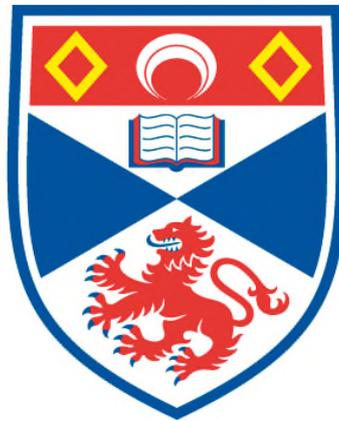


**THE EFFECT OF HIGH PRESSURE GASSES ON
HETEROGENEOUS CATALYSTS**

Robert G. L. Mitchell

**A Thesis Submitted for the Degree of PhD
at the
University of St Andrews**



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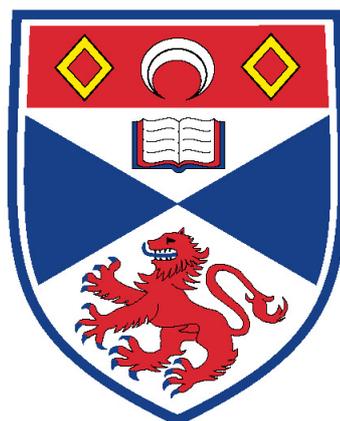
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A thesis presented by

Robert G. L. Mitchell



University
of
St Andrews

The Effect of High Pressure Gasses on Heterogeneous
Catalysts

In application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

August 2008

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Abstract

Several heterogeneously catalysed reactions have been studied at pressures above and below the critical pressure of carbon dioxide in both carbon dioxide and nitrogen. The purpose of this study was to ascertain if carbon dioxide above its critical pressure and temperature would have a beneficial effect on the active life time of the catalysts

When the Beckmann rearrangement of cyclohexanone oxime was studied it was discovered that using carbon dioxide above its critical pressure and temperature was beneficial to catalyst lifetime at both 250°C and 300°C, however the beneficial effect was also observed in nitrogen under the same conditions. It is proposed that the benefits at higher pressures are due to an increased residence time in the reactor or increased competition for active sites. When the process was performed at 380°C, a previously unreported impurity was observed in the collected samples. This was shown to be N-ethyl caprolactam, it is proposed that this is formed by a Ritter style reaction with 5-cyanopent-1-ene known to be formed during the reaction

When the Fries rearrangement of phenyl acetate was studied it was discovered that increasing reactor pressure appeared to have little or no effect on the catalyst; it is thought this is because the reaction temperature of 150°C is

below the boiling point of phenyl acetate, and that the reaction being observed occurs purely in the liquid phase.

When the Diels-Alder addition of isoprene to methyl acrylate was studied, it was discovered that using carbon dioxide above its critical pressure had the effect of improving catalyst lifetime and conversion to desired product, with the greatest effect being at 50 bar. It was discovered that using nitrogen under the same conditions led to a greater improvement in conversion and catalyst lifetime. It is thought that the reactions in carbon dioxide are in a near critical state at 50 bar leading to the maximum effect at this pressure, and at higher pressures the reactions are bi- or multi-phasic, leading to the decrease in the effect.

In the process of studying the above reactions an effective rig for the study of high pressure heterogeneously catalysed reactions was built.

Abbreviations

atm	atmospheres
CBI	Confederation of British Industry
CO ₂	Carbon Dioxide
FEP	Fluorinated Ethylene Propylene
GAS	Gas Anti-Solvent process
H/C	Hydrogen to Carbon ratio
HOMO	Highest Occupied Molecular Orbital
HPLC	High Performance Liquid Chromatography
LUMO	Lowest Unoccupied Molecular Orbital
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance
PGSS	Particles from Gas Saturated Solutions
RESS	Rapid Expansion of Supercritical Solutions
SAS	Supercritical Anti-Solvent process
SEDS	Solution Enhanced Dispersion by Supercritical fluids
SFC	Supercritical Fluid Chromatography
TFE	TertraFlouroEthylene
TOF	TurnOver Frequency
XRD	X-Ray Diffraction

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Chapter 1- Introduction

1-Introduction

Since the critical point of ethanol was first discovered in the 19th century, slow and steady research has been carried out to discover the properties of matter at the critical point and beyond; in the supercritical region. It is only within the last fifteen years there has been an explosion of interest in supercritical fluids, mainly due to their application as environmentally benign alternatives to toxic organic solvents in chemical processes.

This chapter will review the initial research into the properties of supercritical fluids, and then discuss some of these properties in further detail. The current applications of supercritical fluids and the main areas of research will be looked at, with particular reference to their use in the area of heterogeneous catalysis. Finally there will be a brief discussion of catalyst deactivation in heterogeneous catalysis.

1.1-The Peculiar State of Matter

The supercritical phase was first observed in the first half of the 19th century. Baron Charles Cagniard de LaTour was investigating the suppression of the boiling point of liquids by increasing pressure. His experiments involved sealing a ball in a gun barrel containing ethanol¹. During the experiment, by tipping the barrel from side to side, he expected to show that ethanol under pressure would remain liquid beyond its boiling point at atmospheric pressure from listening to the different tone of the ball coming to a halt against the end of

the barrel. However, upon heating he heard the ball bounce rather than come to a halt, suggesting no liquid was present. In order to observe the change visually Cagniard de LaTour performed a similar experiment in a glass container, this time he was able to observe the liquid greatly expand in volume before the meniscus between liquid and gas phases disappeared to yield a single phase of ethanol. He christened his finding the peculiar state of matter, and what we now know as the critical point was given the name of Cagniard de LaTour's point.

Inspired by Cagniard de LaTour's work, Dr Thomas Andrews became an early leader in the field of supercritical fluids. He focused primarily on the behaviour of carbon dioxide and recorded the most accurate values for its critical point for years to come at 31.1°C and 73.8 bar.² It was Dr Andrews that first used the phrase critical point, and his work led to an increased interest in supercritical fluids, ultimately resulting in the publication of a journal devoted entirely to research into supercritical fluids towards the end of the 19th century.³

Indeed, it was Andrews who first described the difficulty at this time of assigning the behaviour of supercritical fluids.⁴ Talking about the properties of his favoured subject, carbon dioxide, he declared that, at just above the critical point, carbon dioxide 'stands nearly midway between the gas and the liquid and we have no valid grounds for assigning it to one form of matter any more than the other.' This led to speculation about the specific liquid-like or gas-like properties that the supercritical phase possessed, and inspired Hannay and Hogarth to look at the liquid property of dissolving solids.⁵ They hypothesised that, if the supercritical state was a continuation of the liquid and gas states, it

followed that a solution could be passed through the critical point without precipitation of the solute occurring. They were able to show that potassium iodide salt could be dissolved in supercritical ethanol.⁶ They went on to show other strongly coloured ionic salts could be dissolved in supercritical ethanol and that the colours of these solutions were not affected by the transition from the liquid phase. The similar behaviour of organic compounds studied showed this result was not exclusive for ionic salts, indeed in some cases the solute remained in solution over 100°C above the critical point of the solvent being studied. Other important observations by Hannay and Hogarth included the shifting of the critical point by addition of the solute and that a fine solid could be precipitated by transition to the gas phase by rapid expansion of the supercritical mixture.⁷ The work by Hannay and Hogarth was truly groundbreaking as solvation had previously been thought to be an exclusively liquid property and it is upon this solvating power of supercritical fluids that nearly all of their modern day applications are based. Understandably this triggered a marked increase in activity in the research into supercritical fluids and Villard produced a review of solubility in supercritical fluids in 1896,⁸ work in this field continued well into the 20th century with several more reviews being published,⁹⁻¹² the most complete overview was provided by Franck.¹³

1.2-Definition of a Supercritical Fluid

When defining a supercritical fluid, it is conventional to look first at a phase diagram with respect to temperature and pressure. Figure 1.1 shows the phase diagram for carbon dioxide; it shows the three more common states of

solid, liquid and gas and the boundaries between these states. The sublimation curve between solids and gases exists until the triple point; this is the only pressure and temperature at which all three phases of matter can co-exist. At the triple point the sublimation curve terminates and splits into the vapour curve, between liquid and gas, and the fusion curve, between liquid and solid. However, whereas the fusion curve seems to extend forever, the vapour curve terminates at the critical point. The critical point, as has already been discussed, is the beginning of the supercritical region; at this point the boundary between liquids and gases is no longer well defined and matter exists as a phase displaying properties both liquid-like and gas-like but cannot be assigned to either state.

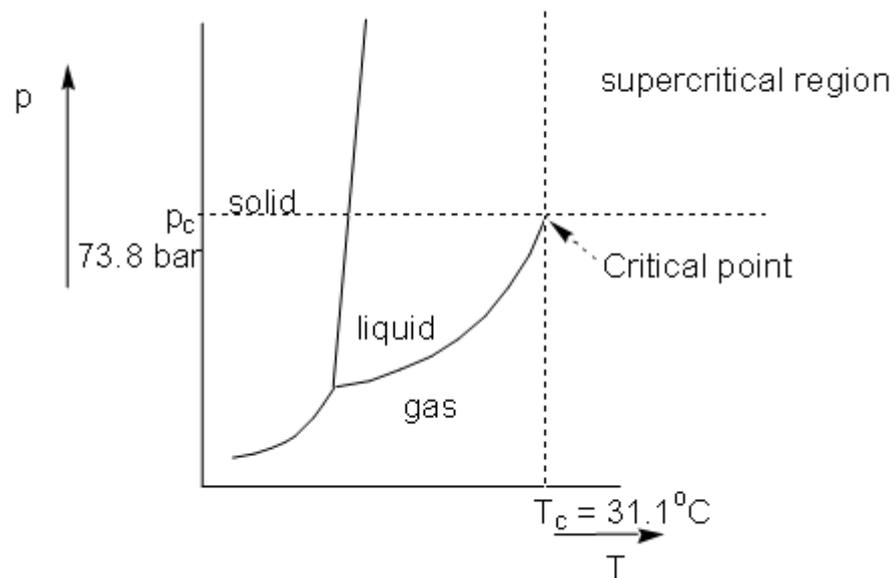


Figure 1.1- Phase Diagram of Carbon Dioxide. Reproduced from reference 14.

The temperature at the critical point is defined as the critical temperature and the pressure as the critical pressure. A supercritical fluid is defined as the

state matter exists in above its critical temperature and critical pressure. In theory the phase diagram for carbon dioxide should be representative of all substances, and a critical point should exist for all substances, however in certain cases decomposition occurs before reaching the critical temperature.

1.3-Properties of Supercritical Fluids

The position of the critical point is different for each substance. In general the critical temperature increases with increasing molecular weight. This trend is obeyed in simple chemical families such as the alkanes as shown in table

1.1.

Alkane	Critical Temperature (°C)	Critical Pressure (bar)
Methane	-83	46
Ethane	32	49
Propane	97	42
Butane	152	38

Table 1.1- Critical temperatures and pressures of simple alkanes

This correlates well with other physical properties such as melting point, as is also true when dealing with simple elements and compounds. Table 1.2 shows a number of such substances and illustrates that both the critical temperature and pressure increase with molecular weight. However, as with

melting points, this general trend is not followed when dealing with hydrogen bonded or polar molecules such as water and ethanol (Table 1.2). The elevated critical temperatures of these compounds come from the extra energy that is required to break the strong polar or hydrogen bonds, rather than just the van der Waals interactions present in the simple cases of less polar compounds.

Element/ Compound	Critical Temperature (°C)	Critical Pressure (bar)
Helium	-268	2
Hydrogen	-240	13
Nitrogen	-147	34
Carbon Monoxide	-140	35
Argon	-122	49
Oxygen	-119	50
Ethene	9	50
Xenon	17	58
Carbon Dioxide	31	74
Ethanol	241	61
Water	374	221

Table 1.2- The critical pressure and temperature of various elements and compounds

Table 1.2 also shows that, in general, the critical pressure increases with molecular weight as is the case for critical temperatures, although this trend is less strictly followed.

As has been previously outlined, a supercritical fluid just above the critical point can be thought of as half-way between a liquid and gas. It therefore follows that the properties displayed by a supercritical fluid are properties that are otherwise associated with either the liquid or gas states. As was discovered by Hogarth and Hannay,⁵ supercritical fluids possess the liquid-like property of solvation, and as was observed by Cagnaird de LaTour they expand to fill all available space like a gas.

Figure 1.2¹⁵ illustrates the dual identity of supercritical fluids. In 1.2(a) we see carbon dioxide below its critical pressure and temperature; under these conditions we see that carbon dioxide exists in both the liquid and gas phases with a clearly defined boundary between the two phases. In 1.2(b) we see the same vessel upon heating, causing both the temperature and pressure to rise as the carbon dioxide approaches its critical pressure and temperature. Here it is seen that the liquid layer expands and the boundary between liquid and gas is less clearly defined. When we look at figure 1.2(c) it can be seen that no phase boundary exists and the carbon dioxide appears to be in a single phase. In this case the carbon dioxide has been raised above its critical pressure and temperature, and it can be seen that the supercritical carbon dioxide, unrestrained by an associated vapour pressure, has expanded to fill all the available space.

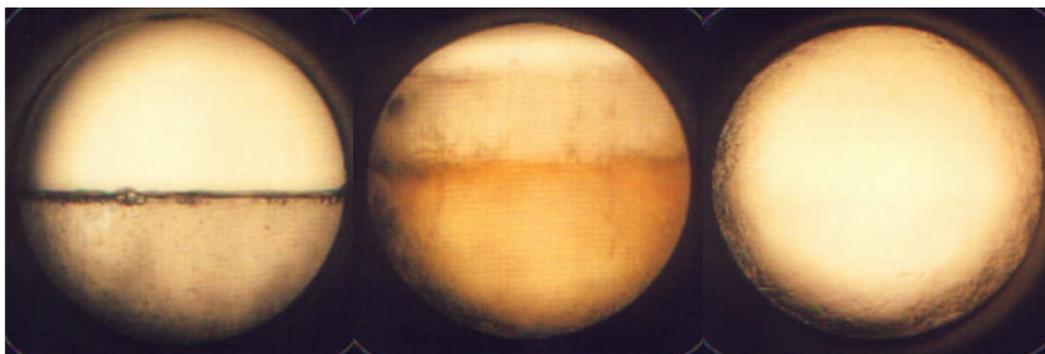


Figure 1.2 (a)- (left) Carbon Dioxide in a sealed vessel below its critical temperature and pressure.

Figure 1.2 (b)- (middle) Carbon dioxide approaching its critical temperature and pressure.

Figure 1.2 (c)- (right) Carbon Dioxide as a single phase above its critical pressure and temperature. Reproduced from reference 15.

The solubility of solids in supercritical fluids differs from the solubility of solids in liquids in an important way. The solubility of solids in supercritical fluids can be tuned by changing the density of the supercritical fluid by varying the pressure or temperature of a system. For example, in figure 1.2 (c) above if the temperature were maintained and the pressure lowered, the supercritical fluid would become diffuse, its density would drop and its solvating power would be reduced. In this case the supercritical fluid is becoming more gas-like in character. Alternatively the pressure could be maintained and the temperature reduced, the density of the supercritical fluid would increase and it would be a better solvent. In this case the supercritical fluid would become more liquid-like in its character. This unique property of supercritical fluids means that, by careful tuning of the density of a supercritical fluid, mixtures can be separated that would be difficult to separate by other means.¹⁶

In addition to their unique solvating abilities, supercritical fluids possess gas-like properties. It has already been shown that a supercritical fluid will expand to fill all the available volume, but they also have gas-like mass transport properties. The rate of diffusion through a medium is inversely proportional to its density; it follows, therefore, that diffusion in a supercritical fluid is much more rapid than in a liquid, although not as quick as in a gas. It also follows that the rate of diffusion can be varied, like solubilising power, by tuning the density. This ability to rapidly transport matter to and away from reaction sites when allied to their unique solvating properties means supercritical fluids are often put forward as alternatives to more traditional reaction media.

However, when considering supercritical fluids as alternatives to more traditional reaction media, several issues need to be borne in mind. Firstly, for reactions which require an activation temperature in excess of the critical temperature of the medium, the density of the medium will be lower than its density at the critical point, and will thus display more gas-like properties. The pressure of the reaction would then have to be raised accordingly to increase the density of the reaction medium. Secondly, the introduction of other components into the medium will effect the position of the critical point and the phase behaviour¹⁷. For a binary system the greater the concentration of the solute the more the critical point of the mixture will move from the critical point of the solvent towards that of the solute. The phase behaviour of multi-component systems is more complex than for a single component system, as the number of components increases the number of phases possible increases as does the

number of phases that can co-exist in equilibrium (equal to the number of components plus two)¹⁷. This means that even for a simple rearrangement with only substrate, product and reaction medium in the mixture there are several combinations of phases possible depending on the concentrations, pressure and temperature, and under the correct conditions it will be possible to have five phases in equilibrium.

1.4-Applications

With their unique combination of properties, supercritical fluids have found applications in many branches of chemistry. Supercritical extraction has been used industrially for many years, but supercritical fluids are now also used as solvents in organic reactions, in chromatography, destruction of toxic waste, polymer synthesis, as well as in both homogeneous and heterogeneous catalysis. Recognition of the growing importance of supercritical fluids was given in 1999 when an entire issue of *Chemical Reviews* was devoted to research in the field.¹⁸

1.4.1-Supercritical Fluid Extraction

Supercritical fluid extraction is an application where supercritical fluids are used in place of conventional solvents to extract chemicals. While it is simpler to use conventional solvents in most cases for extractions, in certain circumstances the properties of supercritical fluids make them ideal for the purpose.

One of the earliest examples of natural product extraction using supercritical fluids was discovered by chance by Kurt Zosel.¹⁹ Zosel was working on the Aufbau reaction, the reaction of triethylaluminium with ethylene for the preparation of primary alcohols, when he made his discovery. His experiments involved adding triethylaluminium to an autoclave filled with ethylene and heating. At room temperature ethylene is already above its critical temperature and the rise in pressure due to heating makes the ethylene supercritical under the reaction conditions. However this was not given any thought at the time. Several years later a licensee researching the Aufbau reaction found large quantities of α -olefins in the product, which had been absent from Zosel's experiments.¹⁹ Zosel hypothesised that in his experiments the α -olefins had been removed by the supercritical ethylene, and quickly realised that this was the basis for a method of separating substances, filing a patent for his process soon after.²⁰

Zosel's discovery was to be of particular significance to the food industry. In this industry conventional solvents have become undesirable as more is understood about their effects upon the human body and the environment. Whereas conventional organic solvents, particularly common halogenated or aromatic solvents, can be extremely toxic to humans and detrimental to the environment, carbon dioxide is completely non-toxic to humans.

As well as being a by-product from human respiration, carbon dioxide is necessary for photosynthesis and therefore necessary for a healthy environment.

However the large quantity of carbon dioxide released annually by industry has led to carbon dioxide being classified as a greenhouse gas and recently western countries have signed up to the Kyoto agreement.²¹ The Kyoto agreement is a commitment by the participating countries to reduce carbon emissions, specifically carbon dioxide and carbon particles, to set levels by 2008 and further by 2012.

The Kyoto agreement is both advantageous and disadvantageous for processes using supercritical extraction. To perform supercritical carbon dioxide extraction a source of carbon dioxide is required, and carbon dioxide is a by-product of several industrial processes, most prominently fermentation. Companies performing fermentation will now be under pressure to reduce emissions of carbon dioxide and one way of doing this would be to collect it and sell it for use in supercritical extraction. This should provide cheap available carbon dioxide. However while not creating any extra carbon dioxide as part of the process, venting of the carbon dioxide at the end of such processes would still be considered as localised emission of carbon dioxide, which would be frowned upon by both the government and the CBI (Confederation of British Industry) and could lead to financial penalties. Therefore, wherever possible, processes should recycle carbon dioxide to avoid this penalty and also reduce costs.

One process that has used supercritical carbon dioxide extraction and recycled the carbon dioxide for several decades is the decaffeination of coffee beans. Decaffeination has been performed for over 100 years, and initially was carried out using benzene, now implicated as a carcinogen. Gradually

chlorinated solvents replaced benzene most commonly trichloroethane, chloroform and carbon tetrachloride. Chlorinated solvents are now known to be mutagens and carcinogens. Given that the process was not 100% efficient at removing the solvents from the coffee beans after extraction, the process was extremely undesirable.²¹ However today over 100 000 tonnes of decaffeinated coffee are produced worldwide using supercritical fluid extraction, completely free of toxic solvents. Caffeine is extracted from coffee beans using supercritical carbon dioxide, which is not harmful to humans. The caffeine is then extracted into water, leaving the carbon dioxide free to be recycled into the extractor. In addition the caffeine can be isolated from water and sold on.

Supercritical fluid extraction is now a widely known technique in the food industry and can be used in a similar way to the decaffeination process to extract undesirable compounds or functional ingredients from a variety of foods and natural sources.²² The technique is not limited to the food industry, having a wide range of applications, and recently supercritical carbon dioxide has been shown to be effective as a environmentally benign cleaning agent.²³ It has been shown that, by passing supercritical carbon dioxide through chemically contaminated soil, it is possible to remove both organic contaminants, such as hydrocarbons, and inorganic contaminants, such as heavy metals and radioactive elements.

1.4.3-Polymers

A major area of research involving supercritical fluids is in the field of polymer chemistry and this is reflected in the volume of reviews in this area. Two main areas of research are polymer particle formation,²⁴⁻²⁶ and polymerization reactions.^{27, 28}

There are several well-known techniques for the formation of particles using supercritical fluids these include RESS (rapid expansion of supercritical solutions), GAS (gas anti-solvent process), SAS (supercritical anti-solvent process), SEDS (solution enhanced dispersion by supercritical fluids) and PGSS (particles from gas saturated solutions). Although commonly used for polymer particle formation these techniques can be used for any substance with the required solubility or insolubility in supercritical fluids, and are used frequently in pharmaceutical research.^{29, 30}

RESS is a process for substances that are soluble in supercritical fluids. The substance is dissolved into a supercritical fluid, this solution is then passed through a nozzle to a lower pressure chamber. Upon this depressurization, the solution is no longer supercritical, resulting in precipitation of the dissolved substance. By changing the dimensions of the nozzle used, it is possible to change the size of particle produced.²⁴

Whilst RESS uses a supercritical fluid as a solvent, GAS, SAS, and SEDS all utilise supercritical fluids as anti-solvents. In all three methods the

substance to be precipitated must first be dissolved in a liquid solvent. In GAS the supercritical fluid is injected into the solution and, as the concentration of supercritical fluid in the solution increases, precipitation occurs. In SAS this process is reversed with the liquid solution being sprayed into a chamber containing the supercritical fluid resulting in rapid precipitation. SEDS differs slightly from SAS. Here the liquid solution and supercritical fluid are sprayed into a precipitation chamber through a nozzle.^{24-26, 29}

PGSS differs from the other techniques described as the supercritical fluid is acting as a solute. The substance to be precipitated is heated until molten or dissolved in a liquid and heated. The supercritical fluid is then dissolved into the system, before the resultant solution is depressurized through a nozzle leading to particle formation.^{24, 30}

The above techniques can be used to produce particles of various sizes, and supercritical fluids can be used as media for polymerization reactions. The obvious environmental advantages of using supercritical carbon dioxide as solvent instead of toxic organic solvents are increased by the non-flammable nature of carbon dioxide and in certain cases higher monomer conversion.²⁷ Two of the most common polymerizations industrially can be performed in supercritical carbon dioxide.

DuPont are constructing a plant for the production of Teflon FEP which will use supercritical carbon dioxide as a solvent instead of the previously used 1,1,2-trichloro-1,2,2-trifluoroethane.^{27,31} As well as replacing a toxic solvent with

an environmentally benign, solvent this has the added advantage that the TFE monomer is less susceptible to ignition in carbon dioxide.²⁷

It has also recently been shown that the formation of Nylon-6 is possible in supercritical carbon dioxide.³² The polymerization of caprolactam with an enzyme catalyst is normally performed in toluene. Again this would replace a toxic solvent with an environmental benign solvent. In this case it was shown that monomer conversion matched that of the reaction in toluene and a slightly wider operating temperature was available.

1.4.4-Homogeneous Catalysis

Supercritical carbon dioxide has been used in homogeneous catalysis research for many years, and has been shown to be a viable solvent for many well known processes including hydrogenation, dehydrogenation, hydroformylation, oxidation, metathesis and numerous oxidation and cyclisation reactions.^{33, 34} One of the major advantages of supercritical fluids is their total miscibility with gases, which can be a problem for purely liquid solvents in homogeneous catalysis. The low critical temperature of carbon dioxide means it is relatively easy to apply to most current homogeneous processes.

Hydroformylation is one of the most studied reactions in supercritical fluids. The reaction was first performed in carbon dioxide in 1991,³⁵ when a cobalt catalyst was used to convert propene to butanal. It was shown that it was possible to obtain selectivities and linear to branched ratios of the desired

aldehyde comparable to those obtained utilising benzene as the reaction solvent. Supercritical fluids are particularly beneficial to hydroformylation reactions as they are much more effective at transporting the required syn gas to the catalyst than organic solvents. Since this initial discovery, a variety of cobalt and rhodium catalysts have been shown to be effective for the process in a supercritical medium.³⁵

Supercritical fluids have also been used in conjunction with ionic liquids.³⁶ In these reactions an ionic catalyst contained in an ionic liquid is used. These reactions take advantage of the solubility of supercritical fluids in ionic liquids combined with the ionic liquid's insolubility in supercritical fluids. This means that the supercritical fluid can transport syn gas and alkene to the reaction chamber and transport aldehyde away but all insoluble ionic material should be left behind. As the catalyst is ionic, leaching of the catalyst to the product stream is reduced considerably.

Recently supercritical fluids have been used in conjunction with organic solvents in the hydroformylation of 1-octene. Carbon dioxide expanded liquids are created when up to half of the organic solvent volume is replaced by supercritical carbon dioxide; this creates a solvent with improved mass transport capabilities.³⁷ When the hydroformylation was performed, TOF, linear to branched ratio, and selectivity were all found to be comparable with or improved by the use of a carbon dioxide expanded liquid relative to results obtained in the absence of supercritical carbon dioxide. It was also possible to perform the reaction under milder than usual conditions.

1.4.5-Analytical Techniques

In addition to providing solvents for reactions, there exist analytical techniques that use supercritical fluids. The most prominent being supercritical chromatography (SFC).

Supercritical chromatography is similar to HPLC and GC, but differs in that it uses supercritical carbon dioxide as a mobile phase as opposed to a liquid or gas.³⁸ As with HPLC and GC, the system can be run with a mass spectrometer attached to give SFC-MS analysis. The main use of SFC is for the separation of enantiomers. Separation of chiral mixtures can be achieved using HPLC; however, the lower viscosity and higher diffusivity of supercritical fluids mean that higher flow rates of the mobile phase can be used. The higher flow rates lead to considerable savings on the time for analysis, in some cases cutting the retention time of compounds to less than half when compared with HPLC.³⁹

Another analytical technique to use supercritical fluids is NMR.⁴⁰ Supercritical NMR is limited by the need to construct specialist high pressure and high temperature cells. Despite this drawback supercritical NMR has proven useful in determining phase behaviour and reaction intermediates in homogeneous catalysis as well as in following polymerization reactions.⁴⁰

1.5-Heterogeneous Catalysis

For the purposes of this project the main area of interest is heterogeneous catalysis. It should be noted that the use of supercritical fluids in heterogeneous catalysis has become a popular area for research worldwide. This review is not an attempt to provide a comprehensive guide to all the work in this field. There are several reviews and books available which provide fuller coverage of the scope of research in this field.⁴¹⁻⁴³

1.5.1-Catalyst Deactivation

This project is concerned with the effect of supercritical fluids on the deactivation rates of heterogeneous catalysts; it is appropriate therefore briefly to consider deactivation of heterogeneous catalysts.

Catalyst deactivation, the loss of catalytic activity over time, is a problem of major concern in the chemical industry. Costs to industry for catalyst replacement and process shutdown total billions of pounds a year worldwide.⁴⁴

Actual timescales for catalyst deactivation vary considerably. In the case of cracking catalysts mortality may be on the order of seconds, while in ammonia synthesis the iron catalyst may last for five to ten years.

While catalyst deactivation is inevitable for most catalytic processes, some of its more immediate consequences can be avoided or postponed. Thus catalyst deactivation issues impact greatly on catalytic chemical research.

In his review on the subject Bartholomew⁴⁴ stated that catalyst deactivation can be split into six main types;

- (i) Poisoning- Strong chemisorption of species on catalytic sites thereby blocking sites for catalytic reaction
- (ii) Fouling- Physical deposition of species from the fluid/gaseous phase onto the catalytic surface and into the catalyst pores
- (iii) Thermal degradation- Thermally induced loss of catalytic surface area, support area, and active phase support reactions.
- (iv) Vapour formation- Reaction of gas with catalyst phase to produce volatile compounds.
- (v) Vapour-Solid and Solid-Solid reactions- Reaction of fluid, support or promoter with catalytic phase to produce an inactive phase.
- (vi) Attrition- Loss of catalytic material due to abrasion.

This report is primarily concerned with the second on the list, fouling, defined as the physical or mechanical condensation of material from the reaction medium onto the catalyst surface, resulting in a loss in activity due to blockage of the pores or active site. There are two main types of fouling, carbon deposition and coking. The former conventionally describes the disproportionation of carbon monoxide to carbon and oxygen leaving a layer of

carbon on the surface, such as in reactions using ‘syn-gas’ (mixtures of hydrogen and carbon monoxide gases), while coking refers to condensation of hydrocarbons onto the catalyst surface. Coke usually consists of polymerised heavy hydrocarbons, but can vary from high molecular weight hydrocarbons to graphite structures depending on the conditions under which the coke was formed and aged.

Menon⁴⁵ suggested that coke forming reactions can be loosely grouped into two types, coke-sensitive and coke-insensitive. In coke-sensitive reactions unreactive coke is layered in the pores leading to a decline in activity, and eventually to the need to replace the catalyst. In coke-insensitive reactions, relatively reactive coke precursors are deposited on the active sites; these can be removed by ‘burning’ out the coke with oxygen or another suitable gas at high temperatures. Further to this hypothesis, Menon also observed that generally the mechanism of the coke formation is significantly different for supported metal catalysts and supported metal oxide catalysts. For this review, it is appropriate to focus on supported-metal oxide catalysts.

In reactions over supported metal oxide catalysts involving hydrocarbons coke formation can occur at several points; in the gas phase, in catalytic pores, on inactive catalytic sites. However all coke is principally formed by cracking style reactions which generate coke precursors. Dehydration and cyclisation reactions generally proceed by the formation of carbocation intermediates on acid sites, these intermediates can react further to form larger carbocations or aromatics, which in turn can react on to yield poly-ringed aromatic structures and condense

out as coke on the catalyst surface. Due to the relatively high stability of larger polyatomic carbocations, they can remain growing for a relatively long time before termination occurs. With this in mind, it is clear that the larger unsaturated hydrocarbons should be more susceptible to coke formation, and a general order of speed of coke formation is; poly-ringed aromatics > benzene derivatives > alkenes > branched alkanes > normal alkanes.

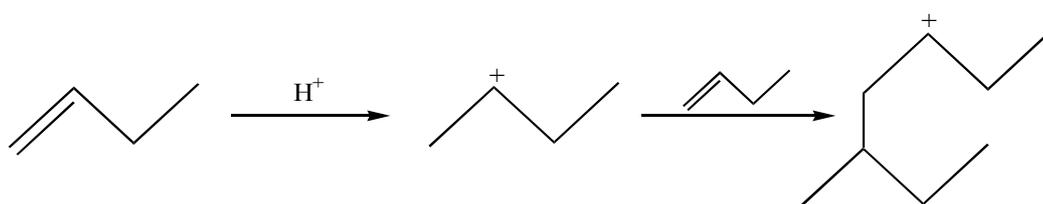


Figure 1.3-Initial formation of a coke precursor from butene

In addition to the structure of the starting material, the acidity and pore-size of the catalyst also play major roles in the rate of coke formation, especially with reference to zeolite catalysts. For catalysts with small pores coking rates are lower. However, a smaller amount of coke can lead to a substantial loss of activity; it is also seen in such cases that there is a large difference in coke yield between surface and pore sites. As carbocation formation plays an important role in coke reactions, it follows that the acid sites are important to coke formation, with a higher concentration of strong acidic sites leading to a more rapid build up of coke precursors in the system. Several studies of coke formation in reactions over zeolites⁴⁶⁻⁴⁸ have all reached similar conclusions; it appears that both acid-site poisoning and pore blockage play a significant role in catalyst deactivation. At low coking rates and coverage, and high temperatures acid-site poisoning is the more prominent factor, whereas at high coking rates

and coverage and low temperatures pore blockage is the major factor. Commercially speaking the latter seems the more important, with catalysts with small pores, such as H-ZMS-5, typically having higher deactivation rates.

The effect of substrate should also not be underestimated, for example using H-ZMS-5 with mesitylene forms coke predominantly on the external zeolite surface whereas with an isobutene substrate, coking occurs inside the pores of the zeolite. When toluene is used large poly-ring aromatic coke structures are formed both in the pores and on the external surface of the zeolite.⁴⁹

1.5.2-Supercritical Fluids and Catalyst Deactivation

With their unique combination of liquid and gas like properties, an increasing body of evidence has built up suggesting that supercritical fluids could be ideal reaction media to counteract catalyst deactivation due to coking.

The possibilities of using supercritical fluids in this way were illustrated by Wei's⁵⁰ study of the dehydrogenation of medium chain length normal alkanes over an alumina catalyst. When this reaction was performed in sub critical conditions, the catalyst deactivated steadily; however when the reaction was performed above the critical pressure and temperature of the alkane being studied an improvement in the rate of the reaction was observed. This improvement was accompanied by an elimination of catalyst deactivation for over one hundred hours.

Subramaniam has carried out in depth studies in the field.⁵¹ Of particular interest was his research on the isomerisation of hex-1-ene over a platinum/aluminium catalyst.⁵² Normally this process would deactivate in under 10 hours. However, using conditions above the critical point of hexane, it was possible to prolong the life of the catalyst as well as halving the lay down of coke (measured as a percentage increase in weight of the catalyst). A more dramatic effect was observed when a feed pre-treated to remove peroxides was used in conjunction with supercritical conditions. In this case no coke lay down was observed over a forty-hour period. The pre-treatment had such a dramatic effect because peroxides form radicals under the reaction conditions, and these radicals promote the coking process.

Another process that has been studied is the alkylation of isobutene over a solid acid catalyst.⁵³ In this case, initial attempts at the process under supercritical conditions at the normal reaction temperature (140°C) slowed the rate of coking but did not prolong the catalyst lifetime greatly. By performing the reaction at a lower temperature (50°C) the yield of the desired alkylate was reduced; however the reaction could be run for over 30 hours without any major loss of catalytic activity.

The concept of coke removal by supercritical fluids was first reported by Tiltcher, when investigating the isomerisation of hex-1-ene on a platinum doped alumina catalyst.⁵⁴ An activity enhancement was observed when the reaction was performed above the critical temperature of hexene and at 500 bar. Tiltcher

attributed this result to the removal of oligomers from the catalyst and cited the increased presence of higher molecular weight oligomers in the effluent stream as evidence.

Tiltscher's findings led to investigation of supercritical fluids for use in regenerating spent catalysts. One such study focused on Zeolite Y catalysts that had been deactivated in the liquid phase alkylation of isobutene.⁵⁵ After the catalyst had been completely deactivated, isobutene was passed over the catalyst at various pressures and temperatures, for various lengths of time. For all of these variables they observed an optimum regenerating value, managing to recover 80% of the original activity in some cases. It was also observed that manipulating the way in which the coke was formed and aged on the catalyst surface would have a knock-on effect on the ability of the catalyst to regain its activity.

A separate study compared the regeneration of different zeolites, deactivated under the same conditions.⁵⁶ Mordenite, Y, and β zeolites were deactivated using the isobutene alkylation reaction. The catalysts were regenerated under supercritical isobutene for one hour. It was found that, while none of the chosen solid acids completely recovered their initial activity, all did display an improvement in catalytic activity due to the regeneration process. It was noted that the loss of activity and regeneration was less pronounced in the cycle for β -zeolite; this was thought to be due to the narrow-pores of the zeolite hindering formation of the major coke precursor.

These results would appear to show that supercritical fluids can extract coke from solid-acid zeolite catalysts. In a review⁵⁷ Subramaniam stated that the reasons for activity enhancement in supercritical fluids were threefold, not simply due to solution of coke precursors;

- (i) Extraction of heavy hydrocarbons from the catalyst surface and their transportation away from the reactive sites
- (ii) Complete miscibility of reactants in reaction mixture and enhanced transportation to active site
- (iii) Control of temperature rises in exothermic reactions

1.5.3-Alkylation Reactions

One of the largest areas of research using supercritical fluids and zeolitic catalysts is alkylation reactions. Of particular interest is isoparaffin alkylation, this reaction is of importance to the petroleum industry where it is used to produce a high-octane blend product. It is run industrially as a homogeneous process because heterogeneous alternatives suffer badly from coking. It has been shown that performing the reaction under supercritical conditions for the reaction mixture can suppress catalyst deactivation.⁵⁸ However, the elevated temperatures required led to the promotion of undesirable side-reactions.⁵⁹

It is possible to lower the critical temperature of the reaction mixture by addition of a co-solvent⁶⁰⁻⁶² with a lower critical temperature. Subramaniam⁶⁰ studied the reaction using carbon dioxide as a co-solvent, and found that at lower

temperatures the undesirable side-reactions were less prevalent. Under these conditions stable conversions to alkylate were observed for over 40 hours.

Querini discovered that the coke left on the surface of the catalyst from such supercritical mixtures is similar in character to that laid down by liquid-phase reactions, having a higher H/C ratio than coke left by gas-phase reactions.⁶³

As discussed above Ginosar et al have shown recovery of catalytic activity is possible by supercritical regeneration of the catalyst.⁵⁶ Further research into regeneration with various supercritical fluids, the nature of the coke deposited, and supercritical co-solvents,⁶⁴⁻⁶⁶ led to the development of a system for in-line catalyst regeneration for a commercial feed for the reaction.⁶⁷ This system performed the reaction in the liquid phase for several hours. The runs of the liquid phase reaction was interspersed with two hour periods under flow of supercritical isobutane to regenerate the catalyst. This system greatly enhanced the catalyst lifetimes. After 3 regeneration cycles, activity was still above 70% of its original value. The authors speculated that, by improving the catalyst and reactor design, even better results could be achieved.

The alkylation of benzene with ethene in supercritical carbon dioxide was investigated by Shi et al.⁶⁸ It was shown that enhanced selectivity and reduced deactivation for the reaction could be achieved for a zeolite Y catalyst when compared to gas or liquid phase reactions. These results were attributed to better solution and transportation of coke precursor from the catalyst surface. In a later

study on the same reaction over a zeolite β catalyst, Gao hypothesised that high-pressure conditions in the near critical and supercritical regions required for these reactions may be harmful for the structure of the catalyst. This was evidenced by the change in structure observed by XRD of the catalyst before and after reaction.⁶⁹

Improved catalyst activity has also been shown for Zeolite β when alkylating benzene with ethene when performing the reaction above the critical parameters for the reaction mixture, although this was accompanied by a loss in selectivity to the desired product when compared to the liquid phase reaction.⁷⁰

The alkylation of toluene with ethylene was studied over zeolite Y using a co-solvent above its critical temperature and pressure, propane.⁷¹ In this case increased catalyst deactivation was observed above the critical parameters. However this was accompanied by an increase in selectivity to the desired product. This 'selective' deactivation was attributed to the loss of Brønsted acidity disfavoured the cracking and coking side reactions.

There have been various other studies of alkylation of aromatics in supercritical fluids.⁷²⁻⁷⁵ All these investigations report improved catalyst lifetime through the use of a supercritical medium in the reaction.

It should be remembered that microporous zeolites are not the only solid acids available for heterogeneous catalysis. Alkylation of both mesitylene and

anisole have been shown to be possible in various supercritical fluids using DELOXAN, a solid supported acid catalyst.⁷⁶

More recently the alkylation of anisole with propan-2-ol in supercritical carbon dioxide was studied over a variety of solid-supported acid catalysts, and zeolite Y.⁷⁷ In general it was discovered that the inorganic supported catalysts, and zeolite Y had higher optimum performance temperatures than the organic supported catalyst studied.

In a similar study, the alkylation of *m*-cresol with isopropanol and propylene in supercritical carbon dioxide was compared over an organic-supported catalyst and γ -Aluminium oxide.⁷⁸ In this case it was discovered that it was possible to perform the alkylation with isopropanol over the aluminium oxide catalyst with good conversions and selectivity. However the authors note that similar conversions can be achieved with no carbon dioxide present.

1.5.4-Isomerization Reactions

Most activity in this field has centred round the isomerisation of hex-1-ene. The initial findings of Tiltscher⁵⁴ and the work of Subramaniam and his conclusions^{51, 52, 57} have already been discussed. More recently Subramaniam has been varying the catalyst used for this reaction,⁷⁹ in particular comparing the rates of diffusion under supercritical conditions through catalysts with different pore-sizes.

The isomerisation of n-butane over a modified zirconia catalyst is of interest to the petroleum industry.⁸⁰ Unfortunately, despite good conversions, the catalyst is prone to rapid deactivation due to coke formation on the catalyst surface, when the transformation is performed as a gas phase reaction. Krasushaar-Czarnetzki et al^{81, 82} studied the reaction above the critical temperature for butane at various pressures. They discovered that, when the pressure was above the critical pressure a steady level of conversion was observed over a three-hour period. An increase in initial conversion of up to 5 times was also observed under supercritical conditions. It was noted that at higher temperatures under supercritical conditions the catalyst became denatured and accordingly deactivated with time. In a separate study similar effects were observed for the isomerisation of n-pentane over a similar catalyst.⁸³

1.5.5-Cracking Reactions

Cracking is another important reaction for the petroleum industry, in which the catalyst suffers rapid deactivation. Dardas et al⁸⁴ showed that the cracking of heptane over zeolite Y is possible under supercritical conditions. In these reactions it was noted that there was an increased concentration of heptane inside the pores of the catalyst and that the deactivation of the catalyst was slowed.

Supercritical fluids have also been used in the cracking of bitumen.^{85, 86} Several different supercritical fluids and catalysts were studied for the process; however it was discovered that to get high conversion and reasonable catalyst

lifetime the use of a supercritical fluid alone was not enough; the presence of hydrogen gas was also required.

1.5.6-Other Reactions

There is a wide range of other heterogeneous reactions that have been performed in supercritical fluids including disproportionation,⁸⁷ etherfication,⁸⁸ Fischer-Tropsch reactions,⁸⁹ hydrogenation,⁹⁰ in supercritical carbon dioxide and oxidation in supercritical water.⁹¹⁻⁹³ This review is far from comprehensive and is only intended to give the reader an outline of the capabilities of supercritical fluids as reaction media for heterogeneously catalysed reactions.

1.6-This Project

The results reported would appear to indicate that supercritical fluids can greatly improve heterogeneous catalysts lifetime when used as the reaction medium. This project intends to look at processes that can be catalysed by simple cheap commercially available zeolites, but suffer from rapid catalyst deactivation. The catalyst activity over time will be compared above and below the critical pressure for carbon dioxide, in the hope of seeing an enhancement in catalyst lifetime.

In order to facilitate the study of heterogeneously catalysed reactions at high pressures and temperatures it will firstly be necessary to design and assemble a rig on which such reactions can be performed. The rig would be

required to meet many criteria. The most important of these requirements being to be able to withstand and control high pressures and temperatures for reaction, facilitate the use of supercritical carbon dioxide, allow access for highly volatile liquids, allow access for gases other than the reaction medium, and provide a simple method of sampling the product stream.

The first reaction to be studied will be the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam. This process is well known industrially as ϵ -caprolactam is used in the synthesis of nylon. Industrially a homogeneous process is used to affect the rearrangement; however, due to a number of perceived short-comings of the homogeneous process there has been extensive research into the possibility of viable heterogeneously catalysed alternative process. Rapid catalyst deactivation has plagued the studied heterogeneous alternatives. This makes the reaction ideal to study in this project. However, the high temperatures required for the heterogeneous process will lower the density of the carbon dioxide used in the reaction at higher pressures. An important area of the study will, therefore, be the comparison of results obtained at high pressures of carbon dioxide to results obtained under the same pressures with nitrogen.

The second reaction to be studied will be the Fries rearrangement of phenyl acetate to hydroxyacetophenones. This process is well known industrially as a route to acylated phenols, and is generally performed as a homogeneous process with aluminium chloride as the catalyst. However, due to the corrosive and toxic nature of aluminium chloride research has been ongoing

into finding an alternative method of this rearrangement, either through use of a heterogeneous process or photolysis. Using photolysis generally leads to poor yields of the desired product and the heterogeneous catalyst studied suffer badly from catalyst deactivation. The process is, therefore, ideal for study in this project. The process can be affected at considerably lower temperatures than the Beckmann rearrangement of cyclohexanone oxime (150°C) and it will thus enable the use of higher densities of carbon dioxide. Once again the comparison of carbon dioxide with nitrogen will form a key part of the study.

The third process to be studied will be the Diels-Alder addition of methyl acrylate to isoprene. This reaction is well known industrially as a route to cyclohexene derivatives, and the process is most commonly performed using a Lewis acid as a catalyst. As these Lewis acid catalysts are generally corrosive and toxic there has been a considerable amount of research into finding a viable heterogeneous alternative. As with the Beckmann and Fries rearrangements above these studies have been plagued by rapid catalyst deactivation. The heterogeneous process is possible under 100°C and is therefore ideal for the purposes of this project to study under higher densities of carbon dioxide. The comparison of the results obtained with carbon dioxide to results obtained with nitrogen will be key in determining the effect of using carbon dioxide as the medium in the process.

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Chapter 2-Catalysis Rig- Design,
Maintenance & Operation

2-Catalysis Rig- Design, Maintenance & Operation

2.1-Introduction

As detailed in the previous chapter, the purpose of this project was to assess the use of carbon dioxide above its critical temperature and pressure as a medium for heterogeneously catalysed reactions. The first step of this project was, therefore, to design and assemble a rig that was appropriate to the work that was intended to be performed.

In the initial project proposal three areas of study were discussed, these were the Cyclar process, the Caprolactam process, and the possibility of immobilised catalysts in hydroformylation. For these processes to be studied using supercritical carbon dioxide the rig would be required to meet many criteria. The most important of these requirements being to be able to withstand and control high pressures and temperatures for reaction, facilitate the use of supercritical carbon dioxide, allow access for highly volatile liquids, allow access for gases other than the reaction medium, and provide a simple method of sampling the product stream.

The design and assembly of a rig meeting these requirements would take a considerable length of time; therefore it was fortunate for this project that at this time an inactive rig was in the possession of the research group to form the backbone of the new design.

2.2-Original Rig Design

The rig (figure 2.1) had been used to investigate the possibility of using solid supported catalysts in hydroformylation in conjunction with supercritical fluids. As would be expected this rig already met many of the requirements for the project. The rig could be broadly split into two sections, a high-pressure section and a low-pressure section. The high-pressure section begins with a Pickel Supercritical Fluid Pump. This, when connected to a carbon dioxide liquid feed cylinder, can deliver carbon dioxide at pressures up to 600 bar. The pressure of carbon dioxide in the system was controlled by an inlet valve (PCV1), which could allow up to 300 bar of gas to pass into the system. Immediately after the inlet valve, there was a pressure gauge, to monitor the pressure before the reactor, and a non-return valve to prevent gas, liquid, or supercritical fluid from the system flowing back to the Pickle pump.

Just before the reactor there were connections to allow the introduction of liquids and gases. A syn gas cylinder was connected to a Haskell gas booster capable of increasing the pressure of syn gas up to 800 bar. This was connected to a dosimeter (D), which controlled the rate at which syn gas was allowed into the system.

After this pair of connections was the reactor. The reactor was made from a 10 cm length of 12 mm stainless steel tubing, resulting in a reactor volume of around 11 ml. The reactor was surrounded by an aluminium heating

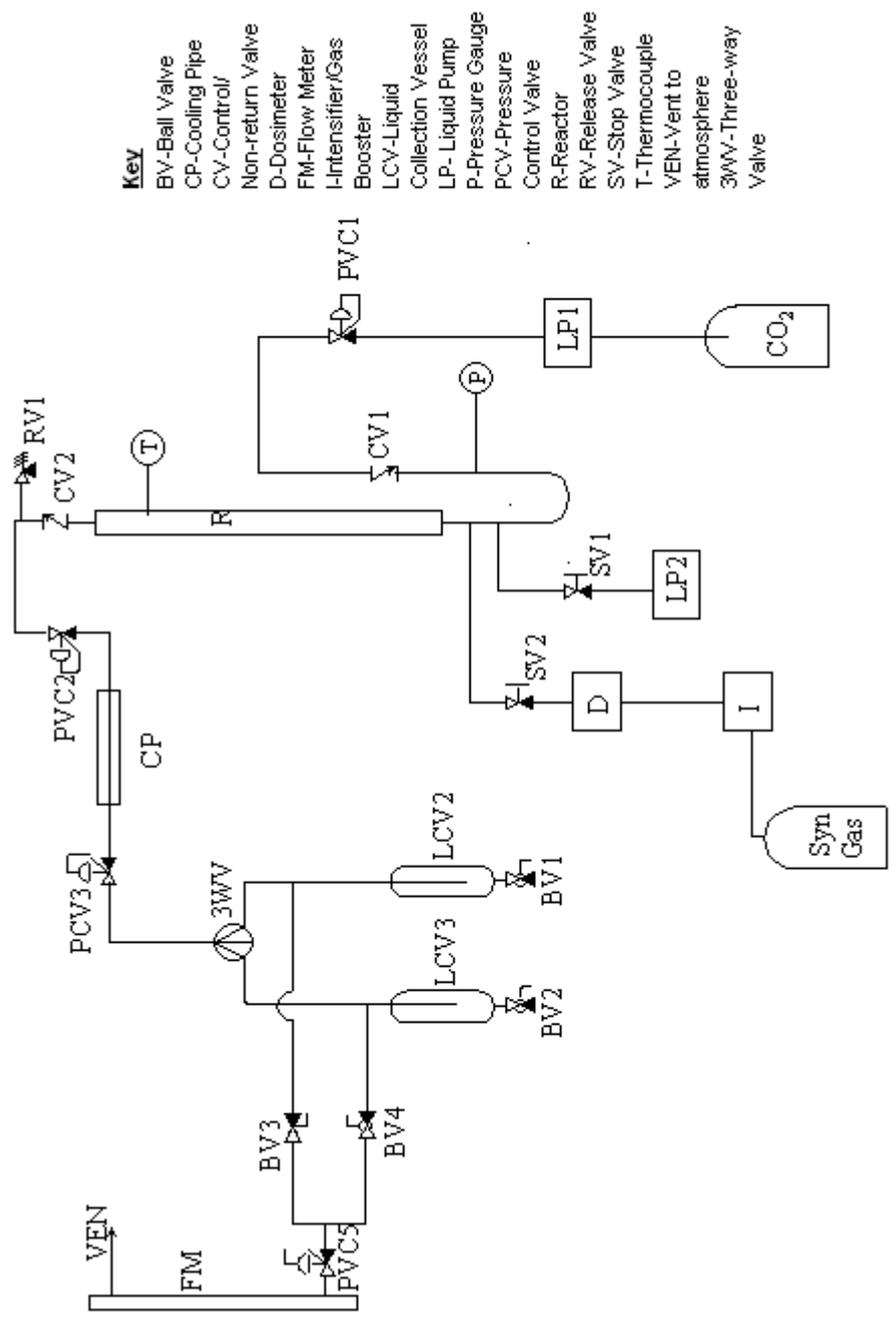


Figure 2.1- Diagram of Rig before the start of the project

block, which was heated by two heating elements. The temperature was controlled using a J-type thermocouple placed inside the reactor and connected to the heating elements.

Downstream of the reactor there was a filter; this was added to the apparatus due to problems of the catalyst blowing out from the reactor. Beyond the filter was a pressure control valve (PCV2), at which point the high-pressure section of the rig crossed to the low-pressure section. This pressure control valve lowers the pressure to below 10 bar; the product stream is then passed through a brass condenser pipe to cool it, before passing through another pressure control valve (PCV3). After this final pressure control valve the product stream can be passed through one of two collection chambers from which samples can be taken without disrupting the flow of gas from the system. Finally the gas is vented from the system through a flow meter, with the rate of venting being controlled by a needle valve located just before the flow meter.

2.3-Design of Project Rig

The original rig design met all of the stated criteria to a certain extent, but there were still several areas in which it was felt that the design could be improved in order to facilitate ease of handling and maintenance of the rig.

Before any work on the rig itself could be performed, it was required to relocate the rig into a new fume cupboard. The original rig was operated in a

cramped fume cupboard, which necessitated that the pumps were outside the fume cupboard. It also meant that it was difficult to isolate faulty equipment for repair without removing several pieces of kit. Fortunately shortly after this project was started, the research group gained access to recently refurbished laboratories, and the rig was moved into a larger fume cupboard that enabled all the pieces of kit to be together and facilitated simplicity of isolation of all the equipment in the rig.

The high pressure and low pressure sections of the rig were attached to a sheet of stainless steel which in turn was supported on a steel framework attached to the back of the fume cupboard and the whole system was earthed by connection to the water pipes.

The plan for the modified rig can be seen in figure 2.2. As with the original design, the rig can once again be split into high pressure and low-pressure sections and, as before, the high-pressure side can be thought of as beginning with the carbon dioxide source. The source of carbon dioxide was kept exactly the same, so it consisted of a liquid feed cylinder of carbon dioxide connected to a Pickel supercritical fluid pump to deliver high pressures to the inlet valve PVC1.

However, an important part of the project would be the comparison of results obtained using carbon dioxide as the reaction medium with results obtained using nitrogen as the reaction medium under the same conditions. For this to be possible it was necessary to add a nitrogen inlet source. For these

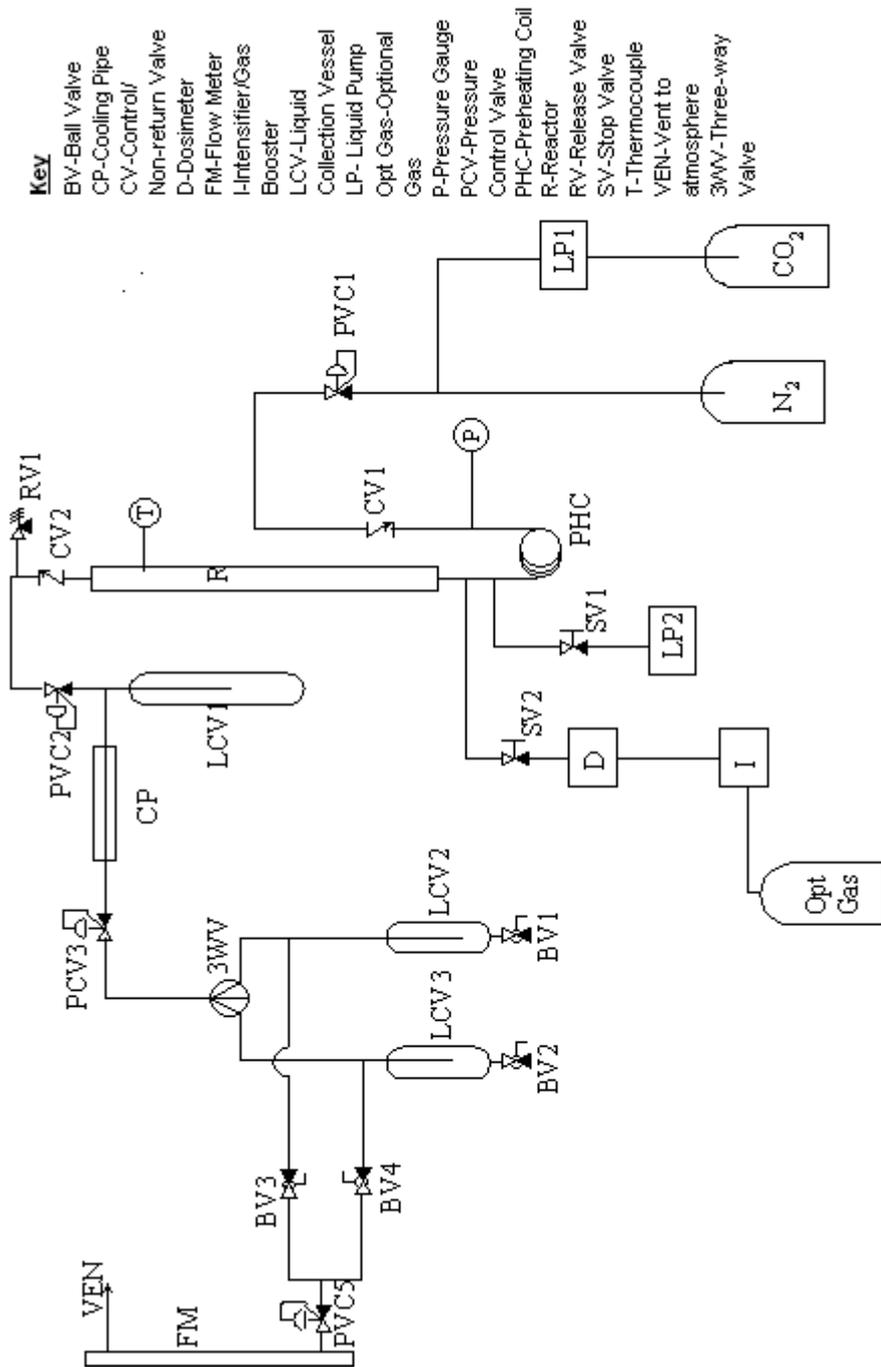


Figure 2.2- Diagram of Rig layout at the conclusion of the project

reactions a nitrogen cylinder was connected to a Haskell gas booster, which in turn could be connected to the inlet valve PVC1. As there was no perceived prospect of performing a reaction that would require the use of nitrogen as the reaction medium and the use of the dosimeter to inject a gas into the system, it was decided that one gas booster could perform both functions.

The next segment of the rig remained largely the same as the original design. The inlet valve was retained, it was rated up to pressures of 300 bar, which would therefore be the upper pressure limit in the high-pressure section of the rig. After the inlet valve, the reaction medium would pass through the original non-return valve to prevent a back flow of medium from the reactor to the pump/booster in the event of a pressure build up in the reactor. After the non-return valve the medium passed through a pressure gauge to monitor the pressure in the high-pressure section of the rig.

The next addition to the rig was a pre-heating coil. The plan for the modification to the rig did not include a pre-heating coil; however the pre-heating coil was added shortly after modifications to the rig were finished, so it is included in this part of the discussion. The pre-heating coil was made by winding 1 metre of stainless steel $\frac{1}{8}$ " tubing round a 2" diameter aluminium cylinder. The aluminium cylinder was heated by two chrome heating elements and the temperature was monitored and controlled using a J-Type thermocouple.

The addition of the pre-heating coil was deemed necessary to ensure that the reaction medium was at the reaction temperature and pressure before entering the reactor. Without the pre-heating coil the reaction medium would enter the reactor at the correct pressure, but below the reaction temperature, meaning that it would require time to heat up to the reaction temperature. Depending on how quick this process was this could mean the bottom of the catalyst bed being below the reaction temperature and possibly inactive in the reaction.

After the pre-heating coil there are two inlets, one for gas substrates and one for liquids as in the original rig. The gas inlet system was taken straight from the original rig. The gas was passed through a Haskell gas booster, and then connected to a Rheodyne gas dosing unit. The dosimeter controls the rate at which gas is allowed into the system. It consists of six ports that sit on top of a disc, this disc has three groves on its surface, and each groove connects a pair of ports (figure 2.3). In this instance, port 1 was the connection to the gas booster, ports 2 and 6 were attached to gas reservoirs, ports 3 and 5 were connected to the rig, and port 4 was blocked off by use of a cap as it was not required for this system. The reservoirs were capped tubes that filled with gas to a pressure set by the gas booster when connected to the inlet. When connected to the system through one of the outlets the gas contained within the reservoir was allowed into the reaction medium. The mechanism for this process can be seen in figure 2.3. In position 1 the inlet to the dosimeter is connected to reservoir 1, filling this reservoir with gas to the pressure of the inlet, at the same time reservoir 2 is connected to one of the outlets to the rig, allowing the gas contained in this reservoir to mix with the reaction medium. Meanwhile the second outlet to the

system is connected to the capped port and is inactive in the mechanism. The disc of the dosimeter is then switched into position 2, now the inlet is connected to reservoir 2, refilling this reservoir with gas from the gas booster, and reservoir 1 is now connected to the rig through one of the outlets, allowing the gas collected in the reservoir in position 1 access to the rig. Once again the outlet not connected to a reservoir is connected to the capped port and is inactive. The disc of the dosimeter is then switched back to position 1 and the cycle is repeated from there.

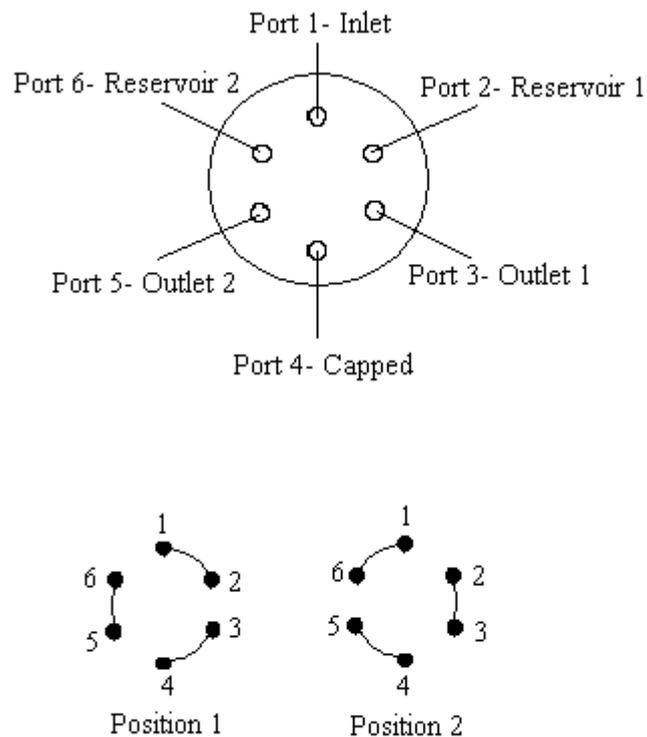


Figure 2.3-Diagram of Gas-Dosing Unit Ports, and connection of ports during Switching

The only modification to the dosimeter from the original was the addition of two 1 ml reservoirs to replace the older reservoirs of unknown volume. This was an important addition as, if the pressure and volume of gas in the reservoir and the pressure and volume of medium in the rig are known, the number of moles of gas allowed into the system upon each switching of the disc of the dosimeter can be calculated as follows; Moles of gas introduced per second = switch rate x volume of reservoir x (pressure in dosimeter – pressure in system). Therefore by adjusting the frequency of the switching the number of moles of gas allowed into the system can be controlled.

Similarly the liquid inlet to the rig was almost identical to that in the original rig. It consisted of a Gilson 305 HPLC pump with a liquid feed tube dipped in the liquid substrate. The pump consists of a metal paddle between a pair of check valves. The check valves prevent flow of liquid from the rig back through the HPLC pump, while the paddle simultaneously draws liquid into the pump from the liquid source and pushes liquid from the pump into the rig.

One perceived problem with the HPLC pump was the temperature of the head of the pump during its operation. When in use the head of the pump heats up considerably. For some applications, a liquid feed of low boiling high volatility liquids might be required. It is probable that such liquids would vaporise in the pump head, stopping the pump from functioning as required.

This problem could be overcome by using an Anachem HPLC cooled-head pump. This piece of equipment operates on the same principle as a

refrigerator and consists of a large box where heat is dissipated and a metal cover for the head of the HPLC pump from which heat is removed. By using a cooled-head it was possible to keep the temperature of the HPLC pump below $-15\text{ }^{\circ}\text{C}$, thus enabling the injection of high volatility liquid substrates to the rig.

After the addition of gas and/or liquid substrates the medium would pass into the reactor (figure 2.4). This part of the rig was unmodified from the original design, consisting of a 12 mm stainless steel tube with a J-type thermocouple to monitor the temperature of reaction. The thermocouple was connected to the aluminium heating block that surrounds the reactor via a heat control box, this controlled the temperature of the heating block through two chrome heating elements, located on opposite sides of the reactor.

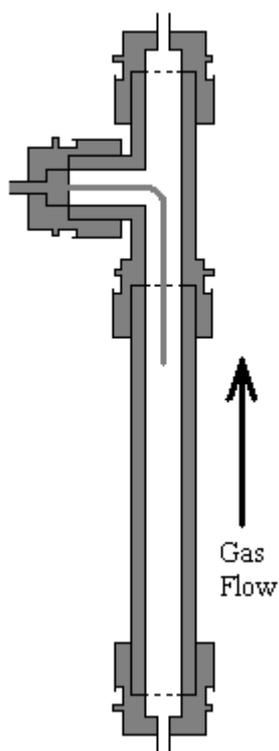


Figure 2.4- Cross Section of Reactor and Thermocouple

The only slight modification to the original design involved the heating elements. Previously these had been connected in series. This meant that if one developed a fault it was impossible to determine which one without removing both and then connecting individually. This problem was simply overcome by re-wiring their connection to the heat control box, so that the two heating elements were in parallel to each other in the circuit. Thus it became possible to remove the element individually, simply and quickly if one developed a fault.

An important consideration, when designing a rig, is whether to use 'up flow' or 'down flow'; referring to the direction in which the reaction medium is passed through the reactor over the catalyst bed. In a 'down flow' reactor it is possible that, when using a fine particle catalyst, the downward force on the catalyst bed can lead to compacting of the catalyst, this in turn can lead to blocking of the reactor. It was due to earlier experiments that the original rig was constructed with an 'up flow' design, and the reason that this design was maintained after consideration for this project. However, it should be noted that, for biphasic reactions, the use of a 'down flow' reactor has the advantage that both phases will pass through the reactor and interact with the catalyst; with a 'up flow' reactor the liquid layer would fill the reactor, leading to observation of only the liquid reaction, as the gas phase will play no part in the reaction.

After the reactor the filter to catch catalyst that blew out of the reactor was retained. Immediately after this filter a new inline sampling port was inserted. When considering the various methods for sampling the product stream

from the reactor, sampling directly from the high-pressure section of the rig, immediately after the reactor, was seen as one of the best options to give a true indication of the make up of the product stream. To this end the inline sampling port was built (figure 2.5). It consisted of a ball valve, a needle valve and outlet for connection to a GC. Both valves would remain closed for the majority of the reaction time. When a sample was required the ball valve would be opened briefly then closed again. This would fill the area between the ball valve and needle valve with a sample of the product stream from the high-pressure section of the rig. By then opening the needle valve, if the outlet were connected to a GC, the sample would be injected directly into the GC.



Figure 2.5-Diagram of Inline Sampling Port

The inline sampling port is the last modification to the high-pressure section of the rig. After passing this port the product stream passes through the expansion valve PVC2 that marks the border between the high pressure and low-pressure sections of the rig.

After passing through the expansion valve PVC2, the expanded gas passes directly into a new collection vessel. In the original design the expanded gas would pass through a condensing pipe and through a second expansion valve

before passing through the collection vessels. However it was felt that the combined effects of the expansion of the reaction medium and the cooling of the medium partially as a result of this expansion, would be enough to condense out any liquids and solids being carried by the reaction medium.

The collection vessel (figure 2.6) was made by connecting two stainless steel containers together. A length of tubing carrying the product stream from the expansion valve PVC2 was dipped into the collection vessel to near the base of the upper steel container, where it was left open to the collection vessel. The product stream should then separate into expanded gas and a liquid product sample. The liquid sample would collect in the lower steel container that had a ball valve at the base for simple removal of the liquid. The expanded gas would continue onwards downstream through the gas outlet at the top of the upper container.

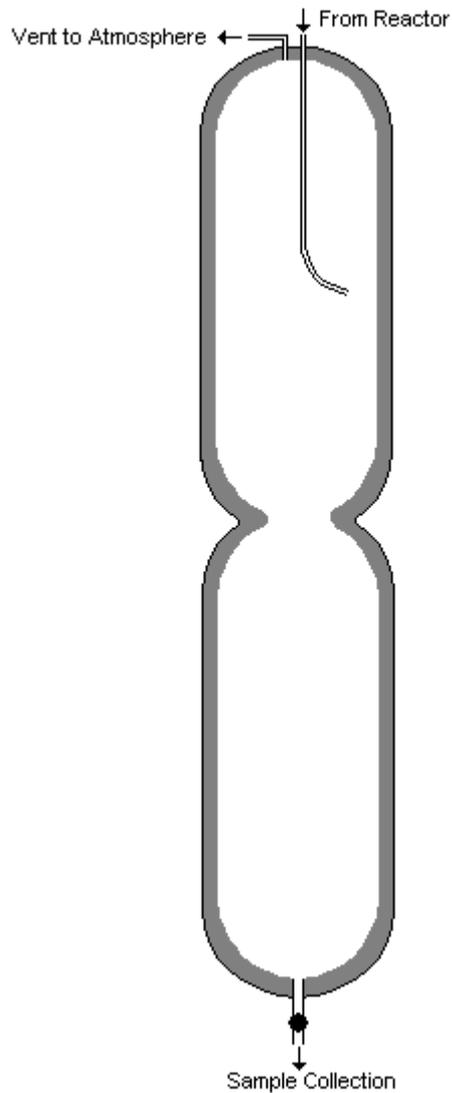


Figure 2.6- Cross-Section of Collection Vessel

After passing through the collection vessel the expanded gas passes through the sampling system from the original rig. This was retained as a back up to the new collection vessel and also as a vent for gas from the system.

The expanded gas passes through a brass cooling pipe and then reaches a second expansion valve PVC3. After passing through this second expansion valve the expanded gas passes through the original sampling system, consisting

of a three-way valve that directs the gas to one of the two collection vessels or closes the system at this point. After passing through one of the collection vessels the expanded gas is vented to the back of the fume cupboard through a flow meter, with the rate at which it is vented being controlled by a needle valve located just before the flow meter.

2.4-Rig Maintenance

The rig that had been constructed would remain largely unchanged throughout the project, indeed the only major change to the apparatus was the integration of a preheating coil, shortly after the completion of the modifications. This has already been discussed.

However the performance of the rig was at times unreliable and several pieces of equipment needed servicing or replacing at regular intervals. Thus the maintenance of the rig and related equipment became a large part of the project.

The most commonly occurring problem with the apparatus was that of dysfunctional pressure control valves. Both the inlet valve and the first expansion valve regularly developed problems. However the second expansion valve, PVC3, never developed any problems and was used for the duration of the project without need of additional attention.

The inlet valve, PVC1, was retained from the original rig, and was rated to withstand inlet pressures of up to and including 300 bar. This value was

therefore used as the maximum pressure for reactions. However, only two reactions were performed at 300 bar, as, after the second reaction, the inlet valve stopped controlling the pressure and in effect became an open section of piping. Inspection of the valve revealed that the metal diaphragm that controls the rate at which gas passes through the valve had buckled and was always fully open. It was concluded that the valve was beyond repair as it would require a new diaphragm, and the valve was discarded. At the time that this decision was made there were no pressure control valves available that could deliver 300 bar to replace the valve. However it was decided that the ability to perform reactions at 300 bar was not vital to the project and that a pressure control valve with a lower delivery capability could be used. At the time of this decision the best immediately available replacement was a Druva high-pressure control valve. The Druva valve could withstand inlet pressures of up to 250 bar, however it was only rated to deliver up to and including 200 bar to the high-pressure section of the rig. Thus 200 bar became the maximum pressure for reactions for the remainder of the project.

While the Druva inlet valve was used until the end of the project, this valve had associated problems itself. The valve required servicing on several occasions, when the valve seized up and would not open, effectively blocking the rig at this point. When this occurred the valve could not be repaired *in situ* and had to be returned to Druva for servicing.

The second pressure control valve (PVC2) was also retained from the original rig. It required occasional servicing due to gradual disintegration of o-

ring seals contained inside the valve. These replacements were both simple and cheap. Eventually, after prolonged use in the rig an internal thread became worn. This meant that the valve became extremely difficult to adjust and began to leak small amounts of gas through it even when fully shut. Unfortunately this meant that the valve had to be discarded and replaced.

At this point in the project, once again, the best available expansion valve was a Druva valve. In this instance it was a high pressure to low-pressure gas expansion valve. The maximum input for this valve was 200 bar, which corresponded to the maximum reaction pressure, and the maximum output was 50 bar, much higher than would be necessary for this project. However the valve had a minimum output of 5 bar and was unreliable when used below this pressure. As with the previous valve the internal o-rings gradually disintegrated and needed to be replaced at regular intervals. As well as this problem the valve regularly stopped delivering a constant pressure of gas and would instead deliver the gas in a series of bursts leading to fluctuations of pressure in the low pressure section of the rig, making control of the overall flow rate impossible. When this occurred the valve had to be returned to Druva to replace the diaphragms inside the valve.

Another area that required a high level of maintenance was the reactor. The heating elements used to heat the reactor needed regular replacement. They had to be removed after every reaction run in order to access the reactor. As the wiring to the heating elements was fragile it is unsurprising that frequently a break in the circuit occurred. Fortunately, due to the rewiring of this section of

the rig so the heating elements were in a parallel circuit, replacement of a heating element was both quick and simple.

The reactor itself needed to be replaced regularly. The Swagelok fittings at either end of the reactor were recommended to be changed after every six opening and closing of the joint. This meant that each reactor that was made should only be used for 3 reactions when cleaning is taken into account. Initially several of reactions were run at temperatures approaching 400 °C, and there appeared to be, in certain instances, a problem of reactor leakage in longer term reactions. After consultation with Swagelok, it was advised not to use the nut and ferrule joints at temperatures above 250 °C, as the particular fittings used were not guaranteed above this temperature.

The only other maintenance carried out on the reactor was the replacement of the thermocouple, due to general wear and tear.

The Haskell gas booster was an important part of the rig, being used for both the source of high-pressure nitrogen as a reaction medium, and to intensify the pressure of substrate gases to be injected into the system. At the start of the project the gas booster was unable to increase the pressure of the gas passed through it. Looking inside the gas booster revealed that the air-drive pin was crooked and replacing this pin returned the booster to optimum performance. However, after this the booster developed a recurring problem with its air-drive section. When this problem occurred the booster would only be able to boost the pressure of gas passing through it slightly; less than 10%, and any attempt to

increase the boost in pressure would cause the booster to vent air through its exhaust. Initially the source of this problem could not be located, and the booster had to be returned to Haskell to be serviced. Haskell reported the problem to be the o-ring seals perishing in the air-drive section. This problem reoccurred on several occasions throughout the project. It is surprising that this should be such a prominent problem as the seals are in the air-drive section, and only come into contact with compressed air and not any gases which pass through the booster.

When the gas booster is used for injection of substrate gases into the rig, it is used in conjunction with a Rheodine gas-dosing unit. This, like the gas booster, is a relatively simple air-driven piece of equipment. The mechanism by which the gas-dosing unit injects gas into the rig has already been described. Problems arose when the reservoirs became blocked. The symptom of this blockage can be subtle. Partial blocking of one of the reservoirs will result in only a slight drop in gas injected. The blocking is a result of small amounts of the substrate mixture diffusing down the dosing unit outlet towards the reservoirs, where organic material crystallises out causing the blockage. This problem is simple to overcome by soaking the affected piece of the apparatus in acetone.

The method for liquid injection into the rig used a Gilson 305 HPLC pump. This was a very reliable piece of equipment. Integral to its mechanism were the two check valves located at the top and the base of the pump head. These check valves ensured that liquid flowed through the pump head in one direction only. The rare occasions that the pump stopped working arose because

small particles lodging in the check valves and preventing them from shutting. The liquid feed to the pump was fitted with a sinter to stop particles getting to the check valve. However, some very fine particles still got through. The particles were removed by sonicating the check valves in an ethanol bath for 1 hour.

2.5-Rig Operation

During the project the rig as described above was used to study three processes, the general procedure for operating the rig during these studies is outlined below.

2.5.1-Beckmann Reactions

Zeolite Y (2 g), prepared as outlined in 2.5.4, was placed in the reactor (R). The bottom of the reactor was filled with glass wool to ensure that the catalyst was tightly packed at the top of the reactor. The reactor was placed in the rig and all pressure control valves were closed. The nitrogen cylinder was opened to give a pressure of 50 bar up to PCV 1. PCV1 was opened to give a reactor pressure of 5 bar, and subsequent PCV2 and PCV3 were opened and adjusted to give a exit flow rate of nitrogen of $67 \text{ cm}^3 \text{ min}^{-1}$. The reactor temperature was then raised to 350°C and the system was maintained at this temperature for 2 hrs in order to remove water or residual organic compounds from the catalyst. After two hours, for reactions to be performed with carbon dioxide as reaction medium, the pressure control valves were closed and the gas feed was switched from nitrogen to carbon dioxide, the Pickel pump was

switched on and allowed to stand for 30 minutes in order for the pump to achieve a temperature at which liquid carbon dioxide was formed. After 30 minutes had elapsed the carbon dioxide cylinder was opened to the pump and the pressure raised to 400 bar, the pressure up to PCV1 was set at up to a maximum of 350 bar depending on the reaction pressure required. If the reaction to be performed used nitrogen there was no need to change the gas connection, however if the reaction was to be performed at a pressure of greater than 5 bar then the gas booster was connected to the air supply and the pressure of nitrogen up to PCV1 was set to 50 bar above the desired reaction pressure. The temperature of the reactor and the pre-heating coil were then set to the required reaction temperature. Once the required reaction temperature has been reached, PCV1 was opened until the reaction pressure was achieved. PCV2 was then opened until a pressure of 5 bar was achieved in the low pressure section of the rig. PCV3 was then opened and the needle valve adjusted to ensure an exit gas flow rate of $67 \text{ cm}^3 \text{ min}^{-1}$. Once the required temperature, pressure and flow rate had been achieved injection of the reactant solution was commenced; the head of the liquid pump was primed with the solution to be injected, the injection rate was set to $2 \text{ cm}^3 \text{ min}^{-1}$. Stop valve SV1 was opened and the liquid pump set to run. Reaction runs were timed from this point. Samples were taken by opening the valve at the base of LCV1 every 15, 30 or 60 minutes during the run, thus the sample would give the average position over the time period since the last sample of the run. Samples were analysed by GC-FID (see 2.5.5 below).

Reactant solutions for injection during the run were prepared by dissolving cyclohexanone oxime (113g, 1 mole) in ethanol, toluene or methanol (1 dm³).

Once the desired run time was completed the liquid pump was switched off, SV1 was shut, the reactor temperature and pre-heating coil temperature were set to 0°C, the nitrogen/ carbon dioxide cylinder was closed and the gas intensifier/ Pickel pump were switched off. Once the residual pressure of gas had diffused out of the system and the temperature had cooled to room temperature, the reactor was removed from the system and cleaned with water and acetone. The clean reactor was then replaced in the system, PCV1 was shut, the liquid pump was connected to an ethanol feed, primed with ethanol, SV1 was opened to the system and the liquid pump set to run at 2 cm³ min⁻¹. During this process PCV2 was left open and the system was allowed to completely fill with ethanol. Once this had been achieved ethanol was allowed to flow through the system for 50 mins, during which time the reactor and preheating coil temperature were raised to 90°C. After 50 mins had elapsed the liquid pump was switched off and SV1 was closed, the nitrogen cylinder was opened to PCV1 to a pressure of 50 bar, the reactor and preheating coil temperature were raised to 150°C and PCV1 was opened to allow a pressure of 10 bar into the system. The system was allowed to dry for 30mins once 150°C had been achieved, after which the nitrogen cylinder was closed and both the reactor and preheating coil temperatures were set to 0°C.

2.5.2-Fries Reactions

Zeolite β or zeolite Y (2.5 g), prepared as outlined in 2.5.4, was placed in the reactor (R). The bottom of the reactor was filled with glass wool to ensure that the catalyst was tightly packed at the top of the reactor. The reactor was placed in the rig and all pressure control valves were closed. The nitrogen cylinder was opened to give a pressure of 50 bar up to PCV 1. PCV1 was opened to give a reactor pressure of 5 bar, and subsequent PCV2 and PCV3 were opened and adjusted to give an exit flow rate of nitrogen of $67 \text{ cm}^3 \text{ min}^{-1}$. The reactor temperature was then raised to 350°C and the system was maintained at this temperature for 2 hrs in order to remove water or residual organic compounds from the catalyst. After two hours, for reactions to be performed with carbon dioxide as reaction medium, the pressure control valves were closed and the gas feed was switched from nitrogen to carbon dioxide, the Pickel pump was switched on and allowed to stand for 30 minutes in order for the pump to achieve a temperature at which liquid carbon dioxide was formed. After 30 minutes had elapsed the carbon dioxide cylinder was opened to the pump and the pressure raised to 400 bar, the pressure up to PCV1 was set at up to a maximum of 250 bar depending on the reaction pressure required. If the reaction to be performed used nitrogen there was no need to change the gas connection, however if the reaction was to be performed at a pressure of greater than 5 bar then the gas booster was connected to the air supply and the pressure of nitrogen up to PCV1 was set to 50 bar above the desired reaction pressure. The temperature of the reactor and the pre-heating coil were then set to the required reaction temperature. Once the required reaction temperature had been reached, PCV1

was opened until the reaction pressure was achieved. PCV2 was then opened until a pressure of 5 bar was achieved in the low pressure section of the rig. PCV3 was then opened and the needle valve adjusted to ensure an exit gas flow rate of $67 \text{ cm}^3 \text{ min}^{-1}$. Once the required temperature, pressure and flow rate had been achieved injection of the reactant solution was commenced; the head of the liquid pump was primed with the solution to be injected, the injection rate was set to $2 \text{ cm}^3 \text{ min}^{-1}$, and the stop valve SV1 was opened and the liquid pump set to run. Reaction runs were timed from this point. Samples were taken by opening the valve at the base of LCV1 every 15 or 30 minutes during the run, thus the sample would give the average position over the time period since the last sample of the run. Samples were analysed by GC-FID (see 2.5.5 below).

Reactant solutions for injection during the run were phenyl acetate provided by Acros chemicals.

Once the desired run time was completed the liquid pump was switched off, SV1 was shut, the reactor temperature and pre-heating coil temperature were set to 0°C , the nitrogen/ carbon dioxide cylinder was closed and the gas intensifier/ Pickel pump were switched off. Once the residual pressure of gas had diffused out of the system and the temperature had cooled to room temperature, the reactor was removed from the system and cleaned with water and acetone. The clean reactor was then replaced in the system, PCV1 was shut, the liquid pump was connected to an ethanol feed, primed with ethanol and SV1 was opened to the system and the liquid pump set to run at $2 \text{ cm}^3 \text{ min}^{-1}$. During this process PCV2 was left open and the system was allowed to completely fill

with ethanol, once this had been achieved ethanol was allowed to flow through the system for 50 mins, during which time the reactor and preheating coil temperature were raised to 90°C. After 50 mins had elapsed the liquid pump was switched off and SV1 was closed, the nitrogen cylinder was opened to PCV1 to a pressure of 50 bar, the reactor and preheating coil temperature were raised to 150°C and PCV1 was opened to allow a pressure of 10 bar into the system. The system was allowed to dry for 30mins once 150°C had been achieved, after which the nitrogen cylinder was closed and both the reactor and preheating coil temperatures were set to 0°C.

2.5.3-Diels-Alder Reactions

Zeolite β or Al-HMS (2.5 g), prepared as outlined in 2.5.4, was placed in the reactor (R). The bottom of the reactor was filled with glass wool to ensure that the catalyst was tightly packed at the top of the reactor. The reactor was placed in the rig and all pressure control valves were closed. The nitrogen cylinder was opened to give a pressure of 50 bar up to PCV 1. PCV1 was opened to give a reactor pressure of 5 bar, and subsequent PCV2 and PCV3 where opened and adjusted to give a exit flow rate of nitrogen of $67 \text{ cm}^3 \text{ min}^{-1}$. The reactor temperature was then raised to 350°C and the system was maintained at this temperature for 2 hrs in order to remove water or residual organic compounds from the catalyst. After two hours, for reactions to be performed with carbon dioxide as reaction medium, the pressure control valves are closed and the gas feed was switched from nitrogen to carbon dioxide, the Pickel pump was switched on and allowed to stand for 30 minutes in order for the pump to achieve

a temperature at which liquid carbon dioxide was formed. After 30 minutes had elapsed the carbon dioxide cylinder was opened to the pump and the pressure raised to 400 bar, the pressure up to PCV1 was set at up to a maximum of 250 bar depending on the reaction pressure required. If the reaction to be performed used nitrogen there was no need to change the gas connection, however if the reaction was to be performed at a pressure of greater than 5 bar then the gas booster was connected to the air supply and the pressure of nitrogen up to PCV1 was set to 50 bar above the desired reaction pressure. The temperature of the reactor and the pre-heating coil were then set to the required reaction temperature. Once the required reaction temperature has been reached, PCV1 was opened until the reaction pressure was achieved. PCV2 was then opened until a pressure of 5 bar was achieved in the low pressure section of the rig. PCV3 was then opened and the needle valve adjusted to ensure an exit gas flow rate of $67 \text{ cm}^3 \text{ min}^{-1}$. Once the required temperature, pressure and flow rate had been achieved injection of the reactant solution was commenced; the head of the liquid pump was primed with the solution to be injected, the injection rate was set to $2 \text{ cm}^3 \text{ min}^{-1}$, and then stop valve SV1 was opened and the liquid pump set to run. Reaction runs were timed from this point. Samples were taken by opening the valve at the base of LCV1 every 15 or 30 minutes during the run, thus the sample would give the average position over the time period since the last sample of the run. Samples were analysed by GC-FID (see 2.5.5 below).

Reactant solutions for injection during the run were prepared by forming a liquid mixture of isoprene and methyl acrylate (3:1 by volume, 2.7:1 by mole).

Once the desired run time had completed the liquid pump was switched off, SV1 was shut, the reactor temperature and pre-heating coil temperature were set to 0°C, the nitrogen/ carbon dioxide cylinder was closed and the gas intensifier/ Pickel pump were switched off. Once the residual pressure of gas had diffused out of the system and the temperature had cooled to room temperature, the reactor was removed from the system and cleaned with water and acetone. The clean reactor was then replaced in the system, PCV1 was shut, the liquid pump was connected to an ethanol feed, primed with ethanol and SV1 was opened to the system and the liquid pump set to run at 2 cm³ min⁻¹. During this process PCV2 was left open and the system was allowed to completely fill with ethanol, once this had been achieved ethanol was allowed to flow through the system for 50 mins, during which time the reactor and preheating coil temperature were raised to 90°C. After 50 mins had elapsed the liquid pump was switched off and SV1 was closed, the nitrogen cylinder was opened to PCV1 to a pressure of 50 bar, the reactor and preheating coil temperature were raised to 150°C and PCV was opened to allow a pressure of 10 bar into the system. The system was allowed to dry for 30mins once 150°C had been achieved, after which the nitrogen cylinder was closed and both the reactor and preheating coil temperatures were set to 0°C.

2.5.4-Catalyst Preparation

All solid acid catalysts were purchased from Zeolyst and used as received, except for Al-HMS which was synthesized as outlined in 2.5.7 below. Difficulties were encountered in early reactions performed, when the fine powder

of the catalysts received from Zeolyst caused blocking of the reactor, this was overcome by increasing the particle size of the catalyst as follows. Solid acid catalysts were pressed under a weight of 1.5 tonnes between stainless steel die ($r = 1$ cm) into pellets. The pellets were crushed in a pestle and mortar and passed through a 30/40 mesh. Catalysts were calcined at 350°C under a flow of nitrogen for 2 hours before each catalytic run, as outlined in the general procedures above.

2.5.5-Analysis

Solid and liquid chemicals were purchased from Aldrich, Acros and Avocado, and used as received. All zeolites were purchased from Zeolyst. All gases were purchased from BOC.

Dichloromethane was distilled over calcium hydride.

Proton NMR spectra were recorded on a Varian 500 NMR 300 MHz spectrometer. ^1H spectra were referenced internally to CDCl_3 ($^1\text{H} \delta = 7.26$ ppm).

Gas Chromatographic analyses were carried out on a Hewlett-Packard 5890 series gas chromatograph equipped with both a flame ionisation detector (GC-FID) (Quantitative analyses) and a Hewlett-Packard 5890 series mass selective detector for qualitative analyses. The gas chromatogram was interfaced with a Hewlett-Packard chemstation for the determination of peak areas by electronic integration. Both the GC-MS and GC-FID determination of products employed a SupelcoTM MDN-35 [bonded and crosslinked, 35% phenyl / 65%

methylpolysiloxane] fused silica capillary column 30 m x 0.25 mm x 0.25 μm film thickness. The carrier gas used was helium and the flow rate was 2.0 $\text{cm}^3 \text{min}^{-1}$ when using the mass selective detector and for the FID it was 2.3 $\text{cm}^3 \text{min}^{-1}$.

Powder X-ray diffraction data were collected on a STOE STADIP diffractometer operating on monochromated $\text{Cu K}\alpha$ radiation. Powder data were collected in transmission mode with the sample mounted between Mylar discs over 2 hours.

BET analysis was performed on a HIDEN intelligent gravimetric analyser. Samples were outgassed for 2 hours at 120°C under vacuum.

Samples from the reaction runs of the Beckmann rearrangement, Fries rearrangement and Diels-Alder reaction were all analysed in the same general method by GC-FID/ GC-MS. Samples for analysis were prepared by dissolving the sample (0.2ml) from the reaction run in dichloromethane (1ml). Retention times and response factors for reactants, products and side products were obtained by running GC's on samples obtained from chemical suppliers. In the case of N-ethylcaprolactam no chemical supplier was available, therefore the sample synthesized (see 2.5.6) was used to confirm/obtain the retention time and response factor.

2.5.6-Synthesis of N-Ethylcaprolactam

A 3-necked flask fitted with a reflux condenser and a calcium chloride drying tube, and under nitrogen, was charged with sodium hydride (2.4 g, 0.1 mol), caprolactam (11.3 g, 0.1 mol) and dichloromethane (200 cm³), the solution was stirred under reflux for 1 hr. After this period bromoethane (22 cm³, 0.2 mol) was added dropwise, and the mixture was then refluxed for a further 2 h. The hot mixture was filtered and the dichloromethane removed at reduced pressure to give a white solid of desired product (9.9 g, 70%). δ_{H} 7.12 (1H, br. s, OH), 3.30-3.20 (4H, m, NCH₂CH₃ and CH₂CH₂CO), 2.46 (2H, m, CH₂CH₂N), 1.68 (6H, m, COCH₂CH₂CH₂CH₂CH₂N), and 0.85 (3H, t, *J* 7, NCH₂CH₃); R_{t} = 8.44; m/z (ES⁺) 141 (M⁺, 100%), 126 (M⁺-CH₃, 60), 98 (M⁺-NHCHCH₃, 60), 85 (37), 58 (57).

2.5.7-Synthesis of Al-HMS

N-hexadecylamine (1.7 g, 70 mmol) was stirred in distilled water (20 cm³) and ethanol (10 cm³). Triisopropyl aluminium (4 g, 30 mmol) and Tetraethoxysilicon (20.8 g, 100 mmol) were added stepwise to the vigorously stirred solution. The suspension was stirred for 48 hrs at ambient temperature. The resulting white solid was collected by filtration and dried under nitrogen. The solid was then calcined at 500°C for 5 hrs in dry air. XRD 2θ = 2.65. BET analysis; surface area = 641 m²/g +/- 21m²/g; uptake of N₂ gas = 25%, microporous

2.6-Rig Development

Throughout the duration of the project the modified rig proved successful in performing the reactions that it was built to make possible. Nearly all of the equipment used proved to be reasonably reliable and did not suffer major faults.

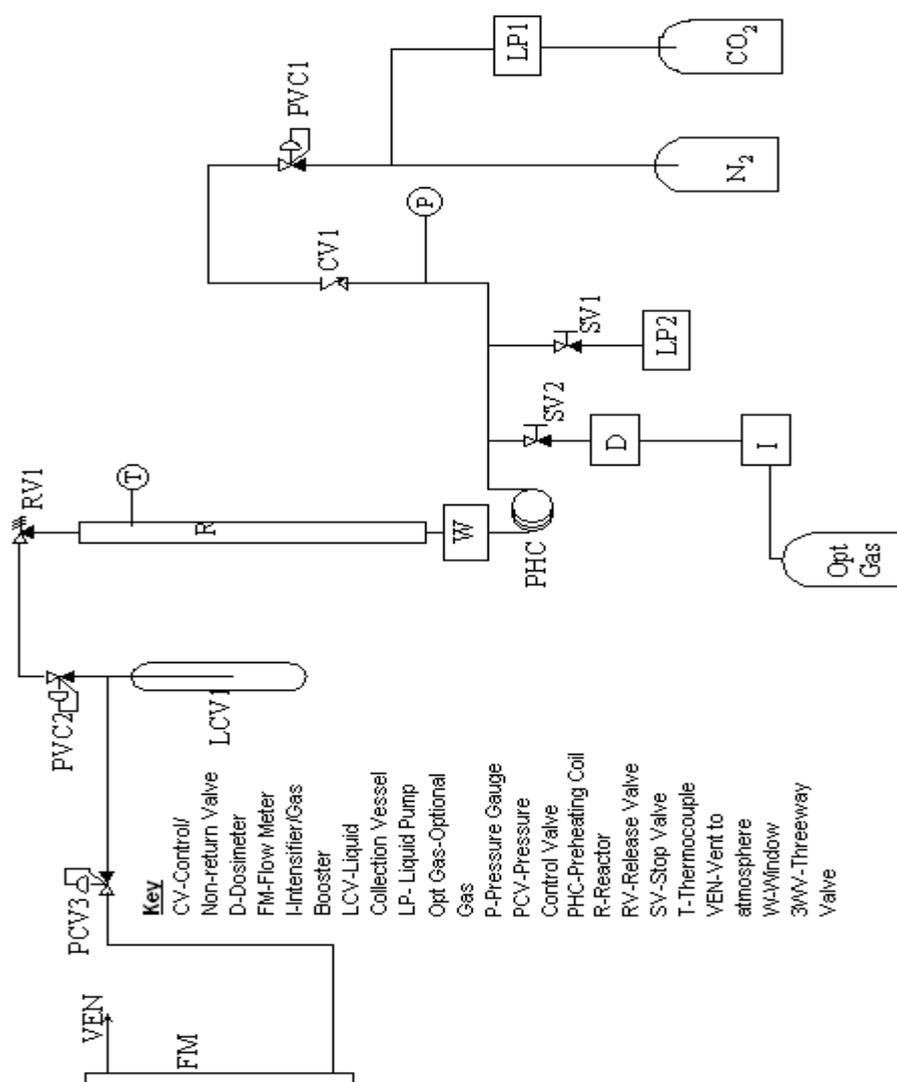


Figure 2.7-Diagram of possible development of current rig

However with the benefit of hindsight there are several areas of the rig, which could be improved upon or made better use of, if the rig were to be used to perform similar reactions in the future. When discussing the development of a rig it is important to remember to try and keep things as simple as possible and to try to minimise dead space in the rig. An outline of the 'future' rig is shown in figure 2.7 showing the areas for possible improvement.

Before talking about areas for improvement, the area before the inlet valve remains unchanged from the project rig. The Pickle Supercritical Fluid Pump never developed a fault throughout the duration of the project, and is retained as a reliable source of high-pressure carbon dioxide.

The Haskell gas booster does appear to have a recurring fault, inspite of this it is an easy to use, generally reliable source of high-pressure nitrogen and so is also retained from the project rig.

Next we come to the high-pressure section of the rig. This section begins with the inlet valve PVC1, and ends with the expansion valve PVC2. During the project both these valves were exchanged for the Druva valves that are currently in place in the rig. Unfortunately both these valves have proven to be exceptionally unreliable, both valves require regular servicing from Druva to replace internal diaphragms and the expansion valve regularly needs to have perished o-rings replaced. With this in mind it is recommend that an alternative,

more reliable make of valve be used in future on the rig. Recently a homogeneous rig used by the research group has switched from Druva valves to Swagelok valves. Swagelok claim their valves to be compatible with supercritical fluids, and to date they appear to be very reliable. Alternatively Boycewood make all metal expansion valves, which would remove perishable o-rings from the system. However with no knowledge of the reliability of the Boycewood valves it is recommend that the inlet valve PCV1 and the expansion valve PCV2 be replaced with Swagelok high-pressure and high-pressure to low-pressure gas expansion valves respectively.

Working downstream through the high-pressure section of the rig from the inlet valve to the expansion valve, the first equipment after the inlet is the non-return valve and then the pressure transducer. Both these pieces of equipment perform a necessary function and have not posed a problem during the project and so are retained.

Continuing downstream the next pieces of apparatus are the preheating coil, and the gas and liquid substrate inlets to the system. Currently both the gas and liquid inlets are located after the pre-heating coil. This is because the pre-heating coil was added after the modification of the rig and was inserted in the only available space before the reactor. Unfortunately this effectively means that after the reaction medium is heated to the reaction temperature in the preheating coil it is then cooled by the addition of gas and/or liquid at room temperature. In an effort to counter this problem in the project rig the gas and liquid inlets were warmed using heating tape. However it is more logical to move these inlets to so

that they inject into the system before the preheating coil, so that the entire substrate mixture is preheated together.

The liquid feed through a Gilson 305 HPLC pump with optional cool-head is retained. On one occasion when the HPLC pump was used to inject a highly volatile liquid utilising the cooled head, the liquid being pumped vaporised in the piping a short distance after the pump head before reaching the rig. This gradually led to gas diffusion back to the pump head stopping liquid injection. By reducing the length of piping between the pump and rig, as well inserting a check valve shortly before injection to the system, the chances of this problem recurring would be decreased.

It has already been mentioned that the gas-dosing unit sometimes blocked due to back diffusion of the substrate mixture and crystallisation of organic compounds in the reservoirs or the pipes after the reservoirs. A possible method to stop this happening, would be to insert a non-return valve between the gas dosing unit and the rig, this would stop any back flow to the dosing unit and therefore any crystallisation blockages from occurring. An alternative to using the gas-dosing unit would be a mass flow controller. A mass flow controller allows a constant controlled flow of gas into the system as opposed to bursts of gas as with the gas-dosing unit. However with a possible solution to the only reliability problem of the gas-dosing unit, the gas dosing unit and non-return valve combination have been used in the 'future' rig.

The next area for discussion is the reactor. There are no recommended changes to the reactor, the temperature control system for the reactor works well. However in the project rig, there is no means of observing the phase of matter either as it enters the reactor or whilst actually in the reactor. Assumptions on the phase of matter must be made from the temperature and pressure of the system. It would be advantageous to insert a high-pressure, high-temperature quartz window immediately before the reactor, thus it would be possible to observe visually if the substrate mixture was indeed a single phase.

An alternative approach to the high-pressure, high-temperature quartz window would be to use a Jerguson gauge. Jerguson gauges are used industrially to observe liquid levels in reactors, and essentially consist of a transparent tube window in parallel with the reactor. The idea for the future rig would be to connect the Jerguson gauge in parallel to the reactor from immediately before it to immediately after it so some of the substrate mixture would pass through the gauge instead of the reactor. Obviously, if this were performed during a reaction, it would mean a portion of the substrate mixture constantly bypassing the reactor giving misleading conversions. Therefore it would be sensible to use a brief dummy run with no catalyst present and the gauge connected to observe the phase of the substrate mixture under reaction conditions, and then perform the reaction with the gauge disconnected.

If it were felt necessary, there is also the possibility of adding a short chamber of glass rings. This would aid the mixing of the substituents before entering the reactor.

Downstream of the reactor on the project rig is the filter. This was retained from the original rig, where it was used to catch any catalyst that blew out from the reactor. In the entire duration of the project this filter was never required, and therefore its removal is recommended.

Continuing downstream the last piece of the rig in the high-pressure section is the inline sampling port, for sampling directly from immediately after the reactor straight to a GC. Unfortunately no suitable GC became available during the project and this port was never used. Nevertheless the port stays as part of the future rig, as if connected to a GC this would give a truer reflection of the product stream than the current sampling method.

Considering the high-pressure section as a whole the set up of the future rig would make insulation after the preheating coil much simpler. We have moved the gas and liquid substrate inlets to before the preheating coil, removing the need for these to be warmed. Now the preheated mixture can pass directly from the preheating coil into the reactor, or through a high-pressure, high temperature quartz window and possible mixing chamber to the reactor. Removal of the filter leaves only the inline sampling port before the end of the high-pressure section, which could lead to a much reduced area of tubing that may need to be insulated.

After the expansion valve PVC2 the product stream passes directly into the collection vessel CV1 that is retained from the project rig. This collection

vessel proved highly successful throughout the project and made the old rig's sampling system, which had been kept as a safety net, redundant. It is thus suggested that the old sampling system of the cooling pipe, three way joint, and pair of collection vessels be removed.

From the collection vessel the expanded gas passes straight to the second expansion valve PCV3, this expansion valve was used mainly to control the venting rate of gas in the project rig, removing the need for a needle valve, which is not present in the future rig.

Finally the gas is vented to the fume cupboard. As with all previous incarnations of the rig this is achieved through a flow meter.

Chapter 3-The Beckmann Rearrangement

3.1-Introduction

In 1886 Beckmann¹ discovered that, by using reagents such as phosphorous pentachloride and acetic anhydride, he could cause ketoximes to rearrange into acid amides, and today such reactions are named after their discoverer. It was 14 years later when the most industrially important Beckmann rearrangement was first reported². Cyclohexanone oxime was converted to ϵ -caprolactam using sulphuric acid as a catalyst (figure 3.1).

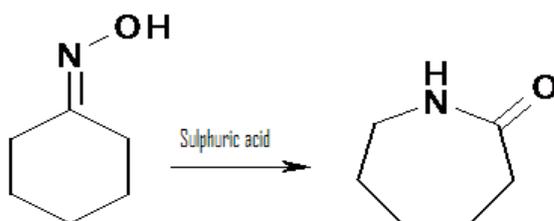


Figure 3.1-Industrially performed Beckmann rearrangement of Cyclohexanone Oxime

The importance of this reaction is a result of the invention in 1935 of nylon-6, 6 at DuPont by Carothers³. The discovery of nylon was to prove to be an important landmark in the chemical industry and the production of nylon-6, 6 was to become one of DuPont's most profitable activities in the period after the second world war. The method DuPont used was the condensation copolymerisation of a diamine, hexamethylenediamine, and a di-acid, adipic acid, and this process was patented by the company.

In order to compete with DuPont rival companies had to find an alternative route to nylon and in the 1950's it was discovered that the ring opening polymerisation of ϵ -caprolactam yielded nylon-6. The most commonly used method of forming ϵ -caprolactam is the acid-catalysed Beckmann rearrangement of cyclohexanone oxime.

Since this process was discovered the production of ϵ -caprolactam using sulphuric acid as a catalyst has become a multibillion dollar industry worldwide, and, despite reports of falling demands⁴ in recent years, seems set to remain as such for the foreseeable future.

While sulphuric acid is widely used as the catalyst for this process, there are several associated problems with this homogeneous process. One mole of sulphuric acid is required to convert one mole of oxime to ϵ -caprolactam⁵, which leads to problems in handling a hazardous and corrosive chemical on a large scale. Once the conversion is complete a stoichiometric amount of base is required to neutralise the acid and isolate the product. This neutralisation forms a large amount of ammonium sulphate, up to 4 tonnes per tonne of product⁶, and these vast quantities of salt have to be disposed, which can lead to conflict with local authorities⁴.

To overcome these problems there is an ongoing search for a viable alternative catalyst. Particular interest has been taken in the possibility of a heterogeneous catalyst^{7, 8}, as this would avoid the difficulties surrounding product isolation in the homogeneous process. Among the most frequently studied are

Zeolites β , ZSM-5 and Y, and mesoporous solids, such as MCM-41 and MCM-22. However all the candidates suffer from loss of activity and/or relatively low selectivity to the lactam.

In order to understand the deactivation of the catalyst it is first necessary to understand the reaction pathway. Until recently it was believed that Beckmann rearrangements followed the stepwise pathway shown in figure 3.2, where protonation of the oxime results in elimination of water, the amide ion then rearranges to give a 7 membered ring, which in turn reacts with the dissociated water to give ϵ -caprolactam.

Recently a study of short chain molecules in ZMS-5 pores supported this theory⁹. However, Yamabe recently showed that, in liquid phase, the Beckmann rearrangement is a concerted process¹⁰, and his work suggested that after protonation the oxime bond is elongated but never broken until oxygen forms a bond with the β -carbon, figure 3.2.

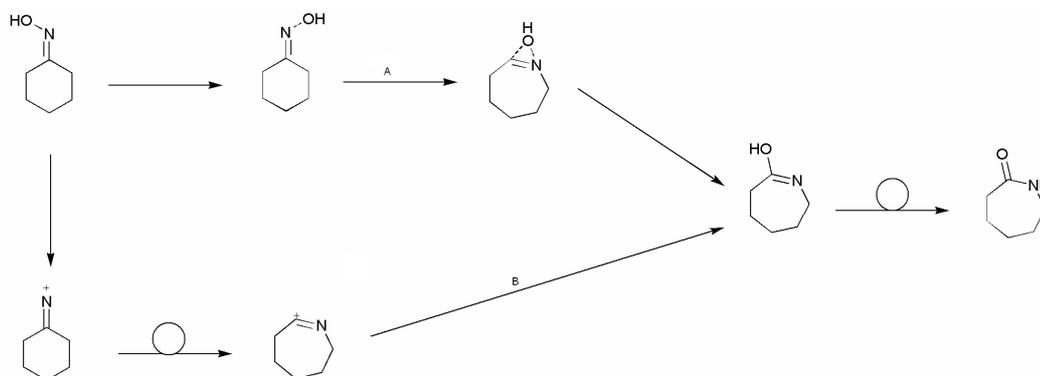


Figure 3.2- Concerted (A) and step-wise (B) pathways for Beckmann rearrangement of cyclohexanone oxime

Whilst the two studies come to differing conclusions on the intermediates of the reaction they both state that an important part of the rearrangement is the coordination of 3 weakly acidic silanol groups to the reactant molecule. Whilst it has been shown that a silanol is not a strong enough acid to catalyse the reaction, they can help to hold the molecule in place during the rearrangement (figure 3.3).

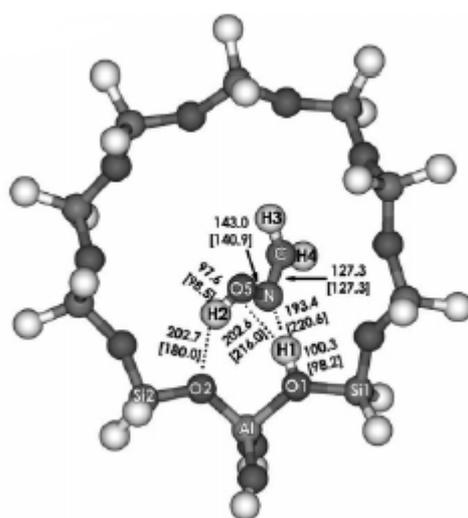


Figure 3.3-Formaldehyde oxime before rearrangement in H-ZMS-5. Reproduced from reference 9.

This shows that weakly acidic sites are important in the reaction, as are strongly acidic sites. A more in depth study into the need for both strong and weak acid sites was performed by Singh et al¹¹. The Si/Al ratio was varied in several zeolites that can be used in the Beckmann rearrangement, and it was found that high aluminum content, giving a larger concentration of strong acid sites, lowers the selectivity to lactam. The main byproducts observed were aniline, cyclohexanone, and hexane nitrile (figure 3.4)

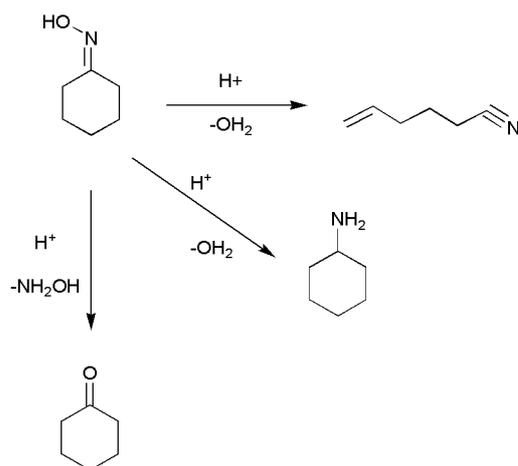


Figure 3.4-The most commonly quoted side-products for the heterogeneously catalysed process

This work has since been verified by the findings of other groups^{12, 13}, specifically it has been shown that lowering the strong/weak acid site ratio increases the selectivity and reduces the rate of deactivation, it has also been observed that the same effect occurs with increasing pore size¹³ for zeolites

It is interesting to note that, when a similar study was performed using MCM-41, it was observed that increasing the aluminium content had no effect on the conversion of oxime and actually improved the selectivity¹⁴. The authors claim that the silanol groups present are not strong enough to effect the desired rearrangement but are strong enough to create the byproducts, and that the much lower concentration of silanol groups in the previously studied zeolite are responsible for the different trends. They also tested polar solvents, methanol and hexan-1-ol as oxime solvents in the process, and found these solvents to be beneficial to both the oxime conversion and selectivity, claiming that water formed by solvent dehydration reduces the acid strength.

It was recently shown that the use of ethanol as a polar solvent greatly improved catalyst lifetime¹⁵, again it is thought that the water produced by solvent dehydration was responsible for the increased catalyst lifetime. However, it was speculated that this was because the water produced shifts the equilibrium that exists on the catalyst surface between the caprolactam and 5-cyanopent-1-ene (figure 3.5). It was assumed that, as an unsaturated molecule, 5-cyanopent-1-ene is the main precursor of coke due to its ready polymerisation.

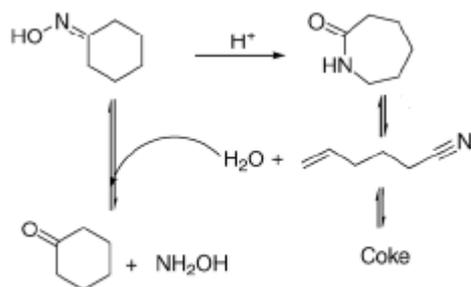


Figure 3.5- The effect of water on the equilibrium on the catalyst surface

The use of H-ZMS-5 modified with noble metals has been shown to give a high lactam selectivity¹⁶ and recent studies suggest that zeolite β may in fact be the best zeolite for the conversion¹⁷⁻¹⁹. However, despite this greater understanding of the reaction and many improvements to the conversion and selectivity of the various available catalysts, there is yet to be discovered a catalyst that can be used continuously without loss of activity. While this remains the case, the pilot plants that exist for the heterogeneously catalysed process continue to have to accommodate costly catalyst regeneration in their design. A good example of this is the pilot plant for the Sumitomo Chemical company of

Japan²⁰ (figure 3.6). This reactor is designed to use a boron doped Zeolite Y catalyst, and features a seeping bed of catalyst to accommodate the catalyst deactivation. In this bed freshly regenerated catalyst is forced in at the base of the reactor, forcing spent catalyst further up the reactor to fall to the regeneration chamber. This chamber is heated to over 700°C to burn out the coke from the zeolite and is also used to preheat the reaction mixture before entering the reaction chamber.

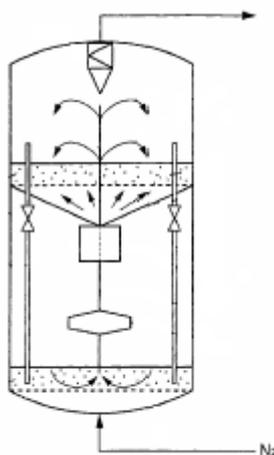


Figure 3.6-Cross-section of Sumitomo reactor for heterogeneously catalysed process. Reproduced from reference 20.

The reactor design shown in figure 3.6 illustrates the amount of time and money spent to get around the problem of catalyst deactivation due to coking in the caprolactam process. It was felt that this would be a fitting reaction to study using carbon dioxide above both its critical temperature and pressure, given the time and money expended on researching heterogeneous catalysts for the project. It was intended to initially perform the reaction under low pressures, similar to those used in the pilot plant operations. The reaction would then be compared to

the same reaction run above the critical pressure of carbon dioxide, paying particular attention to both the rates of catalyst deactivation and the amount of lactam produced by the reactions. An important further set of reactions would be identical reactions run using nitrogen as the reaction medium, this would show if any changes in deactivation or amount of lactam produced were due to carbon dioxide or applicable to any inert gas used under these conditions.

3.2-The Beckmann Process on the Rig

For this investigation it was decided to base the reaction studied on the reaction patented by the Sumitomo Chemical Company²⁰.

As has been related in the introduction to this chapter, a great deal of time and money has been spent on improving the lifetime of catalysts for the heterogeneous process, most commonly the catalyst in question is Zeolite β , Zeolite Y or ZMS-5. The same is true of the catalyst used in the patent here. Zeolite Y has been modified by doping with Boron, by using B_2O_3 in place of Al_2O_3 when forming the zeolite. However, despite the success achieved in prolonging the catalyst life-time for this investigation it was felt that it was advantageous to study a catalyst that, while offering a good initial conversion of oxime, had a short lifetime. With this in mind it was decided to proceed with unmodified Zeolite Y.

The Zeolite Y used had a Si:Al ratio of 2.5 and a unit cell size of 24.35 Å. As can be seen in figure 3.7 the pores in zeolite Y run in three directions, and it is

in these pores and on the surface of the zeolite particles that the rearrangement takes place. The cages located just off the main pores are too small to allow access for the oxime and therefore can be discounted as possible reaction sites.

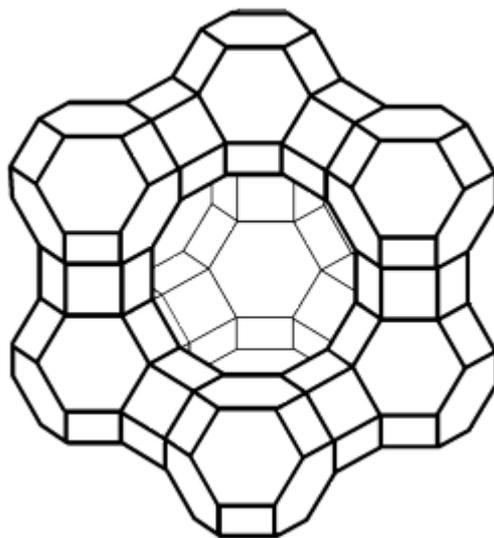


Figure 3.7-Zeolite Y silicon skeleton

Cyclohexanone oxime is a solid at room temperature and so to facilitate its injection into the system, it was required to be dissolved in a suitable solvent. The patent stated that primary alcohols with a carbon chain length of 1 to 10 could be used as such solvents, and for this investigation ethanol was chosen as an oxime solvent. In the patent²⁰ the carrier gas was nitrogen and the reactor pressure was stated as between 1 and 10 bar. The temperature for reaction was between 100 and 700°C. In order to find a set of conditions under which the catalyst had a high initial conversion of oxime, it was decided to work with nitrogen as the reaction medium with a reactor pressure of 5 bar. The temperature of reaction would be steadily increased from 100 °C.

The standard method of analysis for this project would be GC, however at the beginning of this investigation no GC was available, therefore for these initial reactions an alternative form of analysis had to be used. The obvious choice was ^1H NMR as this is a quantitative form of analysis and the spectra of cyclohexanone oxime and caprolactam are sufficiently different to enable simple calculations of approximate oxime to lactam ratios. As can be seen in figure 3.8, caprolactam has a hydrogen atom bonded to the nitrogen, which is not present in cyclohexanone oxime evidenced by a broad peak at δ 6.2, the appearance of this peak in the NMR spectra of the samples would identify if conversion of oxime to lactam is occurring. The ratio of the peak at δ 3.3 in the caprolactam spectrum and δ 2.4 in the oxime spectrum was used to determine the conversion. From this analysis it was decided that the catalyst lifetime should be investigated at 380 °C where the initial ratio of oxime to caprolactam was in the region of 4:1(80%) (figure 3.9).

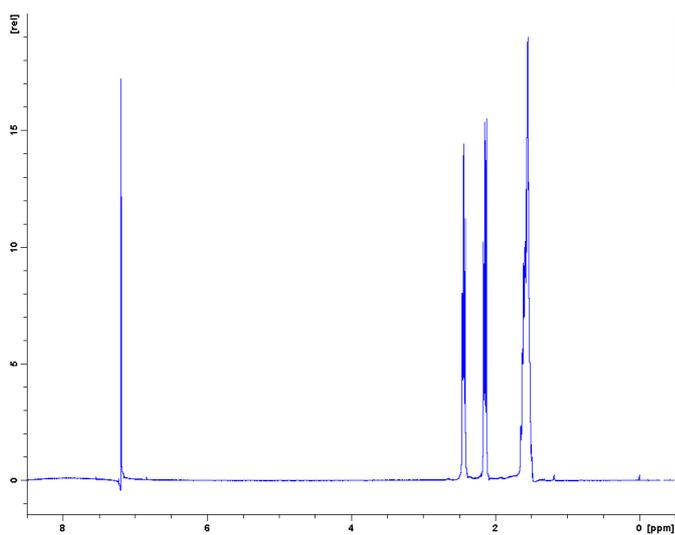


Figure 3.8 (a) ^1H -NMR spectrum of cyclohexanone Oxime

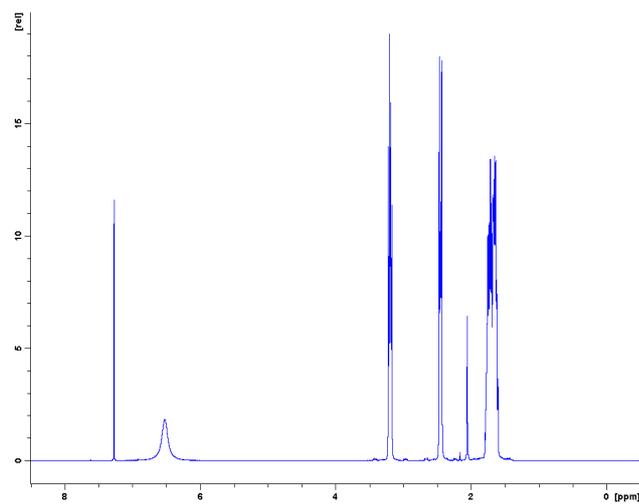


Figure 3.8 (b) ¹H-NMR spectrum of caprolactam

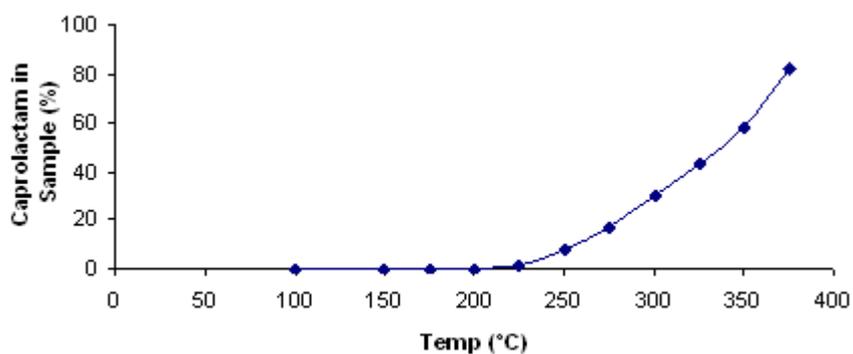


Figure 3.9-Caprolactam in collected sample against temperature, given by comparing peaks in ¹H NMR spectra

3.3-The Caprolactam Process at 380 °C

In general the Beckmann rearrangement of cyclohexanone oxime is performed at around 350 °C industrially; higher temperatures leading to higher conversion of oxime along with more rapid catalyst deactivation. While the second effect is a major disadvantage industrially, for this project both of these effects can be thought of as advantageous; a catalyst that deactivates rapidly due

to coking is ideal to test the ability of carbon dioxide above its critical pressure and temperature to counteract this effect.

To begin with a base run at 380 °C was performed, by passing the oxime solution over the catalyst for several hours using nitrogen as a transport pressure. The GC-trace of a sample collected during the first hour of this procedure is shown in figure 3.10.

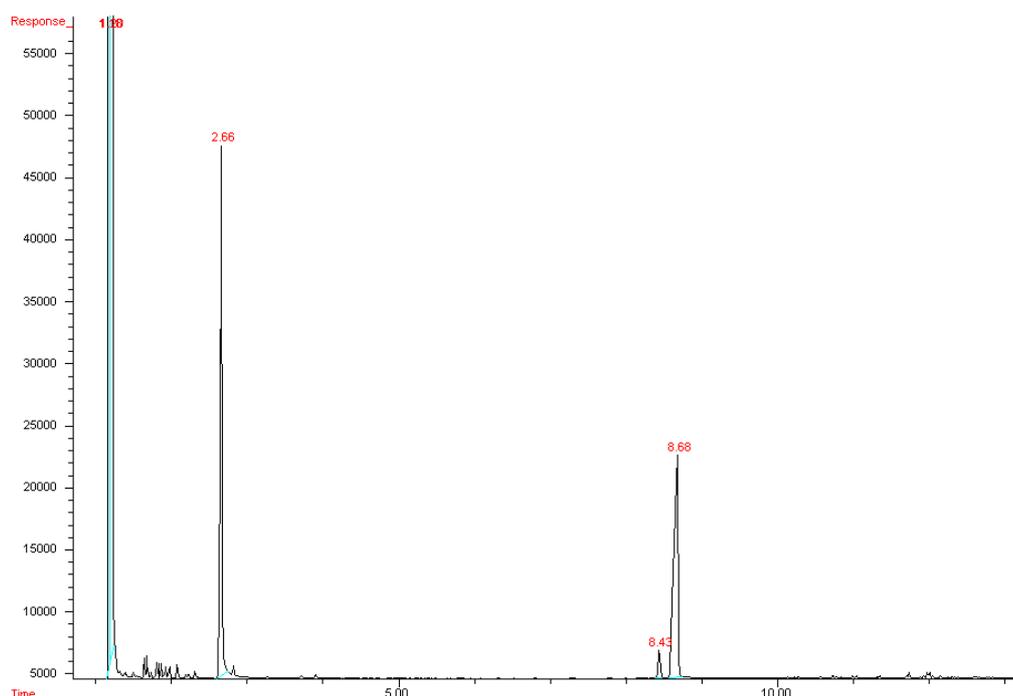


Figure 3.10-GC of sample collected after 1 hour of reaction run at 380°C, showing peaks for Oxime (2.66), By-product (8.43), and Caprolactam (8.68)

Disregarding the large solvent peak, there are three main peaks in the trace. It is interesting to note that none of these 3 main peaks corresponds to 5-cyanopent-1-ene. As referenced in the introduction to this chapter, the literature led us to anticipate 5-cyanopent-1-ene accounting for 7-10 % of the sample.

Indeed given that the catalyst is unmodified zeolite Y and the reaction temperature is greater than 350 °C it would be reasonable to expect an even greater amount of 5-cyanopent-1-ene to be present.

When looking only at the three main peaks in the spectrum, 80% of the sample is caprolactam (8.5) and 9% of the sample is unreacted oxime (2.6). The remaining 11% is an unidentified by-product giving rise to a peak just before the caprolactam peak. When analysed using mass-spectrometry it was discovered that the by-product giving rise to this peak had a molecular weight of 141 amu. This is 28 amu higher than the molecular weight of both cyclohexanone oxime and caprolactam. It was hypothesized that the by-product could be the result of a reaction with the ethanol solvent with either the oxime or caprolactam, resulting in replacement of hydrogen with an ethyl group as this would give an increase in molecular weight of 28 amu.

In order to discover if a solvent interaction was taking place, an experiment was carried out similar conditions but methanol was used as a solvent in place of ethanol. When this experiment was analysed; three main peaks were once more observed on the GC trace. However, while two of the peaks still corresponded to the oxime and caprolactam, the third peak had changed position and accounted for a greater proportion of the sample. Mass-spectrometry confirmed that this was a new by-product as it gave a molecular weight of 127 amu to the compound responsible for this new peak.

This result appears to support the theory of a solvent interaction leading to the by-products, as the difference in atomic weights of the two by-products formed is also the difference in atomic weight of the solvents for the reaction. However, it was still not known what exactly the by-product was and whether it was formed from oxime or caprolactam. As discussed, the most recent theory suggests that the reaction pathway is concerted rather than stepwise, meaning that the O-N bond is elongated during reaction but not broken, this would mean it is unlikely that the reaction with solvent occurs during the rearrangement. It would seem more plausible that after the rearrangement has taken place dehydration of the caprolactam could result in a reaction with ethanol to form O-ethyl-caprolactam.

In the 1950's Marvel and Moyer²¹ published a study on alkyl derivatives of caprolactam. In this study he showed that caprolactams alkylated on the oxygen have a longer retention time than caprolactam itself in GC analysis, whereas a caprolactam alkylated on the nitrogen would have slightly shorter retention times than caprolactam. This would appear to rule out O-ethyl-caprolactam as the by-product, indeed it would suggest that N-ethyl-caprolactam is more likely to be the by-product seen.

To ascertain if the by-product was indeed N-ethyl-caprolactam a sample of the compound was synthesized, this was a simple two step process of reacting caprolactam with sodium hydride to form the sodium salt, then bromo ethane to yield the desired compound. Once synthesized, N-ethyl-caprolactam was found to have the same retention time by GC, and the same MS spectrum as the

unknown by-product. Finally when added to a sample from the rig it was found to co-elute with the unknown by-product. It was therefore concluded that the unknown by-product was indeed N-ethyl-caprolactam.

This answer raised the question of how this by-product is formed. Given that the by-product is a derivative of the product it is logical to suggest that its formation must happen during or after the reaction takes place. As already discussed recent evidence that the reaction is concerted would suggest that it is unlikely that the solvent becomes involved in the transition state, and if it did, this would be more likely to produce alkylation on the oxygen rather than the nitrogen.

Another possibility is the attack of the solvent on the product. In this theory protonation of the solvent leads to loss of water, the resulting cation would then attack the nitrogen on the product to give N-ethyl-caprolactam. However this does not explain why attack is specific and gives only one by-product, in particular if this theory were correct, it would be surprising that no interaction with the substrate was observed. However, this could be explained by the fact that similar attack on the nitrogen in the oxime would lead to a four-coordinate nitrogen centre with no obvious leaving group, indeed it would be most likely to lose the ethyl group to return to the original oxime.

A third theory is that the solvent could interact with the major coke precursor of the process 5-cyanopent-1-ene. Although not observed in our reactions at this temperature this compound is widely acknowledged as the main

deactivating agent as it can polymerize on the surface. It is formed in a reversible dehydration of the product. In this hypothesis, instead of recombining with water, it reacts with ethanol to give N-ethyl-caprolactam. This reaction is not without precedent; the Ritter reaction²² is performed under acid conditions. In the Ritter reaction the ethyl group of ethanol attaches to the nitrogen in a nitrile group, this is followed by hydrolysis which gives the carbonyl group adjacent to the nitrogen (figure 3.11).



Figure 3.11-General scheme of Ritter Reaction

To form N-ethyl-caprolactam the alkyl attack would occur on the nitrile as in the Ritter reaction, this would be followed by a similar hydrolysis cyclisation as occurs when the 5-cyanopent-1-ene returns to caprolactam, only in this case giving the ethyl derivative (figure 3.12). The standard Ritter product would be the non-cyclic amide but it is not observed in the reactions studied.

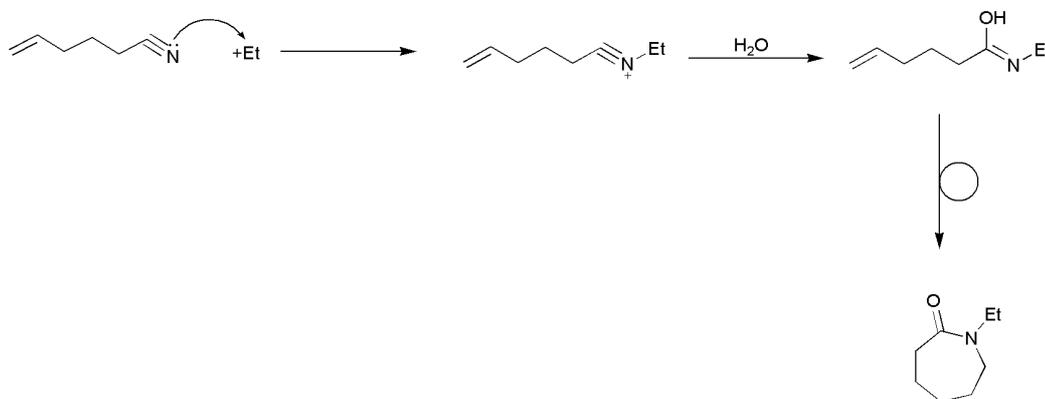


Figure 3.12- Possible Ritter style reaction route to formation of the by-product

N-ethyl caprolactam

A further consideration, when considering the likely route to N-ethyl-caprolactam, is that, in the reactions observed, conversion to the by-product falls much faster with time than the conversion to desired product. It is possible that the water left over from the molecules that react with ethanol to give N-ethylcaprolactam stays in the vicinity of the active site. As more by-product is formed, more water would build up in the pore making it increasingly unlikely that the product would react with solvent as time goes on. However at the temperature and flow rate that the reaction was performed it is unlikely that water would remain in the pores. It is more likely that, as the catalyst deactivates this side reaction is more strongly affected by the loss of acidity inside the catalyst pores and so this reaction appears to die more rapidly than the main rearrangement.

It is believed that N-ethyl caprolactam is formed either by direct attack of ethyl cations formed in the pores on to caprolactam or by a Ritter reaction style attack of ethanol on 5-cyanopent-1-ene followed by cyclisation and hydrolysis. The relatively rapid disappearance of this by-product over time is thought to be due to the high acidity required to form the by-product.

Returning to the reaction at 380°C over a longer period of time (figure 3.14), the already discussed rapid loss of N-ethyl-caprolactam from the collected sample is observed. As well as this a high conversion of oxime to caprolactam is initially observed and as expected the amount of caprolactam in the collected

sample falls steadily with time. However despite the reaction being run for over 50 hours complete deactivation of the catalyst was never observed.

Time (h)	Caprolactam in Sample (%)	By-Product in Sample (%)	Mass balance by Volume (%)
0.5	90	7	77
1.0	68	3	78
1.5	51	1	77
2.0	38	1	75
2.5	32	0	77
3.0	27	0	77
3.5	24	0	77
4.0	22	0	77
4.5	19	0	75
5.0	17	0	73

Table 3.13-Percentage of Caprolactam and By-Product in collected sample by GC analysis, and mass balance of reaction

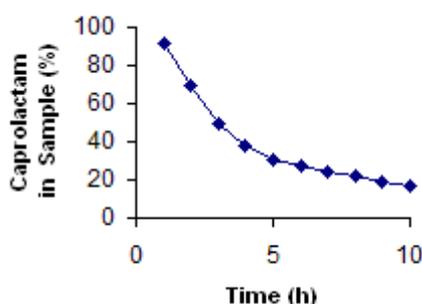


Figure 3.14-Caprolactam in collected sample in Ethanol at 380°C against time

To stop the formation of N-ethylcaprolactam the solvent was changed from ethanol to toluene. When the reaction was performed at 380°C with toluene as the oxime solvent no N-ethyl-caprolactam was observed, as expected. The initial sample contained around 80% lactam, however in this reaction complete deactivation of the catalyst was observed in less than 8 hours (figure 3.16). The obvious conclusion is that toluene promotes catalyst deactivation when compared with ethanol for this particular process. This also is to be expected as polar solvents are most commonly used for the caprolactam process as they encourage

desorption of the product from the catalyst, both freeing the active site for further reaction and decreasing the possibility of coke formation.

Time (h)	Caprolactam in Sample (%)	Mass balance by Volume (%)
1.0	79	78
2.0	42	80
3.0	19	80
4.0	16	78
5.0	8	77
6.0	4	80
7.0	3	78
8.0	Trace	82

Table 3.15-Percentage of Caprolactam in collected sample by GC analysis, and mass balance of reaction by volume

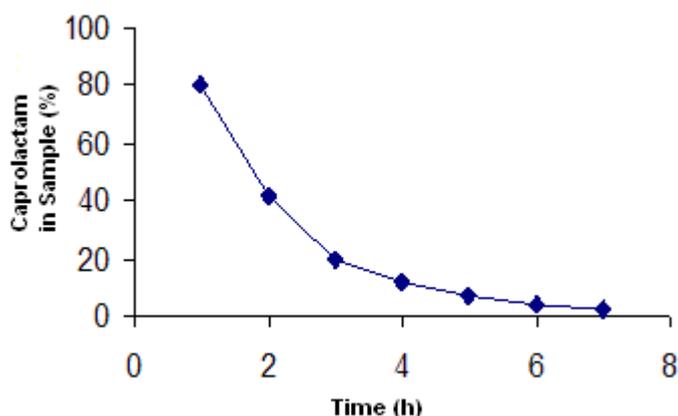


Figure 3.16- Caprolactam in collected sample in Toluene at 380°C against time

Other factors may contribute to toluene's poorer solvent ability for this reaction. The formation of N-ethyl-caprolactam when ethanol is used as a solvent may be due to ethanol reacting with the major coke precursor for this reaction, 5-cyanopent-1-ene, with no analogous reaction when toluene is used as solvent this may also lead to more rapid catalyst deactivation. Alternatively the structure of toluene is similar to the structure of coke on the surface of the

catalyst as it has an aromatic carbon ring. Protonation of toluene when used as a solvent in acidic conditions would lead to the formation of a relatively stable carbocation that would increase the speed at which coke is formed in the pores of the catalyst.

The rapid deactivation of the catalyst when toluene is used as an oxime solvent could be looked upon as a good result, as ideally for this study, a reaction was required that could afford a high initial conversion to lactam combined with a fast deactivation of the catalyst. This was certainly the case when toluene was used, so the reaction would be studied at a pressure above the critical pressure of carbon dioxide at 200 bar.

After one hour of running the reaction with carbon dioxide as a transport vector at reactor pressure of 200 bar the sample of the product stream analysed as 64% caprolactam, 6% unreacted oxime, 6% 5-cyanopent-1-ene, and 24% high atomic mass by-products that could not easily be assigned. The high atomic mass by-products all had atomic masses considerably higher than that of oxime or caprolactam and it is possible that these represent the removal of coke precursors from the catalyst. However, the drop in the amount of lactam in the collected sample had occurred at a similar mass balance to the lower pressure reactions; it would therefore appear that the formation of these higher atomic mass by-products was being favoured by the higher pressure. Nevertheless this result would be interesting if the initial levels of lactam in the sample could be maintained over a period of time. However after 1 hour and 23 minutes the flow of carbon dioxide through the rig stopped and dismantling of the apparatus

revealed a blockage of black tar-like material shortly after the reactor. The tar-like residue was dissolved as much as possible in DCM and analysed by GCMS which revealed it to be similar in composition to the reaction sample taken after 1 hour with a larger percentage of high atomic mass by-products.

To understand more about what had transpired using 200 bar of carbon dioxide at 380°C. The reaction was repeated using nitrogen as the reaction medium. After 1 hour the sample from the nitrogen reaction was of similar composition to the sample taken from the analogous carbon dioxide reaction, with 63% caprolactam and 23% higher atomic mass by-products. Once again the reactor blocked shortly after the 1st sample was taken, and in several attempts the longest this reaction was able to be performed for was just over 3 hours. It was concluded that without major re-structuring of the rig itself a meaningful study of the reaction at high pressures was impossible at this temperature.

Whilst a conclusive study of the reaction at this temperature was impossible, the similar nature of the product stream composition from reactions at high pressure using either carbon dioxide or nitrogen as medium showed that carbon dioxide being above its critical temperature and pressure did not appear to have an effect on the reaction. This result cannot be considered surprising when supercriticality is considered as a function of density. As previously discussed the properties of a supercritical fluid can be tuned, in terms of density this means that the supercritical fluid at lower densities will be more gas-like, and that at higher pressures it will be more liquid-like. The density of carbon dioxide at the critical point is 0.46 g/cm⁻³ and at this point can be thought to be roughly half-

way between liquid and gas. Taking this into consideration in a reaction at 380 °C and 200 bar, the density of carbon dioxide would be 0.16 g/cm⁻³. Essentially this means that the behaviour of carbon dioxide should be very similar to that of a gas. With this in mind it was decided to look again at the earlier work of initial conversion to lactam against temperature of reaction. In an attempt to drive up the density of carbon dioxide at higher pressures available a reaction temperature as low as possible was sought. With an initial conversion of just under 10% it was decided to study the reaction over time at 250°C. Study below this temperature would be impossible as no conversion had been observed.

3.4-The Caprolactam Process at 250°C

As a control reaction the process was performed at 250°C with nitrogen gas as a reaction medium and a reactor pressure of 5 bar. At this temperature no N-ethyl-caprolactam was observed, so it was decided to return to ethanol as solvent for the cyclohexanone oxime. When the reaction was run under these conditions the initial sample collected was observed to be around 6% lactam and as could be expected at these lower catalyst activity only trace amounts of by-products were present. Within 5 hours the amount of lactam in the samples was well below 1% and the catalyst could be considered effectively dead (figure 3.18).

Time (h)	Caprolactam in Sample (%)	Mass balance by Volume (%)
0.5	6.0	78
1.0	2.5	77
1.5	1.7	77
2.0	1.3	75
2.5	1.1	77
3.0	1.0	75
3.5	0.9	75
4.0	0.8	77
4.5	0.7	75
5.0	0.5	75

Table 3.17-Percentage of Caprolactam in collected sample by GC analysis, and mass balance of reaction by volume

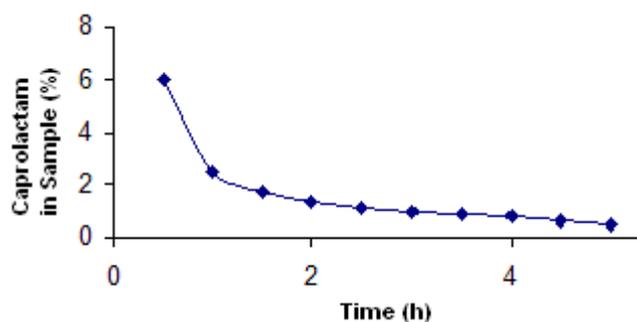


Figure 3.18- Caprolactam in collected sample at 250°C, 5 bar nitrogen

Using this initial run as a basis the reaction was studied using carbon dioxide as the reaction medium instead of nitrogen. First the reaction was run with a reactor pressure of 5 bar, this produced an almost identical result to the run in nitrogen at 5 bar as would be expected. The reaction was then run with carbon dioxide as the medium at 200 bar (figure 3.20). In this run the initial sample collected contained over 5% caprolactam, but the rate at which the amount of lactam in the samples collected fell slowed significantly.

Time (h)	Caprolactam in Sample (%)	Mass balance by Volume (%)
0.5	5.8	78
1.0	4.2	82
1.5	3.6	82
2.0	3.2	80
2.5	2.8	82
3.0	2.7	80
3.5	2.4	82
4.0	2.2	82
4.5	2.0	80
5.0	1.9	82

Table 3.19-Percentage of Caprolactam in collected sample by GC analysis under 200 bar carbon dioxide, and mass balance of reaction by volume

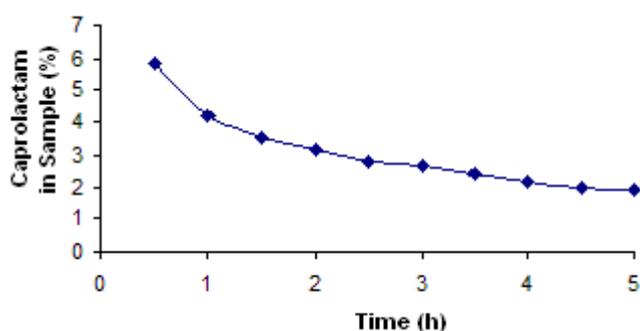


Figure 3.20- Caprolactam in collected sample at 250°C, 200 bar carbon dioxide

This appeared to be a significant result using carbon dioxide as reaction medium above its critical pressure and temperature was reducing the deactivation of the catalyst with time. If this was due to any supercritical nature of the carbon dioxide used then increasing the pressure at the same temperature should increase the density of the fluid, resulting in a better solvent, and a greater improvement in catalyst lifetime. The reaction was run with a reactor pressure of 300 bar, and once again an initial drop in lactam in the sample collected was

observed, but also once again a significant improvement in the catalyst lifetime was observed. To better observe any trend, reactions were performed with reactor pressures of 50 bar and 100 bar (figure 3.22). These reactions fitted in with the previous results having initial percentages of lactam in samples collected between those of the 5 bar and 200 bar reactions and having intermediate deactivation rates as well. The effect on the deactivation of the catalyst can be better observed when looking at a normalised graph (figure 3.23).

Time (h)	Caprolactam in Sample (%)				
	5 bar	50 bar	100 bar	200 bar	300 bar
0.5	6.8	6.2	7.0	5.8	4.3
1.0	2.3	3.7	4.6	4.2	3.9
1.5	1.4	2.7	3.2	3.6	3.4
2.0	1.1	2.0	2.3	3.2	3.0
2.5	0.9	1.5	2.0	2.8	2.7
3.0	0.8	1.3	1.7	2.7	2.8
3.5	0.7	1.1	1.6	2.4	2.4
4.0	0.6	1.0	1.4	2.2	2.3
4.5	0.6	0.9	1.3	2.0	2.2
5.0	0.6	0.9	1.2	1.9	2.1
Time (h)	Caprolactam in Sample (%) / 1st Sample				
	5 bar	50 bar	100 bar	200 bar	300 bar
0.5	1	1	1	1	1
1.0	0.34	0.60	0.66	0.72	0.90
1.5	0.21	0.43	0.46	0.61	0.78
2.0	0.16	0.32	0.33	0.55	0.70
2.5	0.14	0.25	0.29	0.48	0.63
3.0	0.12	0.20	0.25	0.45	0.64
3.5	0.11	0.18	0.23	0.41	0.56
4.0	0.09	0.16	0.20	0.37	0.52
4.5	0.08	0.15	0.19	0.34	0.50
5.0	0.08	0.14	0.17	0.32	0.48

Table 3.21-Percentage of Caprolactam in collected sample by GC analysis at various pressures of carbon dioxide at 250°C, and relative percentage of caprolactam in samples compared to initial sample.

In the normalised graph the percentages of lactam in the collected samples are divided by the percentage of lactam in the first sample collected at each pressure to give the relative amount of lactam compared to the first collected sample against time at each pressure. Here it can be clearly seen that as the pressure is increased, and therefore the density of the carbon dioxide, the deactivation of the catalyst is slowed. This result would appear to confirm that increasing the pressure of carbon dioxide in the supercritical region increases its liquid like qualities and hence its solvating power.

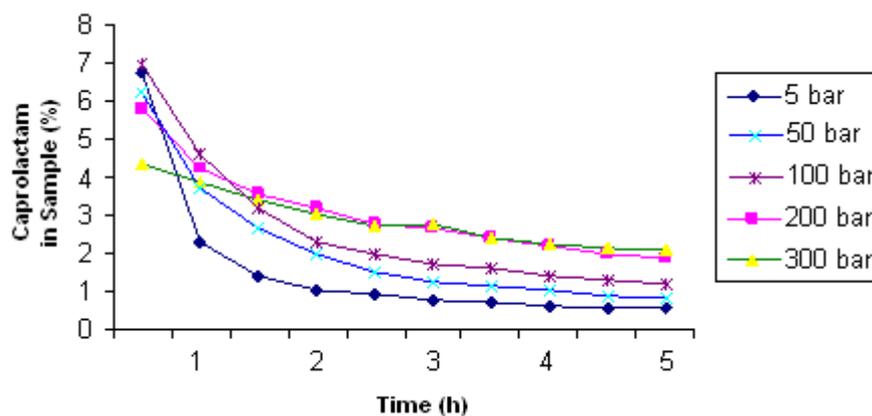


Figure 3.22- Caprolactam in collected sample at 250°C under carbon dioxide, at various pressures

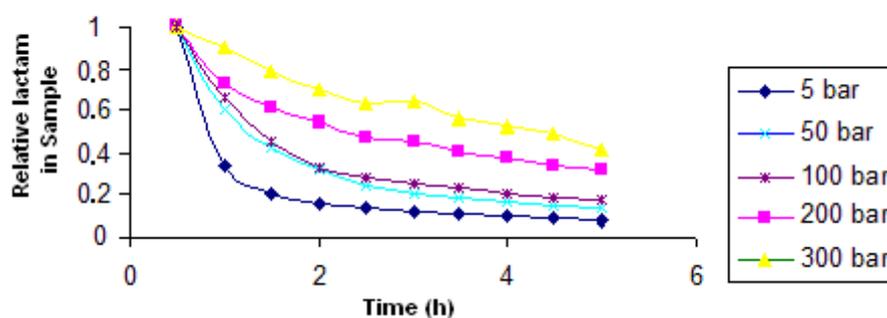


Figure 3.23-Relative Caprolactam in collected sample at 250°C under carbon dioxide

In order to confirm this result it was necessary to perform a control reaction using nitrogen as the reaction medium at a higher pressure. Nitrogen is not considered a supercritical fluid under these conditions, despite being greatly in excess of its critical temperature and its critical pressure, -147°C and 34 bar respectively. It can be thought of as close to an ideal gas for these purposes. A reaction using a reactor pressure of 200 bar of nitrogen at 250°C was run. The result of this run was almost identical to the run performed using carbon dioxide under the same conditions (figure 3.25). This result disproved the conclusions reached above for the reaction in carbon dioxide, and indeed suggests that the observed trends have nothing to do with density at all, as the density of nitrogen under these conditions is quite different from the density of carbon dioxide.

Time (h)	Caprolactam in Sample (%)			
	5 bar CO ₂	200 bar CO ₂	5 bar N ₂	200 bar N ₂
0.5	6.76	5.83	5.98	5.63
1.0	2.28	4.22	2.49	5.34
1.5	1.39	3.56	1.68	4.08
2.0	1.05	3.19	1.31	3.25
2.5	0.92	2.79	1.09	2.92
3.0	0.8	2.65	0.95	2.85
3.5	0.73	2.39	0.86	2.01
4.0	0.64	2.18	0.81	1.85
4.5	0.57	1.99	0.66	1.66
5.0	0.55	1.89	0.59	1.52

Table 3.24-Percentage of Caprolactam in collected sample by GC analysis at various pressures of carbon dioxide and nitrogen at 250°C

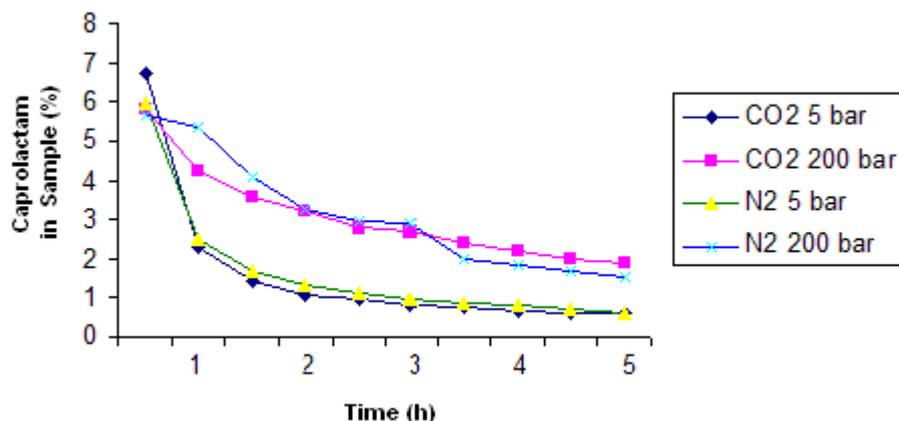


Figure 3.25- Caprolactam in collected sample at 250°C under carbon dioxide and nitrogen at various pressures

The results obtained suggested that reduction in catalyst deactivation was simply due to the increase in pressure. In an attempt to better understand the origin of this effect a number of control reactions was performed.

Firstly the flow rate of carbon dioxide through the rig was varied (figure 3.27). As temperature, reactor pressure and rate of injecting oxime solution was to remain constant, this would have the effect of changing the ratio of the carbon dioxide to reactant molecules in the reactor, and the system in general.

The results show an increase in caprolactam in the initial sample with increasing flow rate, accompanied by a slight increase in the deactivation rate. It is thought that, by increasing the flow rate of carbon dioxide through the reactor the turn over of molecules at the active sites of the catalyst; thus leading to the dual effect of increasing the initial rate of the reaction to form caprolactam and increasing the rate at which the sites are deactivated.

Time (h)	Caprolactam in Sample (%)			
	FR=20	FR=40	FR=60	FR=80
0.5	5.42	6.18	7.07	7.92
1.0	5.42	4.23	4.45	4.65
1.5	4.35	3.46	3.32	3.62
2.0	3.66	2.89	2.74	2.99
2.5	3.33	2.62	2.38	2.60
3.0	3.03	2.30	2.10	2.21
3.5	2.81	2.11	1.88	1.90
4.0	2.59	1.93	1.69	1.65
4.5	2.40	1.84	1.56	1.47
5.0	2.33	1.70	1.58	1.48

Time (h)	Caprolactam in Sample (%) / 1st Sample			
	FR=20	FR=40	FR=60	FR=80
0.5	1.00	1.00	1.00	1.00
1.0	1.00	0.68	0.63	0.59
1.5	0.80	0.56	0.47	0.46
2.0	0.68	0.47	0.39	0.38
2.5	0.61	0.42	0.34	0.33
3.0	0.56	0.37	0.30	0.28
3.5	0.52	0.34	0.27	0.27
4.0	0.48	0.31	0.24	0.23
4.5	0.44	0.30	0.22	0.21
5.0	0.43	0.28	0.22	0.21

Table 3.26-Percentage of Caprolactam in collected sample by GC analysis at flow rates of carbon dioxide at 250°C; 5 bar, and relative percentage of caprolactam in samples compared to initial sample.

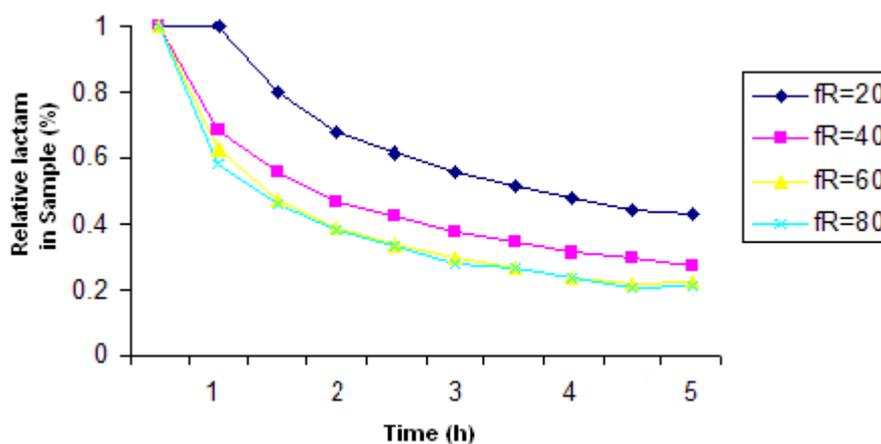


Figure 3.27- Relative Caprolactam in collected sample at 250°C under 5 bar carbon dioxide at various flow rates

The rate of injection of oxime solution into the carbon dioxide was varied at constant reactor pressure and carbon dioxide flow rate. This would again vary the concentration of oxime in carbon dioxide entering the reactor. As would be expected with this set of reactions the initial conversion increased with decreasing injection rate, this is however an illusion, as from the analysis used, the number of moles of oxime converted remained similar as did the deactivation rate of the catalyst when looking at the graph (figure 3.29).

Time (h)	Caprolactam in Sample (%)		Caprolactam in Sample (%) / 1st Sample	
	1ml/min	2ml/min	1ml/min	2ml/min
0.5	11.87	5.83	1.00	1.00
1.0	8.25	4.22	0.70	0.72
1.5	5.53	3.56	0.47	0.61
2.0	4.49	3.19	0.38	0.55
2.5	3.49	2.79	0.29	0.48
3.0	3.19	2.65	0.27	0.45
3.5	3.18	2.39	0.27	0.41
4.0	2.97	2.18	0.25	0.37
4.5	2.76	1.99	0.23	0.34
5.0	2.54	1.89	0.21	0.32

Table 3.28-Percentage of Caprolactam in collected sample by GC analysis under carbon dioxide at 250°C; 200 bar, and relative percentage of caprolactam in samples compared to initial sample.

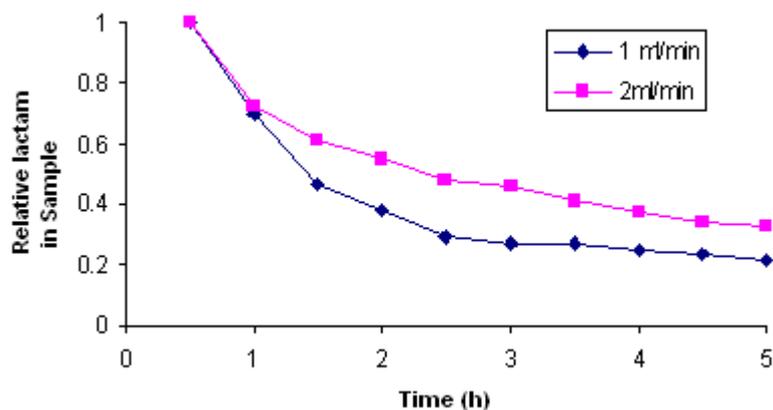


Figure 3.29- Relative Caprolactam in collected sample at 250°C under 200 bar carbon dioxide at various oxime injection rates

A last consideration was the method of the slowing of catalyst deactivation, this may have been due to coke being removed from the surface or may indicate that coke formation on the surface is being inhibited. To discover which appeared to be happening in this case, a sample of catalyst was deactivated by performing a standard run at a reactor pressure of 5 bar of carbon dioxide for 5 hours at which time the catalyst would be dead. Injection of oxime was stopped at this point the reactor pressure was raised to 300 bar and carbon dioxide was allowed to flow through the reactor at this pressure for 5 hours. After this time had elapsed, the reactor pressure was dropped to 5 bar once again and a standard run was again attempted. However the catalyst was still dead after the washing at 300 bar. It was concluded that the slowing of catalyst deactivation must occur due to a prevention of coke being formed on the catalyst rather than removal of the coke/ precursors by high pressure gas.

Overall, when studying the Beckmann rearrangement of cyclohexanone oxime at 250°C, it was found that performing the reaction above the critical

pressure and temperature of carbon dioxide had two obvious effects on the reaction. Firstly the amount of caprolactam initially collected decreased with increasing pressure, and secondly the rate at which the catalyst deactivated was reduced with the increase in pressure. It is clear from the control experiments performed with nitrogen that these effects are due simply to the increase of reaction pressure and not due to any interactions specific to carbon dioxide, it can, therefore, be concluded that the reaction is being observed in the vapor (rather than supercritical) phase. From further control experiments it is clear that the decrease in deactivation rate is due to the inhibition of coke formation rather than promoting the removal of coke or coke precursors from the surface of the catalyst. As the pressure of the reaction is increased with the composition of the mixture entering the reactor remaining the same, the residence time of molecules in the reactor is increased. It is hypothesised that as residence time increases contact time with the catalyst decreases for individual molecules, due to increased competition from the greater number of molecules in the reactor; a decreased contact time would mean a decreased chance of the rearrangement taking place and a decreased chance of coke precursors being formed, which in turn would lead to the decrease in initial lactam formed and the increased catalyst lifetime observed.

3.5-The Caprolactam Process at 300 °C

The findings at 250°C were interesting but appear to be slightly at odds with the brief results obtained at 380°C. At 380°C it appeared that, when the process was run at a higher reaction pressure, the formation of coke precursors

was possibly favoured. In order to see if the findings at 250°C would be replicable at a higher temperature it was decided to investigate the reaction at 300°C.

The process was run in both nitrogen and carbon dioxide at 300°C with a reactor pressure of 5 bar. As expected both runs produced similar results, with a higher initial percentage of caprolactam in the collected sample of over 60% (figure 3.31).

Time (h)	Caprolactam in Sample (%)	
	5 bar CO ₂	5 bar N ₂
0.5	62.28	66.15
1.0	29.08	29.44
1.5	19.95	18.23
2.0	15.99	14.74
2.5	13.62	12.85
3.0	12.83	11.73
3.5	12.24	10.8
4.0	11.47	10.3
4.5	11.01	9.82
5.0	10.38	9.86

Table 3.30-Percentage of Caprolactam in collected sample by GC analysis under carbon dioxide or nitrogen at 300°C; 5 bar

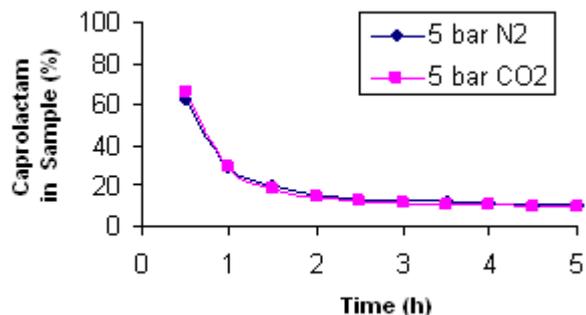


Figure 3.31- Caprolactam in collected sample at 300°C under carbon dioxide and nitrogen at 5 bar

In order to ascertain whether the same effect would be observed at this temperature as at 250°C a run was performed using carbon dioxide as reaction medium at a reactor pressure of 200 bar. If the same sort of effect was to be observed it was expected that a lower initial amount of lactam would be observed combined with a slower deactivation rate. However, when the run was analysed it was discovered that the initial lactam content of the sample had risen to 86%, while the deactivation rate had slowed slightly (figures 3.33, 3.34).

Time (h)	Caprolactam in Sample (%)			
	5 bar CO2	5 bar N2	200 bar CO2	200 bar N2
0.5	62.28	66.15	84.62	86.74
1.0	29.08	29.44	57.52	70.28
1.5	19.95	18.23	45.94	43.21
2.0	15.99	14.74	39.52	31.59
2.5	13.62	12.85	33.65	25.30
3.0	12.83	11.73	28.32	22.11
3.5	12.24	10.80	20.38	19.54
4.0	11.47	10.30	18.59	18.03
4.5	11.01	9.82	19.13	16.97
5.0	10.38	9.86	18.93	16.10

Time (h)	Caprolactam in Sample (%) / 1 st Sample			
	5 bar CO ₂	5 bar N ₂	200 bar CO ₂	200 bar N ₂
0.5	1.00	1.00	1.00	1.00
1.0	0.47	0.45	0.68	0.81
1.5	0.32	0.28	0.54	0.50
2.0	0.26	0.22	0.47	0.36
2.5	0.22	0.19	0.40	0.29
3.0	0.21	0.18	0.33	0.25
3.5	0.20	0.16	0.24	0.23
4.0	0.18	0.16	0.22	0.21
4.5	0.18	0.15	0.23	0.20
5.0	0.17	0.15	0.22	0.19

Table 3.32-Percentage of Caprolactam in collected sample by GC analysis at various pressures of carbon dioxide and nitrogen at 300°C, and relative percentage of caprolactam in samples compared to initial sample.

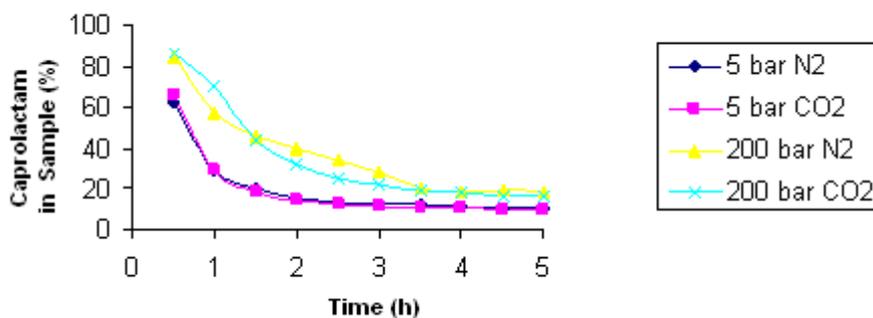


Figure 3.33- Caprolactam in collected sample at 300°C under carbon dioxide and nitrogen at 5 or 200 bar.

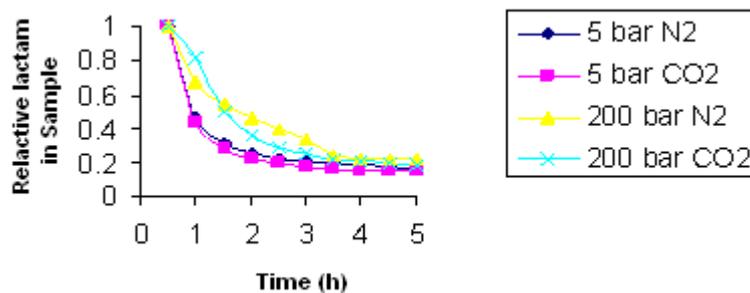


Figure 3.34-Relative Caprolactam in collected sample at 250°C under carbon dioxide and nitrogen at 5 bar and 200 bar

The result seen using a higher pressure of carbon dioxide was replicated when the process was performed using nitrogen at 200 bar. It is believed that while the effect at 250°C may still be occurring and having an effect of the deactivation rate, it was obvious that a second stronger effect was governing the relationship between the rate at which lactam was initially formed and pressure.

A similar effect was reported by Holderich et al in 1999¹⁹. When studying the caprolactam process at 300°C they reduced the pressure to 100 mbar in the hope of achieving better conversions and slower catalyst deactivation. However they observed the opposite of what they expected. While this was at a much lower pressure than our effect it is evidence of a similar effect being observed at the same temperature of reaction.

While the results obtained at 300°C differ from those observed at 250°C, it is believed that the same general effect is being observed. As before the increase in pressure will lead to increased residence time, and increased competition for the active sites of the catalyst between molecules, and in turn a

reduced time on the catalyst surface catalyst for reactant molecules. However, it is possible that at this higher temperature the reaction is expected to be considerably faster and the shorter contact time may be enough to facilitate the rearrangement. This would have the dual effect of freeing up sites for further reaction and reducing the chance that molecules absorbed onto the surface would go on to form coke, leading to an increase initial conversion to caprolactam and a decrease in deactivation rate.

3.6-References

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Chapter 4-The Fries Rearrangement

4-The Fries Rearrangement

When studying the Beckmann rearrangement of cyclohexanone oxime temperatures in excess of 250°C had been required to affect the desired rearrangement. These temperatures are considerably higher than the critical temperature of carbon dioxide, and combined with the pressure limitations of the rig, meant the reactions at higher pressure were performed with a carbon dioxide density considerably lower than that of the critical density. In effect this resulted in the reaction being observed in the vapour phase rather than a supercritical phase. With this in mind it was necessary to study a reaction that could be performed at a lower temperature.

One heterogeneous process that had been reported at lower temperatures was the Fries rearrangement. The Fries rearrangement is a method for forming hydroxyl aryl ketones from phenyl esters as outlined in figure 4.1.

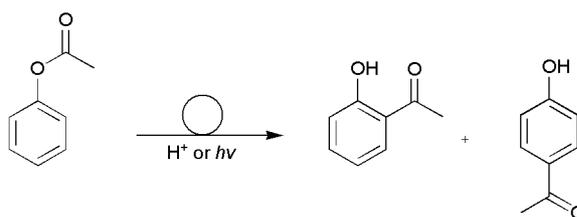


Figure 4.1-General scheme of Fries rearrangement

4.1-Introduction to the Fries Rearrangement

In the first decade of the 20th century German chemist Karl Theophil Fries discovered that, under acid conditions, phenol esters such as phenyl acetate would undergo a rearrangement to yield ortho- or para-acylated derivatives of phenol called hydroxyaryl ketones.^{1,2}

This rearrangement was to become important industrially due to the limitations of Friedel-Crafts acylation reactions. Friedel-Crafts acylation is the standard method for synthesising acylated derivatives of aryl compounds (figure 4.2)³. However this technique is not successful when attempted on phenol and similar compounds. This created a problem as hydroxyaryl ketones are precursors to several important pharmaceuticals, these include paracetamol and salbutamol³.

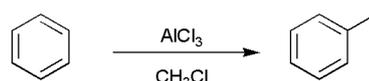


Figure 4.2-Friedel-Crafts alkylation of benzene

The solution to this problem was the Fries rearrangement; this made it possible to synthesise acyl derivatives of phenol by first making a phenol ester and then performing the Fries rearrangement (figure 4.3).

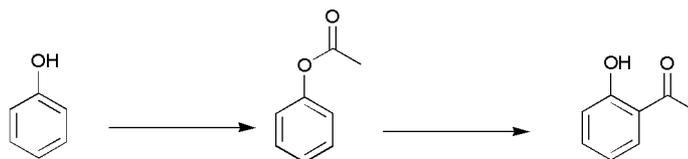


Figure 4.3-Route to substituted phenols through Fries rearrangement

Industrially the catalyst used to perform this rearrangement is the Lewis acid, aluminium chloride. Although aluminium chloride catalyses the reaction well, the catalyst itself is both extremely corrosive and toxic to the environment. For these reasons, alternative catalysts/methods have been sought to perform the rearrangement. It has been shown that the rearrangement can be initiated by photolysis but the low yields from such reactions have prohibited its development as a realistic alternative⁴. The main focus of research has been into the use of heterogenous solid acid catalysts for the process.

Many different solid acid catalysts have been studied for use in the process including zeolites⁵, heteropoly acids⁶, and meso structured materials⁷, both in the liquid and gas phases as both batch and continuous processes. However, these processes suffer from large amounts of generated phenol as well as rapid catalyst deactivation⁸. It is thought that coke is formed in the vapour phase reaction when phenol is formed leaving an acylium ion on the catalyst surface, this ion then forms a ketene which can then dimerise and polymerise on the surface blocking the active sites⁹ (figure 4.4).

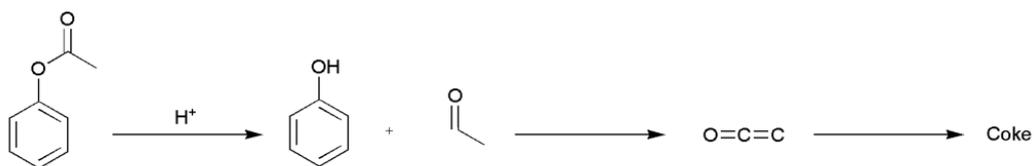


Figure 4.4-Widely accepted route to coke in heterogeneously catalysed Fries rearrangement

4.2-The Fries Rearrangement at 150°C

The literature¹⁰ showed that the Fries rearrangement of phenyl acetate to hydroxyacetophenones could be carried out at temperatures below 200°C. Wang⁶ had shown that zeolite β could be used to perform the rearrangement between 100°C and 200°C. Although no conversion was observed at 100°C, at 200°C conversion from phenyl acetate was over 50%, with 50% selectivity to hydroxyacetophenones.

To obtain a suitable temperature at which to study the process, phenyl acetate was passed over zeolite β under a reactor pressure of 5 bar of nitrogen. The temperature was initially 100°C and this temperature was raised in 25°C increments to 200°C. Analysis showed that conversion to hydroxyacetophenones was just under 10% of the collected sample at 150°C, and it was decided to study the reaction further at this temperature.

Using nitrogen at a reactor pressure of 5 bar as the reaction medium, the Fries rearrangement was performed over 6 hours at 150°C. The initially collected sample was 18% hydroxyacetophenones and 11% phenol. A high

conversion to phenol is to be expected, however in many literature cases the selectivity to phenol is actually higher than that to hydroxyacetophenones. Within the 6 hour reaction time, the amount of hydroxyacetophenones in the collected samples fell to under a tenth of their initial value (figure 4.6), which represented a rapid catalyst deactivation under these conditions.

Time (h)	Product in Sample (%)		Mass Balance by Volume
	Hydroxyacetophenone	Phenol	
0.5	18.62	11.65	83
1.0	7.44	6.87	85
1.5	4.98	4.78	85
2.0	3.31	3.42	87
2.5	2.94	2.92	85
3.0	2.69	2.58	85
3.5	2.31	2.37	87
4.0	2.01	2.13	87
4.5	1.81	2.00	87
5.0	1.63	1.86	87
5.5	1.49	1.74	87
6.0	1.38	1.68	87

Table 4.5- Percentage of hydroxyacetophenones and phenol in collected samples, and mass balance by volume of samples.

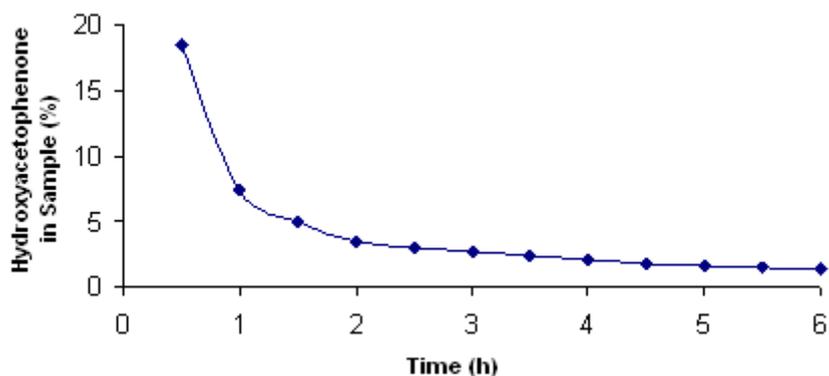


Figure 4.6-Hydroxyacetophenone in collected samples at 150°C, 5 bar N₂

However this result did not correlate with the temperature versus conversion study performed for this process, as already stated this showed that conversion to hydroxyacetophenones at this temperature was around 10%, whereas this initial reaction showed conversions of almost double this figure.

The reaction was rerun at 150°C and 5 bar nitrogen reactor pressure several times. These rerun reactions all gave similar results of initial amount of hydroxyacetophenones of around 8% in the collected samples with a mass balance of 80-85% in all cases. These results correlated well with the conversion versus temperature study, but differed from the 1st reaction run at this temperature.

This would appear to show that the first reaction run under these conditions was a spurious result and not a true reflection of catalyst performance under these conditions, the reason for this is unknown. In all reactions, the same nitrogen cylinder was used, the same batch of phenyl acetate and the same batch of zeolite. The most obvious reason would be that the catalyst was at a higher temperature than it appeared on the temperature control. However the temperature controller was not removed or modified between these reactions, leaving no obvious reason for this discrepancy in results.

The initial spurious result was discarded and the consistent results were taken as the standard for this reaction. The initial sample was around 8% hydroxyacetophenones and over the 6 hour reaction period this percentage fell to

under a sixth of this original value (figure 4.8). This rapid deactivation of the catalyst was ideal for studying using high-pressure carbon dioxide. The major other product, phenol, was observed at a similar conversion to the hydroxyacetophenone, and the conversion to this product fell at a similar rate to that of the conversion to hydroxyacetophenone. Only trace amounts of p-acetylacetophenone, a second impurity known to be formed in the reaction, were present, and no ketene, thought to be the major coke precursor, was observed. The lack of ketene observation would be expected, as the majority of this would not condense on expansion of the reaction media in the sample collection chamber, or would polymerise on the catalyst surface.

Time (h)	Product in Sample (%)		Mass Balance by Volume
	Hydroxyacetophenone	Phenol	
0.5	8.56	8.79	85
1.0	5.68	6.01	87
1.5	4.76	4.99	87
2.0	4.40	4.48	85
2.5	4.06	4.02	87
3.0	3.53	3.39	85
3.5	3.45	3.47	87
4.0	3.08	3.13	85
4.5	2.57	2.72	87
5.0	1.51	1.84	80
5.5	1.40	1.74	82
6.0	1.32	1.68	80

Table 4.7- Percentage of hydroxyacetophenones and phenol in collected samples, and mass balance by volume of samples.

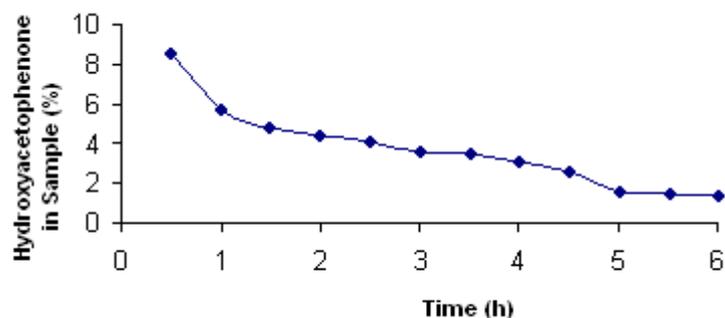


Figure 4.8-Hydroxyacetophenone in collected samples at 150°C, 5 bar N₂

The reaction was performed under the same conditions using carbon dioxide as the reaction medium at a pressure of 200 bar. The initial conversion to hydroxyacetophenones was again around 8% and when the reaction was studied over 6 hours a similar deactivation curve was observed as for the reaction using 5 bar of nitrogen (figure 4.7). This would appear to show that the activity of the catalyst is independent of the reaction medium and pressure at this temperature. To confirm this result the process was repeated using nitrogen at 200 bar reactor pressure and carbon dioxide at 5 bar reactor pressure. In both cases, the runs gave almost identical results to the previous reactions.

Time (h)	Hydroxyacetophenones in Sample (%)			
	5 bar CO ₂	5 bar N ₂	200 bar CO ₂	200 bar N ₂
0.5	8.43	8.56	9.12	8.91
1.0	5.65	5.68	6.20	5.88
1.5	4.97	4.76	5.47	4.90
2.0	4.64	4.40	5.02	4.37
2.5	4.30	4.06	4.56	4.01
3.0	3.71	3.53	4.01	3.74
3.5	3.37	3.45	3.65	3.56
4.0	3.20	3.08	3.37	3.30
4.5	3.03	2.57	3.01	2.94
5.0	2.70	1.51	2.83	2.67
5.5	2.44	1.40	2.64	2.49
6.0	2.28	1.32	2.46	2.41

Time (h)	Hydroxyacetophenones in Sample (%) / 1st Sample			
	5 bar CO2	5 bar N2	200 bar CO2	200 bar N2
0.5	1.00	1.00	1.00	1.00
1.0	0.67	0.66	0.68	0.66
1.5	0.59	0.58	0.60	0.55
2.0	0.55	0.54	0.55	0.49
2.5	0.51	0.50	0.50	0.45
3.0	0.44	0.43	0.44	0.42
3.5	0.40	0.39	0.40	0.40
4.0	0.38	0.37	0.37	0.37
4.5	0.36	0.35	0.33	0.33
5.0	0.32	0.32	0.31	0.30
5.5	0.29	0.29	0.29	0.28
6.0	0.27	0.27	0.27	0.27

Table 4.9- Percentage of hydroxyacetophenones in collected samples, relative amount of hydroxyacetophenones in samples compared to initial sample at 5 bar and 200 bar of nitrogen/carbon dioxide

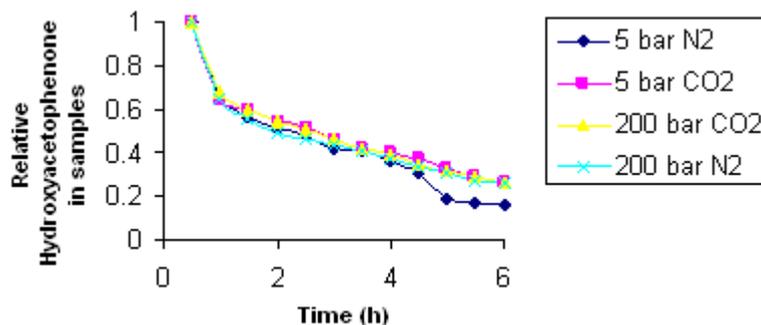


Figure 4.10- Relative amount of hydroxyacetophenone in samples compared to initial sample under 5 bar and 200 bar of nitrogen/carbon dioxide against time

These results seem to confirm that the reaction was unaffected by changes in pressure and medium. One reason for this could be the small pore size of zeolite β , less than 8 Å. This would restrict access to the coke precursors, which would be further hampered by the unidirectional pores possessed by the

zeolite and could lead to diffusion through the pores limiting the reaction. In order to test this, the reaction was repeated using zeolite Y. Zeolite Y has larger pores than zeolite β , and the pores are connect to the cages on 6 sides, giving a 3 dimensional pore structure as opposed to a one-dimensional structure.

The reaction was performed using zeolite Y as a catalyst at 150°C, using nitrogen at 5 bar as reaction medium. The initial conversion to hydroxyacetophenones was lower than when using zeolite β , at around 7.5%. There was a similar conversion to phenol however, and once again only trace amounts of p-acetylacetophenone were detected. No ketenes where present. As with the zeolite β reactions the catalyst was deactivation to under a fifth of its initial activity within 6 hours.

The process was run again using zeolite Y with nitrogen at 200 bar, and carbon dioxide at 5 bar then 200 bar in all reactions the results where almost identical to the 1st run using zeolite Y. This appeared to confirm that the reaction under these conditions is independent of reaction media and pressure. One possible explanation is that a liquid phase reaction is occurring so that the mobile phase does not gain access to the surface. This would explain the observed results. It would also explain the lower than expected conversions to phenol as these are generally lower in the liquid phase reactions than in gas phase⁵. It should also be noted that the boiling point of phenyl acetate is 198°C so it would be a liquid at the reaction temperature. Despite this it is still interesting to note the lack of any effect using carbon dioxide at 200 bar as under these conditions the carbon dioxide should be supercritical, although its density is still lower than

the critical density at 0.33g/cm^3 . Solubility studies of the various reaction components in carbon dioxide at 200 bar and $150\text{ }^\circ\text{C}$ would be instructive.

An alternative explanation is that the coke precursor, presumed in this case to be ketene is very strongly absorbed on the surface undergoes polymerisation to give coke which is insoluble in supercritical carbon dioxide at such a rate that it cannot be extracted and hence the presence of the supercritical fluid has no effect.

Given the results of the reactions and the relatively lower densities of the reaction media used in the study, it is felt that it is most likely that a liquid phase reaction is being observed, with a biphasic feed of phenyl acetate and nitrogen or carbon dioxide. If a liquid phase reaction was occurring with a biphasic system then we would expect the reactor to fill with the liquid phase phenyl acetate, given the up flow direction of the system used, and the gas phase of nitrogen or carbon dioxide bubbling through the reactor having no significant interaction with the substrate/products of reaction. This would lead to the results observed of a change in pressure of reaction medium having no observed effect on the rate of reaction or deactivation of the catalyst.

4.3-References

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Chapter 5-The Diels-Alder Process

5-The Diels-Alder Process

The results at high temperatures for the Beckmann and the Fries rearrangements showed that, using carbon dioxide under the high pressures allowed by the rig, had no effect that would not be seen using nitrogen. In both studies, although above both the critical temperature and pressure, the density of the carbon dioxide was lower than its density at the critical point.

The maximum pressure that the expansion valves on the rig could withstand was 200 bar. At this pressure a temperature of around 100°C is required to study carbon dioxide at densities similar to its density at the critical point.

The Diels-Alder reaction of methyl acrylate with isoprene over zeolite β was reported to be possible at temperatures below 100°C¹. By studying this reaction it was hoped to be able to observe the effect on the reaction of carbon dioxide at high density.

5.1-Introduction

The Diels-Alder reaction is a cyclisation reaction between a diene and a dienophile through a single transition state (figure 5.1).

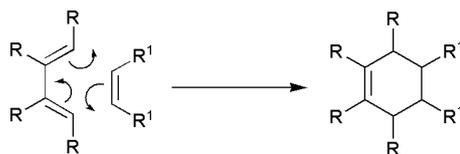


Figure 5.1-General Diels-Alder reaction

The reaction was first reported in 1928² by Otto Paul Hermann Diels and Kurt Alder. The reaction has since become one of the most well-known reactions in organic chemistry, and has even been described as the “Mona Lisa” of organic reaction, due to the low energy required to yield cyclohexene rings³. Diels and Alder eventually received the Nobel Prize for chemistry for their discovery in 1950.

The simplest Diels-Alder reaction is the addition of ethene to 1,3-butadiene (figure 5.2). In this case 1,3-butadiene acts as the diene, and ethene as the dienophile. The reaction goes through a single transition state, during which two new bonds are formed by donation of electron density from the HOMO of the diene into the LUMO of the dienophile. The product of this particular reaction is cyclohexene.

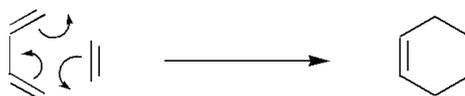


Figure 5.2-Diels-Alder addition of ethene and 1,3-butadiene

The reaction is helped by the presence of electron withdrawing groups on the dienophile, and the reaction can be performed with a wide variety of

substituents on the diene or dienophile. This has led to its importance in organic chemistry, particularly as these substituents lead to the formation of stereocentres during the reaction⁴.

The main use of the Diels-Alder reaction industrially is in the production of fine chemicals and pharmaceuticals⁵. In these processes, Lewis acids such as niobium pentachloride⁶, lanthanum triflate⁷ and aluminium chloride⁵ are used to improve the rate and selectivity.

As with the previous processes studied, the use of these inorganic Lewis acids is undesirable due to their toxicity and harmful effect on the environment. Numerous alternatives to their use have been tried including the use of supercritical carbon dioxide⁸, microwave radiation⁹, and ultrasound¹⁰. There has also been significant research into finding a heterogeneous process that could replace the homogeneous process industrially. This focuses on solid acid catalysts¹¹. However, while many solid acids can perform the cyclo-addition in reasonable conversions, rapid deactivation of the catalyst is a problem. The main source of catalyst deactivation in the Diels-Alder reactions in general is dimerisation or polymerisation of the reactants in the pores of the catalyst, blocking the reactive sites.

5.2-The Diels-Alder Addition of Isoprene and Methyl Acrylate

The Diels-Alder addition of methyl acrylate to isoprene, is a classic Diels-Alder reaction in the sense that the dienophile, in this case methyl acrylate,

has an electron withdrawing group on it, and the diene, isoprene, has an electron donating group. The reaction itself can produce two possible products, either the 3 or the 4 substituted cyclohexene derivative (figure 5.3).

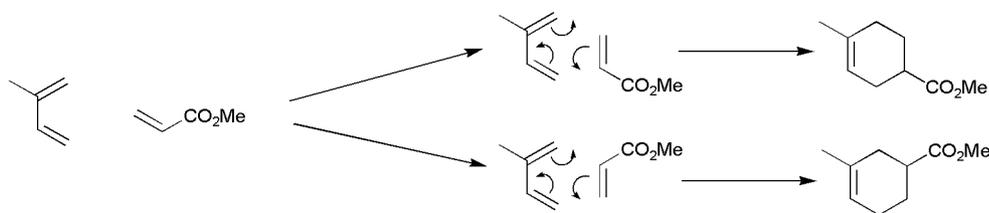


Figure 5.3-Diels-Alder addition of methyl acrylate and isoprene

According to the literature¹, this particular Diels-Alder reaction could be performed below 100°C using zeolite β , indeed the reaction could even be performed in the liquid phase at 0°C. The catalyst activity was stated to decrease over time due to dimerisation of the reactants on the catalyst surface. It should also be noted that methyl acrylate readily polymerises and has to be supplied with a stabilizer present and stored at low temperatures. Any polymerisation of methyl acrylate during the reaction would obviously contribute to the deactivation of the catalyst.

Bearing in mind the stated intention of studying a reaction at a temperature that carbon dioxide at 200 bar is at or above its critical density, initially the reaction was run at 3 temperatures to compare conversion and deactivation rates, 70°C, 90°C, and 110°C. To guard against polymerisation of methyl acrylate, the liquid feed would be a 3:1 ratio of isoprene to methyl acrylate by volume, this translates to a ratio of over 5:1 in terms of moles. As a

result of this all product peaks in GC analysis would be compared to the methyl acrylate peak.

The process was run at the three temperatures using nitrogen as the reaction medium at a reactor pressure of 5 bar. As shown in figure 5.4 the initial amount of cyclohexenes derivatives collected compared to methyl acrylate in the sample increases with temperature slightly as would be expected rising from 32% at 70°C to 37% at 90°C and finally to 41% at 110°C. With this initial rise comes a slightly faster loss of catalytic activity (figure 5.5) again this would be expected as, if the desired reaction is taking place more frequently it is probable that undesired side reactions are also occurring more frequently.

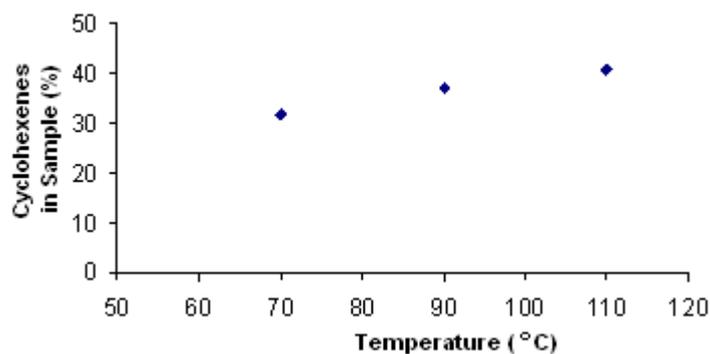


Figure 5.4-Percentage of Cyclohexene isomers in collected samples after 30mins at various temperatures

Time (h)	Cyclohexenes in Sample (%)		
	70°C	90°C	110°C
1.5	32.3	37.1	40.9
2.0	30.0	34.1	37.6
2.5	28.7	31.5	32.7
3.0	27.8	25.6	28.2
3.5	27.1	26.0	25.4
4.0	27.1	26.3	24.1
4.5	26.5	26.7	22.9
5.0	25.2	25.6	20.5
5.5	25.2	22.6	18.0
6.0	24.5	20.4	15.5

Time (h)	Cyclohexenes in Sample (%) / 1st Sample		
	70°C	90°C	110°C
1.5	1.00	1.00	1.00
2.0	0.93	0.92	0.92
2.5	0.89	0.85	0.80
3.0	0.86	0.69	0.69
3.5	0.84	0.70	0.62
4.0	0.84	0.71	0.59
4.5	0.82	0.72	0.56
5.0	0.78	0.69	0.50
5.5	0.78	0.61	0.44
6.0	0.76	0.55	0.38

Table 5.5-Percentage of Cyclohexenes in collected sample by GC analysis at various temperatures under 5 bar nitrogen, and relative percentage of cyclohexenes in samples compared to initial sample

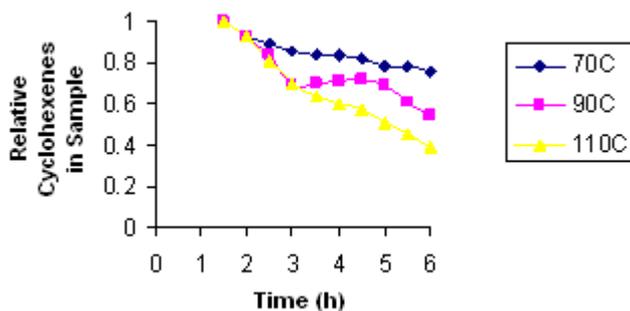


Figure 5.6-Relative Cyclohexenes in collected sample at various temperatures under nitrogen

From these results there is no major difference in looking at the reaction at any of these temperatures. However with the lowest conversion and catalyst deactivation 70°C was not considered, it should also be noted that this temperature is below the boiling point of methyl acrylate (79-81°C) and it was desirable to avoid a repeat of the liquid phase reaction observed when studying the Fries rearrangement.

Following this logic it would appear 110°C would be the obvious choice for temperature to study the reaction since it gives the highest conversion and fastest catalyst deactivation. However considering the previous results it was sensible to study the reaction at as low a temperature as possible, with the density of carbon dioxide at 90°C and 200 bar being 0.53g/cm⁻³ compared to 0.44g/cm⁻³ for carbon dioxide at 110°C and the same pressure. It was therefore decided to study this reaction at 90°C.

Looking at the conversion over the course of the 6 hour reaction at 90°C the catalyst activity only falls by over a third. Throughout the course of the reaction the 4-substituted cyclohexene derivative was the favoured product, accounting for around 90% of the cyclohexene derivatives formed, with the remainder being the 3-substituted isomer formed through the less energetically favourable transition state.

When the reaction was performed using 5 bar of carbon dioxide a similar result to that seen when using nitrogen at the same pressure was observed (Figure 5.8)

Time (h)	Cyclohexenes in Sample (%)	
	5 bar CO2	5 bar N2
1.5	30.8	37.1
2.0	29.2	34.1
2.5	28.1	31.5
3.0	27.3	25.6
3.5	27.5	26.0
4.0	25.6	26.3
4.5	25.1	26.7
5.0	22.8	25.6
5.5	21.0	22.6
6.0	20.8	20.4

Table 5.7-Percentage of Cyclohexenes in collected sample by GC analysis at 90°C under 5 bar nitrogen and carbon dioxide

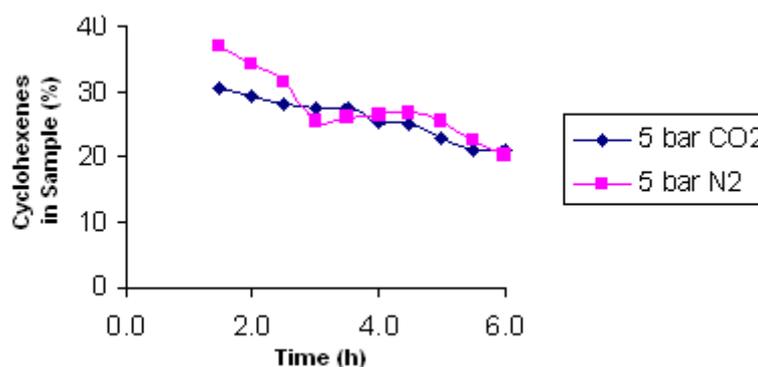


Figure 5.8- Cyclohexenes in collected samples at 90°C and 5 bar nitrogen/carbon dioxide against time

Raising the pressure of the reaction to 200 bar in carbon dioxide led to an increase in initial volume of cyclohexenes compared of acrylate (table 5.9), and there was a slight increase in catalyst lifetime that accompanied this (figure 5.10). However these results are not entirely without precedent. In the literature it has been suggested that higher pressures increase the reaction rate for Diels-Alder reactions that are catalysed homogeneously¹¹.

Time (h)	Cyclohexenes in Sample (%)				
	5 bar	50 bar	100 bar	150 bar	200 bar
1.5	30.8	78.5	49.4	53.6	71.4
2.0	29.2	79.3	47.2	49.3	69.3
2.5	28.1	75.5	46.1	43.9	67.8
3.0	27.3	72.1	44.0	41.4	64.3
3.5	27.5	73.1	43.0	40.6	61.4
4.0	25.6	72.9	43.0	37.8	60.9
4.5	25.1	72.5	42.3	35.8	60.6
5.0	22.8	70.1	40.3	34.9	58.5
5.5	21.0	68.0	39.2	34.3	56.5
6.0	20.8	66.0	40.4	33.3	56.4

Time (h)	Cyclohexenes in Sample (%)/ 1st Sample				
	5 bar	50 bar	100 bar	150 bar	200 bar
1.5	1.00	1.00	1.00	1.00	1.00
2.0	0.95	1.01	0.96	0.92	0.97
2.5	0.91	0.96	0.93	0.82	0.95
3.0	0.89	0.92	0.89	0.77	0.90
3.5	0.89	0.93	0.87	0.76	0.86
4.0	0.83	0.93	0.87	0.71	0.85
4.5	0.82	0.92	0.86	0.67	0.85
5.0	0.74	0.89	0.82	0.65	0.82
5.5	0.68	0.87	0.79	0.64	0.79
6.0	0.68	0.84	0.82	0.62	0.79

Table 5.9-Percentage of Cyclohexenes in collected sample by GC analysis at 90°C temperatures under various pressures of carbon dioxide, and relative percentage of cyclohexenes in samples compared to initial sample

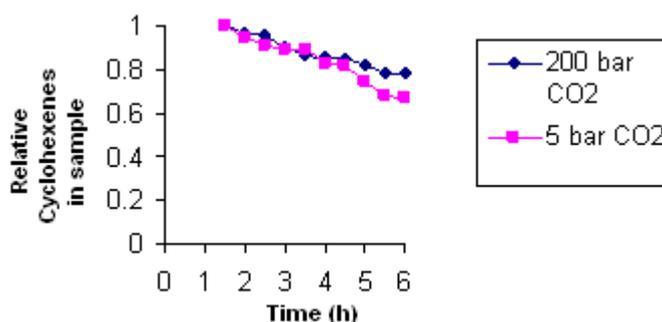


Figure 5.10-Relative Cyclohexenes in collected sample at 90 °C temperatures under carbon dioxide

To better understand the effect of pressure on the reaction a series of runs was performed at intermediate pressures of 50, 100, and 150 bar. Analysis of these reactions revealed that the process had a much higher initial conversion when 50 bar was the reactor pressure than at the other higher pressures (figure 5.11). This higher conversion was accompanied by an improved catalyst lifetime compared to both the run at 5 bar, and the runs at higher pressures (figure 5.12)

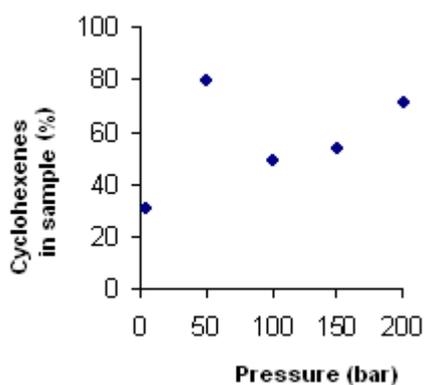


Figure 5.11- Cyclohexenes in samples collected at various pressures of carbon dioxide

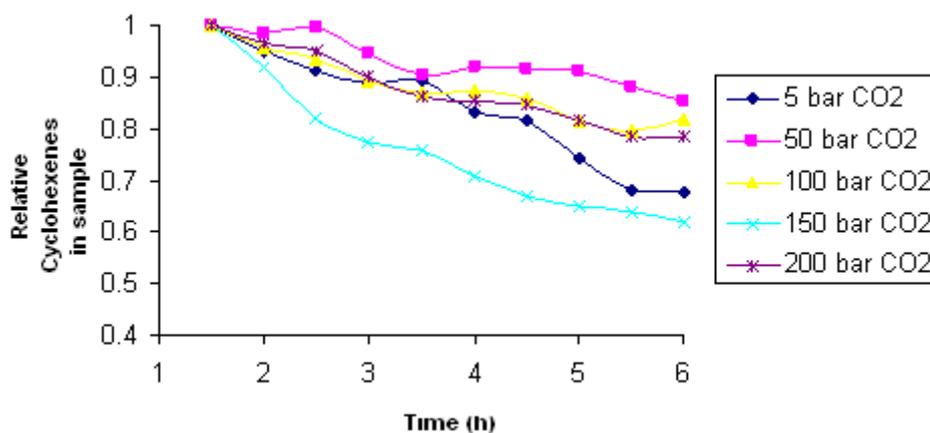


Figure 5.12- Relative Cyclohexenes in collected sample at various pressures of carbon dioxide at 90 °C

Before attempting to explain the effects in high pressure carbon dioxide it was first necessary to perform control reactions in nitrogen in order to ascertain if it would have the same effect as carbon dioxide at higher pressures.

When the nitrogen control runs were analysed they showed that nitrogen at higher pressures did indeed have a positive effect on the reaction, like carbon dioxide. However, unlike the previous reactions studied there was a clear difference between using nitrogen and carbon dioxide at a higher pressure.

Time (h)	Cyclohexenes in Sample (%)				
	5 bar	50 bar	100 bar	150 bar	200 bar
1.5	37.1	93.3	85.2	85.2	94.6
2.0	34.1	91.7	83.4	81.8	94.5
2.5	31.5	90.7	81.8	79.9	94.6
3.0	25.6	89.7	80.3	78.2	93.2
3.5	26.0	89.5	79.1	75.8	90.8
4.0	26.3	89.3	79.4	74.2	89.2
4.5	26.7	88.2	79.0	73.6	86.7
5.0	25.6	86.8	76.8	73.6	85.2
5.5	22.6	86.4	75.4	70.6	84.8
6.0	20.4	85.0	72.8	69.0	85.0
Time (h)	Cyclohexenes in Sample (%) / 1 st Sample				
	5 bar	50 bar	100 bar	150 bar	200 bar
1.5	1.00	1.00	1.00	1.00	1.00
2.0	0.92	0.98	0.98	0.96	1.00
2.5	0.85	0.97	0.96	0.94	1.00
3.0	0.69	0.96	0.94	0.92	0.99
3.5	0.70	0.96	0.93	0.89	0.96
4.0	0.71	0.96	0.93	0.87	0.94
4.5	0.72	0.95	0.93	0.86	0.92
5.0	0.69	0.93	0.90	0.86	0.90
5.5	0.61	0.93	0.88	0.83	0.90
6.0	0.55	0.91	0.85	0.81	0.90

Table 5.13-Percentage of Cyclohexenes in collected sample by GC analysis at 90°C temperatures under various pressures of nitrogen, and relative percentage of cyclohexenes in samples compared to initial sample

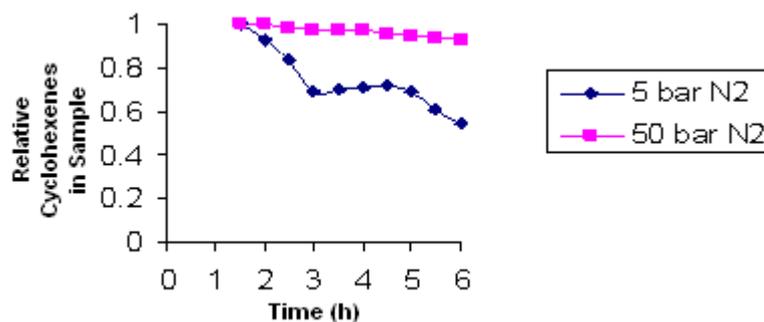


Figure 5.14- Relative Cyclohexenes in collected sample at various pressures of nitrogen at 90 °C

Increasing the pressure to 50 bar led to an increase in volume of cyclohexenes in the initially collected sample (discounting isoprene) to over 90%, this was accompanied by a dramatic increase in catalyst lifetime, from an estimated half-life of just 8 hrs at 5 bar to over 30 hours at 50 bar (figure 5.14).

The result at 50 bar of nitrogen was closely mirrored by the results at higher pressures of nitrogen, in both initial conversion and catalyst deactivation (figures 5.15 & 5.16). Unlike in the carbon dioxide runs there was no obvious optimum pressure for the reaction.

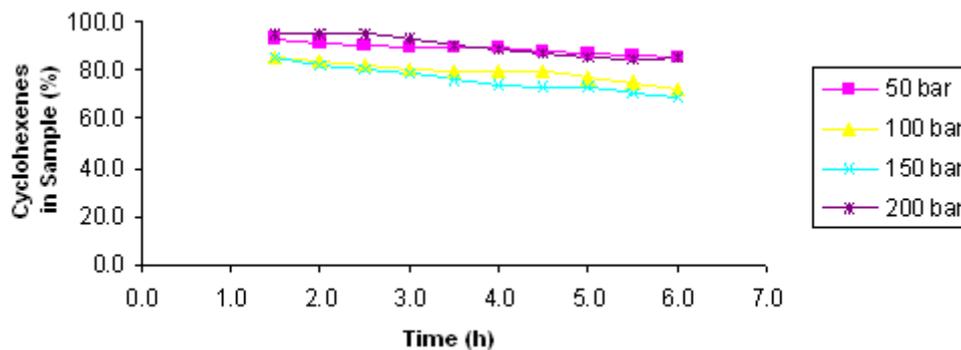


Figure 5.15- Cyclohexenes in collected samples at 90°C under various pressures of carbon dioxide against time

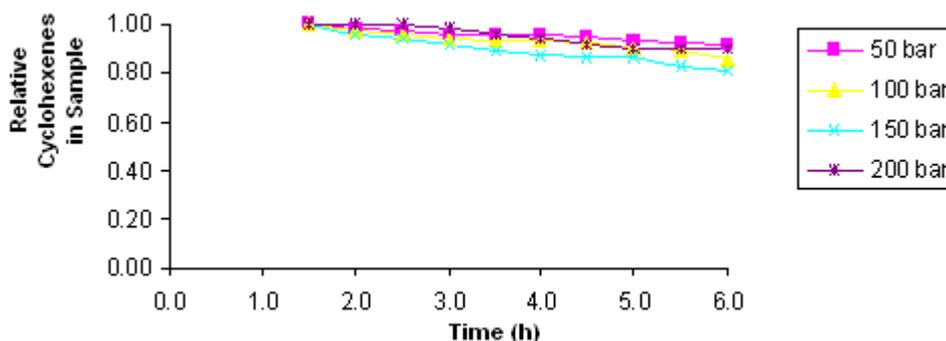


Figure 5.16- Relative Cyclohexenes in collected sample at various pressures of nitrogen at 90 °C

These results clearly show that under the conditions used in the reactions nitrogen is a much better reaction medium than carbon dioxide for this reaction. It is believed that what is being observed in the nitrogen reactions is the purely gas phase reaction. In this case a higher pressure is clearly beneficial to the reaction as would be expected from Le Chatelier's principle. The fact that there appears to be no obvious benefit to increasing the pressure beyond 50 bar may indicate that the catalyst is performing at its maximum for this temperature and reaction.

The fact that these results are not replicated when performing the reaction in higher pressure carbon dioxide would suggest that these are not gas phase reactions. One of the major assumptions of this project was that, as carbon dioxide should be in excess in the reactor, the critical point of the reaction mixture would not vary greatly from that of pure carbon dioxide. The results obtained in the Diels-Alder reaction may suggest that this assumption is incorrect. It would appear that at just 50 bar the reaction mixture is not in the gas phase. It is possible that the presence of the isoprene has lowered the critical point of the reaction mixture to the extent that it is in, or close to, the supercritical region at 90 °C and 50 bar.

The fact that the higher pressure reactions in carbon dioxide show a negative effect on the catalyst could be explained by the reaction mixture moving through or away from the critical point as the pressure increases. There is evidence of this type of behaviour in the literature, both for heterogeneous catalysed reactions, and for the Diels-Alder addition of methyl acrylate and isoprene performed without a catalyst¹³. In both cases, the authors observed a rate enhancement and improved catalyst lifetime at, or in the immediate vicinity of, the critical point. This improved catalyst performance was reduced when moving away from the critical point. It is logical that an increase in temperature would result in a more gas-like supercritical fluid. In this case the pressure is increased and it is speculated that this would lead to a more liquid-like supercritical fluid, in turn meaning that the reaction would tend towards the

liquid phase reaction. Certainly the results would suggest that the reaction is not tending towards the gas-phase reaction.

It has been hypothesised that in certain small pored catalysts, the rate of diffusion through the pores of substrates and products can be the limiting factor on the observed conversion and rate of reactions under supercritical conditions¹⁴. Zeolite β has an average pore size of less than 8 angstroms in diameter, and has a one-dimensional structure. This makes it a strong possibility that diffusion through the pores could be a factor in its use.

Bearing in mind the diffusion rate limiting possibility it was decided to attempt the reaction under the same conditions using a wider pored catalyst.

5.3-Al-HMS Catalyst

Onaka et al had reported that the ‘mesoporous aluminosilicate Al-HMS’ could be used to facilitate the liquid phase Diels alder addition of methyl acrylate to isoprene at -1°C in good yields¹⁵. The reason they had studied the reaction in the liquid phase at such low temperature was to avoid polymerisation side reactions at higher temperatures, which rapidly deactivated the catalyst.

The route to Al-HMS was taken directly from Onaka’s paper¹⁵. Salicylic acid was mixed with aluminium oxide in a water slurry in the presence of both ethanol and an organic template.

Once the synthesis was complete the powder was analysed using X-ray diffraction. When data were collected over low angles the spectrum obtained matched that from the published literature¹⁵ giving a peak at $2\theta = 1.6^\circ$ (figure 5.17), analysis of lower angles was impossible due to the back-stop, which prevents direct exposure of the detector to the beam.

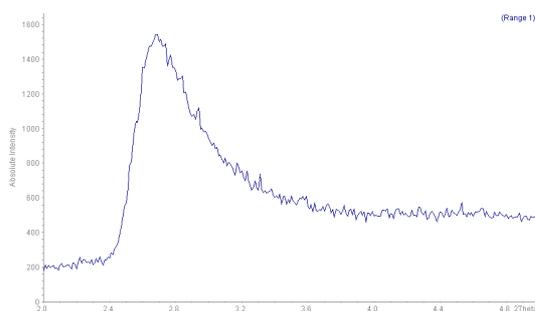


Figure 5.17-XRD trace of synthesised catalyst at low values of 2θ

However despite this seemingly confirming analysis, it should be noted that a collected at higher values of 2θ showed no prominent peaks from 5° upwards. Such spectra are generally indicative of amorphous powder mixtures and would suggest no consistent long-range structure was present in the sample.

The sample was also analysed using BET. The absorption obtained from the sample was characteristic of a microporous rather than mesoporous solid. It showed that there was a constant uptake of gas from low concentrations upwards, whereas in general mesoporous solid display some adsorption at low concentrations and a significant increase in adsorption at higher concentrations.

Microporous solids can have pore sizes of up to 20 angstroms, over twice the pore size of Zeolite β . Indeed the paper from which the synthesis was followed claimed a pore size of a similar magnitude. With this in mind it was decided to proceed with the Diels-Alder reaction using the prepared catalyst.

The reaction was first performed using nitrogen at a reactor pressure of 5 bar. The reaction was run for 6 hours. In the initial sample collected the amount of cyclohexenes in respect to methyl acrylate of over 20% was lower than that achieved with Zeolite β as a catalyst (figure 5.19).

Time (h)	Cyclohexenes in Sample (%)	
	Al-HMS	Beta
1.5	22.5	30.8
2.0	21.6	29.2
2.5	21.0	28.1
3.0	20.6	27.3
3.5	20.3	27.5
4.0	19.9	25.6
4.5	19.3	25.1
5.0	19.0	22.8
5.5	18.8	21.0
6.0	18.6	20.8
Time (h)	Cyclohexenes in Sample (%) / 1 st Sample	
	Al-HMS	Beta
1.5	1.00	1.00
2.0	0.96	0.95
2.5	0.94	0.91
3.0	0.92	0.89
3.5	0.90	0.89
4.0	0.88	0.83
4.5	0.86	0.82
5.0	0.85	0.74
5.5	0.84	0.68
6.0	0.83	0.68

Table 5.18-Percentage of Cyclohexenes in collected sample by GC analysis at 90°C temperatures under 5 bar of carbon dioxide, and relative percentage of cyclohexenes in samples compared to initial sample, for Beta and Al-HMS

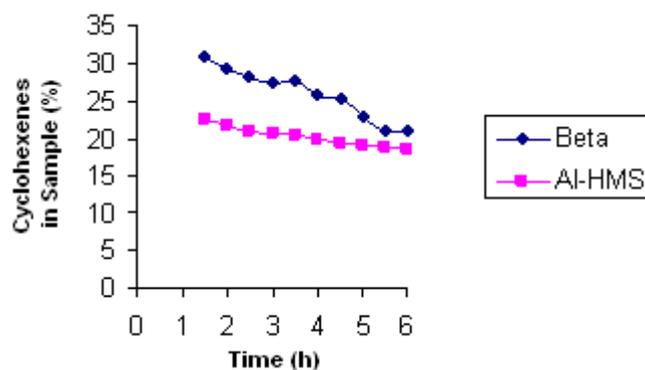


Figure 5.19- Cyclohexenes in collected samples at 90°C under 5 bar of carbon dioxide against time, for Al-HMS and Beta catalysts

Despite this lower initial value of cyclohexenes collected it is interesting to note that when comparing the normalised rate of deactivations for the two catalysts the pseudo-Al-HMS is slightly better than zeolite β (figure 5.20). Also the selectivity for the 4-substituted isomer over the 2- substituted product is similar to when Zeolite β was used.

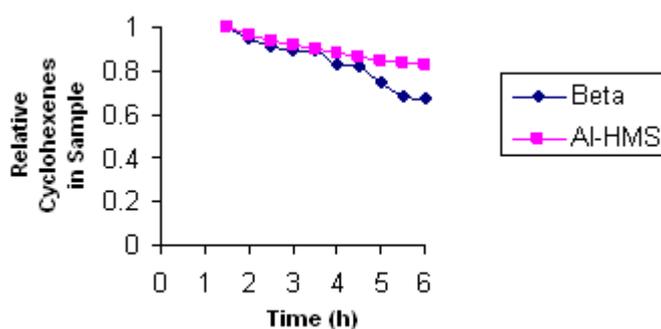


Figure 5.20- Relative Cyclohexenes in collected sample at 5 bar of carbon dioxide at 90 °C against time, for Al-HMS and Beta catalysts

When the reaction was performed using carbon dioxide at higher pressures, a similar improvement was observed in both the initial conversion and the rate of catalyst deactivation (figure 5.22 and figure 5.23) over the reaction at 5 bar. This behaviour is similar to that seen using Zeolite β . Once again the optimum pressure for the reaction appeared to be 50 bar.

Time (h)	Cyclohexenes in Sample (%)				
	5 bar	50 bar	100 bar	150 bar	200 bar
1.5	22.5	67.3	54.9	56.8	56.7
2.0	21.6	67.2	55.3	55.4	56.1
2.5	21.0	66.4	53.1	51.6	51.2
3.0	20.6	65.4	52.7	49.9	52.1
3.5	20.3	64.6	50.9	48.1	48.5
4.0	19.9	63.1	49.2	48.6	45.5
4.5	19.3	63.1	48.7	46.1	48.1
5.0	19.0	61.2	47.1	44.5	44.3
5.5	18.8	60.8	46.3	41.4	43.4
6.0	18.6	60.4	44.6	39.6	41.5
Time (h)	Cyclohexenes in Sample (%) / 1st Sample				
	5 bar	50 bar	100 bar	150 bar	200 bar
1.5	1.00	1.00	1.00	1.00	1.00
2.0	0.96	1.00	1.01	0.98	0.99
2.5	0.94	0.99	0.97	0.91	0.90
3.0	0.92	0.97	0.96	0.88	0.92
3.5	0.90	0.96	0.93	0.85	0.86
4.0	0.88	0.94	0.90	0.86	0.80
4.5	0.86	0.94	0.89	0.81	0.85
5.0	0.85	0.91	0.86	0.78	0.78
5.5	0.84	0.90	0.84	0.73	0.77
6.0	0.83	0.90	0.81	0.70	0.73

Table 5.21-Percentage of Cyclohexenes in collected sample by GC analysis at 90°C temperatures at various pressures of carbon dioxide, and relative percentage of cyclohexenes in samples compared to initial sample

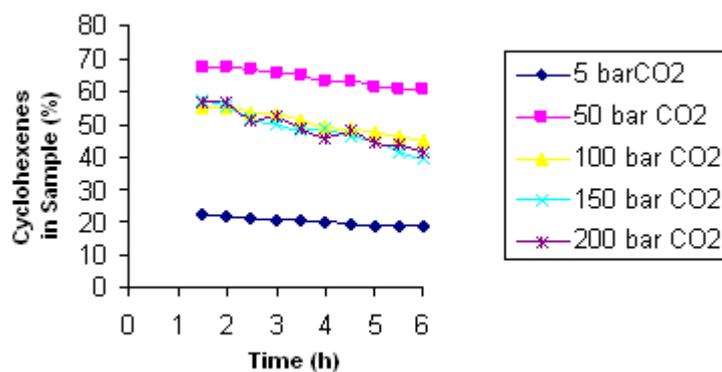


Figure 5.22- Cyclohexenes in collected samples at 90°C under various pressures of carbon dioxide against time

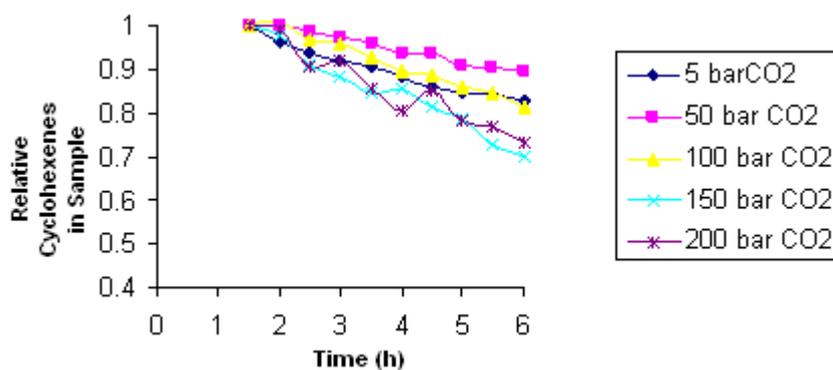


Figure 5.23- Relative Cyclohexenes in collected sample at various pressures of carbon dioxide at 90 °C against time

As before, several control reactions were performed in nitrogen, and as before the high pressure reactions led to a better catalyst performance than carbon dioxide at the respective pressure (figure 5.25).

Time (h)	Cyclohexenes in Sample (%)	
	N2	CO2
1.5	92.2	67.3
2.0	91.8	67.2
2.5	90.8	66.4
3.0	89.3	65.4
3.5	89.7	64.6
4.0	89.4	63.1
4.5	88.1	63.1
5.0	87.5	61.2
5.5	86.6	60.8
6.0	85.1	60.4

Time (h)	Cyclohexenes in Sample (%) / 1st Sample	
	N2	CO2
1.5	1.00	1.00
2.0	1.00	1.00
2.5	0.99	0.99
3.0	0.97	0.97
3.5	0.97	0.96
4.0	0.97	0.94
4.5	0.96	0.94
5.0	0.95	0.91
5.5	0.94	0.90
6.0	0.92	0.90

Table 5.24-Percentage of Cyclohexenes in collected sample by GC analysis at 90°C temperatures at 50 bar of carbon dioxide/ nitrogen, and relative percentage of cyclohexenes in samples compared to initial sample

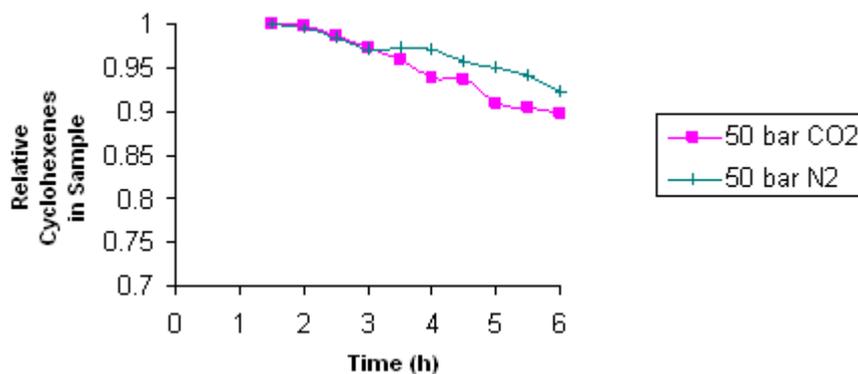


Figure 5.25- Relative Cyclohexenes in collected sample at 50 bar of carbon dioxide/ nitrogen at 90 °C against time

These results suggested that, at this temperature, using carbon dioxide above its critical temperature and pressure was having a clear effect on the reaction when compared to nitrogen as the reaction medium. This effect appears to be detrimental. However it is noted that, without precise knowledge of the exact position of the critical point of the reaction mixture, it is impossible to categorically state that supercritical carbon dioxide is beneficial for this reaction.

The results using the pseudo-AIHMS also suggest that the reactions in carbon dioxide over Zeolite β were not diffusion limited. However it is noted that without conclusive proof that the correct material had been synthesised it is not possible to state this categorically.

5.4-References

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Chapter 6-Conclusion

6-Conclusion

6.1-Catalysis Rig

The first step of the project was to build an effective rig on which to study heterogeneous catalytic reactions. It was fortunate for the project that an old disused rig for solid-supported catalyst was available. By modifying this older rig a viable rig for the study of heterogeneous reactions was made. However, as the project progressed several limitations of the rig became apparent. If further work were to be carried out using this apparatus there are several modifications that would improve the reliability, effectiveness and quality of data obtained from the rig.

The main problem areas with reliability were the expansion valves and the gas booster. The Druva expansion valves used in the rig struggled to cope with pressures below 5 bar and regularly needed to have the o-rings inside the valve replaced, as well as more major problems. It is noted that the St. Andrews group has been gradually phasing out Druva valves and replacing them with Swagelok expansion valves.

The problem with the gas booster occurred occasionally when the booster became unable to increase the pressure of nitrogen. The reason for this problem was never isolated, as it appeared to occur in the air-drive section of the booster, which was not in contact with any chemicals and the o-rings in this section did not appear perished when replaced. It should also be noted that the pressures

used in the course of the project where well below the maximum operating pressures stated for the booster.

A constant question over the nature of the reaction medium being studied persisted throughout the project. By looking at the results of the reactions performed and by calculating the density of the medium used under reaction conditions it was possible to hypothesise over the state of the medium. However it would a vast improvement to the rig to insert a window in series with the reactor in order to be able to physically observe the phase of the reaction medium. A window immediately before the reactor would enable the mixture of substrates with the reaction medium to be observed clearly, and a window immediately after the reactor would enable examination of the mixture of products and reaction medium flowing away from the reactor.

A pre-heating coil was installed to ensure that the substrate stream was at reaction temperature before entering the reactor, this is particularly important when studying a supercritical fluid, as otherwise a non-critical mixture would be entering the reactor. However the position of the preheating coil presented a problem, being situated before the inlets for gas and liquid substrates, this meant that preheated medium would be cooled by room-temperature substrates being injected. The preheating of substrates to counter-act this problem led to an issue of cavitation in the liquid feed.

With these issues in mind it is felt that a repositioning of the pre-heating coil to after the substrate inlets would be advantageous. This would ensure that

the medium and substrates are at the reaction temperature before entering the reactor and should avoid cavitation in the liquid feed. Further, although not used in any of the studies included in this thesis the gas feed suffered from crystallisation of substrates in the dosimeter head, the introduction of a non-return valve in the gas feed may help eradicate this problem.

An important issue when referring to the quality of data was sampling. The method used in this project was adequate however there was undoubtedly the loss of some higher volatility compounds that would not condense out of the product stream upon expansion. A high-pressure sampling valve was added in the re-modelling of the rig, but this was never utilised during the project. By connecting this sampling port with a GC machine it would be possible to gain more accurate data on the make-up of the product stream, in particular with out bias towards lower volatility products inherent in the current method.

A final consideration on the rig is the minimisation of dead space in the apparatus, particularly the old sampling system that if removed would half the volume occupied by the rig.

6.2- The Beckmann Rearrangement

The first process to be studied was the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam over a Zeolite Y catalyst. Initially it was decided to study the reaction at 380°C; although at this temperature the density of carbon dioxide was considerably below its density at the critical point, the

high conversion to lactam and the rapid deactivation of the catalyst at this temperature made it suitable for study.

A surprising feature of the reaction runs at this temperature was the lack of significant amount of the most commonly quoted impurity 5-cyanopent-1-ene and the presence of an unknown impurity. After investigation it was concluded that the unknown impurity was N-ethylcaprolactam, and that this impurity was being formed by a reaction with the ethanol solvent. The formation by solvent reaction appeared to be confirmed when later reactions performed using a toluene solvent show no formation of the impurity, while performing the reaction with a methanol solvent led to the formation of N-methylcaprolactam. The question arises of how this impurity is formed. Given that the impurity is a derivative of the product and no equivalent derivative of the oxime, suggests that the impurity is formed through a side reaction rather than by simple addition to the product, as there is no obvious reason for this to occur solely to the product. It is also worth noting that the concentration of the impurity detected in the reaction samples falls more rapidly with time than the concentration of desired lactam, suggesting that the reaction to form the impurity is more strongly effected by deactivation of the catalyst and the associated drop in acidity. It is considered most likely that the impurity is formed from a Ritter-style reaction of 5-cyanopent-1-ene with the solvent to yield addition of ethanol across the nitrile group. Cyclisation of this compound would yield N-ethylcaprolactam. Although significant amounts of 5-cyanopent-1-ene are not observed in the collected samples the product is simply formed by the dehydration of the oxime and is then known to be strongly bound onto the surface of the catalyst. When reaction with

ethanol occurred it would be in the correct formation to cyclise and desorb from the surface, and given that Ritter reactions require to be performed under extremely acidic conditions the relatively rapid rate of deactivation of this side-reaction would appear consistent with the theory.

The reaction at 380°C was also performed using toluene as a solvent, as noted no N-ethylcaprolactam was observed. Using toluene the apparent loss of catalytic activity was more rapid than when ethanol was used as a solvent. The reasons for this may well be two-fold. Firstly it is widely believed that the polarity of alcohols helps to desorb the desired product from the catalyst surface, there-by prolonging the catalyst life-time. Secondly, protonation of the toluene is much more likely to lead to larger carbocations being adsorbed onto the surface of the catalyst than the equivalent protonation of ethanol. Attempted longer time runs at pressures of 300 bar proved unsuccessful due to blocking of the rig. Analysis of the blockage revealed that the material was largely composed of unknown compounds with an atomic mass of greater than 150 units. Reactions run using both nitrogen and carbon dioxide gave similar results with the rig blocking after a short period of time due to a build up of higher molecular weight compounds after the reactor. The reason for this is unknown. However, the reaction was clearly producing the same result whether nitrogen or carbon dioxide was used, leading to the conclusion that the effect being observed was simply a result of the increase in pressure.

The difficulties encountered at higher pressures at 380°C, combined with the density of carbon dioxide at the maximum available pressure being

considerably below its density at the critical point, meant that studying the reaction at a lower temperature was desirable. It was decided to study the reaction at 250°C as this was the lowest temperature at which conversion to lactam had been observed on the rig.

When the reaction was run over 6 hours at various pressures of carbon dioxide a clear effect was observed; with increasing pressure, the amount of lactam produced and the rate of the catalyst deactivation both decreased. When performing the same series of reactions substituting nitrogen for carbon dioxide as reaction medium the same effect was observed. Nitrogen at this temperature is above its critical temperature. However, its behaviour will be similar to that of an ideal gas, as it is considerably in excess of its critical temperature. These results lead to the conclusion that the reaction is certainly being observed in the vapour phase, and that the effects observed are due to the increase in pressure of the reaction, rather than a change in the properties of the reaction medium.

Further weight was added to this conclusion when a control experiment was performed to see if the slowed deactivation of the catalyst was caused by removal of coke/ precursors or by inhibiting their formation; the reaction showed that the medium did not appear to be removing coke/ precursors from the catalyst, hence the effect must be caused by the prevention of coke/ precursors forming on the surface.

It is thought that effects that were observed were caused by the increased competition for the reactive sites on the catalyst as the pressure increases. As the

pressure of the reaction is increased the composition of the mixture entering the reactor remained the same because, the flow rate of the reaction medium and the injection rate of the oxime solution were maintained across the series of reactions. This would mean that the residence time of molecules in the reactor is increased with increasing pressure. The increased competition for active sites from molecules in the reactor at higher pressures may result in a shorter time on the surface of the catalyst for individual molecules, thus giving a shorter window of time for the rearrangement to take place. In effect the higher pressure leads to a higher turnover of molecules at the active site; as the molecules have a shorter period time to rearrange, the frequency that the rearrangement and undesired side reactions take place will reduce. This will in turn lead to a drop in the amount of lactam being produced against time as well as a decrease in the rate of deactivation of the catalyst.

The findings at 250°C were interesting but appear to be slightly at odds with the brief results obtained at 380°C. At 380°C it appeared that, when the process was run at a higher reaction pressure, the formation of coke precursors was possibly favoured. In order to see if the findings at 250°C would be replicable at a higher temperature it was decided to investigate the reaction at 300°C.

When the process was studied at 300°C the results achieved with carbon dioxide were, once again, closely mirrored by the results achieved with nitrogen at increasing pressure. However, the results were not analogous with those observed at 250°C. Once again the deactivation rate of the catalyst appeared to

decrease with increasing pressure, but this was accompanied by an increase in the amount of lactam observed in the collected samples.

It is thought that a similar effect is being observed at 300°C as was observed at 250°C. However, at this temperature the increase in temperature would be expected to lead to an increase in the rate of the reaction. As described above the increase in pressure would lead to an increase in the residence time in the reactor and increased competition for places, leading to a shorter time at the active site for individual molecules. However, with the increased rate of reaction it would appear that the faster turnover leads to the rearrangement occurring more frequently as the active sites will be freed more quickly after performing the rearrangement. This quicker turnover at the active sites would appear not to give coke precursors long enough on the catalyst surface to build up at a faster rate, leading to the observed increase in catalyst lifetime.

Given the results at 380°C it can be hypothesised that at this temperature the rate of coke propagation is faster than the turnover of molecules at the active site, leading to the observed higher mass molecule formation at this temperature.

It is clear from the effects observed that the reaction was being studied in the vapor phase. However it is noted that the critical point of ethanol (241°C, 61 bar) is close to the lowest temperature that the reaction appeared possible. It would be interesting to study the reaction around the critical point of ethanol with no other reaction medium present.

It would also be instructive to investigate further the route to the formation of N-ethylcaprolactam at 380°C. Reaction with the product could be ruled out by passing a caprolactam solution in ethanol over the catalyst, if the theory proposed above is correct we would expect to observe no ethyl derivative to be formed. Attempting the Ritter reaction of 5-cyanopent-1-ene with ethanol would clarify the feasibility of the theory, and the passing of a solution of 5-cyanopent-1-ene in ethanol over the catalyst would show if the molecule is involved in the formation of the impurity.

6.3- The Fries Rearrangement

The results of the studies of the Beckmann rearrangement showed that the reaction was occurring in the vapour phase. In order to study carbon dioxide at a higher density it would be necessary to study a reaction at a lower temperature given the pressure restrictions of the rig. The Fries rearrangement of phenyl acetate to give hydroxyacetophenones was such a reaction with the desired rearrangement being possible at 150°C

When the reaction was studied using nitrogen at various different pressures it was observed that changing the pressure appeared to have no effect on the reaction or catalyst lifetime. These results were replicated when the same series of reactions were performed using carbon dioxide rather than nitrogen.

Given the results of the reactions and the fact that carbon dioxide is still below its critical density at 200 bar and 150°C, it is felt that it is most likely that a

liquid phase reaction is being observed, with a biphasic feed of phenyl acetate and nitrogen or carbon dioxide. If a liquid phase reaction were occurring with a biphasic system then we would expect the reactor to fill with the liquid phase phenyl acetate, given the up flow direction of the system used, and the gas phase of nitrogen or carbon dioxide bubbling through the reactor would have no significant interaction with the substrate/products of reaction. This would lead to the results observed of a change in pressure of reaction medium having no observed effect on the rate of reaction or deactivation of the catalyst.

After these results it was decided to study a reaction that could be performed at a lower temperature. However, a solubility study of phenyl acetate in carbon dioxide would be instructive, as would the analysis of the critical point of the mixture of phenyl acetate and carbon dioxide in the ratio used in this study. No data was found for the critical parameters of phenyl acetate, if these parameters could be identified it may be possible to study the reaction above the critical conditions for phenyl acetate, in the absence of another separate reaction medium.

The results can also be used to further emphasise some of the shortcomings of the rig. If a window had been installed it would be easy to observe if the phenyl acetate were still in a liquid state going into the reactor. The cooling of the reaction medium by the phenyl acetate upon injection may have contributed to the lack of mixing of the two substances. If the phenyl acetate were injected before the pre-heating coil and warmed with the reaction medium this may have aided mixing of the substances.

6.4-The Diels-Alder Reaction

The last reaction to be studied during the project was the Diels-Alder addition of methyl acrylate and isoprene. The reaction was selected because of the low temperatures ($< 100^{\circ}\text{C}$) at which the addition could be performed over heterogeneous catalysts, thus enabling the reaction to be studied at densities of carbon dioxide similar to its density at its critical point.

The reaction was studied over Zeolite β at 90°C . This temperature was selected as the density of carbon dioxide at 200 bar would be 0.53 g cm^{-3} , and the temperature is above the boiling point of both reactants.

When the reaction was studied using various pressures of carbon dioxide it was observed that the amount of desired product in the collected samples peaked at 50 bar, as did the implied lifetime of the catalyst. Further increasing the pressure of reaction above 50 bar saw an initial drop in product collected followed by a gradual rise, although the rate of deactivation slowed with increasing pressure it never achieved the results obtained at 50 bar within the restrictions of the rig.

When the reaction was studied using nitrogen at various pressures, very different results were observed. While the reaction at 5 bar was similar to the analogous reaction in carbon dioxide, all the reactions performed at higher pressures of nitrogen resulted in a higher percentage of desired product in the

collected samples and a greater implied catalyst lifetime than in the respective reactions performed with carbon dioxide. In addition there was little variation in the results obtained with nitrogen at 50, 100, 150, and 200 bar. It is assumed that the reactions in nitrogen are occurring in the vapour phase, and that the increase in pressure strongly favours the desired reaction. The results imply that the reaction is not occurring in the vapour phase when carbon dioxide is used as the reaction medium. It is believed that the mixture of isoprene and methyl acrylate in carbon dioxide has moved the critical point to a lower pressure than that of pure carbon dioxide to the region of 50 bar. The literature states that the rates of uncatalysed Diels-Alder reactions are greatly improved at or near the critical point of the mixture, and it is believed this is the effect being observed at 50 bar. As the pressure is increased it is likely that the reaction becomes bi- or possibly multi-phasic; the observed results would be explained by a liquid layer composed of mostly methyl acrylate and a vapour phase containing isoprene. The reaction would then be limited by the amount of isoprene dissolved in the liquid layer, so that, as the pressure increases the amount of isoprene dissolved in the liquid layer increases and hence the rate of reaction increases.

It is recognised that without a model of the phase diagram it is hard to draw conclusions on the position of the critical point of the reaction mixture, therefore, if further work is carried out on this reaction it is necessary to procure this phase diagram utilising one of the specialist computer programs available, or measurements of phase behaviour using a windowed autoclave. Once the critical point of the reaction mixture has been identified a series of reactions around the critical point could be run to see the effect on the catalyst under these conditions.

If a positive effect is observed near the critical point there are several possible courses of action. The catalyst could be altered to see if a better conversion is possible using an alternative catalyst from the literature. The composition of the reaction mixture could be altered in order to lower the critical point and attempt to perform the reaction at lower temperatures. It may be possible to attempt the reaction with no carbon dioxide or nitrogen present under supercritical conditions for the reactants.

It has been stated in the literature that the nature of coke laid down is different in supercritical reactions from that laid down in gas phase reactions. It would be possible to gain an indication of whether the reactions in carbon dioxide were in the supercritical phase by performing TGA analysis on the spent catalyst from the reaction for the H:C ratio of the coke being burned off the catalyst and comparing it to that of a catalyst spent in a reaction using nitrogen as the reaction medium.

It has also been shown that reactions in supercritical carbon dioxide may damage the structure of the catalyst. It would be relatively simple to analyse the catalyst by XRD both before and after the reaction and compare the spectra to ascertain whether this was the case with these reactions. Macroscopic changes in morphology could be examined by (electron) microscopy.

The reactions performed using the synthesised Al-HMS did not show the expected improved conversion when compared to Zeolite β , however the analysis

of the synthesised catalyst sample was inconclusive. Unfortunately all of the synthesised material was used up in the reactions and analysis. It would be possible to repeat the synthesis and perform further analysis on the sample obtained. In particular electron microscopy may be able to show if the material is porous, what size the pores are, and how this pore size compares to the literature value.