is directly proportional to the hydrogen pressure in the gas phase. This means that hydrogen mass transport is not limiting at the gas-liquid or the liquid-solid interface. Experimental investigation of the influence of turbulence (as described in detail in the example of the xylose hydrogenation) as well as the activation energy of the rate constant actually could exclude such a mass transport limitation. Fig. 19 shows a typical result for total sulfur concentration plotted against time of reaction. The symbols mark the experimental values for 3 different temperatures and 2 pressures. The curves give the results calculated with optimal regression parameter obtained via Markwards optimization routine. It is clear, that the model is able to describe the pressure dependence of the reaction rate quite well. A statistical analysis shows that the order \( m \) with respect to the hydrogen pressure is practically one in agreement with other literature data.

Summing up experimental as well as theoretical results on high-pressure hydrodesulfurization of gas-oil showed that with catalyst pellets a diffusion limitation exists in the catalyst pellets. The effective order of reaction in accordance with
theory moves closer to unity as soon as mass transport is limiting. On the other hand it turns out that the lumping procedure changes the pseudo-order of reaction towards higher values compared to the molecularity of elementary reactions. Further on, in this case of lumping the width of the initial rate distribution of the sulfur components in a gas-oil is not a physical constant but a function of the chosen reaction conditions. This might be the reason why so many different kinetic models for the description of hydrodesulfurization have been proposed in literature.

V. CONCLUSIONS

The problems discussed in this paper are just a small selection of special problems a reaction engineer will face in case of high-pressure reactions. In any case one can expect special features of the reacting system on study. The equipment as well as the experimental program and theoretical methods for the analysis of the problems must be adapted to the situation. One point seems to be very clear: Even in an industrial situation where energy-saving is an important issue, the additional energy needed to perform chemical reactions under higher pressure can update the economy of a process significantly, indicating that high-pressure reaction engineering needs more attention.
REFERENCES


Figure captions

Fig. 1  Deactivation of a MoO₃/Al₂O₃ catalyst in 1-butene metha-
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Fig. 17 Simulation of desulfurization and experimental results with catalyst powder

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Fig. 19 Desulfurization at different hydrogen pressures with suspended catalyst (simulated and experimental results)
Experiment at $p = 50$ bar H$_2$ with catalyst powder under the influence of H$_2$S. Optimal parameters: $c_{0}(0) = 12.3 \text{ mol kg}^{-1}$ (g sulfur) (1 oil)$^{-1}$; $k_0 = 109.677$ s$^{-1}$ (1 oil)$^{-1}$ (g catalyst)$^{-1}$ (g sulfur)$^{-(n-1)}$; $E_A = 137.5$ kJ mol$^{-1}$; $n = 3.07$.
GAS-LIQUID REACTIONS UNDER PRESSURE:
AN OVERVIEW

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GAS-LIQUID REACTIONS UNDER PRESSURE: AN OVERVIEW

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ABSTRACT

Gas-liquid reactions under elevated pressures, with or without catalysts, with or without solid particles as reactants, are common in industrial practice, particularly for oxidation, hydrogenation, carbonylation and hydroformylation. In some cases, it may be desirable to adopt supercritical conditions. The selection of equipment should be carefully done. The role of fine catalyst particles, fine bubbles, and second liquid phase which may be emulsified, has been brought out and their beneficial effects emphasised.

The characteristic features of high pressure gas-liquid reactors have been covered and the role of backmixing in the liquid and gas phases has been considered. The common strategy of operating semi-batch reactors can be modified in some cases to reduce the batch time. The high pressure oxidation reactors may exhibit an oscillating behaviour in some cases.
Gas-liquid reactions, with or without suspended or pelleted catalysts, are commonly encountered in practice, particularly for oxidation with $O_2$/air, hydrogenation, carbonylation, hydroformylation, etc. Gas sparged, mechanically agitated, loop, etc. reactors are widely used and when pelleted catalysts are used fixed-bed reactor is adopted. High pressure reactors are also adopted for wet-air oxidation of aqueous waste streams containing toxic and refractory dissolved substances. There are instances when two-liquid phases are encountered, such as in the case of catalytic hydration of propylene to isopropanol, oligomerization of ethylene to $\alpha$-olefins in the presence of Ni based homogeneous catalysts, hydroformylation of higher olefins, etc. Doraiswamy and Sharma (1984) have quoted a number of examples of industrial importance. The very large scale removal of acid gases like $H_2S$, $CO_2$, etc. from natural gas, petrochemical, fertilizer, etc. industries, where high pressures are encountered, will not be considered in this overview. Similarly the manufacture of urea, where gas-liquid reactions at pressures of the order of 150 atm are encountered, and which is practised on a grand scale, with global production exceeding 100 mtpa, will not be covered.

In recent years, real large scale, single-site applications have emerged for high pressure gas-liquid reactions in petroleum refining and petrochemical industries and the examples of hydrodesulphurization and hydrocracking stand out as good cases. An emerging example is the manufacture
of methyl tert-butyl ether (MTBE), based on reaction between lean to rich isobutylene and methanol, in the presence of cationic ion exchange resins as catalyst. It is estimated that before turn of the century the production of MTBE will exceed 25 mtpa. Ethyl tert-butyl ether (ETBE) is also an attractive alternative. Yet another emerging area is modified Fischer-Tropsch reaction for conversion of syn-gas to liquid hydrocarbons and middle distillates in slurry reactors and multitubular fixed bed reactors.

The adoption of very high pressures, exceeding 100 atm, is not very common and the manufacture of low density polyethylene still remains an example where pressure exceeds 1000 atm. The older version of carbonylation of methanol to acetic acid, which employed pressures exceeding 500 atm, has given way to new rhodium based homogeneous catalysts which work at 40 to 50 atm. Similarly hydroformylation (Oxo) reactions with rhodium based homogeneous catalysts work at pressures like 40 atm instead of the older cobalt carbonyl based catalyst operating at close to 200 atm.

High pressure operations can be expensive and also hazardous. The application of principles of chemical reaction engineering, coupled with finer aspects of the chemistry of reactions, may well provide avenues to realise higher throughputs and selectivity from the reactors. Since the solubility of solute gases is invariably very low, diffusional resistance on the gas side is uncommon.
Why high pressures?

Most examples of high pressure operation are concerned with sparingly soluble gases like $O_2$, $H_2$, CO, lower olefins (in water), etc. and hence higher pressures allow more throughputs per unit volume of the reactor as the Henry's law is almost always valid over a very wide range of pressures of practical importance. In some earlier examples where Ni or Co carbonyl were used as catalyst it was necessary to adopt higher pressure to keep them in solution and thermodynamic considerations played an important role. The use of noble metal catalysts allowed pressures to be brought down in many hydrogenations which were earlier based on Ni or Co based catalysts.

Sub-critical to super-critical pressures

There are situations in practice where benefits may accrue by adopting super-critical conditions provided they are not harsh. Thus take the case of hydration of propylene or butenes to the corresponding secondary alcohols. The critical pressure and temperature of propylene are 45.4 atm and 350.1 K, respectively. It is thus convenient to change over to super-critical conditions to realise higher throughputs and this may also help in removing substances which foul the catalyst. Further even the product removal may benefit, as a lot of secondary alcohol may be extracted in the gas phase and a minor pressure-swing could allow an easy recovery of the secondary alcohol.
There are claims in the literature that liquid phase oxidation of isobutane with $O_2$ benefits by adoption of super-critical conditions. Modell (1982) has described methods for oxidation of organic materials in super-critical water. Water has a critical pressure of 217.6 atm and critical temperature of 647.2 K. An important advantage of adopting this strategy of carrying out reaction under super-critical conditions, over conventional technique, is that almost total oxidation of the organics could be realized since $O_2$ and $N_2$ are completely miscible with super-critical water in all proportions. Hence stoichiometric amounts of oxygen can be added for the total oxidation of the organics. Dissolved oxygen at higher temperature tends to be corrosive and hazardous and thus materials of construction have to be carefully selected.

Bhise (1983) has described a process for the production of ethylene oxide in which near-critical or super-critical $CO_2$ was first used as a solvent and then as a reactant. Thus, the super-critical fluid medium not only acts as an extractant to remove ethylene oxide from the aqueous stream but also acts as a reactant which enhances the selective conversion of ethylene oxide to ethylene glycol.

Chaudhari and Sharma (1991) have considered absorption of ethylene in concentrated solutions of sulphuric acid to make diethylsulphate. A change of pressure from 50.5 atm to 54.4 atm allowed a substantial increase in the specific rate of
absorption by 73.8%.

Sharma (1983) has made a reference to this subject and quoted examples of making cumene from benzene and propylene in fixed-bed three-phase reactors. It would be useful to consider alkylation of benzene with ethylene or propylene, with dissolved aluminium chloride as catalyst, under super-critical conditions. The critical pressure for propylene is 45.4 atm and that for ethylene is 50.5 atm and the respective critical temperatures are 365.1 and 282.8 K.

Gas-liquid to liquid-liquid mode of operation

When pressures are moderate, at the operating temperature, such as, for instance, in the case of absorption of C\textsubscript{3}/C\textsubscript{4} olefins in a variety of liquids, it is useful to consider a changeover from gas-liquid to liquid-liquid mode of operations as in the latter case it is easy to realise very high interfacial areas and therefore higher throughputs. Even higher specific rates of reaction may be realised when, due to the diffusion film in the liquid-liquid mode while it may occur only in the bulk liquid phase in the gas-liquid mode due to higher value of liquid side mass transfer coefficient.

In the case of the manufacture of MTBE, where cationic ion exchange resin catalysts are used, the liquid-liquid mode does not seem to have been employed even though heat removal is
possibly easier. The reasons for non-adooption of the liquid-liquid mode may have relationship with the selectivity as isobutylene can oligomerise, and perhaps with the life of the catalyst.

Gas-liquid to gas-liquid-liquid mode of operation

It is desirable sometimes to select a solvent in which the liquid products are immiscible so that the separation of products becomes an easy task. This is the case for the oligomerization of ethylene to higher olefins where ethylene glycol is used as a solvent and homogeneous nickel based catalyst is adopted.

It is sometimes desirable to use a second liquid phase to facilitate the reaction in a desired way. Thus hydrogenation of epoxides, with Raney nickel as catalyst, benefits from the use of a small amount of water. In the case of the hydrogenation of \( \text{C}_6\text{H}_5\text{CN} \) the selectivity for benzyl amine is considerably affected by the presence of water [Doraiswamy and Sharma (1984)].

In the case of hydroformylation reaction (Oxo-reaction; Roelen reaction) the recent developments indicate the desirability of having an additional water phase for higher olefins and to have rhodium triphenyl phosphine, with a sulphonic acid group in the meta- position in the benzene ring
which makes the catalyst soluble in water facilitating catalyst recovery.

When, in the oxidation reactions of organic compounds, a small amount of acidic product is obtained which affects the selectivity badly then it is desirable to use a small amount of water which is suitably buffered to remove the acidic impurity. Thus in the oxidation of cumene, where formic acid adversely affects the yield of cumene hydroperoxide, an aqueous carbonate buffer solution is used.

Reactor-separator combo-systems

High pressure reactors provide an opportunity to use membranes in situ to remove the product to allow higher levels of conversion per pass as well as to realise higher selectivity. A claim has been made, in the high pressure air oxidation of cyclohexane to cyclohexanone-cyclohexanol, that a membrane can allow selective permeation of the desired oxidised product, thereby allowing higher per pass conversion than 4 to 6% in the conventional reactors, and higher selectivity to the desired products [Vaughen (1985)].

Selection of contactors

Doraiswamy and Sharma (1984), Ramachandran and Chaudhari (1980), Shah and Sharma (1987) have considered
this subject at length. A specific reference should be made for the adoption of sparged reactors in preference to mechanically agitated reactors for large size equipment to avoid problems of leakage and stability of shaft. The gas flow rate in sparged reactors will generally be in far excess of the stoichiometric requirement and recirculation of gas becomes a necessity. The importance of micromixing should be recognized for reactions where the reaction times and mixing times are comparable.

The loop reactors offer relatively very high interfacial area, approaching even 4000 $\text{m}^2/\text{m}^3$ compared to values around 400 to 600 $\text{m}^2/\text{m}^3$ in sparged and mechanically agitated reactors. The ease with which heat loads can be handled externally lends further support to the utility of this versatile contactor. It is likely that in coming years even polymerization of ethylene / propylene in slurry reactors is conducted in such reactors.

In the conversion of synthesis gas to middle distillates, via the Fischer-Tropsch (FT) process, where heavy paraffins are formed (e.g. in the Shell process), pressures in the range of 40 to 70 atm are encountered and the heat load is very high. For a real large scale plant, where the production of liquid products is of the order of 600,000 tonnes per annum, the uncertainties in the scale-up of slurry reactors, coupled with the problems of backmixing and erosion of catalyst and plant, have deterred the adoption of slurry reactor in practice. A multi-tubular fixed bed reactor with
downflow of gas and boiling water as a coolant has been adopted by Shell in the plant being installed in Malaysia [Eilers et al. (1990)]. (Such a reactor has been considered in the past for MTBE production). Very recently Statoil has reported the development of a slurry bed based FT process.

Fixed bed reactors, with co-current down-flow as well as up-flow, are extensively used for hydroprocessing of heavier petroleum fractions, desulphurization and hydrocracking. For high pressure systems the prediction of the flow regime, which is relevant to characterise hydrodynamics and mass transfer characteristics, is still very difficult and complications arise out of foaming behaviour in some cases. It is important to conduct experiments on a small scale set-up with the actual system under real operating conditions. The up-flow reactors offer better thermal stability due to higher liquid hold-up. The design of liquid distributors in fixed bed reactors is important [Wild et al. (1981)].

It is a common problem in industry, for an operating reactor of specified configuration, to predict the behaviour of alternative feedstocks, new catalysts, etc. Here the problems of "scaled-down" system are encountered. Sie (1991) has discussed problems of this kind and has shown that with a careful choice of the reactor and the catalyst, diluted with fine inert particles, meaningful data can be obtained. Cold flow models can be used to assess the hydrodynamics.
Mechanically agitated, bubble column and loop reactors

Bubble columns are more advantageous than the mechanically agitated reactors in terms of energy efficiency. For a 10 m³ reactor, a comparison between the performance of these two reactors, at the same power consumption, indicates the gas-liquid mass transfer coefficient and effective interfacial area to be 60% higher in bubble columns. The heat transfer coefficient was 40% higher and the solid suspension needed 50% less power input. Bubble columns provide additional advantage of less backmixing in the liquid and gas phases.

Loop reactors can be more advantageous than bubble columns, particularly at higher pressures. The effective interfacial area is 2 to 3 times higher in loop reactors.

The hold-up profile in high pressure bubble column reactors, which governs the entire performance, is yet unpredictable. The prediction of hold-up profile in loop reactors is fairly straightforward. This makes the design procedure more reliable for loop reactors. Further, there is a great degree of flexibility in selecting design parameters (area ratio of riser to downcomer, height to diameter ratio and the sparger location). Because of this, we can make the liquid phase more backmixed or less backmixed depending upon the need.

Loop reactors are particularly advantageous for three phase systems. The power required for solid suspension can be 3 to 4 times lower in loop reactors compared to mechanically agitated reactors.
The residence time distribution in the gas phase occurs mainly due to the gas hold-up profile which is a consequence of the bubble rise velocity and the liquid circulation velocity. The hold-up profile strongly depends upon the column diameter and the superficial gas velocity. Therefore, the gas phase dispersion coefficient obtained from a small scale apparatus can not be extrapolated to a large scale. Earlier correlations for the gas phase dispersion may hold until the hold-up profile is parabolic. In large columns (>2 m) and/or at large superficial velocities (>0.2 m/s), the extrapolated dispersion coefficient could be 3 to 10 times higher than the actual value. This will have a marked influence on the reactor volume when the extent of gas phase conversion is high (>87%). A more rational correlation, recommended by Joshi (1982), takes into account the gradual variation in the gas phase flow pattern with respect to superficial gas velocity and the column diameter. This situation is particularly encountered in high pressure reactors. The following correlations hold:

\[
D_G = 110 \frac{V_G^2 T^2}{\epsilon_G} \quad (1)
\]

for, \(V_G T \epsilon_G^{0.5} \rho_G / \mu_G < 4000\)

and when, \(V_G T \epsilon_G^{0.5} \rho_G / \mu_G > 4000\)

\[
D_G = 2.1 \frac{V_G T}{\epsilon_G^{0.5}} \quad (2)
\]

where

\(D_G\) dispersion coefficient, \(m^2/s\)
\[ V_G \] superficial gas velocity, m/s

\[ T \] diameter of the column, m

\[ \varepsilon_G \] fractional hold-up of the gas phase, dimensionless

\[ \mu_G \] viscosity of the gas, kg/m.s

\[ \rho_G \] density of the gas, kg/m^3

Semibatch reactors

When batch times are measured in hours, it is common to find semi-batch reactors being adopted for oxidation, chlorination, ozonation, etc. There may be stiff requirements for various reasons, for the partial pressure of the solute in the outlet gas to be low due to safety and health hazards. It is common to find very conservative strategy being adopted for mechanically agitated contactors typically employing flow rates of gas which ensures the desired outlet concentration on the basis of the tail-end conditions. The mechanically agitated contactors are usually designed for operating conditions where the flow rate of the gas does not influence the mass and heat transfer coefficients (i.e., the speed of agitation is above the critical speed). Thus a simple controller can be adopted to regulate the flow rate of gas as initially the rate of reaction is relatively very high. Juvekar and Sharma (1977) have considered this problem in detail and have shown that, in some cases, the batch time can be reduced by a factor as high as three.
Reactors for polymerization

It is important to recognise the rheological behaviour of the fluids as it can profoundly influence the mass and heat transfer characteristics. Further complications arise, as in semi-batch reactors, as the fluid properties may change radically over the batch time.

Wastewater treatment at high temperature

Wet-air oxidation converts the COD to CO$_2$ and H$_2$O in the temperature range of 430-570 K and pressure range of 10-200 atm. The spent activated carbon and activated earth can be regenerated by wet-air oxidation. Wet air oxidation is suitable when the effluent COD is in the range of 20,000 and 4,00,000 or when the pollutant is toxic and non-biodegradable. When the COD is high, the exothermic heat of oxidation can be recovered in the form of steam.

For a small capacity thermal treatment, mechanically agitated reactor is attractive, whereas for a large scale application, pipeline reactor would be advantageous. For wet-air oxidation bubble columns are preferable.

Role of fine catalyst particles

The adoption of fine catalyst particles, having size below 20 microns, and even approaching sub-micron dimensions, is expected to be beneficial irrespective of the controlling mechanism. Some aspects of this strategy have been considered by Sharma and co-workers (1982,1985), Deckwer and Alper
(1980), etc. A specific reference may be made to air oxidation, under high pressure, of aqueous solutions of sodium sulphide where fine carbon particles can be immensely helpful. Here even in the absence of the catalyst the reaction is diffusion limited and activated carbon catalyses the reaction. The presence of fine carbon particles led to an enhancement in the rate of absorption by a factor as high as 14 [Pal, Juvekar and Sharma (1982)]. The use of coarser particles having a size more than 20 microns, irrespective of the loading, will not increase the specific rate of oxidation. A simple analysis leads to the following equation for the rate of absorption:

\[ R_A = [A^*] \left( D_A k_1 + D_A k_{SL} a_p \right)^{0.5} \]  \hspace{1cm} (3)

where

\([A^*]\) interfacial gas-liquid concentration of gaseous reactant, kmol/m\(^3\)
\(a_p\) surface area of particle per unit volume of liquid m\(^2\)/m\(^3\)
\(D_A\) diffusivity of dissolved gas in the solution, m\(^2\)/s
\(k_{SL}\) solid-liquid mass transfer coefficient, m/s
\(k_1\) pseudo first order rate constant, s\(^{-1}\)
\(R_A\) specific rate of absorption kmol/m\(^2\).s

If \(D_A k_{SL} a_p \gg D_A k_1\), the rate of absorption is expected to be inversely proportional to the particle size as both \(k_{SL}\) and \(a_p\) are inversely proportional to \(d_p\). A 0.06% (w/w) loading of activated carbon having an
average particle size of 4.3 microns gave an enhancement factor of 2 and a sample of activated carbon with an average particle size of 1.7 microns at the same loading gave an enhancement of nearly 4. However, when catalyst particles of a size of \( \approx 20 \) microns were used, at the same catalyst loading, no enhancement was found to occur.

A very fascinating aspect of fine particles involving supported noble metal catalyst has been brought out by Wimmers and Fortuin (1980). Here a careful selection of the support material (e.g. activated carbon vs zeolite or alumina) can lead to different type of surface active properties and the concentration of the catalyst particles at the gas-liquid interface can be 3 to 4 times higher than on an average basis resulting in a marked improvement in the rate of reaction resulting in increasing the throughput of the reactor per unit weight of the expensive catalyst. The rate of absorption of hydrogen in the presence of Pd/C catalyst particles at a hold-up of 1 kg.m\(^{-3}\) is more than four times higher than with Pd on alumina catalyst. This observation has been explained satisfactorily on the basis of adhesion of fine catalyst particles to bubbles, and the results fit well with their model predictions.

The recovery of fine catalyst particles, particularly those based on noble metals, may pose problems. However, many catalysts like Ni, Co, \( \text{etc.} \) are magnetic and others can be easily magnetised through manipulation of the support material
and high gradient magnetic separators can be used on line besides microfilters.

A special case is encountered in Ziegler-Natta polymerization of olefins such as ethylene and propylene to produce polyolefins which have characteristically broad molecular weight distributions and high values of polydispersity that cannot be explained on the basis of classical reaction modelling. The models for describing this slurry polymerization need to take into account the effect of polymer particles, which are much smaller than the diffusional length scales of the diffusing monomers, especially during the initial period. Typically, the initial catalyst particle size is submicron (0.06-0.3 μm). Since the catalyst breaks up into small fragments on polymer growth, a typical approach would be to use the multi-grain model where the microparticles of the catalyst are encapsulated by the growing polymer. The specific rate of monomer absorption will be significantly influenced by the presence of fine catalyst and growing polymer particles in the diffusion film, especially in the case of exceptionally active catalysts reported [Bhagwat (1991)]. Such models can predict the kinetic behaviour, molecular weight distributions and polydispersities, as well as the effect of different types of active sites.

Role of fine bubbles

Bhagwat, Joshi and Sharma (1987) have analysed in
detail the role of fine size bubbles in a variety of three-phase reactors where solids may be insoluble or soluble reactant or catalyst particle. As an example, consider the case of a fast gas-dissolved solid (sparingly soluble) reaction occurring within the gas-liquid diffusion film.

The presence of micron size bubbles in such a situation even accounting for just 1% of the interfacial area (and a much smaller fraction of the gas volume) can lead to a four-fold enhancement in the rate of absorption. Bhagwat (1980) has further shown that if the fine bubbles are preferentially adsorbed on the solid surface, a further 3-4 fold increase in the rate can be expected.

Role of second emulsified liquid phase

When a solute gas, such as oxygen, lower olefins, etc., is sparingly soluble in aqueous solutions, where we may have dissolved catalyst, then we may well benefit by having a second emulsified liquid phase which exhibits markedly higher solubility. This can result in a marked increase in the specific rate of absorption. Consider a specific case of absorption of isobutylene in aqueous sulphuric acid solutions. When the absorbent liquid is in the form of an emulsion of chlorobenzene (distribution coefficient ≈ 1600) in sulphuric acid having a volumetric hold-up of 5%, the specific rate of
absorption experiences an enhancement factor of 6. In the case of 1-butene, the same emulsion at the same hold-up (distribution coefficient ≈ 2000) gave an enhancement of more than 12. A comprehensive model has been developed for systems with microphase catalysis in general, and the above results closely match the predicted values from this model.

A simple solution, based on the film theory, which is applicable to a wide variety of cases, gives the following equation:

\[
R_A = [A^*] \left[ D_A (k_1 + 1_0 k_{LL} a_p) \right]
\]  

(4)

where

- \(D_A\) diffusivity of A in continuous liquid phase, m²/s
- \(1_0\) fractional volumetric hold up of microphase (based on total liquid + microphase), (dimensionless)
- \(k_1\) forward (pseudo) first order rate constant for consumption (absorption)/generation (desorption) of A, s⁻¹
- \(k_{LL}\) mass transfer coefficient based on external film around microparticle, for uptake/release of A, m/s
- \(a_p\) specific microphase-continuous phase interfacial area per unit volume of microphase, m²/m³
- \([A^*]\) interfacial solubility of A at operating partial pressure on gas side, kmol/m³
- \(R_A\) specific rate of absorption of A, kmol/m²s

**Some aspects of high pressure oxidation reactors**

**Role of mass transfer**

A variety of oxidation reactions (of organic compounds)
are carried out in practice and Doraiswamy and Sharma (1984) have given many examples. An important aspect of the stability of reactors needs to be stressed.

The following steps are involved in the oxidation of a variety of hydrocarbons:

\[ \text{O}_2 + \text{R} \rightarrow \text{RO}_2 \]

\[ \text{RO}_2 + \text{R'}.\text{H} \rightarrow \text{RO}_2\text{H} + \text{R'} \]

At high pressures the chemical rate may control the overall kinetics as the rate of mass transfer of oxygen is sufficiently high and value of the activation energy may lie in the range of 20 to 30 kcal/mol. However, at lower partial pressures of oxygen the process may be limited by mass transfer and the activation energy may be around 3 to 5 kcal/mol. It is prudent to operate reactors with substantial mass transfer resistance as the operation will be stable. Consider a situation where the process is kinetically controlled and a drop in temperature occurs and since the activation energy is very high this will be followed by a further drop in temperature and the reaction rate may come to dismally low level and may even stop. A completely mass transfer controlled situation may lead to lower selectivity as the absence of O\(_2\) in the bulk liquid leads to inadequate scavenging of the alkyl radicals.

Horizontal oxidisers

The pressure drop in the horizontal oxidisers is much
lower than in the case of the vertical oxidisers. Thus for medium pressure applications it may be useful to consider this type of reactor when the requirement from the partial pressure of oxygen in the outlet gas is not at a level below 6% or so. Joshi and Sharma (1976 a,b) have considered mass transfer and backmixing characteristics of such contactors.

Backmixing in liquid phase

When the reaction is first or higher order in the reactant in the liquid phase and the desired degree of conversion is high then the backmixing in the liquid phase becomes important. Bubble column reactors exhibit high level of backmixing and this can be drastically reduced by adopting sectionalisation with radial baffles [Joshi and Sharma (1978)]. The design features of radial baffles have been discussed by Joshi and Sharma (1979) and an additional feature is that baffles can be so designed as to have liquid circulation to remove heat of oxidation. This has been advantageously employed in liquid phase air oxidation of acetaldehyde, dissolved in the product, to give a mixture of acetic anhydride and acetic acid.

Oscillating behaviour

Large size oxidation reactors are employed for the oxidation of p-xylene dissolved in acetic acid to terephthalic acid. Here a cobalt based catalyst is employed and the chemistry of the process indicates that the oxidation-reduction
of cobaltous/cobaltic system may cause an oscillating behaviour which is undesirable from production view point due to the instabilities that this behaviour brings in its wake.

The air oxidation of benzaldehyde catalyzed by Co(II) and Br⁻ dissolved in acetic acid and water is reported to exhibit oscillations in the concentrations of Co(III) and of dissolved oxygen. Changes in operating conditions viz. air flow, temperature, cobalt concentration and benzaldehyde concentration were found to dramatically affect the oscillation frequency [Jensen(1983)]. These oscillations involve an autocatalytic production of Co(III) coupled to a periodic depletion of dissolved oxygen.

The air autooxidation of cyclohexanone catalyzed by Co(II)/Br⁻ has also been reported to show similar oscillatory behaviour in the concentration of dissolved O₂, Co(III) and bromate concentrations [Druliner and Wasserman (1988)].
Conclusions

1. In most cases process conditions, dictated by the chemistry of the reaction, demand higher pressures to realise reasonable throughputs per unit volume of the reactor. In some cases it is desirable to adopt super-critical conditions.

2. The selection of gas-liquid contactor should be carefully made and for large scale applications gas-sparged reactors or fixed-bed reactors should be preferred over the mechanically agitated contactors. For small to medium scale operation loop reactors appear to be attractive. The role of backmixing in liquid and gas phases should be carefully analysed.

3. The adoption of fine size catalyst particles below 20 microns may bestow desirable results. The selection of support material for catalyst should be such that higher local catalyst concentration at the gas-liquid interface is realised.

4. It may be desirable to deliberately have a second emulsified liquid phase, for sparingly soluble gases, to enhance throughput of the reactor.
REFERENCES

Bhagwat, M., (1991), unpublished work


Modell, M., (1982), U.S. Patent, 4338199


Sie, S. T., (1991), Revue de L’ Institut Francais du Petrole, 46, 501

Vaughan, R. J., (1985), U.S. Patent, 4532347


HIGH PRESSURE REACTIONS IN PETROLEUM REFINING

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Introduction

Distillate hydrocracking, residue hydrocracking, hydrotreatment and hydrogenation of distillate, hydorefining of waxes and speciality oil basestocks etc are the few important high pressure processes which are currently being used industrially in the petroleum refineries. These processes are aimed either for making the distillate fuels or to improve upon the quality of feedstocks/products.

Feedstocks used in all such processes is a mixture of various complex hydrocarbons e.g. paraffins, naphthenes, aromatics and olefins. It comprises also the nitrogen and sulfur containing cyclic compounds besides organically bound metals and asphaltenes present mostly in residual feedstocks. The structures and name of the complex organic compounds present is summarized in figure 1.

With the increase of feedstock molecular weight, the complexity aromatics and heteroatom/molecules is increased and the saturation of aromatics and removal of heteroatoms become more difficult.

We are dealing here the upgradation of the feedstock by adding hydrogen in presence of an industriial catalyst under high pressure (55-180 atm) to the feed molecule directly, thus removing the heteroatoms as hydrogen sulfide, ammonia or water and decreasing the molecular weight by hydrogenolysis/hydrocracking or saturation of the feed molecule by hydrogenation. By way of this, the hydrogen to carbon ratio
of the feedstock is increased automatically which helps in getting a product with desired specifications.

**Catalysts**

Catalysts for a given duty are selected based on their activity and selectivity. Activity is important with reference to the maximum product yield/good quality product and the selectivity with reference to the reduction in undesirable reactions which otherwise lead to loss in product yield and higher hydrogen consumption. Catalyst life is equally important as it depends on tolerance of impurities and sintering. In all such processes, sulfur resistance catalysts like combinations of sulfides of cobalt, molybdenum, nickel and tungsten supported on neutral support like alumina (to avoid the undesirable side reactions) or an acidic support (like amorphous silica-alumina or US y-zeolite embedded in silica-alumina matrix are widely used) (Table 10).

Alumina supported Cobalt-molybdenum catalysts are mostly used for hydrodesulfurization (HDS). For hydrodenitrogenation (HDN), nickel molybdenum catalysts supported on alumina have been claimed to be superior to cobalt-molybdenum catalysts. Nickel-molybdenum type of catalysts are also used for mild hydrogenation of less heavier feedstocks. Nickel-tungsten on catalysts are normally utilised when deep hydrogenation is required. This type of catalyst catalyse the hydroisomerisation and hydrocracking reactions also, in
addition to deep hydrogenation, because of some induced acidity. However, this acidity can be suppressed by diluting the catalyst substantially with the alumina support. For hydrocracking, strong and mild acidic bifunctional catalysts like nickel tungsten on amorphous silica alumina or Y-zeolite is chosen.

**Operating Conditions**

Typical operating conditions used in carrying out various reactions in different processes are given in table 1. To compensate the catalyst deactivation, the reaction temperatures are normally increased by about 1 deg F/day during processing.

**Process Flow Scheme**

Design of reactor and the connected equipment alongwith the flow scheme depends largely on the process requirements (Table 10). In case of hydrotreating processes, the reaction is usually carried out in a single stage reactor but in case of hydrocracking process, reactions may be carried out in a single stage or two stage or in series flow. such reactions are usually occured in a fixed bed reactor but fluidised/ebulatting/expanded bed reactors are used for high boiling feed stocks of high Conradson carbon residue and metal content. Typical simplified flow schemes of few of these process are shown in figure 2(a,b,c & d). In case of
hydrotreating processes, the liquid effluent coming from low
pressure separator does not require stripper and
fractionator.

Reactions

The feedstock contains many species which readily form
coke while processing. The double bonds present in these
molecules need saturation, by hydrogenation reactions, and
the saturated product thus formed many further crack
depending upon the reaction conditions used. These reactions
are always in competition with their coke forming reactions.
In order to suppress the coke forming reactions, the hydrogen
pressures are increased.

1 Removal of Heteroatoms

Most of the organo nitrogen, sulfur and metal present in
feedstocks are incorporated in five or six membered cyclic
rings (shown in figure 1) and most of these are unsaturated:

a) Hydrodenitrogenation

Nitrogen removal from the heterocyclic organo cyclic
compounds require hydrogenation of the ring containing
the nitrogen atom followed by hydrogenolysis of the
carbon-nitrogen bond and subsequently removal of
nitrogen as ammonia. The rates of hydrogenolysis
reactions are lower than that of rates hydrogenation and
because of this, the equilibrium of hydrogenation
reactions usually affect the nitrogen removal rates. An unfavourable hydrogenation equilibrium would result in low concentrations of hydrogenated nitrogen compounds undergoing the hydrogenolysis and thus the rates of overall hydrodenitrogenation could be lowered. High hydrogen pressure are generally used to increase the equilibrium concentration of saturated hetero ring compounds to obtain large hydrodenitrogenation rates. Hydrodenitrogenation mechanism of representative heterocyclic nitrogen compounds is shown in figure 3.

b) **Hydrodesulfurisation**
Hydrodesulfurisation of organo sulfur compounds is exothermic and reversible under the reaction conditions used in industrial operations. The thermodynamic data for hydrodesulfurisation of organo sulfur compounds is, in general, favoured at temperatures used in industrial processes.

Removal of sulfur occurs either with or without hydrogenation of the heterocyclic ring. The sulfur removal path via hydrogenated organo sulfur intermediates is inhibited at low pressures and high temperatures because of low concentrations of hydrogenated intermediates. This leads to lower consumption of hydrogen. **Hydrodesulfurisation reactions**
are occurred concurrently under the conditions of hydrodenitrogenation reactions.
Hydrodesulfurisation mechanism of representative heterocyclic sulfur compounds is shown in figure 4.

c) **Hydrodemetalisation**

Hydrodemetalisation results from hydroscission of the organo chain associated with the metal which reduces the solubility of the metal complex and leads to precipitation of metals on the catalyst. The process is similar to hydrocracking with the provision to overcome the deposition of metals on the catalyst which can lead to rapid deactivation of the catalyst.

d) **Hydrodeoxygenation**

Hydrodeoxygenation of organo oxygen compounds is exothermic and irreversible. However, the hydrogenation of organo oxygen compounds which may precede oxygen removal is reversible.

Removal of oxygen can occur through many pathways, including direct oxygen removal and ring saturation prior to oxygen removal.

Hydrodeoxygenation mechanism of representative heterocyclic oxygen compounds is shown in figure 5.
Hydrogenation/Hydrocracking of aromatics

Hydrogenation of aromatics, with or without heteroatoms, are exothermic and reversible. The extent of reaction at equilibrium decreases with increasing temperature. Increase in temperature, to increase rates of other reactions, results in lower equilibrium conversions in hydrogenations of aromatics which are significant at lower reaction pressures. Operation at high hydrogen pressures is necessary to hydrogenate the aromatics to an appreciable extent as shown in figure 6.

In hydrocracking of aromatics, the hydrogenation reactions are superimposed on the cracking reactions. The partial hydrogenation of polycyclic ring followed by rapid splitting of the saturated rings takes place to form substituted monocyclic aromatics. Other reactions are also occurring but are not being dealt herewith as these are not related with the high pressure reactions. In hydrogenation/hydrocracking mechanism of representative cyclic aromatic compounds is shown in Figure 7.

Effect of Pressure on different reactions:

Different reactions which are occurring in petroleum processing have been shown in figures 3 to 6. These are summarized in two groups.
a) The reactions of hydrotreatment e.g., hydrodenitrogenation, hydrodesulfurization, hydrodeoxygenation, hydrodemetalization and hydrogenation of aromatics and olefins.

b) The reactions (cracking) which proceed through a Carbenium ion mechanism e.g. cracking and isomerization. Besides this, other reactions e.g., condensation and dehydrogenation also occur leading to formation of coke.

Reactions of hydrotreatment

The polycyclic aromatic hydrocarbons and the chemically bound cyclic heteroatom (mainly nitrogen) need hydrogenation in order to have a hydrotreated/\(\text{Product}\) hydrocracked/hydrofinished/meeting the specification (as shown in tables 4 to 9) or further cracking in order to get the more valuable products. The reactions of hydrotreatment are favourable at low temperatures. At lower reaction temperature the rate of reactions on the sulfided catalysts (used in refining processes) is relatively lower and therefore in order to work at high temperatures with reasonable reaction rate, the hydrogen pressures are to be increased. This also overcome the thermodynamic limitations and help in saturating the coke precursors and thereby cleaning the surface of the
catalyst which increases the quality/yield of product and life of the catalyst respectively. The thermodynamic and kinetic aspects of these reactions are now discussed.

Thermodynamics

The thermodynamic equilibrium of hydrogenation of different aromatics as a function of hydrogen pressure and temperature respectively is shown in figures 8 and 9. It may be seen that the hydrogenation of aromatics at equilibrium decreases with the increase in carbon atom of the aromatic molecule, with the decrease in hydrogen pressure (at constant temperature) and with the increase in temperature (at constant pressure). Further, the equilibrium conversion of trineuclear aromatics is much less than that of mono and di nucleic aromatics. In order to enhance the saturation of trineuclear aromatics, much higher hydrogen pressures could be used.

Comparison of thermodynamic data for different aromatics with and without nitrogen atom is shown in figure 10 at constant hydrogen pressure and different temperatures. It shows that the nitrogen containing aromatic compounds are much more difficult to hydrogenate than the equivalent aromatic compounds under the same operating temperature.
Influence of hydrogen pressure on reactions of aromatics hydrogenation, hydrodenitrogenation and hydro-treatment of a two stage industrial hydrocracker using vacuum gas oil is shown in table 3. It may be noted that with the increase in pressure, the contents of total aromatics, nitrogen and sulfur in the unconverted feed could be reduced considerably.

Kinetics

The relative rate constants for hydrogenation of various aromatic compounds on an industrial catalyst at identical set of operating conditions are given in table 2. It may be seen that hydrogenation of multi ring aromatics to molecules containing single ring benzene is fairly easy, but that complete conversion of resulting alkyl benzene to a cyclo paraffin or paraffin is about 10 times slower.

Influence of hydrogen pressure on the rate constants for hydrodenitrogenation and hydrodesulfurisation reaction is given in figure 11. Hydrodenitrogenation is found to be more sensitive to hydrogen pressure than hydrodesulfurisation.

This may be due to different reaction mechanism for these two reactions (as the first step of hydrodenitrogenation reaction is the hydrogenation of the nitrogen molecule).
Reactions of Cracking

The reactions of cracking (and also the isomerization) of hydrogenated products proceed through a carbenium ion mechanism. Their rates of reaction decreases with the increase in hydrogen pressure. These are not discussed as they are not high pressure reactions.

Conclusion

Nitrogen removal from the heterocyclic compounds requires hydrogenation of the cyclic ring containing the nitrogen atoms followed by hydrogenolysis of the carbon nitrogen bond in hydrotreatment processes and subsequent scission of the saturated ring in the processes used for hydrocracking. Rate of hydrodenitrogenation is more sensitive to hydrogen pressure than the rate of hydrodesulfurization. In hydrocracking process, the hydrogenation reactions are superimposed on the cracking reactions.

Hydrogenation reactions are equilibrium limited. Aromatic hydrogenation is more difficult when (1) the carbon number of the feed molecule increases (2) the aromatic molecule contains the nitrogen atom (3) the hydrogen pressure/temperature decreases/increases. The
rate of hydrogenation reactions increases with the increase in hydrogen pressure. Further the rate of hydrogenation is much slower than the rate of hydrodesulfurisation (when the hydrogen pressure is increased).

The cracking reactions (occurred in case of hydrocracking process when the cyclic ring is saturated) are not discussed as these are not favorable at high pressures.

Good thermodynamic data to determine the reaction equilibria accurately for equilibrium limited hydrogenation reactions for all mono and multi ring aromatic compounds, with and without sulfur, nitrogen and oxygen compounds are not available. These data are necessary to determine the exact effect of hydrogen pressure on the equilibria at conditions employed in industrial high pressure processes.
Literature cited

1 Michael J. Girgis et al.

2 Bawa J.S. et al.

3 Dufresne P et. al.

4 Martenes A. et. al.

5 Odebunmi et. al.
   J. Cat. 30(1983), 56-89.

6 Laine J. et. al.

7 Cocchetto, J.F et.al.

8 Satterfield C.N. et al.

9 Tamm P.W., et.al.

10 Satterfield C.N., et al.

11 Konings A.J.A. et al.
   J. Cat. 54(1978), 1-6.

12 Satterfield C.N. et. al.
13 Nelson, W.L.
   Oil Gas J. 74(45), 1976, 191-192.

14 Nelson, W.L.;
   Ibid. 74(46), 1976, 72.

15 Satterfield et al.
   A.I.Ch.E.J. 21(1975), 1100-1108.

16 Qadar, S.A.

17 Aboul-Gheit, A.K. et. al.
   Ibid. 59(568), 1973, 188-194.
ACKNOWLEDGEMENT

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<table>
<thead>
<tr>
<th>Typical Operating Conditions for Hydrotreating/hydrocracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature deg C</td>
</tr>
<tr>
<td>Pressure, bar</td>
</tr>
<tr>
<td>LHSV, per hour</td>
</tr>
<tr>
<td>Hydrogen/feed cubic mtr/cubic mtr.</td>
</tr>
</tbody>
</table>
### Table 2

**Relative Rate Constants for Hydrogenation of Different Aromatics**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Rate Constant</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>100</td>
<td>Butene</td>
</tr>
<tr>
<td>Diphenyl</td>
<td>102</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>Toluene</td>
<td>62</td>
<td>Styrene</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>~40</td>
<td>n-Heptane</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>314</td>
<td>Tetralin</td>
</tr>
<tr>
<td>1-Methylnaphthalene</td>
<td>242</td>
<td>2-Methylnaphthalene</td>
</tr>
<tr>
<td>Anthracene</td>
<td>326</td>
<td>2,3-Dimethylbenzene</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>472</td>
<td>2,3,5,6-Dimethylbenzene</td>
</tr>
<tr>
<td>Anthracene</td>
<td>308</td>
<td>2,3-Dimethylbenzene</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>361</td>
<td>2,3,5,6-Dimethylbenzene</td>
</tr>
<tr>
<td>Anthracene</td>
<td>147</td>
<td>2-Methylbenzene</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>158</td>
<td>2,3,5,6-Dimethylbenzene</td>
</tr>
</tbody>
</table>
Table 3  Influence of Hydrogen Partial Pressure on First Stage Hydrotreatment

<table>
<thead>
<tr>
<th></th>
<th>FEED VGO ARABIAN LIGHT</th>
<th>UNCONVERTED FRACTION FROM FIRST STAGE HYDROTREATMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PRESSURE 70 B</td>
</tr>
<tr>
<td>SPECIFIC GRAVITY</td>
<td>0.906</td>
<td>0.864</td>
</tr>
<tr>
<td>N (Wt PPM)</td>
<td>650</td>
<td>10</td>
</tr>
<tr>
<td>S (Wt PPM)</td>
<td>24300</td>
<td>200</td>
</tr>
<tr>
<td>AROMATICS TOTAL</td>
<td>47</td>
<td>31</td>
</tr>
<tr>
<td>U.V. (Wt%) MONO</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>DI</td>
<td>11</td>
<td>6.1</td>
</tr>
<tr>
<td>TRI</td>
<td>12</td>
<td>4.4</td>
</tr>
</tbody>
</table>
**Table 4**

**FEED & PRODUCT QUALITY (TYPICAL)**

1. Hydrostabilization of Cracked Distillates

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Feed</th>
<th>Product (desired)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP/50/IBP</td>
<td>158/240/399</td>
<td>-</td>
</tr>
<tr>
<td>Bromine number</td>
<td>38</td>
<td>1-2</td>
</tr>
<tr>
<td>Sulfur, wt %</td>
<td>0.32</td>
<td>0.04-0.06</td>
</tr>
<tr>
<td>Total Nitrogen, ppm</td>
<td>277</td>
<td>60-70</td>
</tr>
<tr>
<td>Basic Nitrogen, ppm</td>
<td>236</td>
<td></td>
</tr>
</tbody>
</table>

**ASTM Colour**

- **Before Ageing**: D-8, 1
- **After Ageing**: D-8, 1.5

Total sediments (UOP-413) mg/100 ml

<table>
<thead>
<tr>
<th></th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total sediments</td>
<td>86</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 5

**FEED & PRODUCT QUALITY (TYPICAL)**

2. Hydrogenation of Distillate

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Feed</th>
<th>Product desired</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP/50/FBP, deg C</td>
<td>202/290/350</td>
<td>182/266/350</td>
</tr>
<tr>
<td>Cetane Index</td>
<td>26-28</td>
<td>43-57</td>
</tr>
</tbody>
</table>

Table 6

**FEED & PRODUCT QUALITY (TYPICAL)**

3. Hydrocracking of distillate

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM, deg C</td>
<td>350/550</td>
<td><strong>Light Naphtha</strong></td>
</tr>
<tr>
<td>IBP/FBP</td>
<td></td>
<td>RON: 85-87</td>
</tr>
<tr>
<td>Sulfur, wt %</td>
<td>2.0</td>
<td><strong>Heavy Naphtha</strong></td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>770</td>
<td>P : 43-45%v</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N : 45-46%v</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A : 10-11%v</td>
</tr>
</tbody>
</table>

**Kerosene**

- Smoke point: > 25 mm
- Sulfur: < 50 ppm
- Freezing pt.: -50 degC

**Diesel**

- Diesel Index: > 60
- Sulfur: < 100
- Pour Point: -20 degC
### Table 7

**FEED & PRODUCT QUALITY**

4. Hydrocracking of Residues

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cut point, deg C</td>
<td>565+</td>
<td>Yield, wt %</td>
</tr>
<tr>
<td>Sulfur, wt %</td>
<td>5.6</td>
<td>H₂S+NH₃ : 3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₁ to C₃ : 2.7</td>
</tr>
<tr>
<td>CCR, wt %</td>
<td>24.4</td>
<td>C₄₋204°C : 10.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>204-343°C : 17.3</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
<td>170</td>
<td>343-524°C : 27.2</td>
</tr>
<tr>
<td>Nickel, ppm</td>
<td>53</td>
<td>524°C⁺ : 40.0</td>
</tr>
</tbody>
</table>

Quality

- Sulfur of: 0.75
- C₄⁺, wt%
- Sulfur of: 1.8
- 524°C⁺

---

### Table 8

**FEED & PRODUCT QUALITY**

5. Hydrofinishing of Waxes

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point</td>
<td>50-95 deg C</td>
<td></td>
</tr>
<tr>
<td>Oil content, wt%</td>
<td>1.46</td>
<td>FDA test : Passes</td>
</tr>
<tr>
<td>Sulfur, wt %</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Colour, ASTM</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>
Table 9

FEED & PRODUCT QUALITY (TYPICAL)

6. Hydrocracking for Lube Base Stocks

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Feed</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Light Hydro-crackate</td>
<td>Heavy Hydro-crackate</td>
</tr>
<tr>
<td>Viscosity at 98.9°C</td>
<td>7.94</td>
<td>Yield, LV%</td>
</tr>
<tr>
<td>Boiling Range</td>
<td>370-540</td>
<td>LPG</td>
</tr>
<tr>
<td>Sulfur, wt %</td>
<td>0.15</td>
<td>Gasoline</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jet fuel</td>
</tr>
<tr>
<td>Nitrogen, ppm</td>
<td>490</td>
<td>Diesel</td>
</tr>
<tr>
<td>Wax, % wt</td>
<td>17.6</td>
<td>Waxy 100 neutral</td>
</tr>
<tr>
<td>Dewaxed V. l</td>
<td>5.16</td>
<td>Waxy 240 neutral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Waxy 500 neutral</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100N</td>
</tr>
<tr>
<td></td>
<td></td>
<td>240N</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dewaxed V. l</td>
</tr>
<tr>
<td>Process</td>
<td>Operating Conditions</td>
<td>Catalyst/Reactor type</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------------------</td>
<td>------------------------------------------------------------</td>
</tr>
<tr>
<td>1 Hydrocracking of distillate</td>
<td>70-180 350-420 1-2</td>
<td>Ni-W/Silica-alumina (Fixed bed, single/two stage/series flow)</td>
</tr>
<tr>
<td>2 Hydrocracking residue</td>
<td>140-210 400-450 0.5-1</td>
<td>Ni-W/Silica alumina (Ebulliated/expanded bed, single stage)</td>
</tr>
<tr>
<td>3 Hydrocracking of distillate</td>
<td>150-180 380-420 0.5-1</td>
<td>Ni-W/Silica alumina (Fixed bed, single/two stage)</td>
</tr>
<tr>
<td>4 Hydrogenation of distillate</td>
<td>55-100 300-350 1-2</td>
<td>Ni-Mo/Alumina (Fixed bed, single stage)</td>
</tr>
<tr>
<td>5 Hydrostabilisation of distillate</td>
<td>55-80 300-400 1-2</td>
<td>Ni-Mo/Alumina or Ni-Mo-W/Alumina (Fixed bed, single stage)</td>
</tr>
<tr>
<td>6 Hydrofinishing of waxes</td>
<td>55-120 300-370 0.5-1</td>
<td>Ni-Mo or Ni-W on alumina (Fixed bed, single stage)</td>
</tr>
</tbody>
</table>
1. Aromatic Hydrocarbons

1. Pyrene
2. Phenanthrene
3. Anthracene
4. Napthalene
5. Fluoranthene

Figure 1: Structures of Selected Organic Compounds
2. Organosulfur Compounds

- Thiophene
- Benzothiophene
- Dibenzothiophene
- Thianthrene
- Benzo[b]naphtho[2,3-d]thiophene
- Benzo[b]naphtho[1,2-d]thiophene
3. Organonitrogen Compounds

Pyridine

Quinoline

Acridine

5,6-Benzocoumarone

7,8-Benzocoumarone

Indole

Carbazole
4. Organo-oxygen Compounds

Dibenzofuran

Benzofuran

1-Naphtol
5. Organo bound metal compound

Porphyrin
Figure 24: Typical Single Stage Hydrocracking process flow scheme
Figure 2(c) SERIES FLOW HYDROCRACKER FLOW DIAGRAM
Figure 3. Hydrodenitrogenation mechanism of representative heterocyclic nitrogen compounds

Pyridine → \( +3H_2 \rightarrow \) Piperidine → \( +H_2 \rightarrow C_5H_{11}NH_2 \rightarrow +H_2 \rightarrow C_5H_{12} + NH_3 \)

Pyrazole → \( +2H_2 \rightarrow Pyrazolidine \rightarrow +H_2 \rightarrow C_4H_{9}NH_2 \rightarrow +H_2 \rightarrow C_4H_{10} + NH_3 \)

Quinoline → \( +2H_2 \rightarrow \) Tetrahydro-Propyl aniline + \( NH_3 \)

Isoquinoline → \( +2H_2 \rightarrow \) Tetrahydro-Ethyl-hemicyan- \( CH_2CH_2NH_2 \rightarrow +H_2 \rightarrow \) Ethyl-\( CH_3NH_2 \rightarrow +H_2 \rightarrow \) Ethyl aniline + \( NH_3 \)

Indole → \( +H_2 \rightarrow \) Indolene → \( +H_2 \rightarrow \) Ethyl aniline + \( NH_3 \)

Acridine → \( +H_2 \rightarrow \) Dihydro- \( NH_2 \rightarrow +H_2 \rightarrow \) Di phenyl methane + \( NH_3 \)

Di hydro acridine → \( +H_2 \rightarrow \) Phenyl aniline + \( NH_3 \) + Biphenyl
Figure 4 Hydrodesulfurisation mechanism of representative heterocyclic sulfur compounds

Thiophene

\[ +H_2 \rightarrow CH_2=CH-CH=CH_2 \]

Butenes and butane

Benzothiophene

Dibenzothiophene

\[ +H_2 \rightarrow \text{Dibenzothiophene} \]

Tetrahydro-

Bi-phenyl

\[ +H_2 \rightarrow \text{Bi-phenyl} \]

Cyclo hexyl benzene

\[ +H_2 \rightarrow \text{Cyclo hexyl benzene} \]

Bi-cyclo hexane
Figure 5  Hydrodeoxygenation mechanism of representative heterocyclic oxygen compounds

1. Methyl Phenol → Methyl cyclohexene → 1-Naphthol → Methylcyclohexanol
2. Benzofuran → Benzofuran → Alkylphenol → Phenol
3.

Di-benzofuran → Di-phenyl

Phenyl octanol → Cyclohexyl benzene

Products

Products
Figure 6  Effect of Pressure on ring saturation

CALCULATED THEORETICAL MAXIMUM

HIGHER PRESSURE
LOWER SPACE VELOCITY

HIGHER PRESSURE
HIGHER SPACE VELOCITY

LOWER PRESSURE
LOWER SPACE VELOCITY

HIGHER SPACE VELOCITY

CONSTANT $H_2:OIL$

INCREASING RING SATURATION

INCREASING TEMPERATURE
FIGURE - 7 MECHANISM OF REPRESENTATIVE HYDROGENATION / HYDROCRACKING OF CYCLIC AROMATIC COMPOUNDS

(I) NAPHTHALENE + H₂ → TETRALIN → Methylindane + H₂ → C₄H₉ + H₂ → R

(II) PHENANTHRENE → Dihydro- → C-C-C-C
             → ALKYL TETRALIN

(III) PYRENE → HYDROPYRENES AND ISOMERS → PHENANTHRENE AND ISOMERS
             → NAPHTHALENES AND TETRALINS
             → BENZENE
Figure 8 Thermodynamic equilibrium of hydrogenation of different aromatic compounds at different pressures but at 400 deg C

1: benzene  -  2: toluene  
3: naphthalene  -  4: decylbenzene  
5: paraxylene  -  6: mesitylene  
7: Phenanthrene.
Figure 9  Thermodynamic equilibrium of hydrogenation of aromatic compounds at different temperatures but at 100 bars

1: benzene  2: toluene  
3: naphthalene  4: decylbenzene  
5: paraxylene  6: mesitylène  
7: phenanthrene.
Figure 10  Comparison of thermodynamic data for hydrogenation of aromatic compounds (with and without nitrogen atoms) for different temperatures but at 100 atm.

% Naphtene

1 : benzene - 2 : toluene - 3 : pyridine - 4 : aniline
Figure 11 Influence of pressure on rate constants for hydrodenitrogenation & hydrodesulfurisation

Feedstock: coker gas oil
Catalyst: NiMo/Al₂O₃
SYNTHESIS OF POLYMERS UNDER HIGH PRESSURE

G. Luft

Institut für Chemische Technologie
Technische Hochschule Darmstadt
Petersenstraße 20; 6100 Darmstadt
Germany
1. GENERAL

As in the case of a large number of chemical reactions, polymerization reactions are also pressure-sensitive. Monomers which do not polymerize at ambient pressure give appreciable yields of polymer at high pressure due to the effect of pressure on the equilibrium between the monomer and the growing chain. The rate of reaction of nearly all polymerization reactions is accelerated by an increase in pressure, this being essentially due to the increase of the overall reaction rate constant and to the increase of the volumetric concentration of the reacting species resulting from the high compressibility of gaseous monomers. The outstanding feature of high pressure polymerization is that, due to the different dependence of the rates of the elementary reactions on the pressure, an increase in pressure leads to significant changes in the ratio of these rates: subsequently this leads to significant changes in the molecular weight, in the structure and generally in the properties of the polymers.

In order to elucidate the above mentioned influence of high pressure on the polymerization, the way in which the pressure acts should be evaluated. The effects will be quantified by first considering the thermodynamic and kinetic relationships. From this knowledge the changes in the molecular structure and of some macroscopic properties of the polymer can be understood.

Various laboratory polymerization facilities are available to investigate kinetics and the dependency of polymer properties on the synthesis conditions. As an example a continuously operated polymerization unit is shown.

At the end of the paper some trends in the industrial manufacturing of polymers under high pressure are discussed.
2. EFFECTS OF HIGH PRESSURE

2.1 Thermodynamics

Using the equilibrium between the monomer and the growing chain it is possible to predict if the probability to polymerize a monomer will increase when high pressure is applied.

2.1.1 Equilibrium between the monomer and the growing chain

The thermodynamics of the addition of a monomer to a chain radical and of the competing chain-depropagation reaction can be described by an equilibrium constant $K_{MP}$. The following relation exists between $K_{MP}$ and the molar Gibbs energy $\Delta G_{MP}$ of the transition from the monomer M to the polymer P

$$\Delta G_{MP} = -RT \ln K_{MP}$$

with

$$\Delta G_{MP} = \Delta H_{MP} - T \Delta S_{MP}.$$ 

Usually both the change of the enthalpy $\Delta H_{MP}$ and of the entropy $\Delta S_{MP}$ are negative. At a well-defined temperature $T_C = \Delta H_{MP}/\Delta S_{MP}$, the so-called ceiling temperature, $\Delta G_{MP}$ becomes zero. Above $T_C$ the formation of highly polymerized polymer will not occur, but the formation of low molecular weight products is not precluded.

The ceiling temperature is affected by the pressure according to the following equation

$$\frac{dT_C}{dp} = C = \frac{\Delta V_C}{\Delta H}$$

After integration of Equ. 2 one can see that $\ln T_C$ changes linearly with the pressure:

$$\ln(T_C)_P = \ln(T_C)_1 \text{ bar} + \left(\frac{\Delta V_C}{\Delta H}\right) \cdot P$$

[3]
2.1.2 Equilibrium between monomer and polymer phases

Another type of thermodynamic equilibrium, namely phase equilibrium, is involved in high pressure bulk and solution polymerization processes.

As an example, the equilibrium between ethylene-rich and polyethylene-rich phases will be discussed, which has been intensively investigated because of the industrial importance of the high pressure polymerization of ethylene. The pressure at the cloud point when the phase separation starts was determined visually in an autoclave equipped with pressure-resistant sapphire windows. Simultaneously the composition of the phases was determined by taking samples from the ethylene and the polymer-rich phases. In Figure 1 the pressure at the cloud point is plotted against the composition of the phases. The thick line is the cloud curve which encloses the two phase region. Under conditions beyond the cloud curve the mixture is homogeneous. The thin lines are the coexistence curves which give the fraction of polymer in the phases for different total polymer concentrations. The coexistence curves on the left hand side show the weight fraction of polymer in the

![Fig. 1. Phase equilibrium of ethylene polyethylene mixtures. Temperature 433 K. Coexistence curve (a) 6.1 wt%. (b) 11.4 wt%. (c) 18.6 wt%. (d) 28.0 wt%. (e) 36.5 wt% total concentration of polymer. —— Cloud curve; ——— Shadow curve; —— Coexistence curve.](image-url)
ethylene-rich light phase, the so-called sol phase. The curves on the right give the fraction of polymer in the dense or gel phase. Decreasing the pressure, the concentration of polymer in the sol phase decreases and increases in the gel phase.

Besides pressure and total concentration of polymer, the main influence on the phase behaviour comes from the temperature, the molecular weight of the polymer and its structure. When the temperature decreases or the polymer molecular weight increases the two phase region extends toward higher pressures. The mutual solubility is also reduced when the polymer molecules are less branched as in the case of high density or linear low density polyethylene.

The addition of a comonomer like vinyl acetate, methyl acrylate, acrylic and methacrylic acid etc. results in a smaller two-phase region.

Depending on the phase equilibrium the polymerization can proceed in a single phase or under two-phase conditions. This affects not only the reaction path and the rate of polymerization but also the texture of the resulting polymer.
2.2 Kinetics

Both from the scientific and the industrial point of view the main interest has been devoted to the radical high pressure polymerization rather than to the ionic or insertion polymerization. The mechanism of the polymerization of vinyl monomers will be considered to illustrate the main features of the kinetics of radical polymerization under high pressure.

2.2.1 The elementary reaction steps

Omitting thermal initiation and initiation by radiation the radical polymerization starts by the reaction of the monomer with radicals from the decomposition of an initiator I.

\[ \text{I} \xrightarrow{k_d} \text{I}^* \quad [4] \]

\[ \text{I}^* + \text{M} \xrightarrow{k_1} \text{R}_1^* \quad [5] \]

By successive addition of monomer molecules M, radical chains are formed

\[ \text{R}_n^* + \text{M} \xrightarrow{k_{n+1}} \text{R}_{n+1}^* \quad [6] \]

whose growth is terminated either by disproportionation or combination

\[ \text{R}_i^* + \text{R}_j^* \xrightarrow{k_{t1}} \text{P}_i + \text{P}_j \quad [7] \]

\[ \text{R}_i^* + \text{R}_j^* \xrightarrow{k_{t2}} \text{P}_i + \text{P}_j \quad [8] \]

giving polymers P with different molecular weights. Apart from these main reactions, chain transfer reactions with the monomer can take place.

\[ \text{R}_i^* + \text{M} \xrightarrow{k_{tr1}} \text{P} + \text{R}_1^* \quad [9] \]

By intermolecular chain transfer the radical is transferred to a mid-chain carbon atom where growth continues and long, highly mobile side chains are formed

\[ \text{R}_i^* + \text{R}_j^* \xrightarrow{k_{tr2}} \text{P} + \text{R}_i^* - \text{R}_j^* - \text{R}_j^* \quad [10] \]

while the intramolecular hydrogen transfer

\[ \text{R}_i^* - \text{R}_j^* \xrightarrow{k_{tr3}} \text{R}_i^* - \text{R}_j^* - \text{R}_j^* \quad [11] \]

gives short and relatively rigid side chains.
2.2.2 Rate of polymerization

The rate of polymerization depends on the concentration of the monomer, the concentration of the polymerization initiator or catalytically active species and on the reaction rate constant.

\[ R_{pol} = k_{pol} [M][I]^{1/2} \]  \[12\]

The overall rate constant \( k_{pol} \) is a composite quantity which contains the separate constants of the rate-determining steps.

\[ k_{pol} = \frac{k_d^{1/2}}{k_t} \]  \[13\]

The effect of pressure on each rate constant \( k_i \) can be expressed by means of the expression

\[ \frac{\partial \ln k_i}{\partial p} \bigg|_T = -\frac{\Delta V''}{RT} \]  \[14\]

in which \( \Delta V'' \) is the volume of activation.

From [13] and [14] the following relation for the overall volume of activation results:

\[ \Delta V''_{pol} = \Delta V''_p + \Delta V''_d/2 - \Delta V''_t/2 \]  \[15\]

Where \( p, d \) and \( t \) stand for chain propagation, initiator decomposition and chain termination.

Experimentally determined overall activation volumes of polymerization reactions were always found to be negative, their values being up to -20 to -30 cm\(^3\)/mol.

In general, high pressure increases the concentration of the monomer \([M]\) as well as that of the catalytically active species \([I]\) and the rate constant \( k_{pol} \). Thus radical polymerization is greatly accelerated by increasing the pressure. The change of \( R_{pol} \) with increasing pressure is shown in Figure 2 for the radically initiated polymerization of ethylene. At first the rate of polymeri-
zation increases steeply and then less steeply with increasing pressure. At the high pressure of 1750 bar the reaction rate is around 10 times higher than at the low pressure of 500 bar.

Fig. 2. The effect of pressure on the rate of the photosensitized polymerization of ethylene. Initiator Diphenyl disulfide. Temperature (○) 405 K. (△) 417 K. (x) 426 K. (▲) 437 K. (▲) 445 K. (▲) 454 K. (■) 462 K. (■) 472 K.
2.2.3 Chain propagation and termination

The individual rate constants $k_p$ of chain propagation and $k_t$ of chain termination can be determined by the rotating sector method or by the laser technique. From the results of photochemically-initiated polymerization tests under steady, as well as unsteady-state conditions, the effect of both pressure and temperature on $k_p$ and $k_t$ can be evaluated separately.

The shape of the rate constant to pressure curves observed in the synthesis of polyethylene is typical for radical addition polymerization. As shown in Figure 3 the rate constant of chain propagation, as well as that of chain termination, increases with increasing temperature. With increasing pressure, $k_p$ increases as a result of the decrease of the volume in the transition state by the addition of monomer units to the growing chain. The rate con-

![Graphs showing the influence of pressure and temperature on the rate constants of chain propagation and termination.](image)

**Fig. 3.** Influence of pressure and temperature on the rate constant of chain propagation (a) and chain termination (b).
stant of chain termination decreases rapidly with increasing pressure because the termination reaction is diffusion controlled.

The activation volume $\Delta V_p$ of chain propagation is negative, and is in the range of $-18$ to $-26$ ml/mol. The activation volumes of chain termination vary between $+7$ and $+25$ ml/mol.
2.3 Structure and properties

The ratio of the rate constants of the elementary reactions involved in the polymerization determines not only the overall rate but also the molecular weight and the structure of a polymer, from which a large fraction of processing and application properties depend. Because of the influence of the pressure on the individual reaction rate constants, high pressure effects strongly the polymer properties.

2.3.1 Molecular weight

The course of the molecular weight to pressure curves of polystyrene and polyethylene presented in Figure 4 is typical for radical polymerization under high pressure. The molecular weight first increases steeply with increasing pressure. At high pressure the curves level-off.

![Graph showing molecular weight vs. pressure](image)

**Fig. 4.** Effect of pressure on the molecular weight. (a) Polystyrene formed at 60°C with 430 mol ppm dibenzoyl peroxide. (b) Polyethylene yielded at 180°C with 10-20 mol ppm oxygen.

The effect of pressure on the molecular weight of the polymer can be discussed when Eqn. [16] is considered. It gives the average degree of polymerization $\bar{DP}$ for radical polymerization with an initiator $I$ and in the presence of a chain transfer agent $S$.

The first term on the right hand side takes into account the ending of a growing chain by mutual termination. The second term represents chain termination by radical transfer to the monomer,
and the remaining term results from chain transfer to a transfer agent which can be a solvent.

\[
\frac{1}{\text{DP}} = \left(\frac{k_d \cdot k_t}{2}\right)^{1/2} \cdot \frac{1}{k_p} \left[\frac{[I]}{[M]}\right]^{1/2} + \frac{k_{tr1}}{k_p} + \frac{k_{tr4}[S]}{k_p [M]} \quad [16]
\]

As mentioned before, the rate constant \(k_p\) of chain propagation increases strongly with increasing pressure, whereas the rate constant \(k_d\) for initiator decomposition decrease. Also the rate constant \(k_t\) of chain termination is reduced at high pressures when this reaction step is diffusion-controlled. The rate constants \(k_{tr1}\) and \(k_{tr4}\) of transfer processes change nearly as much with pressure as \(k_p\), thus the ratios \(k_{tr1}/k_p\) and \(k_{tr4}/k_p\) are less dependent on pressure. The first term of Equ. 16 therefore governs the effect of pressure on the degree of polymerization. As this term initially decreases rapidly with increasing pressure, \(\text{DP}\) should rise. At high pressure the changes in \(k_d\), \(k_t\), and \(k_p\) cancel out and \(\text{DP}\) reaches a constant value as observed in the experiments.
2.3.2 Branching

Intermolecular chain transfer results in branched polymer molecules when chain growth continues by addition of monomers at the radical sites. The activation volume of intermolecular chain transfer is less negative than that for chain propagation, and high pressure therefore hinders the formation of long side chains.

The influence of the pressure on long chain branching was investigated in the synthesis of low density polyethylene. As expected, the long chain branching frequency decreased rapidly with increasing pressure (Figure 5). Surprisingly high values were found at low pressures under two phase conditions (Figure 5, left hand side). This is contradictory to the assumption that the reduced mobility of the polymer chains in the polyethylene rich phase should minimize long-chain branching.

![Graph showing long chain branching frequency as a function of polymerization pressure.](image)

**Fig. 5.** Long chain branching frequency of polyethylene as a function of polymerization pressure. Polymerization temperature: 200°C. Residence time: 30 sec. Initiator: tert-Butyl perpivalate. Initiator concentration: 60 to 220 ppm.
The effect of pressure on the frequency of short chain branching for polyethylene is demonstrated in Figure 6. In the polymerization of ethylene the short chain branching frequency was found to be higher than the formation of long side chains by a factor of 10 to 30 subsequently decreasing with increasing pressure.

A low number of short side branches allows the close arrangement of the polymer molecules resulting in a high density of the polymer formed under high pressure and vice versa.
2.3.3 Tacticity

In Figure 7 three different configurations of a polymer chain consisting of the unit -CH\(_2\)-CHR- are shown. The units can be incorporated in such way that all substitues are above the plane (isotactic polymer). They can be arranged alternating above and below (syndiotactic polymer) or in an irregular sequence (atactic polymer).

The effect of pressure on the configuration of monomer units in the polymer chain has been studied by several authors in the polymerization of methyl methacrylate under various pressures. Although only a fairly small change in tacticity was observed, even at the very high pressure of 8 kbar, there was still a clear increase in the isotacticity and atacticity accompanied by a corresponding decrease of the proportion of syndiotactic polymer when the pressure was raised.

Fig. 7. Different configurations of a polymer chain.
(a) Isotactic. (b) Syndiotactic. (c) Atactic.
2.3.4 Properties

A number of functional and mechanical properties of the polymer are connected to the molecular weight and the structure, and are therefore affected by the polymerization pressure. It must be remembered though, that the macroscopic properties of the polymer are not solely determined by these parameters, the history of the thermal treatment or of the processing also having an important effect.

The degree of short-chain branching determines primarily the density and the percentage of crystallinity. As shown in Figure 8 the density increases with increasing pressure due to an decrease in the short chain branching frequency. The crystallinity follows the same pattern. The crystallinity itself mainly influences the properties which are related to the mobility of polymer segments such as the melting point, the stiffness, Young's modulus etc.

![Diagram of properties vs. pressure]

Fig. 8. Change of properties of polymer with polymerization pressure. (a) Properties depending mainly on degree of short chain branching. (b) On long chain branching. (c) On molecular weight.
The frequency of long-chain branching is a decisive factor for rheological properties of the molten polymer.

With an increasing degree of long-chain branching the non-Newtonian behaviour increases together with the melt recovery, whereas the critical shear rate decreases and the extensibility of the melt lowers.

The average molecular weight mainly determines the physicochemical properties such as solubility, permeability by gases and water. Furthermore, the molecular weight affects the tensile strength.

The change of the properties of the polymer with pressure is depicted in Figure 8. With increasing pressure density, melting point, Young's modulus, stiffness, crystallinity, critical shear rate, extensibility, molecular weight and tensile strength increase whereas degree of short and long-chain branching, non-Newtonian behavior, melt recovery, solubility and permeability of the polymer decrease.
3. LABORATORY APPARATUS FOR POLYMERIZATION UNDER HIGH PRESSURE

The experimental data presented earlier were obtained by means of a laboratory polymerization unit which operated continuously and contained the main features of a large-scale commercial pant.

The ethylene is taken from bombs and compressed by means of a multistage diaphragm compressor (Figure 9). The maximum pressure is 2500 bar. The throughput is maintained constant by means of a mass flow controller in the suction line. The ethylene feed can be varied from 0 to 3 m³/h. Two diaphragm compressors are available at the high pressure laboratories.

Fig. 9 Diaphragm compressor

The center-piece of the polymerization unit is a small stirred autoclave in which the polymerization can carried out at pressures of up to 2400 bar and temperatures of up to 350°C.
The autoclave reactor is shown in Figure 10. It is equipped with a fast running stirrer and a magnet-drive. The gaseous monomer is fed at the top through the shaft of the magnet-drive. The polymerization initiator is dissolved in a hydrocarbon and metered into the reactor through syringe-type pumps which can be seen on the left hand side. A membrane pump is used to feed liquid comonomers and modifiers. Gaseous modifiers are passed into the reactor through a metering device not shown in this figure.

After the reactor the polymer formed is separated from the unreacted ethylene and comonomer by pressure release.

Depending on its molecular weight, the polymer is obtained as a pulp or flocks. It is collected in different separators arranged after the reactor, one of which receive product until a steady state is attained (Fig. 10, bottom).
For safety reasons the polymerization unit is located within a high pressure building. It is operated by means of a computer which is also used to monitor the data (Fig. 11).

Fig. 11 Operation Panel
In order to evaluate the trends in the manufacture of polymers by high pressure processes I would like to present the development in the production of polyethylene in Western Europe as a typical example.

![Polyethylene Production in Western Europe](image)

**Fig. 12** Polyethylene Production in Western Europe

In terms of the quantities produced polyethylene is the most important polyolefin. The discovery of the polymerizability of ethylene in 1933 was a milestone in the development of high pressure processes. Since the beginning of the fifties the commercial production of LDPE was doubled every five years and achieved a maximum of nearly 4 million tonnes per annum in 1978. This rapid development was made possible by the progress achieved in high pressure engineering, in control engineering and last not least in process technology which has made possible an increase of 10 to 20 times in the production capacity of a high pressure polymerization reactor within the last 20 years. LDPE is highly branched. It contains both long chain branches and a large number of short chain branches. The large number of short chain branches gives a low density of 0.915 - 0.935 g/cc.

In 1953 a low pressure process was invented which uses transition metal catalysts to manufacture an other type of polyethylene the so-called HDPE which has a different structure. The polymer molecules are linear and exhibit only a small number of short chain
branches and consequently a high density. In the following years around 30% of the polyethylene were manufactured by this low pressure process.

The competition had become more severe by the introduction of further low pressure processes in 1978. By polymerization in gas phase, solution or slurry a third type of polyethylene can be yielded. LLDPE has also a linear structure with varying number of side chains. The density reaches from 0.900 typical for LDPE to values as high as those of HDPE. The branches are generated by incorporation of \(\alpha\)-olefins like 1-butene or 1-hexene. It is suggested that LLDPE growth will accelerate to 800 thousand tons up to 1990.

The share of the competitive processes in Western Europe is shown in Figure 13. In 1987 the total capacity was around 7 Mio tons. More than 50% of polyethylene was manufactured by high pressure processes. It is expected that this fraction will decrease to around 40% through 1990. This decline will be mainly compensated by an increase of LLDPE manufactured by low pressure processes from 15 to 25%.

**Fig. 13 Competitive Process Capabilities**
(Western Europe, 1987)
This change is due to the lower manufacturing costs of LLDPE. The polymerization in both gasphase, slurry or solution under low pressure requires only 70% in investment, 50% utilities and 70% in operational labor. The costs of raw material are more or less the same in both processes (Figure 14).

**Fig. 14** Comparison of Manufacturing Costs of LDPE and LLDPE

An other advantage of the new low pressure processes is the broad range of properties of LLDPE. As shown in Figure 15 the density ranges from 0.91 to 0.97 g/ml and melt index of 0.01 to 100 g/10 min can be achieved.

**Fig. 15** Performance of High and Low Pressure Processes
One way to defend the position of the high pressure process is therefore to extend the product range to high density grade. This could be achieved by the use of Ziegler catalyst in existing high pressure plants with only low additional investment (Figure 16).

Fig. 16 Use of Ziegler-catalysts in High Pressure Polymerization

The main trend in the development of high pressure polymerization processes is the manufacture of different kinds of copolymers containing vinyl acetate, acrylates or acids. Polar monomers cannot be polymerized in the low pressure processes because of deactivation of the catalysts used.

The advantage of the use of catalysts also in the high pressure process has been already mentioned.

Last but not least also in high pressure polymerization computer models will be increasingly applied for the design of optimal reactor configuration and for the evaluation of optimal operation conditions.
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Reaction Engineering under Supercritical Conditions

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Abstract

The objective of this paper is to give a review of the field of reaction engineering under supercritical conditions. Besides fundamental aspects of pressure effects on reaction rates, interest is focused mainly on heterogeneous catalytic conversions under conditions where the fluid phase is either in the liquid, gaseous or supercritical state. Reaction engineering advantages of using a supercritical fluid reaction mixture in the near sub- or supercritical region are presented with respect to an increase of space time velocity, the control of yield and selectivity of complex reactions, the increase of the effectiveness factor and the prolongation of the lifetime of heterogeneous catalysts. Several examples of experimental techniques for kinetic measurements are presented.

1. Introduction

Recent years have witnessed a remarkably increasing interest in investigations of fluid media in the critical or supercritical region /1,2/, mainly due to their importance in new separation techniques /3,4/. Apart from the evident advantages in separation processes, which already found practical application in large scale production plants (e.g. the decaffeination of coffee or tea /5/, etc.), the utilization of the specific effects of pressure and temperature on physicochemical fluid properties as a measure of reaction control - especially in the near critical region - is a new field of chemical reaction engineering /6,7/.

By exploiting the outstanding solvent properties of supercritical fluids (SCF), it may be possible to enhance reaction rates while maintaining or improving selectivity. Also, the separation of products from reactants, catalyst and unwanted byproducts, can be facilitated by the adjustment of the solvent power of an SCF solvent /8/. In principle there are two ways, to make use of supercritical conditions: either the reaction medium itself acts as an SCF and participates in the conversion or an SCF medium acts only as the solvent medium for the reactants, catalysts and products. In this manner reactions can run in a single-phase, and then interphase mass-transfer limitations are avoided.

In order to make use of an SCF reaction medium and not to fail with side-effects, it is necessary to be cognizant of the phase behavior which is exhibited by the reaction mixture at high pressures. In comparison with separation processes, the situation with reacting systems is far more complicated, since the phase behavior will often change with the degree of conversion. When operating a conversion in the mixture critical region, the location of phase border curves in the pressure-temperature-composition (P,T,X) space is of great importance. These phase border curves, which separate regions of differing states of matter, can be liquid-vapor boundaries or two-phase liquid-liquid boundaries, three-phase liquid-liquid-vapor or solid-liquid-vapor boundaries, and in certain cases even four-phase solid-solid-liquid-vapor or liquid-liquid-solid-vapor boundaries (for a review see /9,10/).

As shown in Figure 1 for the alkylation of benzene with propene, the critical points of the ternary reaction mixture propene-benzene-cumene are located on a critical surface, where the exact position depends on the composition. The full lines refer to the border curves liquid-vapor and the dashed lines correspond with the critical curves of the binary mixtures. If the reaction of benzene with propene should run at all degrees of conversion under supercritical conditions, this phase behavior as depicted in the diagram has to be considered, and mainly the increase of the critical pressure, when propene is mixed with benzene has to be taken into account. Otherwise a separation into a propene enriched gaseous phase and a benzene enriched liquid phase might occur.
Fig. 1: P-T-diagramm for the system propene/benzene/cumene.
The dashed lines define the critical surface ($K_p$ : critical point). The values of the material properties are characteristic for liquids, gases and super-critical fluids in the near critical region.

The object of this paper is to present a survey of the manifold possibilities using pressure variation on chemical reactions with the reaction phase in different fluid states. The effects range from influences on reaction rates (homogeneous, as well as heterogeneous catalytic surface reactions), to mass transfer between the catalyst and fluid phase and to transport processes inside porous catalysts.

In chemical reaction engineering elevated pressures have unquestionably long been an instrument for reaction control /11/. Here novel approaches shall be defined and compared with usual techniques.

In many cases the rate ($r$) of a single homogeneous reaction ($i$) in a multi-reaction system can be expressed satisfactorily as a function of the concentration ($c$) of the components ($i$) and the rate constant ($k$). The main advantage in application of high pressure to gas phase reactions is seen by the increase of the concentrations of the reactants due to compression. Thus, reaction rates increase and equilibrium conversions, which result in a reduction of the number of moles, produce higher yields according to the principle of Le Chatelier and Braun. For multiple reactions (in systems with parallel and/or consecutive reactions where the components enter into single reactions with different order $n$) yield and selectivity can be directed according to the increase in the concentrations due to compression. This technique of reaction control by pressure is, in principle, a method of concentration control. With the knowledge of the $p,V,T$ - behavior of the system one can calculate these pressure effects, here defined as "thermodynamic pressure effects".
Methods of Reaction Control

Single reactions: \[ r_j = k_j \prod_i c_{i,j}^{n_{i,j}} \]

Multiple reactions:

Consecutive reactions: \[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

Parallel reactions: \[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

\[ \Delta n_{i,1} = \Delta n_{i,2} = \Delta n_{i,j} \rightarrow \text{concentration control ('thermodynamic pressure effect')} \]

\[ E_{a,1} = E_{a,2} = E_{a,j} \rightarrow \text{temperature control} \left( \frac{\partial \ln k}{\partial T} \right)_p = \frac{E_a}{RT^2} \]

\[ \Delta V_i^i ≠ \Delta V_j^j = \Delta V_j^i \rightarrow \text{pressure control ('kinetic pressure effect')} \left( \frac{\partial \ln k}{\partial p} \right)_T = \frac{\Delta V^i}{RT} \]

Fig. 2: Principles of reaction control by the variation of concentration, temperature and pressure

On the other hand, it is less known that the rate coefficient of a single reaction also depends on pressure. A measure for this so-called "kinetic pressure effect" is the volume of activation.

When the \( \Delta V^i \neq \) values for reactions in a system are different, one may at first glance expect reaction control possibilities comparable to those using temperature control. Contrary to activation energies of normal reactions, volumes of activation \( \Delta V_i^i \neq \) can be either positive or negative. This means some reactions will be accelerated and others retarded by increasing pressures.

2. Theory of pressure effects on chemical reactions

The problem of interpreting and predicting the effects of high pressures on reaction rates is principally one of understanding the volume changes that occur in the activation processes. These volume changes vary with the compression of the reaction system and may be partly determined by other material properties such as the dielectric constant, which are also pressure-dependent. By means of the transitions state theory (TST) thermodynamic concepts are introduced into the theory of rate processes /12,13/. On this basis it is nowadays convenient to describe pressure effects on reaction rates in dense fluid systems, and this concept also holds for supercritical conditions.
2.1 Homogeneous reaction systems

The concept of TST is schematically summarized in Figure 3. For a bimolecular reaction a chemical equilibrium is assumed between the reactants A and B and the transition state X≠. The reaction proceeds via a gradual rearrangement of atomic positions between those of reactants and those of products.

\[
\frac{\partial \ln k}{\partial p} = -\frac{\Delta V^\ddagger}{R \cdot T}
\]

\[
\Delta V^\ddagger = \bar{V}_{X^\ddagger} - \bar{V}_A + \bar{V}_B
\]

\[
\Delta V^\ddagger = \Delta V_R^\ddagger + \Delta V_S^\ddagger
\]

Uncertainty:

\[
\Delta V^\ddagger = f(p,T)
\]

\[
k = f(p,T)
\]

Fig. 3: Simplified hard-sphere model which illustrates the basic concept of transition state theory and volume profile along the reaction coordinate.

The energy of the system however, increases initially to a maximum, the transition state, before falling to that of the products. The transition state, although being only metastable, is ascribed all the thermodynamic properties of a normal species, i.e. energy, entropy, volume, etc. The rate of reaction is actually the rate at which the transition state passes along the reaction coordinate to products. Partial differentiation of the rate coefficient with respect to pressure gives the volume of activation, \( \Delta V^\ddagger \), as a measure for the pressure dependence of the rate coefficient.

With these assumptions \( \Delta V^\ddagger \) is the difference between the partial molar volume of the transition state and the sum of the partial molar volumes of the reactants which can be immediately seen from the volume profile along the reaction coordinate.

This definition predicts an increase or decrease in rate with pressure if the transition state occupies a smaller or larger volume than the total volume of the reactants respectively. Just as the partial molar volume of a stable molecule may be considered to be made up of two parts, the same division may be made for
the volume of activation. These parts are: the intrinsic part or Van der Waals volume, \( \Delta V_{\text{intr}} \) and the solvation part \( \Delta V_{\text{solv}} \) (eq.1), which relates to changes in the volume of solvating medium when the transition state \( X^\# \) is formed.

\[
\Delta V^\# = \Delta V_{\text{intr}}^\# + \Delta V_{\text{solv}}^\#
\]  

(1)

Since volumes of both reactants and transition state change with pressure and since there is no a priori reason for their having similar compressibilities, plots of \( \ln k \) against pressure are more or less curved towards the pressure axis. A relationship which describes satisfactorily this behavior up to very high pressures and even under supercritical conditions gives the following equation (2) /14/.

\[
\Delta V^\#_{(p,T)} = \Delta \phi^\# - \Delta \Pi \frac{\delta V_F(p,T)}{\delta p}
\]  

(2)

The parameter \( \Delta \phi^\# \) may be regarded as a measure of the volume change due to the variation of atomic distances during transition state formation and \( \Delta \Pi^\# \) as a measure of the interaction of the reacting species with the surrounding solvent, e.g. the reaction mixture.

With the help of eq. (2) volumes of activation and their variation with pressure can be easily calculated. The diagram in Figure 4 gives a typical example for

![Diagram](image)

Fig. 4: Experimental (circles: data from /15/) and calculated (line) pressure dependence of the volume of activation for the formation of tetraethyl-ammonium iodide in acetonitrile.
a conversion of the Menshutkin-type. The activation parameters, $\Delta \phi \neq$ and $\Delta \Pi \neq$, were determined from experimental data at pressures up to 1.8 kbar. The calculated course (line), agrees well with the experimental data (circles) up to 3 kbar.

The main advantage in reaction engineering, which arise from this theory of the compression of the reaction sphere, may be seen in the prediction of rate coefficients (eq. 3).

$$\ln k(T) = \ln k_0(T) - \frac{\Delta \phi}{RT} (p - P_0) + \frac{\Delta \Pi}{RT} (V(p,T) - V_0)$$

Thus with the knowledge of $k_0(T)$, $\Delta \phi \neq$, $\Delta \Pi \neq$ and the $p,V,T$-behavior of the system one can calculate the field of $k = f(p,T)$ over wide ranges. The validity of this relationship for polar reactions (e. g. formation of alkyl-/-aryl-ammonium, -phosphonium, -arsonium and -stibonium salts in different solvents) at pressures of up to 3 kbar and temperature intervals of up to 80 K which means a corresponding variation of the rate coefficient of almost three orders of magnitude, could be ascertained extensively until now. Recent indications show that this concept also holds for nonpolar reactions /16/ and even for heterogeneous catalytic surface reactions /17/18/. When the $\Delta V \neq$ -values for reactions in a system are different, one may at first glance expect reaction control possibilities comparable to those using temperature control. For complex reaction systems with positive and negative volumes of activation one obtains additional possibilities for reaction control, since some reactions will be accelerated and others retarded with pressure. Such opposing effects can bring about significant changes of yield and selectivity.

An example is given in Figure 5 for a system of consecutive reactions of first order A to B to C. When the ratio of $k_1$ to $k_2$ is 1:10, one obtains at normal pressure and at a constant temperature a course with time of the intermediate B according to the lowest curve. When the reaction from A to B is accelerated with pressure according to a volume of activation of - 20 ml/mol and the reaction of B to C is retarded according to + 20 ml/mol, an increase of pressure in steps of 1 kbar up to 4 kbar effects an increase of the maximum yield of B according to the dashed line.

Two characteristic features should be stressed:
- first, the pronounced increase of the yield from about 9 % at normal pressure up to more than 90 % at 4 kbar, and
- second, there is only a negligible small shift of the positon of the maximum yield on the time axis.

The advantages of pressure control become evident, when they are compared with the more familiar technique of temperature control, which can be demon
strated with the diagrams in Figure 5 below. When the reaction from A to B shows a temperature dependence according to an activation energy of 42 kJ/mol and the reaction from B to C of 84 kJ/mol, the equivalent increase of

\[ k_1 \quad k_2 \]

\[ A \quad \rightarrow \quad B \quad \rightarrow \quad C \]

**Pressure control**

- \( k_{1,\text{ref}} = 5 \times 10^{-4} \text{ s}^{-1} \)
- \( k_{2,\text{ref}} = 5 \times 10^{-3} \text{ s}^{-1} \)
- \( \Delta V_1 = -20 \text{ cm}^3/\text{mol} \)
- \( \Delta V_2 = +20 \text{ cm}^3/\text{mol} \)
- \( T = 323 \text{ K} \) const.
- \( p = 1 \ldots 4000 \text{ bar} \)

**Temperature control**

- \( k_{1,\text{ref}} = 5 \times 10^{4} \text{ s}^{-1} \)
- \( k_{2,\text{ref}} = 5 \times 10^{-3} \text{ s}^{-1} \)
- \( E_{a1} = 42 \text{ kJ/mol} \)
- \( E_{a2} = 64 \text{ kJ/mol} \)
- \( p = 1 \text{ bar} \) const.
- \( T = 234 \ldots 323 \text{ K} \)

**Fig. 5:** Comparison of the methods of pressure control with temperature control for the shift of the yield of an intermediate B of first order consecutive reactions. The time axis in the case of temperature control has a logarithmic scale.

The maximum yield of B can be gained by a decrease of the temperature from 323 K to 234 K. But contrary to pressure control a drastic shift of the position of the maximum yield on the time axis occurs. E.g. in the given case the maximum yield is gained after a reaction time of about 3 weeks. The kinetic pressure effect in homogeneous reactions is predominant only in dense fluid systems and thus also hold for SCF conditions. In low density gas phase reactions the increase of concentrations usually masks the alteration of the rate coefficient.

### 2.2 Heterogeneous catalytic systems

The analysis of pressure effects on heterogeneous catalytic surface reactions is normally even more complex due to the interaction of transport, sorption and surface reaction. But it turned out that comparative studies with the reaction phase either in the liquid, gaseous, or supercritical state is a suitable tool to simplify the analysis of such complex systems /19/.

The strategy of pressure and temperature variations for this purpose is shown schematically in the p,T-diagram of a pure substance in Figure 6. The arrows give the directions of the p,T-variations. Conditions with respect to the phase
behavior are always defined in such a way, that the heterogeneous catalytic system contains only two phases: the solid catalyst and either a liquid, gaseous, or a supercritical phase. In practice, it is necessary to be cognizant of the phase behavior exhibited by the reaction mixture at high pressures, which may also change with the degree of conversion.

The use of pressure induced fluid state variations, gaseous supercritical, is based on the connected variation of physicochemical fluid properties, which in turn effects reaction behavior. As shown in Figure 1, the diffusivity of a supercritical fluid (SCF) exhibits behavior more like that between a liquid and a gas. The viscosity is also more gas-like in the near supercritical region, however, densities in the supercritical region are comparable to liquids.

![Diagram](image)

**Fig. 6:** Scheme of pressure and temperature variations in the different fluid states (S: solid; L: liquid; G: gas; Tr: triple point; \( p \): critical pressure; \( T_c \): critical temperature; SCF: supercritical fluid; \( r_T \): isothermal pressure dependence of reaction rate; \( r_p \): isobaric temperature dependence).

Typical changes of density and viscosity with pressure from the gaseous to the supercritical state are shown in Figure 7. The curves refer to a temperature only 2 K above the critical temperature \( T_c \). The pronounced increase of material properties within small pressure intervals is significant and holds phenomenally well for other systems also.
Fig. 7: Variation of density ($\rho$) and viscosity ($\eta$) with pressure from the gaseous into the supercritical region. The data refer to a reaction mixture of n-pentane, benzene and 1,4-diisopropylbenzene.

3. Experimental techniques for reaction engineering measurements

In the past, a number of experimental reactors have been developed to study heterogenous catalytic processes. These reactors are primarily designed for low pressure gas phase operation and cannot be easily adapted to reactions with liquids and/or highly compressed gases without changing the conveying systems.

A differential recycle reactor, especially for kinetic measurements in heterogeneous systems with the fluid phase in different states, was recently constructed for pressures even up to 2 kbar and temperatures up to 570 K or at lower pressures up to 900 K /20,21/.

Besides the advantages for kinetic measurements gradientless reactors are especially suited for investigations with fluid state variations. Mainly in the near critical region in this way one can ensure, to keep the reaction mixture in the
desired fluid state. The most difficult problem to be solved was the construction of a conveyor for the realization of an internal recycle, satisfying

- a continuous, pulsation-free flow through the catalyst bed, against the back pressure produced by dense fluid systems, and

- the conveyance of both liquids (pump) and/or gases (compressor) over a wide range of space velocities.

A solution is a screw conveyor, utilizing the viscous properties of the fluid medium as hydrodynamic seal. A rotor equipped with grooves on its outer surface rotates inside a fixed cylinder and thus moves the fluid in a circumferential direction due to adhesion and viscosity. In this way the fluid is conveyed axially by the screw motion. The volumetric flow rate \( V \) (laminar flow) can be calculated for a square thread using the speed of rotation \( n \), geometric and physical properties, and pressure drop \( \Delta p \).

For an optimized construction of the screw conveyer one obtains the operation eq. (4) for the calculation of the volumetric flow rate.

\[
\dot{V} = D_1 \left( n - \frac{\Delta p}{\eta} D_2 \right)
\]

(4)

The parameters \( D_1 \) and \( D_2 \) combine all the geometric data for the constructive design; \( n \) refers to the speed of rotation and \( \Delta p \) means the pressure drop and \( \eta \) the dynamic viscosity. A cross-section of this type of high pressure differential recycle reactor is shown in Figure 8.

![Schematic cross-section of a high pressure internal recycle reactor for dense fluid systems and fixed bed arrangement of the catalyst.](image-url)
The main parts of the reactor are the pressure vessel with a Bridgman-type self-sealing closure, the cover, catalyst cage, rotor with screw conveyer, and guide bearing. The opening serves as an inlet for the reactants and simultaneously enables thermocouples and internal heating devices to be introduced. Openings in the rounded end of the reactor allow the insertion of an additional thermocouple, an opening for the drive shaft, and an outlet for the reaction mixture.

In addition, usually a number of measuring and control devices are required, due to the extremely variable conditions of a continuously operated high pressure laboratory unit at different fluid states. If the pressure range can be restricted to that of HPLC applications (about 500 bar), one can use commercially available equipment. But in most cases, no commercially sized devices for the upper pressure region are suitable, due to the precision required. This is especially true for pressure, temperature, and flow control and self-designed constructions are necessary; an example of a flow-diagram is shown in Figure 9.

![Flow-diagram](image-url)

**Fig. 9:** Example of a flow-diagram for continuous operation of a high pressure laboratory unit.

In the past physical ‘in situ’ measurement techniques have gained importance for online determinations of physical properties in the near critical region. The use of common analytical techniques, e.g. sampling under pressure, is restricted, since they change pressure or composition to a high extent. A suitable solution is given with optical techniques /22/, since for many reactions some change in the spectrum will occur. The introduction of optical probes with imaging optics and optical fibers /23/ in combination with diode array spectroscopy opens new ways not only for kinetic measurement but also for mass transfer measurements between fluid phases and for studies on the sorption behavior on catalysts /24/ under sub- or supercritical conditions.
4. Heterogeneous catalytic surface reactions

Since pressure effects on heterogeneous catalytic surface reactions can be masked by pressure effects on transport processes, precautions have to be made in order not to fail with macrokinetic effects. Besides the influences of the phase behavior of the system, which may change with the degree of conversion, the efficiency of clearing up pressure effects on heterogeneous catalytic microkinetics, depends greatly on the experimental set-up, the reaction system, and the catalyst chosen.

The objective for the analysis of pressure induced fluid state interactions on the course of heterogeneous catalytic surface reaction is summarized in Figure 10.

![Diagram showing reaction rate vs. pressure]

**Fig. 10:** Steps on a solid catalyst and schematic graph of the variation of the reaction rate for a first order reaction with pressure

For a given first order reaction $A \rightarrow B$ an increase of pressure, which means at very low pressure levels an increase of the concentration of the reactant, will result in a decrease of the reaction order. When all active sites are occupied during catalytic process the order with respect of $A$ is zero. A further increase of pressure at subcritical temperatures leads to a liquid reaction phase (with high density, high viscosity and low values for diffusion coefficients) and at supercritical temperatures to a supercritical reaction phase (high density, low viscosity and high values for diffusion coefficients). The basic question is, if there is a significant difference, when the catalytic conversion runs at almost the same density (= concentration) level, but with distinctly different material properties.

Double-bond and cis-/trans-isomerization of $\alpha$-olefins, on $\gamma$-Al$_2$O$_3$ turned out to be well suited for such investigations from several points of view /25/:

- physical properties, especially the critical data of the reactant do not differ
significantly, thus conditions can be easily adjusted to keep the reaction system at different degrees of conversion in the desired fluid states
- product formation occurs via a system of coupled parallel and consecutive reactions
- trans-isomers are thermodynamically more stable than cis-isomers, but their formation at high pressures is more restricted kinetically because of steric effects, and
- there exists detailed information about the kinetics at very low pressures in the literature /26/.

When the degree of conversion is kept on a low level, the reaction scheme simplifies strongly, as shown in Figure 11 for the isomerization of 1-butene. In order to avoid influences of internal mass transport effects shell catalysts with very low catalytic activity, a macroporous structure and a thickness of the catalytic layer of only several microns have to be used.

![Reaction scheme diagram]

Model equations according to a Langmuir–Hinshelwood mechanism

\[
\begin{align*}
-r_{1-Bu} &= \frac{K_{1-Bu}k_{1}p_{1-Bu} + K_{1-Bu}k_{2}p_{1-Bu}}{1 + \sum_{i=1}^{n} K_{i}p_{i}} \\
-r_{2-\text{cis-Bu}} &= \frac{K_{2-\text{cis-Bu}}k_{1}p_{1-Bu}}{1 + \sum_{i=1}^{n} K_{i}p_{i}} \\
-r_{2-trans-Bu} &= \frac{K_{2-trans-Bu}k_{2}p_{1-Bu}}{1 + \sum_{i=1}^{n} K_{i}p_{i}}
\end{align*}
\]

\[K_{1-Bu} = \text{adsorption equilibrium constant} \]
\[k_{1} = \text{surface rate constant 1-butene} \rightarrow 2\text{-cis-butene} \]
\[k_{2} = \text{surface rate constant 1-butene} \rightarrow 2\text{-trans-butene} \]
\[p_{1-Bu} = \text{partial pressure of 1-butene} \]

Fig.11: Reaction scheme of 1-butene isomerization of very low degrees of conversion and kinetic equations /26/.

The variation of the total reaction rate with pressure under different fluid state conditions can be seen from Figure 12. All experimental data refer to the same degree of conversion (10 %) for the isomerization of 1-butene. The lowest curve (reduced temperature \(T_r = 0.976\)) describes the variation of the reaction rate with pressure, when fluid state changes from gas to liquid. The upper curve \((T_r = 1.036)\) is determined by change in fluid state from gas to supercritical.
In the region of low system pressure \((p < p_c)\), when the gas phase has low density, the isotherm at 435 K shows the characteristic shape of Langmuir adsorption when a first order reaction is given. Contrary to that, for \(p = p_c\), reaction rate increases significantly with pressure. For example, when pressure increases from 35 bars to 45 bars \((p_c = 39\) bar) the change in reaction velocity of a component is nearly doubled.

![Figure 12: Variation of total reaction rate of 1-butene isomerization with pressure in different fluid states.](image)

From this experimental results it can be concluded, that by raising pressure in the near critical region the microkinetic of a heterogeneus catalyzed surface reaction can be influenced. Obviously this activation of the reaction by pressure can be described as an interaction of the fluid phase and the processes on the catalyst surface. Effects of the observed magnitude cannot be explained by the raise in concentration through increasing pressure.

5. Mass Transfer between catalyst and fluid phase

Pressure has a pronounced effect on the transport properties like the molecular diffusivity, thermal conductivity or viscosity. Since in multi-component systems these effects usually cannot be calculated by thermodynamic methods as can be done for thermodynamic properties, detailed experimental determinations are necessary.

Generally, mass transfer resistances can have an important influence on the behavior of catalysts, mainly at high pressures. Limitations under gas-phase conditions can be widely repressed, when a heterogeneous catalytic conversion is operated in the near critical or supercritical region of the reaction mixture. The
increase of pressure in connection with variation of physico-chemical fluid properties result in two major effects:

- increase of the solvent power, in certain cases up to several orders of magnitude, in the supercritical region mainly at temperatures near $T_c$ (for utilization of this phenomenon see literature on supercritical gas extraction/3,4/)

- increase of mass transfer between catalyst and fluid phase when all other parameters of the system besides fluid properties remain constant.

By adjusting pressure and temperature in a way that the reacting medium reaches the supercritical state, low volatile compounds deactivating the catalyst under subcritical conditions can be stripped from the catalyst surface /27/. In this manner, the activity of a catalyst can be regenerated periodically, or, running the reaction at supercritical conditions, may maintain high levels of catalytic activity for longer periods of time.

In principle supercritical conditions are achievable either by an increase of temperature and/or an increase of pressure. The latter can be performed either with the reaction mixture itself or by use of a suitable diluent. There are no general rules about the best way, since it depends on the type of catalytic reaction and the phase behavior of the system. E.g. the use of a diluent with a low critical temperature may be advantageous if the reaction mixture itself has very high critical temperatures, as with aromatic compounds.

![Conversion-time plot for the isomerization of hexene-(1) on a shell catalyst under continuous operation (CSTR). Catalyst deactivation (DA) occurs by side-reactions (oligomerizations) in the gas-phase and reactivation (RA) under supercritical conditions.](image-url)
The potential advantages of supercritical fluid reaction mixtures for inline catalyst regeneration are demonstrated in Figure 13.

It is well known that gas phase isomerization reactions of olefins on acid-base catalysts like $\gamma$-Al$_2$O$_3$ cannot be performed without deactivation caused by formation and deposition of low volatile higher molecular products on the active surface sites. Such a typical deactivation course for fixed-bed isomerization of hexene-1 on a shell catalyst with very low catalytic activity ($\gamma$-Al$_2$O$_3$ / glass; specific surface about 5 m$^2$/g) shows the lowest curve (Fig.13). At 15 bar and 523.2 K under CSTR-conditions the expected degree of conversion according to the dashed line for stationary conditions cannot be reached with a gaseous reaction phase. The colourless liquid product contains the isomeric hexenes only (hexene-(1); cis-hexene-(2); trans-hexene-(2); trans-hexene-(3).

An increase of pressure at the same temperature to well above the critical pressure of the reaction mixture effects a dark brown shading of the liquid product mixture. After readjustment of stationary conditions the conversion agrees with the expected value. In spite of the essentially higher reactivity, mainly as a result of the kinetic pressure effect, under these conditions no catalytic decay occurs even after extremely long reaction times.

The dark brown oily product contains besides the hexene-isomers, considerable amounts of oligomers (C12 to C30). Under conditions of a gaseous reaction phase these oligomeric compounds, formed by side reactions, remain on the catalyst surface due to their low volatility and finally cause complete coking.

Whilst pressurization at a constant temperature of a gaseous reaction phase usually favors sorption processes in heterogeneous catalytic reactions and thus hinders desorption of low volatile compounds, increase of pressure in the supercritical region causes the opposite effect. The pressures required for the reactivation are in the same range as for supercritical gas extraction. Prerequisite for successful inline regeneration is to keep catalyst coking at a precoke-level ensuring that the solvent power is strong enough to overcome sorption forces.

6. Interaction of internal transport processes and chemical reactions

There exist little knowledge about pressure effects on transport processes inside porous catalysts with the reaction mixture in the near critical region. The interactions between transport phenomena and chemical rate processes have great importance for catalytic processes. Transport limitations may effect the activity, selectivity and yield of catalysts, expressed e.g. by the catalyst effectiveness factor. Since pressure in different fluid states may influence physical transport processes in a different way than chemical reactions, one gains by pressure variations an additional tool for the control of heterogeneous catalytic conversions.
In the case of highly porous catalysts, e.g. of zeolite type, the situation is far more complex due to the distinct bimodal pore structure with a high portion of micropores. But it turned out that comparative studies with the fluid reaction mixture in different states are well suited to get a deeper insight to analyse reaction behavior.

![Diagram of Heterogeneous Catalysts]

**Pore sizes:**
- macro pores: \(40 \text{ nm}\)
- micro pores: \(0.5 \text{ nm}; 0.35 \text{ nm}\)

**Reaction System**

\[
\text{Benzene} + \text{Propene} \rightarrow \text{Cumene}
\]

<table>
<thead>
<tr>
<th>Benzene</th>
<th>Propene</th>
<th>Cumene</th>
</tr>
</thead>
<tbody>
<tr>
<td>TB [K]</td>
<td>353.3</td>
<td>225.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>425.6</td>
</tr>
</tbody>
</table>

Fig. 14: Alkylation of benzene with propene on a zeolite of faujasite-type (micropore size: 0.5 nm) and on a commercial catalyst or mordenite-type (micropore size: 0.35 nm).

Alkylation of benzene with propene on zeolitic catalysts was chosen for this purpose from several reasons:

- the reaction product cumene has a low volatility
- formation of higher substituted alkylates is favored due to the thermodynamic equilibrium
- the system allows to study olefinic and aromatic coking, and finally
- this synthesis is of great practical importance.

The conditions with respect to the catalyst are summarized in Figure 14. Two types of catalysts (Mg 13 X and Zeolon 900 Mg) with distinctly different micro-
pores were applied. One essential intention was to compare conventional contacts with shell catalysts, made from the identical catalytic material but with a different thickness of the catalytic active material.

Fig. 15: Variation of the degree of conversion of propene with pressure from the gaseous (p = 30 bar) into the supercritical region (p > 60 bar).

The upper diagram in Figure 15 shows the course of the degree of conversion of propene under CSTR-conditions after isothermal pressure variations from the sub- into the supercritical region. The lower diagram shows the corresponding course of the reduced pressure $p_r$ and the reduced temperature $T_r$ of the reaction mixture. Striking is the significant increase of the degree of conversion when the pressure is raised into the supercritical region (e.g. from 30 bar to 60 bar) and the resulting reduction of losses of catalytic activity in the dense fluid region. But different compared with macroporous shell catalysts with very low catalytic activity in the case of microporous systems, the decay of catalytic activity can be influenced by fluid state variations only to a minor extent (see Figure 16).
The reason for this behavior may be seen as the result of two deactivation mechanisms of zeolite-type catalysts. Whilst intercristalline deposits on a precoke level can be removed by SCF-treatment, intracristalline deposits cannot. Thus, the use of an SCF-reaction mixture offers the ability to study deactivation processes in micropores of catalysts with bimodale pore structure. If precautions are made to suppress micropore deactivation, the lifetime of zeolite-type catalysts can be prolonged significantly. For instance it was found that the time on stream of modified zeolite-type catalysts (e.g. Mg 13 X) for the alkylation of benzene with olefines under supercritical reaction conditions appear to be longer by a factor of more than 20 than under usual gas phase conditions.

![Graphs showing catalytic activity over time](image)

**Fig. 16:** Comparison of the variation of catalyst activity with time for different microporuous catalysts with gaseous, liquid and supercritical reaction mixtures.
Conclusions

The aim of this paper was to demonstrate new trends in high pressure chemical reaction engineering and to focus interest on applications of elevated pressures. The main reason for the present increasing interest in high pressure technology may be seen in the specific effects of pressure on chemical and physical processes and on properties of reaction systems in different fluid states, especially in the near supercritical region. Whilst the advantages of SCF-media for new separation processes are already utilized on a large scale, their application as a measure of reaction control, mainly in heterogeneous catalysis, is new and still in the state of laboratory testing. Since critical pressures of the most organic compounds are in the region of about 50 bar, SCF-conditions are also of interest for technical synthesis.

7. References

/1/ Paulaitis, M., J.M. Penninger, R.D. Gray, and Ph. Davidson, Chemical Engineering of Supercritical Fluid Conditions, Ann Arbor Science, 1983


/14/ Tiltischer, H., Habilitationsschrift 1982; Annual Report of Technical University, Munich, 1983

/15/ Foag, W., Dissertation, Technical University Munich (1981)


/21/ Schelchshorn, J., Dissertation, Technical University Munich (1983); IDEA-Verlag, Puchheim, 1983

/22/ Buback, M., Angew. Chem. 103 (1991) 658


/24/ Ertel, H., and H. Tiltischer, Applied Optics, submitted for publication


HIGH PRESSURE PROCESS MACHINERY FOR CHEMICAL PLANTS

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High-Pressure Machinery for Chemical Plants

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Abstract
Because of severe stresses, it is necessary to design, structure, and fabricate high-pressure machines very carefully. Experience shows that, in high-pressure processes, the machines, that is high-pressure pumps and compressors, present the most problems as regards life-time and maintenance. In process and production engineering, high pressure is generally understood to include the range from 100 to 4000 bar. Nearly all important applications also fall within this range [1].

1. Special Features of High-pressure Machines
High-pressure machines are expensive to research, develop, produce, supply with energy, maintain, and repair. Since the components are subject to high stress, a careful stress analysis is necessary. For dynamic stresses, a design with few notches and with excellent surface quality is required.
At points that are especially prone to risk, the local material properties must be improved, and stress peaks must be reduced.
The solution of sealing problems, especially under dynamic stress, requires a great deal of experience. The piston seals of reciprocating displacement pumps present special problems. Such pumps overcome very high pressure differences (up to several thousand bar) in one stage.
The sealing of difficult fluids, such as suspensions and materials with low viscosity and poor lubricating action, absolutely requires special measures.
In selecting materials for high-pressure components, special attention should be paid to high strength, good isotropy, homogeneity, and toughness. Quality assurance is extremely important. Besides high-strength ferritic tempering steels, fabricated with special purity, soft martensitic, semiaustenitic and precipitation hardening chrome-nickel are increasingly being used. Homogenity is achieved by the smelting method and isotropy is achieved by forging the slugs all around as much as possible.
In the field of dynamic seals, all capabilities of modern materials development for plastics, bronzes, sintered metal carbides, and layers of hard material are utilized. The special material properties of fluids at high pressures, such as compressibility, viscosity changes, density, and solidification temperature, must be taken into account.

2. Creation of Pressure by Pumps and Compressors
The approximately isentropic change of state during a pressure increase (Fig. 1) causes a temperature rise which is small in liquids but large in gases. This temperature rise limits the pressure ratio produced by one stage in compressors. The required technical energy is generally determined by the difference of the total enthalpies.
For gas compressors, efficiency data refer alternatively to isothermal or isentropic changes of state, which implies considerable differences.
For reciprocating piston machines, the clearance volume, fluid compressibility, and working-space elasticity determine the volumetric efficiency (also transfer or discharge level), which represents a measure for utilization of the structurally determined swept volume. With high-pressure piston compressors, a multi-stage arrangement with intermediate cooling, to approximate the energetically favorable
isothermal change of state, is economical. The pressure ratios produced by one stage here amount to 2 - 5 in the case of process gas compressors (Fig. 2, left).
By contrast, piston pumps for liquids overcome very high difference pressures in a single stage, because the liquids are much less compressible (Fig. 2, right). The fatigue of the pump component with a cyclical interior pressure [2, 3] and the life-time of the piston seals set limits here.
With rotating displacement machines, e.g. gear pumps, interior leakage losses play the decisive role for the volumetric efficiency. For high-pressure applications, such pumps are suitable only for highly viscous fluids.
When pressure is generated hydrodynamically, as in turbomachines (Fig. 3), the circumferential speed of the commonly used radial wheels is of essential significance for the pressure increase per stage \( \Delta p = \Psi p u^2 / 2 \) (where \( \Psi \) is the so-called coefficient of pressure, \( p \) is the fluid density). The rotor stress limits the circumferential speed for pumps to about 100 - 200 m/s. For turbocompressors, the speed of sound, about 300 - 400 m/s, sets a limit; generally one stays with Mach numbers safely below 0.7.
In any case, pressure increases per stage of 50 - 250 bar are achieved for liquids, depending on the power. For gas compression, one needs more stages than for liquid pumps, because of the lower fluid density, and in particular one needs intermediate cooling.
Compared to hydrodynamic turbomachines, hydrostatic displacement machines exhibit pulsation of the flow rate (Fig. 4). As a rule, for comparable power, better efficiency speaks in favor of displacement machines, whereas their smaller size, their smaller space requirement, and their better quiet running speaks in favor of turbomachines.

3. Pumps
In high-pressure systems, pumps are used for volumetric metering, for transfer, circulation, and pressure maintenance. Volume flows here extend from about 1 ml/h to over 10^8 m^3/h. The pressure range generally extends up to 300 - 1000 bar, more rarely into the range of 1000 - 4000 (10,000) bar (Fig. 5).
The characteristic curves of pump construction types differ mainly in their pressure stiffness (Fig. 6a). Because of their pressure-elasticity curve, centrifugal pumps can also be regulated by throttling (Fig. 6a: The operating point shifts from A to B). Regulation of the rotational speed is already more favorable energetically (Fig. 6a: Operating point shifts from A to \( B' \)). Bypass regulation is also customary for large machines and low energy costs.
Displacement machines have pressure-stiff characteristic curves; consequently, they impress their flow rate on the pumping system (Fig. 6a: Lines O and R). As a rule, the flow rate depends approximately linearly on the regulated variables (rotational speed \( n \), stroke length \( h \)) (Fig. 6b). With reciprocating displacement pumps, the high pressure difference shifts the characteristic curve from the origin, through elasticity effects from the working space and the fluid [4]. The same applies to rotating displacement pumps at higher difference pressures, through the interior clearance leakages. With rotational speed \( n_0 \) (e.g. gear pump) and stroke length \( h_0 \) (e.g. reciprocating metering pump), the flow rate is 0. Only in the case of reciprocating displacement pumps is there proportionality between the flow rate and the regulated variable \( n \), because the interior leakage currents vanish as a rule (Fig. 6b).
3.1. Reciprocating Displacement Pumps

In high-pressure engineering, reciprocating piston- and diaphragm-pumps are used in many variants up to extreme pressures of 10,000 bar. They may have electrical, hydraulic or pneumatic, linear or mechanical, crank- or eccentric-drives, and their stroke, or speed may sometimes be adjustable. The following explanations refer to metering and transfer-pumps, and are oriented in terms of important applications.

3.1.1. Metering Pumps

For very small, pulsation-free metering flows (e.g. $10 - 10^3$ ml/h), hydraulic and mechanical (spindle) linear drives are familiar for pressures up to several 1000 bar. By operating two systems in parallel, these can also be controlled without interruption (Fig. 7a and b) [4].

By superposing two displacement pistons or by controlling the angular velocity with a special cam drive, one achieves small metering flows with rather low pulsation, up to a pressure range of about 700 bar. This can even be done with leak-free hydraulic diaphragm pump heads (Fig. 7c and d). Applications for such pumps also occur in HPLC-analysis [5, 6].

If high-frequency metering flow pulsations do not interfere with the process, as is the rule with most applications, reciprocating piston- or diaphragm-metering pumps with adjustable stroke and speed are used.

Magnetic linear drives (Fig. 7e) are distinguished by their ease of activation and their small construction size. This is a favorable solution for the range below 1 l/h, for pressures up to 500 bar, with diaphragm pump heads.

For larger metering flows, reciprocating metering pumps with an adjustable stroke and with mechanical transmissions have proven themselves. For metering several components, or to smooth out pulsations, these can be designed with several cylinders (Figs. 7f and g) [7]. The automation systems are activated through stroke actuators or through drives with variable speed.

Diaphragm metering pumps with an hydraulic diaphragm drive have proven themselves up to the highest pressures. Up to about 500 bar, their diaphragm consists of polytetra-fluoro-ethylene; beyond this, up to about 3000 bar, it consists of metal (e.g. chrome-nickel steel) [7, 8]. The leak-free design operates reliably, is easy to maintain, presents no problems with hazardous fluids, and circumvents piston sealing problems.

With smaller metering flows, drives by spring-loaded cam drive systems predominate because they make it possible to adjust the stroke without backlash (Fig. 7h). For larger metering flows (hydraulic power up to 50 KW per metering element), all types of drive designs with adjustable stroke are in use. All of these are based more or less on the familiar ordinary crank mechanism (Fig. 8).

The life time of PTFE diaphragms, which are primarily used (up to 500 bar) far exceeds 10,000 h. Diaphragm rupture can be signalled through sandwich diaphragms [9, 10]. For very high pressure (greater than 1500 bar), diaphragm pumps with metal diaphragms have gained entry only for laboratory and pilot systems, because they are quite sensitive in this pressure range.

Reciprocating high-pressure metering pumps therefore predominantly tend towards diaphragm technology. Exceptions are the above-mentioned piston designs for HPLC analysis, where extremely favorable operating conditions prevail.

For process and production engineering, piston metering pumps with a low-frequency, long-stroke linear drive (Fig. 9, also called pressure converters) continue to prove themselves for very high pressure (1500 bar - 4000 bar) (Fig. 7i). The
uniform, slow piston motion leads to an operationally reliable piston seal and, when two pump heads are superposed, to low pulsation of the flow rate [11]. For a pressure range of several thousand bar, such as is required for metering purposes in poly-olefin production or for water-jet cutting, the piston heads are designed with coaxial pump valves to avoid the notch effect (see Fig. 12). Hydraulic pressure converter pumps can also be driven easily speed-controlled at high powers for automation purposes.

3.1.2. Transfer Pumps

In contrast to metering pumps, which generally have a single cylinder and an adjustable stroke, transfer pumps are always designed with several cylinders (e.g. triplex) in a multi-head structure, in order to smooth out pulsations in the flow rate (Fig. 7g). Powers over 1 MW are achieved in a vertical or horizontal mode of construction. At this time, piston pump heads still predominate. Drives for multi-head piston- and diaphragm-pumps greatly resemble one another (Fig. 10a).

At high pressure, and when using corrosion-resistant high-strength steels, the monoblock mode of construction is replaced by a component mode of construct (Fig. 11c). The advantage is that the parts which are most subject to fatigue can be replaced more easily. Beginning with 100 - 300 bar, a coaxial valve arrangement is suitable because, in this way, the notch stresses can be reduced by at least a factor of two compared to the customary T-intersection of the pump head bores. Such designs can deal with differential pressure up to about 1500 bar, in an operationally reliable and long-term manner. Such pressures are presently required in high-pressure cleaning technology and elsewhere (Fig. 12).

Diaphragm transfer pumps in a multi-head structure with powers up to about 1 MW have recently also been built for the pressure range up to 1000 bar (Fig. 10b) [9, 12]. The avoidance of piston seals with fluid contact and of their leakages leads to remarkable operating reliability. For this reason, multi-head diaphragm pumps are economical for hazardous fluids at high pressures, as compared to multi-head piston pumps, despite the higher investment costs.

With the development of pipeline transport of coal or ores, the chemical refining of ore, and coal hydration, which still remains current, high-pressure pumps are currently being used for suspensions that are loaded with solids. There are various methods to keep abrasive particles away from the piston seal, e.g. hydraulic isolating lines, sedimentation spaces, and flushing systems [13].

For predominantly aqueous, abrasive slurries with a high concentration of solids, multi-cylinder diaphragm pumps are suitable up to a pressure range of 200 bar and for powers of about 1.5 MW. They generally have a four-cylinder arrangement and elastomer diaphragms [14].

An entirely new branch of "high-pressure engineering" is the conveyance of materials with high consistency, e.g. mortar, concrete, sludge, slurries, along longer distances. Up to 200 bar pressure may be necessary for this. This can be done with slow hydraulic long-stroke piston displacement elements if the inlet opening of the two-cylinder arrangement is controlled with sliding switches which operate as valves [15].

3.1.3. Rotating Displacement Pumps

At high difference pressures, rotating displacement pumps are suitable only for viscous fluids. As the viscosity increases, the internal sealing clearances seal better and better, and the pump efficiency as well as the attainable pressure difference reach satisfactory values. Gear pumps and screw pumps are suited for process engineering
applications up to 300 bar, beginning with fluid viscosities of about 100 mPas.
Typical applications for gear pumps are the injection, conveyance, filtration, and
spinning of polymer melts (viscosities till above 10⁶ mPas). Delivery pressures up to
450 bar occur in these applications. In the case of hot and direct spinning processes,
the heated high-pressure gear pump with a large entry cross-section takes the
polymer melt from a reactor, which may possibly be under vacuum, and presses it,
via filters, towards the gear spinning pumps, whose flow rate is especially uniform
and does not depend greatly on the delivery pressure. Gear pumps are used behind
compounding extruders to increase the pressure, e.g. from 100 to 300 bar, and to even
out the extruder output which tends to fluctuate (Fig. 13 and 14) [16 - 20].

3.2. Centrifugal Pumps
High circumferential speeds and several or many stages are needed at high pressure
differences. Economic application of centrifugal pumps in this area depends on the
specific speed of the single stage (at least 10 - 20 min⁻¹) and thus on the magnitude
of the flow rate and the hydraulic power.

3.2.1. Multi-Stage Centrifugal Pumps
High-pressure centrifugal pumps have long been known as feed pumps for steam
boilers [21, 22]; their power extends to beyond 30 MW, their pressures up to 400 bar.
The design of high-pressure centrifugal pumps for process engineering varies
according to the pressure level, the temperature conditions (including during
starting), the operational requirements, as well as the directives of the international
regulatory works.

In the area of high-pressure process engineering, centrifugal pumps with vertically-
split barrel construction have established themselves for powers above about 1 MW
in petro-chemistry and in petroleum/natural gas exploration, here especially as
injection pumps [23, 24]. Injection pumps for surface and sea water impose much
more stringent requirements of the corrosion and erosion strength of their
components (power up to about 20 MW, pressure up to 300 bar). The entire running
gear can be withdrawn without disassembling the housing, which facilitates repairs
(Fig. 15). For pressures below 250 bar and lower powers, multi-stage centrifugal
pumps are also used with staged housing or modular construction. They require
lower investment costs in general. For the pressure range up to 150 bar, a
longitudinally divided (horizontally split) housing design (pipeline pump) is suitable
for certain applications.

3.2.2. High-Speed Centrifugal Pumps
The introduction of high-speed single-stage and two-stage centrifugal pumps has
become noteworthy in recent years (Fig. 16). They now represent a quite significant
alternative to multi-stage centrifugal pumps in the range up to 100 m³/h. The
required high circumferential speed (max. 200 m/s) is effected by high rotor speed
through gears (rpm to about 30,000 min⁻¹), so that pressure increases per stage up to
about 200 bar are possible. Their efficiency is generally poorer than in the case of
multi-stage pressure arrangement, but on the other hand, high-speed centrifugal
pumps have a compact construction.

Two-stage gear-centrifugal pumps achieve still higher pressure than single-stage
pumps (Fig. 16b). But here the shaft seal of the second stage is exposed to higher
pressure; the slow-running booster stage that is shown in Fig. 16b is used to increase
the suction pressure and improve NPSH-conditions.
For hydraulic powers below 1 MW (pressures from 100 to 300 bar), only a detailed cost-benefit calculation will generally indicate the most favorable choice between multi-stage centrifugal pumps, high-speed one- or two-stage centrifugal pumps, or reciprocating multi-head-piston or diaphragm-pumps. The consumption of energy and expenses for investment and maintenance determine the optimal solution.

3.2.3. Hermetic Centrifugal Pumps
With centrifugal pumps, too, there is a trend towards avoiding leakages and problems with shaft seals by means of a leak-free design. Normally, the shaft seals of centrifugal pumps are exposed only to intake pressure, and thus can be dealt with relatively easily. With higher intake pressures or system pressures, it is recommended that centrifugal pumps with a canned motor drive be used, especially in the power range below 500 KW, if the fluids are toxic or hazardous [26, 27]. Experience is available up to system pressures of 1000 bar. Especially the support of the thin-walled containment shells of austenitic steel in the grooved stator against the high pressure should be noted here. The rotor bearings, lubricated by the delivery fluid, are now frequently made of silicon carbide.

Fig. 17 shows a single-stage canned-motor centrifugal pump with separate water-cooling circuit for the motor, such as is used, for example, to circulate carbon dioxide at 300 bar system pressure. The pump rotor is mounted in the motor area; the pump stage in supercritical extraction systems and the cooling-circuit impeller operate over-mounted on both sides of the bearing. The entire cooling flow passes the canned motor (slit, shaft boring) for cooling.

Permanent magnet drives for pumps and agitating mechanisms are increasingly entering high-pressure technology [26, 28, 29]. But here, with the magnet drive - in contrast to canned motors - the containment shell must take up the full pressure difference and must have appropriately thick walls.

If larger flows of non-problematic fluids must be circulated at high system pressure (e.g. carbon dioxide at 400 bar), two-stage mechanical seals with pressure blockage are sometimes used. The axial thrust is taken up, for example, by a segment bearing (Fig. 18). Hydrodynamic mechanical seals make it possible to control system pressures up to 300 bar even in a single stage [30].

4. Compressors
Development has led to optimal compressor types for the various power ranges. Fig. 19 [31] was calculated on the basis of 1 bar intake pressure and an isothermal efficiency of 64 %. It can give only approximate reference points for the most favorable area of application, which can vary depending on the manufacturer. If the intake pressure is greater than 1 bar, as is the rule, it is necessary to recalculate. (Example: Ethylene compression 6400 kg/h = 51130 Nm³/h from 231 to 2151 bar, corresponds to a real intake volume flow of 161 m³/h and a power consumption of 8200 KW.)

The application boundary between piston- and radial-turbo-compressors lies approximately at 10¹⁴ m³/h intake volume flow (power > 1 - 5 MW). In individual cases, the most economical solution must be determined in the boundary range.

Development of piston compressors has partially stagnated in recent years. Rotating screw-type compressors and turbo-radial machines have taken over certain areas. For large, multi-stage horizontal process-gas piston-compressors, built up to powers in excess of 10 MW, development is largely concluded. The trend toward radial-turbo-compressors dominates here for reasons of economy. They operate with little
vibration and pulsation, they are more easily sealed, and they require little space. All of these are favorable factors.

4.1. Piston Compressors

At lower powers (< 2 MW), there is a lively development of piston compressors in the direction of a higher stroke frequency, a more compact modular construction (Fig. 20), dry-running compression, sparing lubrication, and simpler maintenance [32 - 35]. The dry-running range for continuous operation extends up to about 300 bar, depending on the type of gas. Labyrinth- and piston-ring-compressors here have their characteristic fields of application. The completely encapsulated labyrinth compressor with a pressure-proof housing is attractive for gases that are not too light (Fig. 21). Dry-running piston-ring compressors can be used universally as far as gas density is concerned; to achieve satisfactory running times (> 10,000 h), modern design and material concepts must be implemented for the piston rings. The so-called sparing lubrication also plays a role here in reducing the lubricant contamination of the gas. However, the predominant portion of all high-pressure piston compressors is designed with lubrication. In that case, trouble-free running times above 10,000 h are the rule.

Ethylene secondary compressors occupy a special position. These compress typically from about 200 - 300 bar to 2000 - 3500 bar in two stages, and are built up to powers of about 10 MW [36 - 38]. In contrast to crank compressors, their drives are designed with an interior, robust cross-head guide (Fig. 22) and pair-wise opposite cylinders. The top-most principle is to keep away any transverse forces from the piston seal. For components subject to cyclical pressure, notches are avoided (Fig. 23). Valve bodies with cone-valves at large capacities several arranged in parallel, are used here. Super-pressure compressors mainly work with stationary piston sealing elements; here there is an essential difference from standard piston compressors with mobile piston rings. But only with a stationary sealing arrangement does one achieve the required effective high-pressure lubrication, which also requires extremely hard, smooth, and precisely machined plunger pistons.

4.2. Diaphragm Compressors, Laboratory High-Pressure Compressors

The diaphragm compressor, one of the oldest leak-free machines, is limited to lower powers (< 100 KW) because of its sensitive metal diaphragms, which must be chosen because of the high compression temperatures. Its applications include laboratories, pilot installations, and special production facilities. An attractive feature is their very high pressure ratio produced by one stage, up to 20, as a result of the small clearance volume and good cooling.

At every stroke, the diaphragm is pressed against the upper contact surface through excess hydraulics (smallest clearance volume). However, it does become sensitive to particles, coatings, liquid droplets, and surface defects, so that its life-time generally is less than 5000 h (Fig. 24). It is possible to signal diaphragm rupture by means of sandwich diaphragms [40].

Diaphragm compressors are built for pressures up to 4000 bar, at least for short-term operation. They are economical if absolutely tight operation and no gas contaminations whatsoever are required at small volume flows and at high pressure. For very small delivery quantities (0.1 - 1 m³/h) against pressures up to 2000 bar, air-driven piston- and diaphragm-compressors (Fig. 25) are suited for refilling and compressing gases. Because of their compact construction, their explosion protection, and their ease of regulation, such machines are attractive for short-term operation in
research facilities.

4.3. Turbo-Compressors
For large volume flows (2 x 10^3 - 10^5 m^3/h), radial turbo-compressors have now largely displaced process-gas piston compressors even in the range above 150 bar. Typical applications in urea-, ammonia-, and methanol-plants, for compressing synthesis-, natural-, and refinery-gas, as well as for transporting and injecting gas, extend up to the pressure range of 400 bar [41].
For high-pressure technology, radial compressors are designed similar to high-pressure centrifugal pumps, in vertically split barrel construction (Fig. 26); for hazardous gases, this is already done beginning at about 80 bar, in contrast to liquid pumps, on account of the more favorable seal. There are good possibilities for compensating the axial thrust by an appropriate arrangement of impeller stages with intermediate cooling.
It should be mentioned that multi-stage gear-radial turbo-compressors are suitable as preliminary stages for high-pressure stages for pressure ratios up to about 50 bar [42, 43].
For pipeline gas transport, single-stage and two-stage vertically split barrel designs have been produced for final pressures up to 80 bar and for powers above 20 MW. These designs are easy to install and maintain.
A series of prototypes were developed to expand the fields of application of turbo-compressors. By way of example, Fig. 27 shows a six-stage high-pressure stage (350/800 bar). The impellers have been machined smooth and are composed of two disks (e.g. by soldering); an exit gap of a few millimeters can be achieved here. Nevertheless, the shaft seals here must seal against the suction-side pressure level (350 bar); they work with pressurized oil blockage [44].

5. Other High-pressure Machines
The problems of sealing rotating shafts recur with high-pressure agitators and high-pressure extruders, which greatly resemble rotating pumps [28, 29, 16 - 20].
High-pressure sluices for bulk goods present special sealing problems [45].
A new type of "high-pressure machine" has arisen in the area of high-pressure extractors with automatically opening locks [46].

6. Special Problems involving High-Pressure Machines
6.1. Strength of Components
Since high-pressure components generally are subject to high stress, a precise strain analysis is necessary, possibly with the finite element method or with strain optics. This is especially true for impellers that have a high circumferential speed, also for the vibrational analysis of rotor shafts.
In general there is no special problem about dealing with strains in statically stressed pressure housings especially since a suitable stress flux can achieve a favorable strain (e.g. vertically split barrel design). By contrast, it is much more difficult to dimension components that are stressed in cyclical fashion by internal pressure. The largest cyclical internal pressure stresses occur with reciprocating liquid pumps. The permissible dynamic material stress lies below the yield point of the material. The maximum stresses occur at notch points. Compared to the "undisturbed" thick-walled pipe, the usual notch points (Fig. 28) have notch factors from 1.5 to 3.5 [3, 47].
Studies on ferritic tempering steels, and recently also on soft martensitic, semiaustenitic, and precipitation hardening highly alloyed chrome-nickel steels, make
it possible to design dynamically loaded thick-walled components [48 - 56].
With tough, highly alloyed chrome-nickel steels, an increase of their dynamic
loadability by autogenous autofrettage has been observed, which explains the
experimentally familiar favorable behavior of these steels.
Studies show that thick-walled forged pieces can exhibit anisotropy noticeably often,
and that the surface quality has a perceptible influence. Furthermore, the
characteristic values of the material depend on the purity of the material (slag
inclusions). With components subject to very high stress, the use of especially pure
steel grades, smelted under inert gas or in vacuum, is therefore always
recommended. Allaround forging promotes isotropy.
At very high pressures, and for parts made of rather brittle steels and subject to
cyclical stresses, there is a clear discrepancy between the characteristic data of the
material for uniaxial and thick-walled samples. [52]. Various researches prove that the
penetration of pressure into the micro-cracks (e.g. slag inclusions), which are always
present in the material, creates a noticeable additional stress. With highly alloyed
chrome-nickel steels, these stresses appear rather to be reduced by local plastification.
For thick-walled components, the following design measures help to deal with
cyclical pressures:
a) Avoiding notches, for example, by a coaxial arrangement of the pump valves (Fig.
12). If this is not achievable, the point that is subject to the greatest stress must
be rendered safe by giving it a Y-shape instead of a T-shape (rounded) (Fig. 29).
A tangential layout of the intersecting bores can also yield advantages [56],
b) Application of compression pre-stresses, in the limiting case up to pure cyclical
pressure stress by autofrettage, cold-working, shrinkage, or local shot-peening.
c) The use of pure, isotropic materials that are as tough as possible, and the
avoidance of corrosion as a result of which the fatigue strength is greatly reduced
[58]. Reliable data on the fatigue strength of thick-walled components have
recently become available for moderate, high-strength soft-martensitic (e.g. 1.4405,
1.4313), semiaustenitic (e.g. 1.4462), and hardened (e.g. 1.4548) steels [3].
In general, the design of components that are subject to cyclic pressure requires great
experience. In compressor construction, the problems generally are easier to solve
because of the lesser pressure amplitudes.

6.2. Seals
In high-pressure technology, metallic seals - lenses, ring joints, cuts - are used as
static seals. Self-sealing elastomer sealing rings, e.g. O-rings, have also proven
themselves for easily loosened connections, to the extent that the pressure,
temperature, and fluid permit this.
Where such seals are unfavorable, for example, with horizontally split compressor
housing, structural measures, e.g. vertically split barrel housing, are used to
guarantee a reliable seal.
The clamping and sealing of diaphragms for diaphragm pumps and compressors
occupy a special position [9]. These represent a form of static seals with special
function requirements.
The actual problem points in high-pressure machines are the dynamic shaft- and
piston-seals. Seals create special problems when they slide rapidly under high
pressure and if the fluid being sealed does not have any lubricating power. Cyclical
stress additionally creates fatigue problems for the parts of the seal. Non-contacting
seals with defined narrow clearances, such as labyrinth seals, are less problematical
in connection with the generally low difference pressures (< 50 bar); however, the fluid should not have an erosive effect (Fig. 30). Difference pressures up to several hundred bar occur at the axial thrust compensation pistons of centrifugal pumps and compressors, but these are distributed among many labyrinth stages. Labyrinth seals on reciprocating pistons require very precise alignment, and are limited to gases that do not have too low a molecular weight, as well as to pressure differences $p < 150$ bar (Fig. 30b).
The leakage flow of non-contacting gap- and labyrinth-seals is considerable, and must be recycled internally. With the "floating ring seal", a typical shaft seal for high-pressure sealing oil system sets a slight over-pressure compared to the gas pressure at the floating ring (Fig. 31), so that the sealing problem is reduced to the gap seal for the oil [45].
Mechanical seals for liquids, without special measures, are clearly limited to pressures below 100 bar [59]. The limits are determined by the product of the sliding speed $v$ and the difference pressure $\Delta p$, whose rule of thumb is approximately $\Delta p \cdot v < 2000$ to 5000 bar m/s. This value is physically based on the friction power arising in the gap. With pressures above 100 bar, sealing pressure blocking systems are used to reduce the difference pressure, to avoid evaporation, to improve lubrication, and to provide cooling [30].
High-pressure mechanical seals are needed for centrifugal pumps only if there is a high system- or vapor-pressure. With smaller powers, leak-free canned motor pumps are generally applied in these cases.
It is especially difficult to seal reciprocating motions of pistons. Piston rings are suitable as piston seals in piston compressors up to pressures of about 1500 bar; above 250 bar, generally with lubrication. With dry-running or sparsely lubricated piston compressors, the concept of piston rings made of PTFE composite materials has proven itself. This is shown in Fig. 32. It competes with non-contacting labyrinth seals for pistons. At high pressure, the "captive piston ring" is especially interesting (Fig. 32, stage 3). It is supported after a run-in process, and thus makes contact at low compression [60]. For lubricated high-pressure stages up to 700 bar, metallic piston rings are used. Generally these are made of perlitic gray cast iron. At still higher pressures (up to 1500 bar), piston rings made of forged bronze have also proven themselves.
Piston seals of ethylene secondary compressors in diaphragm systems occupy a special position (Fig. 33). Supercritical ethylene is here compressed from 300 - 350 bar, in two stages, to 3000 - 3500 bar. (Specific volume at 4500 bar; 1.5 dm$^3$/kg). Good experience has been made with stationary bronze seals, which run against metal carbide pistons. The sealing elements consist of a sequence of radially and tangentially slotted rings, generally preceded by a throttle ring. Oil, as a lubricant, is injected between the individual sealing elements against the high pressure produced by the compressor [61].
Similar sealing elements are also successfully used for sealing piston rods at pressures up to 500 bar [62].
Piston seals for reciprocating displacement pumps must master the greatest dynamic pressure differences because the compression always occurs in a single stage. To this must be added the large spectrum of fluid properties (toxicity, corrosion, low vapor pressure). Lubrication is often ineffective because the pumped fluid often has the character of a solvent. The seals have a rich variation of designs in terms of form and material. PTFE composites (solid, braided) are often used. The piston should be
designed hard, smooth, and geometrically precise. Guided centrically, it should run in the seal "without any coercion". The sealing elements should press just hard enough as is required for sealing. Dry-running must be avoided, possibly by lubrication or flushing (for design forms, see Figs. 12 and 29). Spring-tensioned chevrons with lubrication are used successfully up to the highest pressures (up to 3000 bar). As the pressure increases, the life-time decreases quite drastically (e.g. 3000 h at 500 bar; 1000 h at 3000 bar). Packing rings with a separately clamped lubricating or flushing chamber have proven themselves to be a robust design for the pressure range from 200 to 300 bar. With heterogeneous fluids, or with fluids that cannot be lubricated readily, it is advantageous to inject a flushing fluid into the working space (Fig. 34, item 1).

The maintenance and installation of piston seals requires a great deal of experience; the necessary flushing and lubricating systems are sometimes quite complicated. Frequently, the optimal design (3000 to 8000 h life-time) must be determined empirically by systematic troubleshooting.

At very high pressure (> 1000 bar), special measures are needed: pistons and guide bushings of sintered hard metals; extremely precise, smooth machining; seal made of PTFE with carbon, graphite, ceramic, or metal powder admixture. To this is added a support for the lubrication, as well as a form of the sealing elements which operates as automatically as possible under pressure. A low piston speed reduces the friction power and increases the life-time of piston sealing elements. In this respect, hydraulic linear drives are more favorable (Fig. 9). With high-pressure piston seals for suspensions, the particles must be kept away by injection flushing or by sedimentation spaces, as experience with coal slurry pumps (3000 bar) has shown [13].

A quite decisive measure to circumvent problems with piston- or shaft-seals is to avoid them totally by using hermetic diaphragm- or canned-motor-pumps.

6.3. Wear, Vibrations

The literature references [64 - 70], which are specific to high pressure, mainly refer to the wear of automatic pump valves, and to the determination of pressure oscillations through reciprocating pumps and compressors.
References


22 Matthias, H.B.: Speisepumpen für Dampfkraftwerke und Nuklear-Kraftwerke bis 1300 MW Blockleistung. Pumpen und Pumpenanlagen, Lexika-Verlag 1979


35 N.N.: Industrial Gases Committee (IGC): Kolben-Verdichter für Sauerstoffbetrieb. IGC-Dok. 10/81/D


38 Traversari, A.; Beni, P.: Approaches to Design of a Safe Secondary Compressor for High Pressure Polyethylene Plants, Safety in High Pressure PE-Plants. AIChE 1974


44 N.N.: Turboverdichter für sehr hohes Druckniveau. Mannesmann-Demag Druckschrift MA 25.69 dt/11.81, 1981


59 Mayer, E.: Axiale Gleitringdichtungen. VDI-Verlag Düsseldorf, 1982


62 de Haas, P.: Besondere Merkmale von Borsig-Kolbenkompressoren. BORSIG-Druckschrift


64 Vetter, G.; Schweinfurter, F.: Vermeidung störender und gefährlicher Druckschwingungen durch Hochdruckpumpen. VDI-Berichte Nr. 748, 1989, p. 21 ff


Fig. 1:
Isentropic change of state (carbon dioxide)
A - B gases
C - D liquids
E - F supercritical fluids
$T_c$ critical temperature
$p$ pressure
$v$ specific volume

Fig. 2: Gas and liquid compressor (pump) in a p-V diagram
Left: five stage gas compression
Right: single-stage liquid compression
$p$ pressure, $V_h$ stroke volume, $V_T$ clearance volume, $\Delta p_A$ pressure increase per stage
Fig. 3: Principles of pressure generation
a) piston pump, single stage
b) piston compressor stage (double-action)
c) multi-stage centrifugal pump (or turbo-compressor)
d) high-speed single-stage centrifugal pump

Fig. 4: Time behavior of the fluid flow
a) hydrodynamic pump or compressor
b) hydrostatic (double-action) piston machine
$V_m$ average volume flow
$V(t)$ time volume flow
Fig. 5: Capacity range of various pump types for high pressures
1 micro-metering pumps (piston-, diaphragm-, gear-, spinning-pumps);
2 metering pumps for laboratory and pilot systems (K, MH); 3
metering pumps (K, MH); 4 ultra-high-pressure piston pump; 5 multi-
cylinder piston pump; 6 multi-cylinder diaphragm- pumps; 7
centrifugal pumps (high speed, single-/two-stage); 8 centrifugal
pumps (multi-stage); 9 rotating displacement pumps (gear, spindle) K
piston, MH diaphragm/hydraulic

Fig. 6: Characteristic curves for various types of pumps
a) pump in the system, throttle/rpm regulation of centrifugal
pumps
b) regulation characteristics of displacement pumps
K centrifugal pumps
R rotating displacement pumps
Q reciprocating displacement pumps
V fluid flow
Δp pressure difference
n rpm, speed
$h_k$ stroke length
A, B, B' operating points
a, b characteristic curve for the installation system
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Fig. 7: Types of reciprocating metering pumps
K piston pump head
MH diaphragm pump head (hydraulic)
Fig. 8: Diaphragm metering pump with stroke adjustment through an eccentric adjustment system (LEWA)
1-7 eccentric adjustment drives; 8 piston; 9 diaphragm; 10, 11 pump valves; 12 pump cylinder; 13 replenishing valve; 14 piston seal; 15 hydraulic supply container; 16 sliding gate valve; 17 relief valve; 18 venting valve

Fig. 9: Superposition system with hydraulic linear drive (UHDE)
a) principle of the arrangement
b) pulsation of the fluid flow
1 single cylinder piston pump; 2 two-cylinder linear drive (like Fig. 9a)
x, y basic effect of reduced volumetric efficiency through elasticities
$V_m$ average medium flow; $t$ time
Fig. 10: Process diaphragm-pump for high pressure (LEWA)
   a) drive system with straight thrust crank drive for multi-head arrangement
   b) diaphragm pump head for the pressure range up to 500 bar
      1 sliding gate valve for controlling the position of the diaphragm; 2
diaphragm (PTFE, sandwich form); 3 hydraulic cylinder; 4 piston with
       seal; 5 pump valves

Fig. 11: Mono-block and component mode of construction (URACA)
   a) monoblock, valves displaced
   b) monoblock, valves flush
   c) component mode of construction
Fig. 12: Coaxial arrangement of the pump valves
1 piston; 2 piston seal; 3 suction valve;
4 pressure valve

Fig. 13: High-pressure gear pump (heated) for polymer melts (MAAG) [20]

Fig. 14: Compounding extruder with high-pressure gear pump (1) and pressure regulation through the extruder (2) speed (3)
Fig. 15: Six-stage vertically split barrel housing centrifugal pump (SULZER)

Fig. 16: High-speed gear-centrifugal pumps (SUNSTRAND)
   a) single stage
   b) two-stage with booster stage for improving the NPSHr

I, II stages
B Booster stage
Fig. 17: Single-stage canned motor centrifugal pump for carbon dioxide circulation (HERMETIC)
1 rotor; 2 bearings; 4,5,6 canned motor; 8 cooling-circuit impeller; 9 cooler

Fig. 18: Two-stage high-pressure centrifugal pump for circulating carbon dioxide at a system pressure of 300 - 400 bar (GRASSEL)
1 pump stages; 2 blocked high pressure mechanical seal (two-stage); 3 radial bearing; 4 axial bearing
Fig. 19: Power and capacity range of various compressor types for high pressures
M diaphragm compressor, K1 piston compressor, dry running (piston ring, labyrinth); K2 piston compressor, lubricated (piston ring); K3 ultra-high-pressure compressor, lubricated (plunger, piston); TR radial turbo-compressor; TA axial turbo-compressor; S screw compressor

Fig. 20:
Piston compressor in modular construction
(NEUMANN & ESSER)
Fig. 21: Sealing concepts for labyrinth compressor [34]
   a) pressure-proof housing
   b) spacer
   1 labyrinth piston; 2 cylinder; 3 labyrinth piston rod seal; 4 spacer; 5 oil wiper; 6 piston rod; 7 guide bearing; 8 cross head; 9 crank shaft; 10 mechanical seal; 11 oil separator

Fig. 22: Designs of propulsion systems for high-pressure piston compressors
   a) crank, vertical
   b) crank, horizontal
   c) crank, horizontal (double action)
   d) sliding block, horizontal
Fig. 23: Final stage of an ultra-high-pressure secondary compressor (NUOVO PIGNONE)
a) overall arrangement
b) valve block
1 plunger piston; 2 stationary sealing elements; 3 valve block; 4 compressor valve arrangement; 5 plug valve

Fig. 24: Diaphragm compressor (HOFER) [39]
1 diaphragm; 2 working space; 3, 4 suction/pressure valve; 5 diaphragm cover; 6 perforated plate; 7 hydraulic cylinder; 8 relief valve; 9 oil return; 10 cooling; 11 check valve; 12 drive system; 13, 14 cooling; 15 hydraulic space; 16 oil injection; 17 compensation pump; 18 check valve; 19 oil supply
Fig. 25: Two-stage filling compressor with pneumatic linear drive (HASKEI)

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1 compressor stages, 2 vertically split barrel housing; 3 interior housing (modular construction type); 4 bearing; 5 thrust balancing piston; 6 shaft seal
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1 rotor with compressor stages; 2 stage housing; 3 vertically split barrel housing; 4 seal for vertically split barrel housing

Fig. 28: Typical notch points in thick-walled high-pressure components
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1 piston; 2 piston sealing elements; 3 valve head; 4 Y-intersection;
5 lubrication; 6 cooling

Fig. 30: Labyrinth seals
a) radial impeller
b) labyrinth piston
Fig. 31: Floating-ring shaft seal for high pressure (MANNSMANN-DEMA)
1 rotor shaft; 2 floating rings; 3, 4 oil pressure system

Fig. 32: Various designs of piston- and rod-seals for piston compressors
(NEUMAN & ESSER)
Fig. 33: Plunger piston seal of an ethylene ultra-high-pressure compressor 2000 - 3000 bar (NUOVO PIGNONE)
1 plunger piston; 2 sealing housing; 3 sealing rings; 4 compressor cylinder; 5 oil supply

Fig. 34: Piston seal with packing rings, lubrication and injection flushing (URACA)
1 injection; 2 piston; 3 injection bushing; 4 high-pressure seal; 5 flushing, lubricating; 6 guide bushings, 7 low pressure seal
HIGH PRESSURE REACTIONS BY HOMOGENEOUS CATALYSIS

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1. INTRODUCTION

Reactions under pressure have wide ranging applications in the production of chemical feedstocks as well as speciality products. Almost in every field of chemical processing, high pressure reactions are encountered. Some important examples are: Hydrogenation of organic compounds, hydrodesulfurization of residuum oils, Fischer-Tropsch synthesis, polymerization of ethylene, carbonylation of methanol to acetic acid, Oxo synthesis (hydroformylation) and ammonia synthesis. In the development of commercial processes, it is a common objective to obtain highest possible rate of reaction in a given capacity reactor. The pressure reactions have played an important role in this aspect, especially in the development of multiphase catalytic processes involving gas and / or liquid phase reactants. The special features of reactions under pressure are:

- The liquid phase reactions which require temperatures higher than the boiling point of the reactant/solvent, can be conveniently carried out under pressure.

- For gas-liquid reactions, the solubility of gaseous reactants increases with increase in pressure, thus leading to higher reaction rates. Similarly, in gas-solid catalytic reactions, the adsorbed concentration in most cases increases with increase in pressure, leading to higher rates.

- The high pressure conditions also favour equilibrium reactions, not feasible at atmospheric pressure. This feature is commonly observed in C1 Chemistry (carbonylation reactions), wherein the active catalytic complexes consisting of metal carbonyls are stable only under high pressure conditions. An important example of this class is the Co catalyzed hydroformylation of olefins (see Figure 1). For this reaction the active catalyst, HCo(CO)4 is stable only at very high pressures (Cornils, 1980).
In addition, the changes in the physicochemical properties of the system under pressure can also lead to favourable conditions for obtaining higher rates and selectivity.

In the development of high pressure technologies for production of chemicals, catalysis has played an important role. A major portion of the basic chemical feedstocks are produced using homogeneous or heterogeneous catalytic reactions. This can be realized from the examples shown in Table 1, which are the products with more than one billion pounds production in US. Although, bulk of the chemical processes are based on heterogeneous catalysis, homogeneous catalysis has also been important in some areas.

The aim of this lecture is to present the current status and future challenges in homogeneous catalytic reactions carried out at high pressures. The most important homogeneous catalysts are consisting of metal complexes that are soluble in the reaction medium and are generally employed for the reactions of gas and liquid phase reactants. While, these catalysts are useful in principle, in a large variety of reactions, they have been found to be particularly attractive in oxidation, carbonylation, hydroformylation, oligomerisation, hydrocyanation and polymerization reactions (see Table 2). Homogeneous catalysts have the following advantages over the heterogeneous catalysts:

- Feasibility at milder operating conditions compared to heterogeneous catalysts.

- Higher selectivity is an important feature of homogeneous catalysts. These catalysts are discrete molecules with one or more metals and their surrounding ligands. Hence, the nature of active species is better understood and very often, the activity and selectivity can be tailored with proper selection of a ligand. An important example of this case is the recent development in sterspecific synthesis of optically active isomers by homogeneous catalysis (e.g. manufacture of L-dopa by hydrogenation, Parshall and Nugent, 1988).

- Heat and mass transfer resistances can be easily eliminated leading to better control of temperature at catalytic sites unlike heterogeneous catalysis in which hot spot formation is often observed.

- The ability to activate substrates such as hydrogen, carbon monoxide, oxygen and olefins at milder operating conditions is another important feature of these catalysts.
In spite of these advantages, the application of these catalysts was limited in industry due to the following disadvantages:

- Separation of the products and catalyst is difficult
- Expensive catalyst recycle and recovery processes.
- Handling and storage of catalysts and deactivation due to trace impurities
- Corrosion and product contamination.
- Expensive high pressure equipment.

Nevertheless, in recent years, several new developments have taken place in the direction of overcoming these drawbacks. The activities in homogeneous catalysis got priorities due to the oil crisis in early 70’s, when the alternatives to the petroleum feedstock needed to be developed. Particularly, homogeneous catalysis played an important role in the development of C₁ Chemistry and technologies via CO and syngas (CO + H₂) as feedstocks. In these processes, new product/catalyst separation technologies have also been evolved. The most significant achievement in this direction has been the use of water soluble homogeneous catalysts in biphasic systems. This approach has been successfully used in a new hydroformylation process commercialized by Ruhrchemie jointly with Rhone-Poulenc (Kuntz 1987). Similarly, the expertise in high pressure engineering has been developed considerably. Several new applications of homogeneous catalysts are also emerging in the manufacture of specialty chemicals (Parshall and Nugent, 1988).

2. COMMERCIAL PROCESSES

Some examples of homogeneous catalytic reactions operating on a commercial scale under high pressure conditions are summarized in Table 3. The important features of these include high pressure operations, homogenous catalysis and utilization of cheaper and easily available feedstocks. A few important cases are described here.

2.1 Carbonylation of Methanol to Acetic Acid

Acetic acid is a major industrial chemical used in the manufacture of vinyl acetate, cellulose acetate, pharmaceutical, dyes and pesticides. While it is manufactured by different processes, the most important process followed in recent days involves homogeneous catalytic carbonylation of methanol:
\[
\text{CH}_3\text{OH} + \text{CO} \xrightarrow{\text{catalyst}} \text{CH}_3\text{COOH} 
\]

(i)

The first commercial process developed by BASF, Germany is based on a Cobalt carbonyl catalyst with an iodine compound as a promoter. Cobalt acetate or iodide is commonly used as a precursor for in situ generation of \( \text{Co}_2(\text{CO})_8 \) and HI. This process is carried out industrially at 210°C and 700 atm pressure. The major drawback has been the very high pressures and lower selectivity. The major improvement in this process was with introduction of the Monsanto process based on a low pressure Rhodium complex catalyst along with alkyl iodide promoter. In this process, homogeneous Rh complex catalyst is used which is generated in situ and is believed to be \([\text{Rh}(\text{CO})_2\text{I}_2]^-\). The process is operated commercially at about 180°C and 30-40 atm pressure with a selectivity for acetic acid or its methyl ester greater than 99%. Though, the pressure required in the Monsanto process is considerably lower than the BASF process, a critical factor in this technology is a specialized material of construction. Most of the new plants for acetic acid via methanol have been built using this process and the minimum capacity of such plants is 80,000-100,000 tpa.

The recent developments in this field are based on new catalyst systems consisting of non-noble metals, cheaper than rhodium, which retain the features of high activity and selectivity. The results on Ni complex catalyst modified with suitable ligands are very promising in this respect.

2.2 Oxo Process: Hydroformylation of Olefins to Aldehydes/Alcohols

Oxo synthesis or Hydroformylation is the well-known process used commercially for the manufacture of aldehydes and alcohols. It involves a reaction of olefin, CO and \( \text{H}_2 \) in the presence of a homogeneous catalyst. The reaction is described as:

\[
\text{R-CH}=\text{CH}_2 + \text{H}_2 + \text{CO} \xrightarrow{\text{catalyst}} \text{R-CH}_2\text{CH}_2\text{CHO} 
\]

(ii)

\[+ \text{R-CH-CH}_3 \]

\[\text{CHO} \]

This reaction was discovered by Roelen of Ruhrchemie in 1938 and is an example of one of the large scale application of homogeneous catalysis in industry, also involving high pressure technology. The world capacity of hydroformylation products is around 6-7 million tpa in which a further increase is anticipated. The basic
products cover aldehydes and alcohols containing 3-20 carbon atoms. The major uses of oxo products are as solvents and as intermediates for the production of plastisizers, lubricants, detergents and other surfactants. The production of plastisizer alcohols is the major application of oxo technology, and, of these, 2-ethyl hexanol via hydroformylation of propylene, is the most important one. The principle applications of the oxo products are summarized in Table 4. Total installed capacity throughout the world to produce butyraldehyde alone exceeds 3 million tpa. The first commercial oxo process based on Roelen's original work uses a homogeneous cobalt complex catalyst and operates at 250-350 atm pressure and 140-180°C. For the manufacture of higher alcohols, only this process or a modified cobalt catalyzed process developed by Shell is used. Higher pressure of CO is required because of the instability of the catalyst at lower pressures. This process has several drawbacks besides the severity of operating conditions. The hydrogenation of propylene to propane, condensation of aldehydes to form acetal derivatives are major side reactions. An important requirement of the oxo process performance is the higher n/iso aldehyde ratio. For this process, the n/iso ratio is typically in the range of 3.5:1. In a modified cobalt catalyzed process developed by Shell the catalyst consists of cobalt-hydridocarbonyl trialkylphosphine complex (HCo(CO)₃PR₃). This requires lower operating pressure in a range of 40-50 atm and temperature of 180-200°C. This process gives improved n/iso ratio and has been used to manufacture directly the oxo alcohols. In both these cobalt catalyzed processes, the separation of products from the catalyst and recovery of cobalt in a form suitable for reuse is a complicated and relatively expensive operation.

The development of a low pressure oxo process based on rhodium complex catalyst has been a major breakthrough in the oxo technology. Around 1976, the first plant was started using the process developed jointly by Union Carbide, Davy Mckee and Johnson Matthey. This process uses a homogeneous rhodium complex catalyst (HRh(CO)(PPh₃)₂), and requires 20 atm pressure and 100°C temperature. The n/iso ratio obtained is as high as 10:1, and also the side reactions leading to hydrogenation and condensation products are negligible. A comparison of the different oxo processes is shown in Table 5. This process is mainly used for the conversion of propylene to n-butyraldehyde and about 13 commercial plants are operating or under construction throughout the world based on this process. The total capacity of butyraldehyde licensed to date using this process is in excess of 1.1 million tpa.

While low pressure oxo process development has been a major achievement, it's application has been limited to butyraldehyde manufacture due to the simplicity in product separation and catalyst reuse. For the conversion of higher olefins, the low pressure oxo catalyst is also highly selective but the product separation is extremely
difficult due to nonvolatile products. In order to eliminate this difficulty, Ruhrchemie and Rhone-Poulenc have jointly, developed a water soluble rhodium complex catalyst, such that the product aldehydes can be separated easily by phase separation. The process based on this catalyst is already commercialized by Ruhrchemie for the production of n- butyraldehyde (Kuntz, 1987).

In the case of oxo process, development of novel catalyst has played a major role in the improvement of technologies. Considering the growing demand of oxo products and rather large capacities, the improvement is bound to continue and therefore continuing efforts on R and D on this subject are most essential.

2.3 Acetic Anhydride via Carbonylation of Methyl Acetate

Acetic anhydride is an important intermediate chemical with applications in cellulose acetate fibres and plastics. A new process for acetic anhydride is the most successful example of conversion of coal to chemicals. The key step in this process involves a reaction of CO with methyl acetate in the presence of a rhodium complex catalyst alongwith iodine containing promoter.

\[
\text{CH}_3\text{COOCH}_3 + \text{CO} \xrightarrow{\text{catalyst}} (\text{CH}_3\text{CO})_2\text{O}
\]

The catalytic species has been found to be \([\text{Rh(CO)}_2\text{I}_2]^–\) similar to that in the carbonylation of methanol to acetic acid. The typical reaction conditions are 190°C and 50 to 70 atm pressure. Tennessee Eastman company has setup a plant to produce acetic anhydride of 500 million lb/year capacity based on the technology jointly developed by Eastman and Halcon SD group. This plant has demonstrated a technology with lower production cost based on coal, an abundantly available feedstock. The key features of this technology are a novel homogeneous catalyst and high pressure equipment with specialized material of construction.

2.4 Propionic Acid via Carbonylation of Ethylene

Propionic acid is an important intermediate in the manufacture of esters, cellulose derivatives and agrochemicals. The reaction of ethylene and CO with water to form propionic acid is an example of an industrially operated hydroxycarbonylation process (Reppe process):

\[
\text{C}_2\text{H}_4 + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{CH}_3\text{CH}_2\text{COOH}
\]
This reaction takes place in the presence of a homogeneous catalyst consisting of Ni(CO)$_4$, at 200-240 atm. pressure and 270-320°C. The catalyst, Ni(CO)$_4$ is formed in situ from Ni propionate by reaction with CO. After the reaction, Ni(CO)$_4$ present in the product is reconverted to propionate via air oxidation in the presence of propionic acid and recycled to the reactor. BASF has operated this process on industrial scale since 1952 with a capacity of 30,000 tpa.

### 2.5 Acrylic Acid via Carbonylation of Acetylene

Carbonylation of acetylene to acrylic acid represents one of the older Reppe process using homogeneous catalysis.

\[
\text{C}_2\text{H}_2 + \text{CO} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{CH}_2=\text{CHCOOH} \quad (v)
\]

This process is carried out using homogeneous NiBr$_2$ catalyst in the presence of Cu halide as a promoter and tetrahydrofuran as a solvent. The typical reaction conditions are 160-200°C and 40-55 atm pressure. Even today BASF is using this process for the manufacture of acrylic acid. However, in most of the new plants an alternative process via oxidation of propylene is followed.

### 2.6 Oligomerization of Olefins to alpha Olefins

Oligomerization of ethylene is a large scale process used to manufacture alpha olefins by Shell Oil Co. A Ni complex catalyst is used in this process and the active Nickel hydride catalyst is generated by reduction of Ni salts in the presence of a chelating ligand such as diphenylphosphinoacetic acid. In practice, a catalyst thus prepared is allowed to react with ethylene in a solvent like ethylene glycol at 100°C and 40 atm pressure. A rapid reaction occurs to form a mixture of linear alpha olefins. The chain lengths are typically distributed as follows:

\[
\begin{align*}
\text{C}_4 - \text{C}_8 & = 41 \% \\
\text{C}_{10} - \text{C}_{18} & = 40.5 \% \\
\text{C}_{20} + & = 18.5 \%
\end{align*}
\]

The C$_{10}$ to C$_{18}$ olefins, for which ready market exists, are separated by distillation. The higher and lower boiling products are used in a complex sequence of reactions to give a mixture of C$_5$ to C$_{41}$ oxo alcohols (see Figure 2). Since 1977, the Shell
process has been operating industrially in a 200,000 tpa plant in USA. This process is a part of the Shell complex for complete utilization of ethylene (See Figure 2). It is important to note that the major part of this complex involves homogeneous catalytic processes such as oligomerization and hydroformylation under high pressure conditions.

2.7 Epoxidation of Propylene to Propylene Oxide

A new application of homogeneous catalysis was announced by Halcon Corporation to synthesize propylene oxide by catalytic transfer of oxygen from an alkyl hydroperoxide to propylene.

\[ \text{CH}_3\text{-CH}=\text{CH}_2 \quad + \text{ROOH} \xrightarrow{\text{catalyst}} \quad \text{CH}_3\text{-CH}_2\text{-CH}_2 \quad + \text{ROH} \ (\text{vi}) \]

Epoxide

This process has a potential to displace the conventional chlorohydrin route for propylene oxide (PO). PO, is an important raw material for propylene glycol, glycerin and polyethers. Oxirane Corporation is using this process in which propylene is reacted with ethyl benzene hydroperoxide or t-butyl hydroperoxide. By-products such as 1-methyl-benzyl alcohol and t-butanol have important applications. In the commercial process, excess liquid propylene is used with Mo(CO)₆ catalyst at 90-130°C and a 15-65 atm. pressure. About 86% yield of PO is reported.

2.8 Oxidation of Hydrocarbons

The largest scale application of homogeneous catalysis is the oxidation of hydrocarbons by molecular oxygen. Some of the important processes and their applications are shown in Table 6. Of these, the processes such as oxidation of xylene, cyclohexane and n-butane are carried out on remarkably large scale. While most of these are carried out at moderate pressures (10-30 atm), the processes for oxidation of butane to acetic acid is carried out under relatively higher pressure conditions (60-80 atm). A brief description of these processes are given below:

2.8.1 Oxidation of p-xylene to terephthalic acid (TPA)

TPA is mainly used in polyethylene terephthalate manufacture and hence has always gained importance. The fibre grade TPA is manufactured by oxidation of
p-xylene using a homogeneous catalyst. The Amoco process using a catalyst combination of Co and Mn acetates in 95 % acetic acid is most widely used for TPA. A mixture of NH₄Br and tetrabromoethane serves as a co-catalyst, however, a co-catalyst in the form of CoBr₂ or MnBr₂ is also practiced. p-Xylene is oxidized at 190-205°C and 15-30 atm pressure using air as the oxidant. Both batch and continuous processes have been standardized. The plants of the order of 10-50,000 tpa are operating today. This process exclusively uses homogeneous catalyst and involves a complex product purification process besides catalysis.

2.8.2 Adipic acid via oxidation of cyclohexane

Adipic acid is another bulk chemical required in the manufacture of Nylon. The commercial process involves direct air oxidation of cyclohexane using a soluble Co or Mn naphthenate catalyst at 140-165°C and 10 atm pressure. Usually a two stage process is used wherein the first stage involves oxidation of cyclohexane to cyclohexanone and cyclohexanol and in the second stage this mixture is oxidized to adipic acid. In the second step, Cu, and Mn acetate catalyst is used at 80-85°C and 6 atm pressure.

The processes involving oxidation of acetaldehyde to acetic acid, o-xylene to phthalic acid and toluene to benzoic acid are on similar lines.

2.8.3 Acetic acid via butane oxidation

Oxidation of butane to acetic acid is carried out using homogeneous cobalt complex catalyst at 160-200°C and 60-80 atm pressure. This process is important from the point of view of a relatively cheap and abundant feedstock such as n-butane. The products include acetic acid, propionic acid and 2-butanone, all of which have commercial values.

The above processes for oxidation are generally designed for much higher pressures than the operating pressures due to the explosion hazards associated with these systems.

3. DEVELOPMENT OF NEW PROCESSES

The recent developments in homogeneous catalytic processes has gained momentum mainly after the oil crisis in 70’s, when a search for alternative feedstocks for basic chemicals became important. At this time, research in C₁ Chemistry got priority with the objective of conversion of coal to chemicals. Extensive R & D efforts on
the conversion of synthesis gas and carbon monoxide to chemicals were undertaken in several laboratories. Homogeneous catalysis as well as high pressure engineering played a vital role in the development of new concepts/routes for important chemicals. The new processes therefore have been largely based on CO and syn gas as feedstocks and these are summarized in Table 7.

3.1 Syngas to Chemicals

Among the processes for the conversion of syn gas to chemicals, the following cases can be considered as most important for commercial applications in which homogeneous catalysis is used.

- Conversion of syn gas to acetic acid
- Conversion of syn gas to ethylene glycol
- Homologation of alcohols

The various chemicals that can be produced involving syn gas as the raw material are shown in Figure 3. Many of these processes are based on homogeneous catalysis under high pressure.

3.1.1 Syn gas to acetic acid

Texaco Chemical Co has developed a catalyst for direct conversion of syn gas to acetic acid which consists of a homogeneous ruthenium-cobalt complex in the presence of Bu₄PBr as a promoter. The reaction is carried out at 220°C and 482 atm pressure with syn gas as a feedstock and selectivities greater than 70 % have been reported. In addition to acetic acid, propionic acid and esters of acetic acid, methane and CO₂ are also produced. In this process, the major difficulties are the requirement of very high pressure, lower selectivity and complex separation of products.

3.1.2 Syn gas to ethylene glycol

Ethylene glycol is an important raw material in chemical industry and various alternative routes for its manufacture have been investigated (Table 7). It is believed that the direct conversion of syn gas to ethylene glycol can be the most economical route. The process for direct conversion of syn gas to ethylene glycol has been investigated by Union Carbide upto a semicommercial scale. The key feature of this
process is the high pressure rhodium catalyzed reduction of carbon monoxide. The reaction is:

\[ 2\text{CO} + 3\text{H}_2 \xrightarrow{\text{catalyst}} \text{HO-CH}_2\text{-CH}_2\text{OH} \quad (vii) \]

In this process a homogeneous catalyst consisting of mononuclear complexes such as \( \text{Rh(CO)}_2(\text{acac}) \) or the Rh carbonyl clusters like \( \text{Rh}_4(\text{CO})_{12} \) or \( \text{Rh}_6(\text{CO})_{16} \), are used at 210- 250°C and 500-600 atm pressure. In another process of DuPont, CO hydrogenation in the presence of a homogeneous cobalt complex catalyst has been reported at about 3000 atm pressure. In the rhodium catalyzed process 70 % yield of ethylene glycol has been reported. This process has major economical potential if the following problems can be solved.

- High pressure conditions (greater than 500 atm are required to prevent decomposition of the catalyst)
- The side products such as propylene glycol and glycerol pose difficulties in product separation
- With the present state of the art development of catalyst and process, even at higher pressures sufficient activity and selectivity is not achieved for commercial viability.

Nevertheless, with improvement in the activity and selectivity of the catalyst for this process, the direct conversion of syn gas to ethylene glycol has a great potential in future.

3.1.3 Homologation of alcohols

Homologation of methanol to ethanol is carried out in the presence of homogeneous catalysts such as \( \text{Co}_2(\text{CO})_8 \), at 180°C and 300 atm pressure. The reactions involved are:

\[ \text{CO} + 2\text{H}_2 + \text{CH}_3\text{OH} \xrightarrow{\text{catalyst}} \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \quad (viii) \]

Other catalysts consisting of rhodium and ruthenium complexes are also reported. This process can also be used for the production of a mixture of higher
alcohols which may be further useful for production of synthetic fuels. The major side products are ethers, esters, acetals, acids and alkanes. However, no industrial application of this process is reported yet due to the lower activity and selectivity of the catalyst obtained even at high pressure conditions.

3.1.4 Vinyl acetate from syn gas and methanol

A new route for the manufacture of vinyl acetate from syn gas and methanol has been reported by Halcon. In this process, the reaction of CO and hydrogen with methyl acetate in the presence of a rhodium complex catalyst along with 3-picoline and iodine containing promoters gives ethylidene diacetate (EDA) as a product. EDA is then converted to vinyl acetate with the loss of acetic acid. The reactions involved are:

\[ 2\text{CH}_3\text{COOCH}_3 + 2\text{CO} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{CH}_3\text{CH(OOCCH}_3)\text{OCH}_3 + \text{CH}_3\text{COOH} \quad (ix) \]

\[ \text{CH}_3\text{CH(OOCCH}_3)\text{OCH}_3 \xrightarrow{\text{catalyst}} \text{CH}_2=\text{CH-OOCCH}_3 + \text{CH}_3\text{COOH} \quad (x) \]

The first step, is carried out at 150°C and 140 atm pressure. The total scheme of vinyl acetate manufacture from methanol is shown in Figure 4.

3.2 Carbonylation of Butadiene to Adipic acid

Adipic acid being an important chemical intermediate in the manufacture of Nylon, there is a need for developing new processes from different feedstocks. A recent analysis by Arco Chemical Co. (See Table 8) indicates that carbonylation of butadiene could be a very attractive route for adipic acid compared to the conventional cyclohexane oxidation from economic considerations.

In this direction, the first process was developed by BASF in which hydrocarbonylation of butadiene was carried out in the presence of methanol at 300 - 600 atm pressure and 140–200°C using a cobalt complex catalyst. The major product formed was dimethyl adipate and the overall reaction is:

\[ \text{C}_4\text{H}_6 + 2\text{CO} + 2\text{CH}_3\text{OH} \xrightarrow{\text{catalyst}} \text{CH}_3\text{COO(CH}_2)\text{OCH}_3 \quad (xi) \]

\[ \text{DMA} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{HOOC(CH}_2)\text{OCH}_3 + 2\text{CH}_3\text{OH} \quad (xii) \]

BASF has proposed a (Kesling 1987) 70,000 tpa commercial plant based on this technology.
Arco Chemical Co. has developed a process involving oxidative carbonylation of butadiene which operates at 100°C and 120 atm pressure. In this process a redox catalyst system consisting of Pd(II) and Cu(II) complexes has been proposed.

### 3.3 Carbonylation of Nitro Compounds to Isocyanates

Isocyanates are important raw materials in the manufacture of polyurethane foams and elastomers. The commercially important products are toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). These are commercially produced via phosgenation route which have several drawbacks due to the toxic and hazardous nature of phosgene and corrosion due to by-product HCl. A new alternative route for isocyanates is based on homogeneous catalytic carbonylation of nitro compounds. The overall reaction is:

\[
\text{RNO}_2 + 3\text{CO} \xrightarrow{\text{catalyst}} \text{RNCO} + 2\text{CO}_2
\]  

The corresponding processes for the manufacture of TDI and MDI are described below.

#### 3.3.1 Toluene diisocyanate (TDI)

TDI can be produced by carbonylation of 2,4 dinitrotoluene (DNT) in the presence of homogeneous palladium, rhodium or ruthenium complex catalysts in the presence of metal halide promoters. The reaction conditions are 100-180°C and 100-200 atm pressure. A complete conversion of DNT with 70-80 % selectivity for TDI has been reported. This route has several advantages over the phosgenation route:

- Is a single step process.
- Involves less hazardous chemicals.
- Corrosion problems due to phosgene and HCl are eliminated.

Mitsui Toatsu Chemicals Inc., (Tokyo) and Arco Chemical Co., (USA) have plans for commercialization of this route for the manufacture of TDI (Mullen, 1980).
3.3.2 Methylene diphenyl diisocyanate (MDI)

The new non-phosgene route for MDI synthesis is described in Figure 5. The key step in this process is carboxylation of nitrobenzene to ethyl phenyl carbonate (EPC). This reaction is carried out using a homogeneous catalyst consisting of Pd(py)$_2$Cl$_2$ with FeCl$_3$ as a promoter at 130-150°C and 60-100 atm pressure. It is possible to achieve EPC yield over 95%. The selectivities of the order of 90-95% are also achievable in the other two steps. The important features of this route include a less hazardous and non-corrosive process and high selectivity for monomeric MDI. Asahi Chemicals, Japan has carried out pilot plant trials and has plans to commercialize this technology.

3.4 Methyl Methacrylate (MMA)

Methyl Methacrylate polymers have wide ranging applications in advertising displays, lighting fixtures, molding and extrusion resins and water based latex paints. Due to hazardous nature of HCN which is used in the conventional process, various alternative routes are proposed for MMA production based on different feedstocks as shown in Figure 6. In each of these schemes, homogeneous catalytic carboxylation is involved under high pressure conditions.

3.5 Hydroformylation of novel organic substrates

Hydroformylation of olefinic substrates can be extended to develop new routes for some of the industrially important products. With the development of water soluble homogeneous catalysts, this technology can be applied for the production of even the non-volatile products. Some of the new processes via hydroformylation are:

- Butanediol via hydroformylation of allyl alcohol.
- Hydroformylation of 2-butene 1,4 diol as an important step in the new Vitamin A process (see Figure 7) (Parshall, 1988)
- Hydroformylation of acrylonitrile: an important step in a process for sodium glutamate.
- Hydroformylation of higher olefins to aldehydes/alkohols.
3.6 L-Dopa by homogeneous hydrogenation

L-dopa is an important drug used in the treatment of Parkinson’s disease. Monsanto has developed stereoselective synthesis of L-dopa via asymmetric hydrogenation. The key step in the l-dopa synthesis is the hydrogenation of a prochiral olefin to a specific optical isomer of phenylalanine derivative, as shown in Figure 8.

The stereoselective hydrogenation is conducted in the presence of a homogeneous rhodium complex catalyst with a chelating biphosphine ligand (DIPAMP). The hydrogenation is carried out at 50°C and 3 atm pressure to obtain the required l-isomer with 95% enantiomeric selectivity. The process has already been commercialized by Monsanto.

4. NCL ACTIVITIES IN HOMOGENEOUS CATALYSIS

National Chemical Laboratory (NCL), Pune, is actively involved in research in the area of homogeneous catalysis, with the aim of developing new catalysts/processes for industrially important chemicals. The following processes have been developed.

4.1 Acetic Acid by carbonylation of methanol

NCL has developed a cheaper, non-noble metal catalyst (ENCICARB 1) for carbonylation of methanol to acetic acid. The catalyst is highly active and selective and operates under reaction conditions comparable to the Monsanto process. Novel features of NCL process are:

- Uses low pressure, non-noble metal catalyst with high activity and selectivity.
- The selectivity and operating conditions are comparable to the Monsanto process.
- Catalyst is more economical than the conventional catalysts for identical performance.
- The process yields 90-95% product in crude stage, thus consuming less energy in purification steps.
- Recovery of spent catalyst is simple and may not require sophisticated process control equipment.
• Smaller capacity plants are feasible and a more economical process is envisaged.

Based on this process, a semicommercial plant of 2 tpd capacity has been designed by NCL and Davy Power Gas jointly for GAAC Ltd, Ahmedabad. This plant is expected to be commissioned by end of 1992. NCL process has also been granted a U.S. Patent (US Patent No. 4902659) in February 1990. At present two US companies are negotiating with NCL for using the NCL catalyst in commercial plants to be set up in USA and Venezuela.

4.2 Propionic acid from ethanol

This technology is based on the novel catalyst (ENCICARB 2) developed by NCL for carbonylation of ethanol. Further work on commercialisation is undertaken by GAAC, Ahmedabad, where a 2000 tpa plant is proposed. The novel features of the technology are:

• Uses low pressure, non-noble metal catalyst with high activity and selectivity.

• Ethanol is used as a feed stock, petroleum based ethylene is not required.

• The process yields 90-95 % propionic acid in crude stage, thus consuming less energy in the purification steps.

• Recovery of spent catalyst is simple and does not require sophisticated process control equipment.

• Operating conditions are milder compared to BASF process and also selectivity to propionic acid is high.

• This will be the first plant using ethanol as a feed stock, and it can be advantageous in Indian context, where ethanol is available at cheaper prices.

4.3 Toluene diisocyanate (TDI) via carbonylation

A process involving catalytic carbonylation of 2,4 dinitrotoluene (DNT) to TDI has been developed. The NCL catalyst consists of a homogeneous Pd-Fe bimetallic complex and typical reaction conditions are 150-180°C and 150 atm pressure. A conversion of DNT> 99 % with a TDI selectivity of 75-80 % has been achieved.
4.4 Hydrogenation of organic compounds

NCL has developed several liquid phase hydrogenation processes which involve use of pressure reactors. Some examples are:

- Glucose to sorbitol
- Butynediol to butenediyl and butanediyl
- Chloronitrobenzene to chloroaniline
- Nitrobenzene to aniline
- o-Nitroanisole to o-anisidine

Thus, NCL has acquired expertise in high pressure reactions using both homogeneous and heterogeneous catalysis.

5. FUTURE SCOPE

The recent developments in C₁ Chemistry indicate that homogeneous catalytic reactions under pressure, have a wide scope in developing new processes based on cheaper feedstocks as well as bringing improvements in the existing ones. Particularly, the applications in the following areas appear to be very promising.

- Direct conversion of syn gas to acetic acid and ethylene glycol.
- Development of new processes/routes for fine chemicals/agrochemicals and pharmaceuticals.
- Synthesis of stereo-selective intermediates for pharmaceuticals.
- Use of CO₂ gas as a chemical feedstock
- Development of non-phosgene, non-HCN routes for major chemicals like pharmaceuticals, isocyanates, carbamates and acrylic derivatives
- Development of catalyst systems without using corrosive iodine containing promoters.

As we observed, in addition to homogeneous catalysis, expertise in high pressure equipment design will be equally important for the success in this areas.
6. REFERENCES


Table 1
Production of Major Organic Chemicals in the United States
(Lyons, 1984)

<table>
<thead>
<tr>
<th>Elemental Composition</th>
<th>Chemical Product</th>
<th>U.S. Production (billions of lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, H, O</td>
<td>Acetic Acid</td>
<td>2.82</td>
</tr>
<tr>
<td></td>
<td>Acetic Anhydride</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td>Alkyl Acrylates</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>Adipic Acid</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>Ethylene Glycol</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>Ethylene Oxide</td>
<td>4.95</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
<td>5.77</td>
</tr>
<tr>
<td></td>
<td>Isopropyl Alcohol</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>7.00</td>
</tr>
<tr>
<td></td>
<td>Methyl tert-butyl ether</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>Phenol</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td>Pthalic anhydride</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Propylene oxide</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>Terphthalic acid</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>Vinyl acetate</td>
<td>1.92</td>
</tr>
<tr>
<td>C, H, N</td>
<td>Acrylonitrile</td>
<td>1.83</td>
</tr>
<tr>
<td>C, H, Cl</td>
<td>Ethylene dichloride</td>
<td>9.97</td>
</tr>
<tr>
<td></td>
<td>Vinyl chloride</td>
<td>6.46</td>
</tr>
</tbody>
</table>

- Produced by Homogeneous Catalysis
Table 2
Applications of Homogenous Catalysis in Industry
(Parshall, 1980)

<table>
<thead>
<tr>
<th>Reactions and Products</th>
<th>Approximate 1977 Production* (thousands of metric tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbonylations</strong></td>
<td></td>
</tr>
<tr>
<td>Oxo alcohols (hydroformylation)</td>
<td>780</td>
</tr>
<tr>
<td>Acetic acid (from methanol)</td>
<td>180</td>
</tr>
<tr>
<td><strong>Olefin polymerisation</strong></td>
<td></td>
</tr>
<tr>
<td>Polybutadine (coordination catalysis)</td>
<td>345</td>
</tr>
<tr>
<td>Ethylene polymers (solution processes)</td>
<td>500</td>
</tr>
<tr>
<td><strong>Olefin additions</strong></td>
<td></td>
</tr>
<tr>
<td>$\alpha$ - Olefins</td>
<td>177</td>
</tr>
<tr>
<td>Adiponitrile</td>
<td>200</td>
</tr>
<tr>
<td>Diene dimers and trimers</td>
<td>40</td>
</tr>
<tr>
<td>Chloroprene</td>
<td>166</td>
</tr>
<tr>
<td><strong>Olefin oxidation</strong></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>410</td>
</tr>
<tr>
<td>Propylene oxide (Oxirane process)</td>
<td>418</td>
</tr>
<tr>
<td><strong>Alkane and arene oxidation</strong></td>
<td></td>
</tr>
<tr>
<td>Terphenyl acid and esters</td>
<td>2277</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>698</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>986</td>
</tr>
<tr>
<td>Benzoic, isophthalic acids</td>
<td>86</td>
</tr>
<tr>
<td><strong>Condensation polymerisation</strong></td>
<td></td>
</tr>
<tr>
<td>Polyester fiber</td>
<td>1660</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>8923</td>
</tr>
</tbody>
</table>

* In U. S.
### Table 3
Commercial processes by Homogenous Catalysis under pressure

<table>
<thead>
<tr>
<th>Process</th>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature °C</td>
<td>Pressure atm.</td>
</tr>
<tr>
<td>Oxidation of</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Co or Mn napthenate</td>
<td>140 -165</td>
<td>10</td>
</tr>
<tr>
<td>Butane</td>
<td>Co complex</td>
<td>160-200</td>
<td>60-80</td>
</tr>
<tr>
<td>Propylene</td>
<td>Mo(CO)₆</td>
<td>90 -130</td>
<td>15-65</td>
</tr>
<tr>
<td>Carbonylation of</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>Rh-I complex</td>
<td>150-200</td>
<td>30-40</td>
</tr>
<tr>
<td></td>
<td>Co - I complex</td>
<td>200-220</td>
<td></td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>Rh-I Complex</td>
<td>170-200</td>
<td>50-70</td>
</tr>
<tr>
<td>Ethylene</td>
<td>Ni(CO)₄</td>
<td>270-320</td>
<td>200-240</td>
</tr>
<tr>
<td>Acetene</td>
<td>NiBr₂</td>
<td>160-200</td>
<td>40-50</td>
</tr>
<tr>
<td>Hydroformylation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>HCo(CO)₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oligomerization of</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>Ni Complex</td>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>Polymerization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td>Al(Bu)₃, TiCl₄</td>
<td>250</td>
<td>60-80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 4
**Principle applications of oxo products**

<table>
<thead>
<tr>
<th>Starting olefin</th>
<th>Product</th>
<th>End use / Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene (C₂)</td>
<td>n-propyl alcohol</td>
<td>solvent, printing inks, grain preservative, agriculture chemicals.</td>
</tr>
<tr>
<td></td>
<td>propionic acid</td>
<td></td>
</tr>
<tr>
<td>Propylene (C₃)</td>
<td>Butyl alcohols</td>
<td>solvent, paints adhesives, plastisizers, agriculture chemicals.</td>
</tr>
<tr>
<td></td>
<td>butyraldehydes</td>
<td></td>
</tr>
<tr>
<td>Butene (C₄)</td>
<td>C₅ alcohols</td>
<td>Lubricants, cetane improvers, oil additives, metal extractive agents.</td>
</tr>
<tr>
<td></td>
<td>C₁₀ alcohols</td>
<td>Plastisizers</td>
</tr>
<tr>
<td>Pentene (C₅)</td>
<td>C₆ alcohols</td>
<td>oil additives plastisizers</td>
</tr>
<tr>
<td>Hexene (C₆)</td>
<td>C₇ aldehyde</td>
<td>fragrances</td>
</tr>
<tr>
<td>C₇₋₁₁</td>
<td>C₈₋₁₂ alcohols</td>
<td>Plastisizers</td>
</tr>
<tr>
<td>C₁₁₋₁₉</td>
<td>C₁₂₋₂₀ alcohols</td>
<td>Detergents</td>
</tr>
<tr>
<td>Process</td>
<td>BASF</td>
<td>Shell Oil Co.</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>----------</td>
<td>---------------</td>
</tr>
<tr>
<td>Catalyst</td>
<td>HCo(CO)$_4$</td>
<td>HCo(CO)$_3$-PR$_3$</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>110-180</td>
<td>160-200</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>200-300</td>
<td>50-100</td>
</tr>
<tr>
<td>Selectivity w.r.t.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aldehydes</td>
<td>medium</td>
<td>low</td>
</tr>
<tr>
<td>alcohol</td>
<td>medium</td>
<td>high</td>
</tr>
<tr>
<td>n-isomers</td>
<td>medium</td>
<td>higher</td>
</tr>
<tr>
<td>iso-products</td>
<td>medium</td>
<td>lower</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>Sensitivity towards catalyst poisons</td>
<td>low</td>
<td>low</td>
</tr>
</tbody>
</table>
### Table 6
Industrial Oxidation of Hydrocarbons (Parshall, 1980)

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Oxidation Product</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>Cyclohexanol and</td>
<td>Converted to adipic acid and caprolactum (polyamide precursors)</td>
</tr>
<tr>
<td></td>
<td>cyclohexanone</td>
<td></td>
</tr>
<tr>
<td>Cyclododecene</td>
<td>$C_{12}H_{25}OH$ and $C_{12}H_{22}O$</td>
<td>Oxidised to dodecanoic acid lauryl lactum (polyamide precursors)</td>
</tr>
<tr>
<td>Butane</td>
<td>Acetic acid</td>
<td>Solvent, vinyl acetate polymers</td>
</tr>
<tr>
<td>Toluene</td>
<td>Benzoic acid</td>
<td>Phenol synthesis</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>Isophthalic acid</td>
<td>polymers and plastisizers</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>Terephthalic acid</td>
<td>Polyester fibers, films and plastics</td>
</tr>
<tr>
<td></td>
<td>Terephthalate esters</td>
<td></td>
</tr>
</tbody>
</table>
Table 7

Syngas-based routes to ethylene glycol
(King and Grate, 1985)

<table>
<thead>
<tr>
<th>Method</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct synthesis (CO hydrogenation)</td>
<td>(2\text{CO} + 3\text{H}_2 \rightarrow \text{HOCH}_2\text{CH}_2\text{OH})</td>
</tr>
</tbody>
</table>
| Oxidative carbonylation of methanol        | \(2\text{CH}_3\text{OH} + 2\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{O}_2\text{CCO}_2\text{CH}_3 + \text{H}_2\text{O}\)  
\(\text{CH}_3\text{O}_2\text{CCO}_2\text{CH}_3 + 4\text{H}_2 \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} + 2\text{CH}_3\text{OH}\) |
| Formaldehyde condensation                  | \(2 \text{HCHO} \rightarrow \text{HOCH}_2\text{CHO} \xrightarrow{\text{Hydrogenation}} \text{HOCH}_2\text{CH}_2\text{OH}\) |
| Reductive carbonylation of formaldehyde    | \(\text{HCHO} + \text{CO} + 2\text{H}_2 \rightarrow \text{HOCH}_2\text{CH}_2\text{OH}\) |
| Carbonylations of formaldehyde             | \(\text{HCHO} + \text{CO} + \text{HOH}(\text{R}) \rightarrow \text{HOCH}_2\text{CO}_2\text{H}(\text{R})\)  
\(\text{HOCH}_2\text{CO}_2\text{H}(\text{R}) \xrightarrow{\text{Hydrogenation}} \text{HOCH}_2\text{CH}_2\text{OH} + \text{HOH}(\text{R})\) |
Table 8
Comparision of Adipic Acid Processes (Keshing, 1987)

<table>
<thead>
<tr>
<th>Raw Materials-</th>
<th>c/Lbs</th>
<th>cyclohexane oxidation</th>
<th>Butadiene oxicarboxylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene</td>
<td>50.0</td>
<td>-</td>
<td>22.6</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>21.7</td>
<td>-</td>
<td>11.1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.6</td>
<td>-</td>
<td>0.4</td>
</tr>
<tr>
<td>Methanol</td>
<td>26</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>125</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>70.4</td>
<td>50.7</td>
<td>-</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>13.2</td>
<td>14.5</td>
<td>-</td>
</tr>
<tr>
<td>Pd($/ounce)</td>
<td>375</td>
<td>-</td>
<td>2.7</td>
</tr>
<tr>
<td>Others</td>
<td>5.3</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>By-product credit</td>
<td>-</td>
<td>(6.0)</td>
<td></td>
</tr>
<tr>
<td>Total raw Materials</td>
<td>70.5</td>
<td>36.4</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1

Stability of the hydroformylation catalysts HCo(CO)$_4$ + Co$_2$(CO)$_8$ in relation to temperature and partial pressure (Cornils, 1980)
Figure 2

A block diagram of Shell Higher Process to illustrate complete utilization of ethylene (Parshall, 1980)
Figure 3

Syngas as a building block (Cornils, 1987)
Figure 4

Vinyl Acetate via Syngas (Cornils, 1987)
\[ \text{O} - \text{NH}_2 + \text{CO} + \frac{1}{2} \text{O}_2 \xrightarrow{\text{EtOH}, \text{Catalyst}} \text{O} - \text{NHCOOEt} + \text{H}_2\text{O} \]

EPC

OR

\[ \text{O} - \text{NO}_2 + 3\text{CO} \xrightarrow{\text{EtOH}, \text{Catalyst}} \text{O} - \text{NHCOOEt} + 2\text{CO}_2 \]

EPC

Methylene diphenyl diurethane (MDU)

2 \[ \text{O} - \text{NHCOOEt} + \text{HCHO} \]

\[ \text{EtOOC}\text{HN} - \text{CH}_2 - \text{O} - \text{NHCOOEt} + \text{H}_2\text{O} \]

(MDU)

Thermal decomposition of MDU TO MDI and ethanol

\[ \text{MDU} \xrightarrow{\Delta} \text{OCN} - \text{CH}_2 - \text{O} - \text{NCO} + 2\text{EtOH} \]

(MDI)

**FIGURE 5: A NEW NON-PHOSGENE ROUTE FOR MDI**

(ASAHI PROCESS)
Figure 6

Alternatives to the acetone cyanohydrin route to MMA (Cornils 1987)
FIGURE 7: BASF PROCESS FOR TOTAL SYNTHESIS OF VITAMIN A (PARSHALL AND NUGENT, 1988)
FIGURE 8: l-DOPA SYNTHESIS
HAZARD ANALYSIS OF HIGH PRESSURE SYSTEMS

K.V. Raghavan

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HAZARD ANALYSIS OF HIGH PRESSURE SYSTEMS

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Adyar, Madras 600 020 India

A wide range of industrially important chemicals are manufactured employing high pressure technologies. Typical examples are ammonia and methanol syntheses, Fischer Tropsch synthesis, ethylene oxidation, carbonylation, oxy and hydrocarbonylations, hydrocracking etc. Fig.1 shows the pressures typical of the above processes. The employed pressures are compromises between yield or reaction rate improvements and higher costs of pressure installations. There is no sharp dividing line between high and low pressures and the basic design of high pressure equipments is executed on similar lines upto 6000 atm pressures above which special design approaches are required. Ultra high pressure region begins at a pressure of about 8000 atm. This is the probable strength limit of simple elastic cylinders at which it becomes necessary to use special types of construction such as wire wound vessels. The present paper attempts to highlight the strategies to be adopted for hazard identification and quantification in high pressure chemical plants.

The use of high pressure significantly enhances the amount of energy stored in the concerned installation and accordingly, its hazard potential. High pressures associated with high and/or low temperatures and/or aggressive materials further enhances the hazard potential. The major causative factors responsible for higher damage levels in accidents in high pressure installations are:

i. Enhanced fluid leakages due to higher pressure differentials

ii. Rupture of pipelines/vessels due to internal explosions

iii. High thermal stresses induced during start-up and shutdown periods

iv. Low temperature or hydrogen embrittlement leading to pipe/vessel rupture

v. Loss of control action due to malfunctioning of critical instruments
An explosion and fire occurred (1) in the hydrocracker section of a major UK refinery when a low pressure separator vessel (20 tonnes capacity) failed catastrophically releasing large quantities of flammable gases and liquids. The vessel disintegrated and fragments weighing up to 2 tons each travelled a distance of 1.2 kms from the seat of the blast. This accident occurred due to the failure of control mechanism of liquid flow between high (155 atm) and low pressure (9 atm) gas-liquid separators. The process was operated from a local control room using electro pneumatic control system.

Hazard Identification

Hazard identification in high pressure installations requires a detailed study on the impact of pressure in combination with high or low temperature on materials of construction, process fluids and the process itself. Pressure has a strong influence on the following system properties and its precise effect needs to be understood in order to make a realistic hazard assessment and to model the system failure under the influence of high pressure.

Enhanced Corrosion Effects

The synergistic effect of high pressure and corrosion in high stress environments may lead to failure of materials well below their normal yield strength (2, 3). The phenomenon of stress corrosion cracking is not well understood. Table 1 highlights typical environments which are conducive to stress corrosion cracking. Hydrogen embrittlement can occur rapidly after a stressed body is exposed to hydrogen environment at high temperatures and pressures.

Enhanced failure rates at high stress concentration areas

Voids, cracks, side entry ports, notches, regions where bore diameter changes, locations with thermal discontinuities and other areas of high stress concentration are prone to higher failure rates at elevated pressures.

Vibrations induced in pipelines carrying high pressure fluids can assume serious proportions in cryogenic installations. Vibrations are conveyed from rotating and reciprocating machinery, cavitation in suction side of high pressure compressors, multi phase flows in the pipelines and pressure surges created by the sudden stoppage of fluid flow. In addition to static stress, pressure piping is also subjected to dynamic stresses created by vibration which can be bending, axial, torsional or radial depending on the dimensions and layout of the
piping. The different types of vibrations can occur simultaneously with possible large amplitude of movement and pipe material damage through fatigue. In corrosive environment, the piping material can rupture at substantially lower amplitude or load cycles than if the process fluid is non-corrosive. Klapp (4) studied the vibrational phenomena in pressure equipment and proposed mathematical models to predict their responses to the external stimulation.

**Effects on System Properties**

**Single phase systems**

Pressure is an important variable in the control of transport properties of fluid and solid phases. Gases become liquidlike at sufficiently high pressure even if the temperature is higher than critical temperature. At still higher pressure, further condensation occurs to form a solid phase. The behavior of gases at high pressures can be computed by modified equations of state. The properties of gas mixtures can be obtained from measurements on the pure components by employing the fugacity concept.

The physical properties of most crystalline materials do not change appreciably with pressure unless there is a phase change. Properties of porous and polycrystalline solids may be more strongly affected by pressure as particles are crushed together and pressure cycling may lead to irreversible changes in their properties. The thermal conductivity of insulating materials decreases with increasing gas pressure.

**Multiphase Systems**

Vapor-liquid-solid and solid-solid-liquid equilibria and solid-solid transformations are strongly influenced by pressure. Fig. 2 illustrate the associated phase behavior. Structural, electronic and magnetic transformations occur in solids on application of high pressure.

**Large Inventories**

It is usual in some of the chemical processes to handle very large inventories of flammable materials at high pressures and temperatures which are capable of sustaining a major fire or air explosion. Such damage can be extensive. Flixborough accident is an important example of this category.

**Modelling of pressure vessel and pipeline failures**

Current knowledge base in high pressure design technology and material sciences is sufficiently advanced to predict the pressure vessel and pipe failures with an acceptable degree of
engineering precision.

**Vessel Fragmentation**

Pressure vessels (upto 1000 atm) are fabricated from special materials of construction which are ductile under operating conditions. In case of their rupture, fracture occurs where cracks appear and the parts may break away. The stored energy in the pressure vessel could generate a shock wave and accelerate the speed of travel of vessel fragments. The stored energy is dissipated as kinetic energy of fragments, shock wave energy, plastic energy imparted to fragments and energy for heating surrounding air. Saville (5) observed that 80% of available energy is transformed into shock wave energy for brittle type failures.

Considerable interest has been generated in recent years on the simulation of pressure vessel failure modes and their consequences. Failure mechanisms based on Maximum Principal Stress, Maximum Shearing Stress, Maximum Elastic Strain and Octahedral Shearing Stress theories have been reported. According to maximum Principal Stress Theory, failure of a pressure vessel is imminent when the tensile stress of the wall drops below its stress levels at inner surface. Good correlation between prediction and actual failure is achievable if vessel wall temperature and pressure histories are accurately assessed (6). Fig. 3 shows the simulated time variant pressure and temperature profiles in a pressurised storage vessel engulfed in fire. The simulation results are then employed for assessing the vessel failure.

Prediction of vessel fragment number, size and direction of propulsion is of practical utility for hazard analysis. Empirical correlations are reported (7 to 10). The rupture process of vessels under the influence of detonation is highlighted by Engan (11).

**Prediction of leak before break behavior**

The size of initial leak is vital for modelling the chemical release rate and source strength as a function of time in case of accidents in high pressure installations. Several models have been reported for assessing the leak rates through small cracks in pressure vessel and pipe walls. Abdollahiam (12) modelled the leak employing modified Bernoulli's equation and homogeneous fluid state assumption for evaluation of critical mass flux. Amos et al (13), employing homogeneous fluid state assumption, estimated the leak level as a function of crack size. His model also assumes that the liquid boiling starts as soon as the local pressure in the crack has dropped to the saturation pressure corresponding to the fluid stagnation temperature. The model proposed by John et al (14) considers several liquid discharge
modes depending on possible stagnation states of liquid upstream of the leak. The model proposed by Collier (15) considers thermodynamic non-equilibrium and employs empirical correlation for the relaxation towards the equilibrium state.

Transient and Surges in Pipelines

Long distance pipeline transportation of pressurized liquids frequently encounter temperature, pressure and velocity transients and pressure surges. They could contribute to pipeline ruptures and leaks. Pressure surges occur due to sudden conversion of kinetic energy into potential or pressure energy, and can be modelled by employing equations of continuity and motion with appropriate initial and boundary conditions. Several studies have been reported for assessing the pressure and velocity changes associated with the surges. Streeter and Wylie (16) employed the method of characteristics to solve pressure and velocity transient problems in pipelines. Rockford and Ramsey (17) considers fluid frictional and compressibility effects. Hein (18) reported a simple computer program for surge analysis in a pipeline employing Streeter and Wylie method. Koshy et al (19) examined the transient and surge effects in a cryogenic propylene transportation line equipped with a feed pump, a check valve at the upstream end and a time controlled block valve at the downstream end. Fig. 5 shows the simulated pressure and velocity transients in the pressurized liquid pipeline.

Typical Process Hazards at High Pressures

Chemical reactions are executed at high pressures to increase yield and reaction rate and in gas/vapor phase reactions to reduce the size of the reactor. The product yield in reactions with volume decrease are enhanced by pressure. In catalytic reactions, pressure increases the surface density of adsorbed molecules and may increase or decrease molecular diffusion flux rates.

Internal burning in oxidation processes

This is a complex subject. The ability of free radicals and peroxides to ignite flammable mixtures well below the autoignition temperature is reported in case of oxidation reactions. In normal reaction conditions, burning does not occur. However, dispersion of air into small bubbles enables the high specific interfacial area to dissolve oxygen rapidly into an initially oxygen free liquid. This very quickly reduces the oxygen content of the bubbles to below the level which will sustain combustion. Other possibilities are (a) involvement of peroxide deposits as an ignition source (b) presence of pyrophoric and catalytic deposits and (c) frictional heating between two metal surfaces inside the sector. An analysis of past accidents indicate that (a) hydrocarbon backflow into air line
(b) development of airlines within the vessel (c) concentration transients during start up (d) change in process flows during off gas recycle (e) liquid diversion and (f) oxygen enrichment have to be closely watched to prevent internal burning in pressure reactors. Fig. 4 highlights the details.

Thermal Explosions

Several high pressure reactions are exothermic. They tend to accelerate if the rate of heat removal in the reactor is insufficient to control the temperature rise. The reactor can attain a level of thermal loss control resulting in explosion of reaction vessel and associated large release of toxic and/or flammable gas/vapor into the near environment. The subsequent hazards due to gas/vapor cloud ignitions and explosion, boiling liquid and expanding vapor explosions, dust-hydrocarbon explosions and toxic gas releases can be very damaging. It is usually pressure generation, not thermal runaway, that causes rupture and maximum damage to process and high pressure storage installations.

From process control angle, temperature and pressure are be considered as reliable runaway reaction precursors. A three tier reactor control system is the most appropriate strategy for achieving intrinsic safety. It consists of providing (a) built-in cooling system taking charge of normal operating temperature control within allowable limits of temperature excursions (b) online detection facility for monitoring runaway reaction precursors followed by measures for restabilization of process parameters and (c) emergency pressure release through properly designed vent system.

Process Hazard Quantification

Lumped parameter approach for process hazard rating

Adiabatic Temperature Rise (ATR), Unit Process Hazard Rating (UPHR), Fire and Explosion Index (F&EI) and Runaway Index (RI) are some of the reported methods (20 to 23) based on lumped parameter approach. F&EI is widely used for first level screening of hazardous unit processes. The adverse effects of pressure on the process is explicitly evaluated in terms of a special hazard factor. The penalty is directly related to set pressure of relief valve.

Parametric sensitivity approach for thermal runaway

Hot spots are usually observed in the steady state temperature properties along tubular (empty and fixed bed) reactors in which exothermic reactions are carried out under pressure. They not only pose severe constraints in the scale up and design of polymerization and oxidation reactors but also lead
to thermal explosions. Under certain operating conditions, the magnitude of the hot spot may become quite sensitive to small variations in the input parameters. This phenomenon has been referred to as parametric sensitivity (24). For hazard analysis purposes, it is important to know a priori the locations of the boundaries between the sensitive and non-sensitive regions in the parameter space for both the temperature and product distribution.

A considerable amount of work on parametric sensitivity has been reported for fixed bed reactors (25 to 30). Recently, Raghavan (31) suggested computer assisted offline method for identification of parametric sensitive regions in fixed bed reactors for a series-parallel reaction scheme. A two dimensional heterogeneous transport model was employed. Its utility was demonstrated for two commercially important partial oxidation processes with different levels of reaction vigour and exothermicity. The method can also be applied to high pressure reaction systems.

Tjahjadi et al (32) studied the parametric sensitivity in tubular polymerization (chain) reactors. Using conditions typically encountered for high pressure polyethylene systems, they obtained detailed parametric sensitivity plots which could be used to obtain safe operating conditions. Chemburkar et al (33) have shown that the generalized sensitivity criterion developed for tubular reactors can easily be applied in the case of a CSTR. A generalized region of parametric sensitivity was identified where the reactor temperature is parametrically sensitive to all input parameters.

Table 2 presents the details of the parametric sensitivity studies highlighted above. Fast pressure relief systems in high pressure ethylene polymerization in tubular reactor are described in patented literature (34 to 36). One of the major drawbacks of parametric sensitivity approach is the lack of experimental support for the a priori projections made through computer analysis.

Thermochemical investigations for assessing thermal and pressure effects

Thermochemically, runaway reactions and exothermic decompositions at high pressures operate on similar mechanisms because they are characterized by accelerated self heating resulting in exponential increase in reaction rate and temperature. The basic objective of thermochemical investigations is to determine the temperature and pressure ceilings below which a chemical reactor can be safety operated. As stated earlier, temperature and pressure are the two important thermochemical precursors and measurement of rate of their increase forms the
critical part of thermochemical analysis.

The dynamic behavior of runaway pressure reactions can be studied effectively through Accelerated Rate Calorimetry (ARC). The self accelerating temperature and pressure rises can be measured and recorded at operating range of 0-500° and 1 to 150 atm. All operations are controlled by a microprocessor system along with the logic to search for and follow exotherms and exobars to permit user selection of runaway parameters and to provide online display of critical variables. A search for a reaction exotherm is accomplished by elevating the sample temperature by a fixed increment (step heat) and then checking to see if the sample self heat rate exceeds a user selected threshold. Once an exotherm is detected, automatic collection of time, temperature and pressure data is carried out until the reaction is finished and the self heat rate has dropped below the threshold value. Fig. 6 shows the typical temperature and pressure profiles.

The pressure information is very important in thermochemical analysis. Pressure versus temperature and pressure versus inverse temperature are two ways of interpreting the pressure rise during a reaction. A plot of pressure rate versus temperature rate can show reaction mechanism changes that otherwise might not be obvious. Important to hazard prediction is the ability to use exotherm and exobar data for vent sizing in process and storage situations.

Thermokinetics for prediction of runaway behaviour

Process kinetic data from classical techniques is usually obtained at conditions far removed from runaway situation and is not valid for predicting the thermal explosions. The chemistry and mechanism of a runaway reaction is often complex and a precise understanding of its kinetics is difficult and time consuming. Thermokinetic analysis based on microcalorimetric techniques relies on data on total heat and pressure production as a result of all reactions occurring under runaway conditions.

Classical kinetic studies from isothermal data depends upon periodic sampling and analysis of reaction mixture to obtain concentration of reactants and products under isothermal and isobaric conditions. Sampling of adiabatic reaction mixtures under runaway conditions is highly impractical. Thermokinetic investigations, therefore, make use of thermal and pressure responses for kinetic parameter estimation. Kinetic constants like activation energy, Arrhenius preexponential factor and reaction velocity constants applicable for runaway conditions can easily be evaluated by selecting appropriate reaction mechanism.
Models for consequence assessment of chemical releases from high pressure systems

Several models have been reported for calculating the chemical release effects and damages. They can be applied to the chemical release cases from high pressure installations on their failure due to process and non-process events. Fig. 7 highlights the typical chemical discharge modes and applicable consequence models (Table 3). The widely accepted damage criteria for thermal radiation, explosions and toxic chemical effects are highlighted in Table 4. The process and non-process hazards of high pressure systems can be quantified with the help of consequence analysis which makes use of material and chemical properties as influenced by high pressure environment. The vessel/pipe fragmentation modelling will be helpful in assessing the size of the chemical leaks.

SUMMARY

Hazard analysis of high pressure system provides exciting challenges to chemical and mechanical engineers in modelling the accident scenarios.

Acknowledgements

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NOMENCLATURE

$S_i, \overline{S}_i$  Sensitivity and adjoint variables
$F_i$  $dy_i/dM$
$M$  $f(t)$
$t$  Independent variable
$y$  State variable
$\theta$  Input parameters
$\theta_P$  Catalyst particle temperature
$\theta_i$  Catalyst particle temperature at point of inflexion
$\theta_s$  Limiting particle temperature
$T$  Bulk fluid temperature
$T_i$  Bulk fluid temperatures at point of inflexion

subscript
$0$  Inlet value
REFERENCES


02. Takayani, I., Koatsu Gasu 8(6), 384 (1971)

03. Tamoyashi, N and Mamoru, F., Koatsu Gasu., 8(6), 350 (1971)


24. Bilous, O and Amundson, NR., AIChE. J 2, 117 (1956)


TABLE 1: TYPICAL ENVIRONMENTS CONDUCIVE TO STRESS CORROSION CRACKING

<table>
<thead>
<tr>
<th>Materials of Construction</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Carbon Steels</td>
<td>i. Caustic solutions</td>
</tr>
<tr>
<td></td>
<td>ii. Calcium, ammonium and sodium nitrite solutions</td>
</tr>
<tr>
<td></td>
<td>iii. Mixed acids (sulphuric and nitric)</td>
</tr>
<tr>
<td></td>
<td>iv. Hydrogen sulphide solutions</td>
</tr>
<tr>
<td>ii. Stainless Steels</td>
<td>i. Acid chloride solutions</td>
</tr>
<tr>
<td></td>
<td>ii. Caustic - hydrogen sulphide solutions</td>
</tr>
<tr>
<td></td>
<td>iii. Salt - hydrogen peroxide solutions</td>
</tr>
<tr>
<td>iii. Monel and Nickel</td>
<td>i. Fused caustic soda</td>
</tr>
<tr>
<td></td>
<td>ii. Hydrogen fluoride and hydro-fluoro silic acid</td>
</tr>
<tr>
<td>iv. Inconal</td>
<td>i. Caustic solutions</td>
</tr>
</tbody>
</table>
TABLE 2: PARAMETRIC SENSITIVITY IN CHEMICAL REACTORS

1. High Pressure Polymerization (9)

<table>
<thead>
<tr>
<th>Kinetic Scheme</th>
<th>Free radical polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transport Model</td>
<td>Plug flow (steady state) in a tubular reactor</td>
</tr>
<tr>
<td>Input parameters</td>
<td>Initiator concentration, feed temperature, heat of reaction, rate constants and activation energy</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>Thermal and Molecule weight</td>
</tr>
</tbody>
</table>
| Algorithm | \[
d\frac{\text{dyn}}{d\phi j} = \sum_{i=1}^{n} S_i(0) \cdot \bar{S}_i(0) + \int_{0}^{t} S_i \cdot \frac{\partial F_i}{\partial \phi_j} dt
\]

2. Partial oxidation of hydrocarbons (8)

| Kinetic scheme | Series - Parallel; first order |
| Transport Model | Two dimensional heterogeneous (Packed bed) model with intra particle, interphase and bulk fluid gradients |
| Input parameters | Hydrocarbon concentration, feed temperature, heat of reaction, rate constants and activation energy |
| Sensitivity | Thermal |
| Algorithm | \[
\frac{d (t-T_i)}{dt} = \frac{t_i - T_i}{t_i - t_s}
\]
# TABLE 3: MATHEMATICAL MODELS FOR CONSEQUENCE ANALYSIS

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Phenomenon</th>
<th>Applicable Models</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>OUTFLOW</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>Bernoulli flow equation; phase</td>
</tr>
<tr>
<td></td>
<td>Two phase mixtures</td>
<td>equilibria; multiphase flow</td>
</tr>
<tr>
<td></td>
<td>Gas/Vapour</td>
<td>models; orifice/nozzle flow equations; Gas laws; critical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>flow criteria</td>
</tr>
<tr>
<td>2.</td>
<td>DISCHARGES</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spreading liquid</td>
<td>Spreading rate equations for</td>
</tr>
<tr>
<td></td>
<td></td>
<td>non-penetrable surfaces based</td>
</tr>
<tr>
<td></td>
<td></td>
<td>on cylindrical liquid pools</td>
</tr>
<tr>
<td></td>
<td>Vapour jets</td>
<td>Turbulent free jet model</td>
</tr>
<tr>
<td></td>
<td>Flashing liquids</td>
<td>Two zone flash vaporization model</td>
</tr>
<tr>
<td></td>
<td>Evaporation of liquids</td>
<td>Spreading boiling and moving</td>
</tr>
<tr>
<td></td>
<td>on land and water</td>
<td>boundary heat transfer models;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Film and metastable boiling phenomenon; cooling of semi-infinite medium</td>
</tr>
<tr>
<td>3.</td>
<td>DISPERSIONS</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Heavy gas</td>
<td>(i) Buoyancy dominated, stably</td>
</tr>
<tr>
<td></td>
<td></td>
<td>stratified and passive dispersion models</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) 3D models based on momentum mass and energy conservation</td>
</tr>
<tr>
<td></td>
<td>Neutral gas</td>
<td>Gaussian dispersion models for</td>
</tr>
<tr>
<td></td>
<td>Atmospheric stability</td>
<td>neutrally buoyant plumes</td>
</tr>
<tr>
<td></td>
<td>Consequences</td>
<td>Boundary layer theory (turbulence); Gaussian distribution models</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Probit model for toxicity</td>
</tr>
<tr>
<td>Sl No</td>
<td>Phenomenon</td>
<td>Applicable Models</td>
</tr>
<tr>
<td>------</td>
<td>--------------------------------</td>
<td>-----------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>4.</td>
<td><strong>HEAT RADIATION</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid pool fires</td>
<td>Burning rate, heat radiation and incident heat correlations (semi-empirical); Flame propagation behaviour models</td>
</tr>
<tr>
<td></td>
<td>Jet fires</td>
<td>Jet dispersion model</td>
</tr>
<tr>
<td></td>
<td>Fireballs</td>
<td>API fireball models relating surface heat flux of flames; geometric view factor and transmission coefficients</td>
</tr>
<tr>
<td></td>
<td>Fire engulfment of vessels</td>
<td>Transient heat radiation, conduction and convection in multilayered containers</td>
</tr>
<tr>
<td></td>
<td>Consequences</td>
<td>Probit model for thermal radiation</td>
</tr>
<tr>
<td>5.</td>
<td><strong>EXPLOSIONS</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boiling liquid expanding vapour explosion</td>
<td>Fireball and physical overpressure models; deflagration and detonation models; ID gas dimensional computations</td>
</tr>
<tr>
<td></td>
<td>Consequences</td>
<td>Probit model for overpressures</td>
</tr>
</tbody>
</table>
### TABLE 4: DAMAGE CRITERIA

<table>
<thead>
<tr>
<th>HEAT RADIATION</th>
<th>EXPLOSION</th>
<th>TOXIC GAS DISPERSION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident flux</td>
<td>Damage</td>
<td>Peak over pressure,</td>
</tr>
<tr>
<td>$\text{KW/m}^2$</td>
<td></td>
<td>bar</td>
</tr>
</tbody>
</table>

| 37.5 | 100% lethality; Heavy damage equipment | 0.3 | Heavy (90%) |
| 25   | 100% lethality; non piloted ignition   | 0.03| Repariable (10%) |
| 12.5 | 100% lethality; piloted ignition       | 0.01| Damage of glass |
| 4    | Not lethal; 1st degree burns           |     | Crack of windows |
| 1.6  | No discomfort even after long exposure |     |                   |

The extent of damage depends upon the concentration of the toxic compound in the atmosphere; The relation between percent of injuries and the toxic load is normally given in the form of Probit functions.
FIG. 1 PRESSURE PYRAMID APPLICABLE TO CHEMICAL TECHNOLOGIES
Fig 3: Modelling and simulation of failure of a pressure vessel (LPG filled) engulfed in fire.
Fig. 4 Internal burning hazards in liquid phase oxidation reactors
Fig. 5. Simulated Pressure and Velocity Transients in Liquid Pipelines
FIG. 6 TYPICAL THERMAL RESPONSE PATTERNS FROM A RUNAWAY REACTOR
Panel Discussion
PANEL DISCUSSION

Chairman: Prof. Y.T. Shah
Members: Prof. H. Hofmann
Prof. G. Luft
Prof. H. Tiltcher
Prof. G. Vetter
Prof. M.M. Sharma
Dr. K.V. Raghavan
Dr. R.V. Chaudhari
Dr. P.D. Patel
Dr. V.V. Chavan
Dr. P. Sawhney

Y.T. Shah proposed that the panel discussion can be focused on the following aspects: 1) Basic Science 2) Engineering and 3) Safety and cost.

H. Tiltcher: Development of clean, precise and practical experimental techniques for studies of high pressure reactions is necessary. New techniques required in the use of NMR and IR need to be developed under pressure and particularly near supercritical conditions need to be developed. There is, in general, a lack of information on physicochemical properties for complex molecules under critical conditions.

H. Hofmann: It is necessary to have predictive correlations, for thermodynamic properties under high pressures.

P.D. Patel: Are there any correlations based on molecular level thermodynamics available for comparison with experimental data?

H. Hofmann: At present no correlations and experimental data are available.

Uday Sankar: Critical properties are available only for hydrocarbons. New correlations for other classes of compounds need to be developed.
**H. Tiltscher:** Techniques are not available to measure properties at near critical conditions for practical systems.

**Y.T. Shah:** What is the status at present regarding the equations of state at high pressures?

**H. Tiltscher:** Equations of state are not available for mixtures. However, they are available for single compounds.

**M.M. Sharma:** Super critical fluid chromatography can be effectively used to determine properties at near supercritical conditions and the experimental techniques are relatively simple. The problem of adsorption and role of entrainers are well understood.

**Y.T. Shah:** Data are available for some systems using super critical fluid chromatography. The status of transport properties under high pressures conditions is however, not clear.

**H. Hofmann:** There is lack of experimental data on mass transport and kinetic parameters under high pressures.

**Y.T. Shah:** What would be the difference in transport properties under normal and high pressure conditions?

**H. Hofmann:** There are bound to be differences, however, the exact trends of pressure dependence not yet well understood.

**R.M. Mashelkar:** Under critical and near critical conditions the ‘continuum equation’ breaks down and measurements are difficult.

**Uday Sankar:** What is the methodology and experimental techniques available to study the behavior of systems under supercritical conditions.

**B.D. Kulkarni:** Presently available knowledge may be sufficient, to model behavior at near critical points for mixtures. Averaging may not work at the near critical regions. It has to be looked at microscopic level.

**V.V. Chavan:** Even at microscopic levels some assumptions are needed
to model. What are those assumptions?

**B.D. Kulkarni:** Ideally, no assumptions are necessary if the approaches of modelling is based on molecular chaos.

**R.V. Chaudhari:** What about prediction of transport properties? The equations available are qualitative in nature.

**H. Tiltischer:** What is the definition of near critical region for Chemical Engineering? Is there any known process operating at critical conditions?

**M.M. Sharma:** How about designing a supercritical fluid?

**Y.T. Shah:** How to predict critical properties for mixtures?

**G. Luft:** There is a need for generating thermodynamic data to predict these properties. The data predicted with existing correlations differ greatly with experimental values, for example, in viscosity values of ethylene at 800 and 2000 bars. Most of the existing equations fail near critical conditions.

**Y.T. Shah:** What about reactions under supercritical conditions? What is the influence of pressure on the rate constants and other physicochemical properties of fluids? The properties could vary widely due to solvation effects. The variation could be of the order of few thousand times.

**R.V. Chaudhari:** In order to understand the influence of supercritical conditions on rate parameters, homogeneous reactions with known mechanism can be used as model systems.

**M.M. Sharma:** A good example is the Diels Alder reaction. High pressure conditions are known to change the mechanism as well as the products obtained.

**Y.T. Shah:** What we should not be doing?

**R.M. Mashelkar:** Not to operate process at conditions which cause criticality. Also do not operate at transition regions where the behavior is not well understood. The conditions which could lead to transition regions
should be known and avoided.

**Y.T. Shah:** Let me pose some questions on high pressure engineering: 1) What about the mechanical design of reactors and pumps at high pressure conditions? 2) What are the analytical tools available?

**G. Vetter:** Design of these equipment are dictated only by the process needs. Mechanical design is generally satisfactory. In general, cost is not a major issue. Fatigue and corrosion under high pressure conditions are not properly understood. The mechanical seals have a definite life time. The reason why and where the leak occurs is not known. Wear and tear depends on dry and lubricated conditions. Particle influence on the seals is more significant for smaller particles. Complicated mechanical parts are difficult to model. Efforts should be directed to develop leak proof systems.

Cavitation criteria is important at high pressures. Temperature rise should also be taken into consideration as it is known that a temperature rise of nearly 20 °C can take place in the pumps.

**Y.T. Shah:** What are the diagnostic tools available?

**G. Vetter:** These are well developed for turbo compressors. However, for reciprocating and rotary pumps these are not developed.

**K.V. Raghavan:** For the purpose of safety analysis, what would be the range of parameters we would be using in the next decade? Failure mechanism for high pressure systems should be known. The order of toxicity, hazard during explosion should also be known. On line diagnostic techniques should be developed. Instruments and techniques at high pressures should be developed.

**M.M. Sharma:** Understanding creep behavior of equipment is essential. Use of cast tubes might enable reaching high temperatures and pressures. New developments in this area is necessary.

**G. Vetter:** There are no developments being made in crystalline alloys. More research is required for the development of anisotropic materials for high pressure operations.
Y.T. Shah: What do we do about cost and safety?

G. Luft: Cost can be reduced by reducing the size of the reactor. More laboratory scale work required to optimize operating conditions and equipment sizing.

K.V. Raghavan: The level of manual operation should be reduced in high pressure experiments.

Y.T. Shah: Should it be computer controlled?

K.V. Raghavan: In some cases, 'yes'. However, manual supervisory control is also necessary.

M.M. Sharma: Future efforts should be directed to bring down the high operating pressures. Intrinsically safe processes need to be developed. Ambient pressure processes are preferable.

H. Tiltscher: New techniques to reduce the volume of operation would be preferred to reduce the hazards in case of an accident.

B.I. Bhatt: Inspection procedures should be standardized for equipment so as to reduce equipment failure.
PROGRAMME OF INDO-GERMAN WORKSHOP ON
"HIGH PRESSURE TECHNOLOGY - ENGINEERING"

AT
NATIONAL CHEMICAL LABORATORY, PUNE, INDIA
SPONSORED BY: CSIR(INDIA) & KFA (GERMANY)

Venue: Lecture hall of Chemical Engineering Division

3 January, 1992

09.00 - 9.30 hrs  Registration

09.30 - 9.35 hrs  Welcome Remarks, by Dr. R. A. Mashelkar, Director,
    National Chemical Laboratory, Pune, India

9.35 - 10.30 hrs  Professor H. Hofmann, University of Erlangen-Nurnberg, Germany
    "SOME PROBLEMS IN HIGH PRESSURE REACTION
    ENGINEERING"

10.30 - 11.00 hrs  Tea

11.00 - 12.00 hrs  Professor M. M. Sharma, Department of Chemical
    Technology, Bombay, India
    "GAS-LIQUID REACTIONS UNDER PRESSURE:
    AN OVERVIEW"

12.00 - 13.00 hrs  Dr. T. S. R. Prasada Rao, Indian Institute of Petroleum,
    Dehradun, India
    "HIGH PRESSURE REACTIONS IN PETROLEUM PROCESSING"

13.00 - 14.00 hrs  Lunch

14.30 - 16.00 hrs  NCL Foundation Day Function in NCL Auditorium

16.00 - 16.30 hrs  Tea

16.30 - 17.30 hrs  Professor G. Luft, Technische Hochschule Darmstadt, Germany
    "SYNTHESIS OF POLYMERS UNDER HIGH PRESSURE"

19.30 hrs  Dinner at NCL Guest House lawns
4 January, 1992

9.00 - 10.00 hrs  Professor H. Tiltscher, Technical University of Munich, Germany
"REACTION ENGINEERING UNDER SUPERCRITICAL CONDITIONS"

10.00 - 11.00 hrs  Professor G. Vetter, University of Erlangen-Nurnberg, Germany
"HIGH PRESSURE PROCESS MACHINERY FOR CHEMICAL PLANTS"

11.00 - 11.30 hrs  Tea

11.30 - 12.30 hrs  Dr. R. V. Chaudhari, National Chemical Laboratory, Pune, India
"HIGH PRESSURE REACTIONS BY HOMOGENEOUS CATALYSIS"

12.30 hrs  VISIT TO LABORATORIES

13.00 - 14.00 hrs  Lunch

14.00 - 15.00 hrs  Dr. K. V. Raghavan, Central Leather Research Institute, Madras, India
"HAZARD ANALYSIS IN HIGH PRESSURE TECHNOLOGY"

15.00 - 15.30 hrs  Tea

15.30 - 16.30 hrs  PANEL DISCUSSION : "FUTURE DIRECTIONS IN HIGH PRESSURE TECHNOLOGY"
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Prof. M.M. Sharma  
Dr. T.S.R. Prasada Rao  
Prof. G. Luft  
Prof. H. Tiltscher  
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Chairman Panel Discussion:  
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