Synthesis of ethyl ethanoate from ethanol by heterogeneous catalytic dehydrogenation, hydrogenation and purification

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Synthesis of Ethyl Ethanoate from Ethanol by Heterogeneous Catalytic Dehydrogenation, Hydrogenation and Purification

Stephen William Colley

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Doctor of Philosophy

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Chapters 1-6 and Appendices

Intellectual Property and Confidentiality

This report is covered by the agreement between Davy Process Technology and The University of Durham dated 10th June 1996. Particular attention is drawn to articles 6 and 7 covering these issues, as some of the concepts herein are commercially sensitive.

The material in this thesis has not been submitted for examination for any other degree or part thereof, at The University of Durham or any other institution. The material contained herein is the sole work of the author except where formally acknowledged by reference.

Some of the catalysts used for this work were obtained from specialist catalyst manufacturers under strict non-analysis agreements and hence precise details of the physical and chemical properties could not be given in the text that follows. For further information and samples of these catalysts, the suppliers must be contacted directly.

Acknowledgements

I would like to thank Davy Process Technology for sponsoring me through the five years of this degree. I would particularly like to thank Norman Harris for allowing me to begin the study, Mike Wood for his patience and understanding during the last five years, and all of the chemists and engineers who worked on the ethyl ethanoate project. I would especially like to thank all of those chemists who worked shifts, operating the test equipment on a 24 hour basis; the ethyl ethanoate process and this thesis could not have been completed without your help.

I would also like to thank Prof. Ken Waugh and Dr. Javad Tabatabaei for their help in characterizing the ethanol dehydrogenation catalyst.

ABSTRACT

A study has been carried out into the reactions of ethanol over transition metal dehydrogenation catalysts, with particular emphasis on the reaction of ethanol to ethyl ethanoate. The reaction is of commercial interest, and the testwork has been aimed at the development of a process that would yield ethyl ethanoate at commercially acceptable purity.

Copper based catalysts have been shown to selectively promote the formation of ethyl ethanoate. Experimental work has been carried out to identify an optimised catalyst and reaction conditions for the ethanol to ethyl ethanoate reaction. A copper based catalyst that yields >95% selectivity to ethyl ethanoate, at >40% conversion of ethanol, has been identified. A purification scheme has been devised that incorporates selective hydrogenation using either nickel or ruthenium heterogeneous catalysts to remove aldehyde and ketone by-products. The purification scheme includes a novel distillation section.

The catalyst system developed can be used to synthesise ethyl ethanoate at a purity of >99.98% from industrially available ethanol that contains up to 5% 2-propanol. A commercial plant producing 50,000 tonnes of ethyl ethanoate per annum, using the technology described in this thesis, has been in operation since April 2001.

Four patents, based on the technology described in this thesis, have been applied for or granted.

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Abbreviations used

DEE	Diethyl Ether
DPT	Davy process Technology
EtOAc	Ethyl Ethanoate
FOB	Free on Board
GC	Gas Chromatography
GC/MS	Gas Chromatography with Mass Spectrometer detector
HP	High Pressure
HT	Heating Tape
LHSV	Liquid Hourly Space Velocity
LP	Low Pressure
MFC	Mass Flow Controller
MFM	Mass Flow Meter
PSD	Pressure Swing Distillation
RFC	Reactive frontal Chromatography
SEM	Scanning Electron Microscopy
SLPH	Standard Litres per Hour
PI	Pressure Indicator
Rx	Reactor
TC	Thermocouple
TPD	Temperature Programmed desorption
TPRS	Temperature Programmed reaction Spectroscopy
Tm	Temperature at Maximum
TPA	Tonnes per Annum
UMIST	University of Manchester Institute of Science and Technology
VLE	Vapour Liquid Equilibrium

Chapter 1

Dehydrogenation of Ethanol To Produce Ethyl Ethanoate

1.1 Aims

The aim of this work is to develop a commercial process to produce ethyl ethanoate from ethanol using heterogeneous catalysts. The study involves

i) Testing and development of catalysts for high activity (>40% conversion of ethanol) over an extended life. High activity for at least 1000 hours is considered acceptable.

ii) Development of the process to achieve high selectivity (>90%), and the recovery of products by standard industrial techniques such as distillation. The methods chosen should be successfully demonstrated in the laboratory.

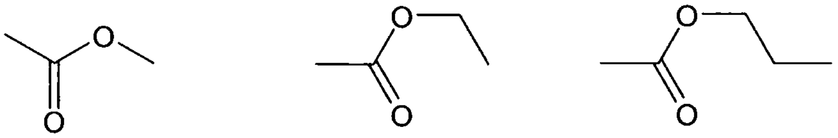
iii) Development of a kinetic model, suitable for use in designing a large scale (50,000 TPA) industrial plant.

iv) Development of the laboratory process to one that can utilise industrially available ethanol sources, including sources that contain significant quantities of impurities.

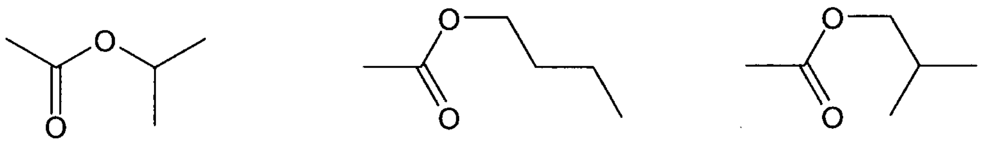
iv) Determination of the mechanism for the synthesis of ethyl ethanoate and significant by-products

1.2 Commercial Background

Ethyl acetate, the widely used trivial name for ethyl ethanoate, is an industrially important bulk chemical[1] used primarily as a solvent in the paints, coatings and inks industry. Its manufacture is linked with that of other low molecular weight acetate (or ethanoate) esters – methyl ethanoate, iso-propyl ethanoate, n-propyl ethanoate, iso-butyl ethanoate and n-butyl ethanoate – with many manufacturers operating multi-product plants capable of producing a range of esters on a batch basis. Total world production of acetate esters in 2002 approaches 2,400,000 metric tonnes per annum in the proportions methyl ethanoate 3%, ethyl ethanoate 51.8%, butyl ethanoates 37.5%, propyl ethanoates 7.7%[1]. Three companies dominate the world manufacture of ethanoate esters – BP-Amoco (25%) Celanese (15%) and Eastman (10%) and whilst BP and Celanese produce world-wide, Eastman produce only in the United States. Manufacture methods for ethanoate esters are detailed in section 1.3, below.



Methyl Acetate Ethyl Acetate Propyl Acetate



iso-Propyl Acetate Butyl Acetate iso-Butyl Acetate

Figure 1.1 – Common Acetate (Ethanoate) Esters.

Typical costs for the feed materials – ethanoic acid, the various alcohols, and product esters are given below. All costs are quoted in US dollars and are for a metric tonne – prices are taken from Chemical Marketing Reporter, June 2002. Typically the price quoted is FOB (Free on Board – or before local taxes) and in the case of ethanol is the non duty-paid price.

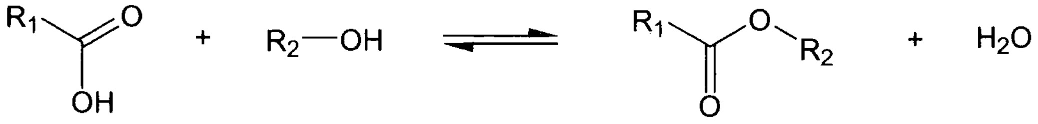
Material	**Price (US$/tonne)**
Ethanoic acid	980
Methanol	200
Ethanol	530
2-propanol	760
1-propanol	1410
iso-butanol	1230
1-butanol	1230
Ethyl ethanoate	1280
1-propyl ethanoate	1460
1-butyl ethanoate	1340
iso-butyl ethanoate	1340

1.3 Commercial Synthesis of ethyl ethanoate

There are a number of commercial acetate ester processes – some are used to produce the entire range of esters and some for individual esters. These processes are detailed below.

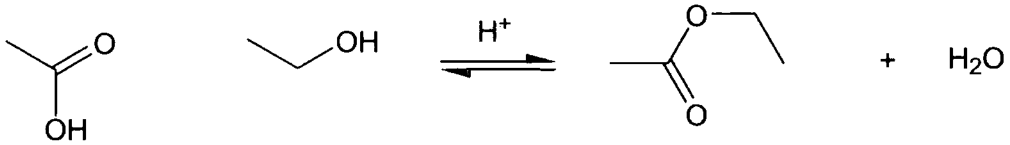
1.3.1 Esterification

Fischer esterification[2] is used to produce all acetate esters and is the most widely used commercial method. The process involves the reaction of acetic acid with an alcohol in the presence of an acid catalyst, usually sulphuric or sulphonic acids. Most processes involve the addition of the alcohol to a reactor containing acetic acid. The reaction is equilibrium limited, and in most cases the water of reaction is removed by distillation in order to drive the equilibrium to completion [3].



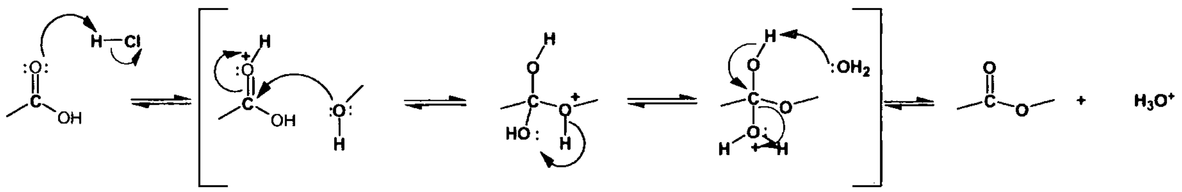
Carboxylic Acid + Alcohol Ester + Water

Specifically, for Ethyl ethanoate

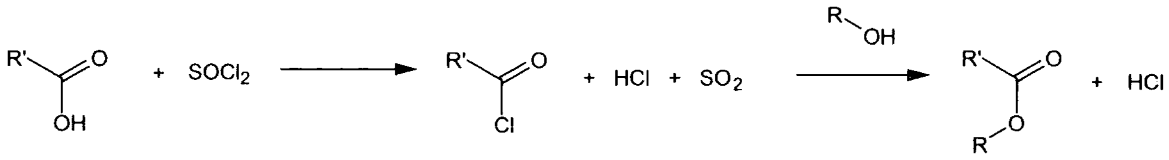


Ethanoic Acid + Ethanol Ethyl Ethanoate + Water

The mechanism of reaction is shown below [4]. The acid catalyst protonates the carboxylic acid, activating it and allowing nucleophillic attack by the alcohol. The intermediate tetrahedral carbon decomposes to form the ester.



Laboratory or small scale ester synthesis is more commonly achieved by the reaction of an acid chloride with an alcohol according to the scheme shown below:



but is only applicable to high value esters and to esters that have no other hydroxy containing functional groups. The reaction does not require the use of a catalyst and in practice is not equilibrium limited.

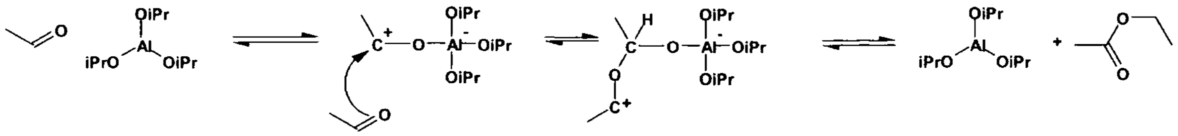
Industrial processes are complicated by the existence of azeotropes of the ester and alcohol[5], and separation of the products being complicated in some instances. Much of the equipment in an ester production unit is required to purify the ester product and recycle unreacted feed alcohols. Typical specifications of ethyl ethanoate and butyl ethanoate are given below[1]:

	Ethyl Ethanoate	Butyl Ethanoate
Ester wt% (min)	99.5	99.5
Alcohol wt% (max)	0.5	0.5
Water wt% (max)	0.01	0.01
Carbonyls wt%(max)	0.01	0.01

Several minor synthetic methods for ethyl ethanoate synthesis are discussed below:

1.3.2 Tishchenko Mechanism

The disproportionation of two moles of ethanal to form ethyl ethanoate is termed the Tishchenko reaction[6] . It is catalysed by aluminium alkoxides and activated by aluminium and iron chlorides.



This process is operated commercially by Eastman in the United States and by various suppliers in Japan, where it is the leading source of ethyl ethanoate.

When used with a single aldehyde, symmetrical esters are produced. When two or more aldehydes are used a mixture of esters is produced. There are no commercial producers of mixed esters using this process.

1.3.3 Hydrocarbon Oxidation

The primary source of acetic acid prior to the introduction of the Monsanto acetic acid process was the oxidation of butane and naptha[7]. Acetic acid is formed as a significant side-product, and this acid was used to produce ethyl ethanoate by esterification. Hydrocarbon oxidation is not now a major source of acetic acid or ethyl ethanoate and is therefore not considered further.

1.3.4 Transesterification

Trans-esterification[8], or ester exchange as it is known industrially, is used commercially to produce ethyl ethanoate by the reaction of polyvinyl acetate and ethanol. The products are ethyl ethanoate and polyvinyl alcohol. The process can be either acid or base catalysed. Butyl and higher acetates are manufactured by reacting ethyl ethanoate and butanol in the presence of base catalysts such as titanium isopropoxide.

1.4 Survey of Ethanol to Ethyl Ethanoate Literature

There exists a large body of literature on the theme of catalytic dehydrogenation, generally concerned with the production of carbonyl compounds from alcohols, and unsaturated hydrocarbons such as styrene, propene and butene from ethyl benzene, propane and butane (see below). There is little specific literature on the dehydrogenation of alcohols to form esters, and what little there is concentrates on methyl formate from methanol and ethyl ethanoate from ethanol. While there are a number of chemical methods[9] that can be utilised to dehydrogenate alcohols, for example DMSO, these are not industrially important outside the field of pharmaceuticals. Dehydrogenation of bulk chemicals is invariably carried out catalytically, and almost exclusively over heterogeneous catalysts. The literature review presented here reflects the predominance of heterogeneous catalysis and industrial applications.

1.4.1 General Principles of Catalysis

Heterogeneous catalysts are defined as 'solids that increase the rate of a reaction by virtue of the specific properties of their surfaces'[10], and they remain unchanged at the end of the catalytic cycle. The position of equilibrium of the reaction is unchanged by a catalyst which, however, speeds up the rate of the forward and backward reaction. For a reactant such as ethanol, there are several reactions that are thermodynamically feasible. Catalysts are chosen for their ability to speed a particular reaction over others – this relates to the selectivity of the catalyst. Ethanol decomposition by dehydrogenation is the favoured reaction when using a metallic copper catalyst. The reaction proceeds to either ethanal or ethyl ethanoate, depending on reaction conditions:

$CH_3CH_2OH \rightarrow CH_3CHO + H_2$

$2\ CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + 2H_2$

However, over an oxide catalyst such as alumina the decomposition reaction that is favoured is dehydration, resulting in ethene or diethyl ether:

$CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$

$2\ CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 + H_2O$

Clearly the nature of the catalyst influences the reaction path, and given that both reactions are thermodynamically possible the nature of the catalyst is all important in the development of an industrial process.

Following the examples shown above, heterogeneous catalysts can be grouped into types, according to their physical properties such as electrical and thermal conductivity, which relate to their areas of application. The primary functions of metals (copper, platinum, palladium etc) are for hydrogenation and dehydrogenation, while those of metal oxides are oxidation and reduction. The table below [10] lists the functions of heterogeneous catalysts:

Class	Metals	Metal oxides and sulphides		Salts and acids
Conductivity Type	Conductors	Semi-conductors	Insulators	
Major Uses	Hydrogenation Dehydrogenation Hydrogenolysis	Oxidation Reduction Dehydrogenation Cyclisation	Dehydration Isomerization	Polymerisation Isomerization Cracking Alkylation Hydrogen transfer
Minor Uses	Oxidation Reduction	Hydrogenation	Hydrogenation	

Table 1.1 General Classification Of Catalyst Types

Metals and semi-conducting oxides catalyse dehydrogenation and hydrogenation reactions by their ability to adsorb hydrogen and the parent molecules (ethanol in the case of ethyl ethanoate), whereas insulating oxides such as alumina tend to catalyse dehydration due to their ability to adsorb water. The differences in selectivity of semi-conducting and insulating oxides and sulphides are associated with the ability to depart from stoichiometry in the lattice oxygen. Oxygen atoms in semi-conducting oxides are fairly easily removed or added to the lattice. Consequently, they are good oxidation and reduction catalysts. In contrast, insulating oxides are not capable of this form of departure from stoichiometry and are not good oxidation / reduction catalysts. Alumina and silica, which fall into this latter group, are however important as they can adsorb water and act as good dehydrating agents.

1.4.2 Surface adsorption and catalysis

In order to react, reactants must first be adsorbed onto the catalyst from the 'less dense phase' – the liquid or gas that is in contact with the catalyst. It is a general principle that the catalysis occurs on the surface of the catalyst, not in the bulk of the active catalyst. Figure 1.2 indicates the state of an atom at the surface of a crystal: in the bulk phase each atom is close packed and surrounded by and bound to a number of other atoms co-ordinating to the atoms. At the surface of the crystal not all the bonding preferences of the surface atoms can be satisfied and there are, in principle, unpaired electrons associated with the atoms at the catalyst surface. The unpaired electrons result in the surface having an energy similar in concept to the surface energy of liquids. Adsorption at the surface of the solid involves these free valency sites. The adsorbing molecule interacts with the surface atoms and in the process loses energy as it is now stationary and bound at the catalyst surface rather than in free motion. Given these losses in free energy in the system, the process of adsorption must always be exothermic. One point to note is that if the adsorption of the reactant or product on the catalyst surface is a very energetic process, the concentration at the catalyst surface may well block transfer of reactants to and from the surface. In this case the strongly adsorbing molecule could be termed a poison. Dehydrogenation reactions commonly generate products that are more strongly adsorbed onto the catalyst surface than the reactant molecules and so self-poisoning of the catalyst by the product is a problem that will be discussed in later sections. Conversely, if the reactants are not adsorbed strongly, it is likely that the catalyst will be poor in terms of rate enhancement. There is therefore a range of adsorption energies that makes for an efficient catalyst, and the rate of catalysis will be a relationship between the strength or heat of adsorption and catalytic activity.

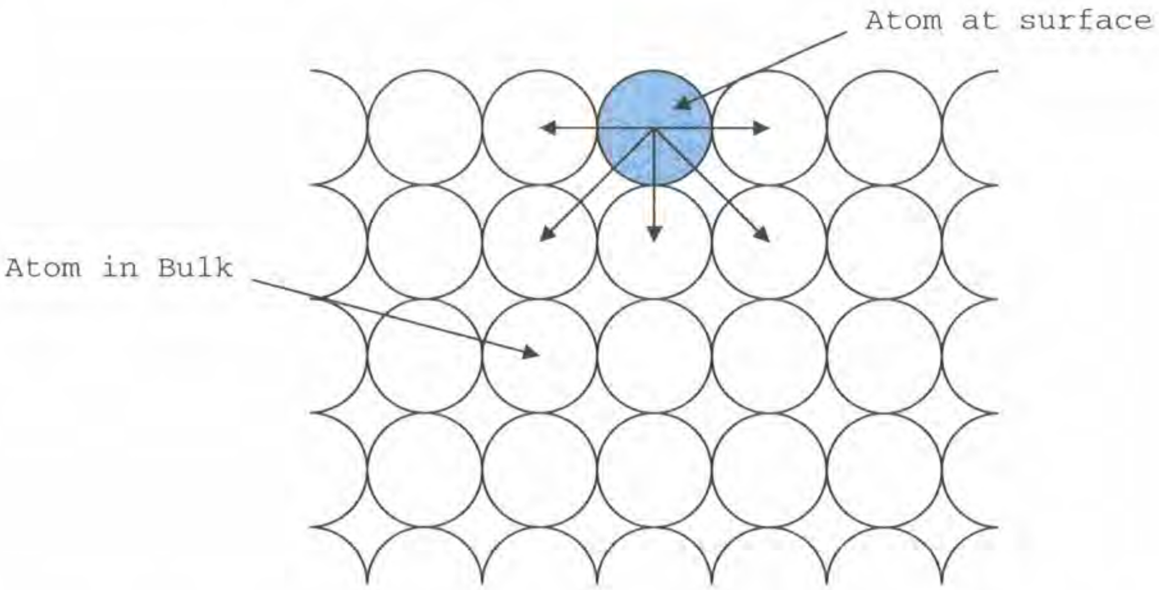


Figure 1.2: State Of An Atom At The Surface Of A Crystal, Illustrating Near Neighbours With Which It Interacts.

The efficient absorption of a molecule on a surface depends on a number of factors, but it centres around the stabilisation of transition states within the reaction. The Absolute Rate Theory[11] states that the rate of a reaction is governed by the rate of crossing of an energy barrier or of forming an activated complex. The rate difference between a heterogeneous and homogeneous process is predicted by the theory to be in the order of $10^{-12\pm3}$ times exp.($\Delta E/RT$), that is the rate for a homogeneous process is very much faster than for a heterogeneous process.. The rates are calculated for $1cm^2$ of surface and $1cm^3$ of gas, and ΔE is the difference in activation energy. Given that in the present context, the rate of the heterogeneous catalysed reaction is faster than that of the homogeneous, uncatalysed reaction, the heterogeneous reaction must either have an activation energy considerably smaller than that of the homogeneous reaction or the catalyst must exhibit a very large surface area. Given that for most metal catalysts, surface areas lie in the region of $10\text{-}30m^2/g$ (10^5 cm^2/g) there is a difference in activation energy that must be accounted for. In fact, the range of activation energy differences of surface processes[12] has been found to be in the region of 20-40 $Kcal/mol^{-1}$. In the case of a homogeneous reaction of two atoms, the transition state can only be achieved if energy is removed in some manner, such as through the collision with a third atom. Heterogeneous catalysts stabilise the transition state by lowering the energy of the atoms bound to the surface compared with those in the less dense phase. Other factors, such as the activation of the reactants by breaking bonds in the reacting molecule and making bonds between the molecule and the catalyst surface also have major effects, especially in hydrogenation and dehydrogenation reactions. A case in point is the hydrogenation of molecules having a double bond in the presence of precious metal catalysts. The reaction is extremely slow in the homogeneous phase due to the strength of the double bond that has to be broken before reaction can take place. It is believed that when an alkene is adsorbed onto the catalyst surface it assumes the shape and configuration of the parent alkane. The double bond is broken and is replaced by two carbon-metal bonds, which are then broken by reaction with adsorbed hydrogen. The exact distances between the metal centres have an effect on the energy of the transition state. The closer the interatomic distances on the metal surface are to the interatomic distance of the absorbed species, then the closer to the minimum energy state the transition state will be. This can be illustrated conceptually in Figure 1.3 below: States A and C are the case when the interatomic distance is less or greater than the optimal, state B is when it is close to optimal. The energy barrier to overcome is at a minimum for state B: in cases A and C there is an energy barrier to overcome in adsorbing the molecules due to strain in the bonds between the adsorbed molecule and the catalyst surface.

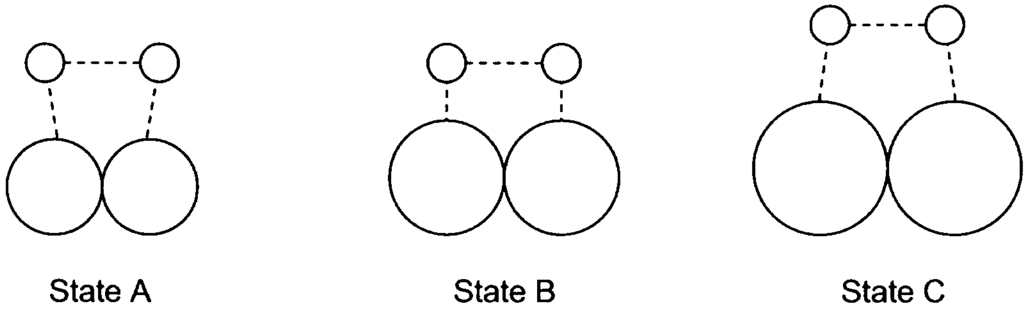


Figure 1.3 Illustration Of Bond Configuration Between Adsorbed Molecules And Catalyst Surface

There are two types of adsorption that occurs on a surface – Physical adsorption or Van der Waals adsorption, and chemisorption. The two differ in fundamental ways in relationship to catalysis. Physical adsorption, or physisorption, occurs when the adsorbed molecule is held at the catalyst surface by weak Van der Walls forces, and not by chemical bonds. The adsorption is weak and occurs at low temperatures below the critical temperature of the adsorbing molecule. At higher temperatures the amount of physisorption is low and is not a significant factor in catalysis. There is little energy release on the adsorption of the molecule and the adsorption is not an activated process. In contrast, chemisorption is a process where the molecule and surface take part in a reversible chemical reaction that results in strong adsorption that occurs over a wide temperature range. There is a release of energy on adsorption and the free energy of the adsorbed molecule and the catalyst surface is reduced. Figure 1.4 below (after Dowden)[13] shows the different adsorption processes of a diatomic molecule that dissociates on adsorption, in terms of potential energy.

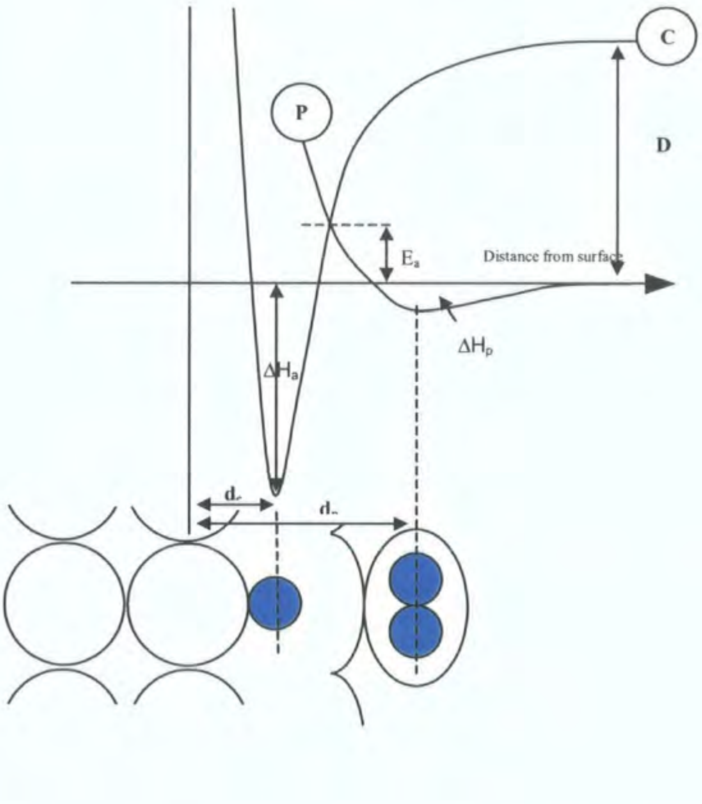


Figure 3 Adsorption and Van der Waals Adsorption At A Catalyst Surface.

See Text For Key To Symbols

The difference between the energy profiles of the chemisorbed atom, 'C' and physisorbed molecule, 'P', can be clearly seen. The curves showing heats of adsorption (ΔH_a and ΔH_p) vs. distance from the surface show markedly different characteristics in terms of magnitude and shape. The curves intersect at the activation energy E_a, the barrier to adsorption, as illustrated. The value of the activation energy can be anything from zero to D, the heat of dissociation of the molecule to atoms, depending on the relative shapes of the two curves. The distances d_c and d_p denote the relative closeness to the surface of the chemisorbed and physisorbed molecules.

Adsorption of oxygen is observed for most metals and some non-metals, but it is generally the case that metals that have a filled d-band are unable to adsorb significant quantities of permanent gases other than oxygen[14, 15, 16, 17]. There is a commonly cited group of gases used for this type of study, listed below in order of strength of adsorption on metals:

$O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 > N_2$

Metals are classified into groups (A, B1, B2, C, D, E, F) by their ability to adsorb these gases, group A adsorbing all the gases, group B1 all except N_2, B2 all except N_2 and CO_2 and so on . The table listed below details the adsorption (A = is adsorbed, NA = not adsorbed).

		GASES						
Group	Metals	O_2	C_2H_2	C_2H_4	CO	H_2	CO_2	N_2
A	Ca, Sr, Ba, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, (Re)	A	A	A	A	A	A	A
B_1	Ni, (Co)	A	A	A	A	A	A	NA
B_2	Rh, Pd, Pt, (Ir)	A	A	A	A	A	NA	NA
C	Al, Mn, Cu, Au	A	A	A	A	NA	NA	NA
D	K	A	A	NA	NA	NA	NA	NA
E	Mg, Ag, Zn, Cd, In, Si, Ge, Sn, Pb, As, Sb, Bi	A	NA	NA	NA	NA	NA	NA
F	Se, Te	NA	NA	NA	NA	NA	NA	NA

It is apparent that transition metals make up the majority of groups A, B_1 and B_2 and this arises due to the metals having unfilled d-electron bands. The exceptions to this rule are copper and gold, which can be explained by the relatively low energy of excitation from the s- to d- band. Micro-crystalline copper also has the ability to adsorb H_2 at room temperature, possibly due to the differing nature of this form of copper over evaporated films. Calcium, strontium and barium have overlapping s-, p- and d- bands which result in these metals having some characteristics of transition metals.

1.5 Dehydrogenation Reactions

Catalytic dehydrogenation can be split into two fields: dehydrogenation of hydrocarbons and dehydrogenation of alcohols. The two fields are very different in terms of catalysts and reaction conditions and there are few if any parallels between the two processes, and so they cannot be considered as a whole. Industrially, the dehydrogenation of hydrocarbons is by far the larger and more important subject area, with a number of important industrial chemicals; e.g. styrene, butene, being produced in this way[18]. Short reviews of hydrocarbon and alcohol dehydrogenation are presented below. The subject of oxidative dehydrogenation is one that has received some attention in the scientific and patent literature, and is a method used for both hydrocarbon and alcohol dehydrogenation and so will not be considered in isolation.

1.5.1 Hydrocarbon dehydrogenation

Hydrocarbon dehydrogenation can be further subdivided into dehydrogenation of alkanes to alkenes, and dehydrogenation of alkyl aromatics, such as ethyl benzene to styrene. Hydrocarbon dehydrogenation is an apparently simple process complicated by the fact that the reaction is highly endothermic and thermodynamically equilibrium limited[19]. These complications mean that for relatively low conversion (50%) of alkanes to alkenes, high temperatures of operation (750-1000°K) are required. At these temperatures the reactions of alkanes and alkenes are dominated by thermal cracking, aromatisation and isomerization, reducing the yield of alkene and therefore limiting its usefulness as an industrial or synthetic process. Consequently, dehydrogenations are typically carried out at lower temperatures and low conversion, typically in the 10-20% range.

The amount of energy required to remove hydrogen from an alkane is almost independent of the molecular weight, and the adiabatic temperature decrease – the decrease in temperature of a reacting gas or liquid during dehydrogenation - for alkane dehydrogenation is large. Figure 1.5 plots the theoretical temperature decrease[19] that must be overcome to dehydrogenate alkanes in the C_2 to C_{10} range; the figures have been calculated at the equilibrium temperature and are on a weight rather than molar basis.

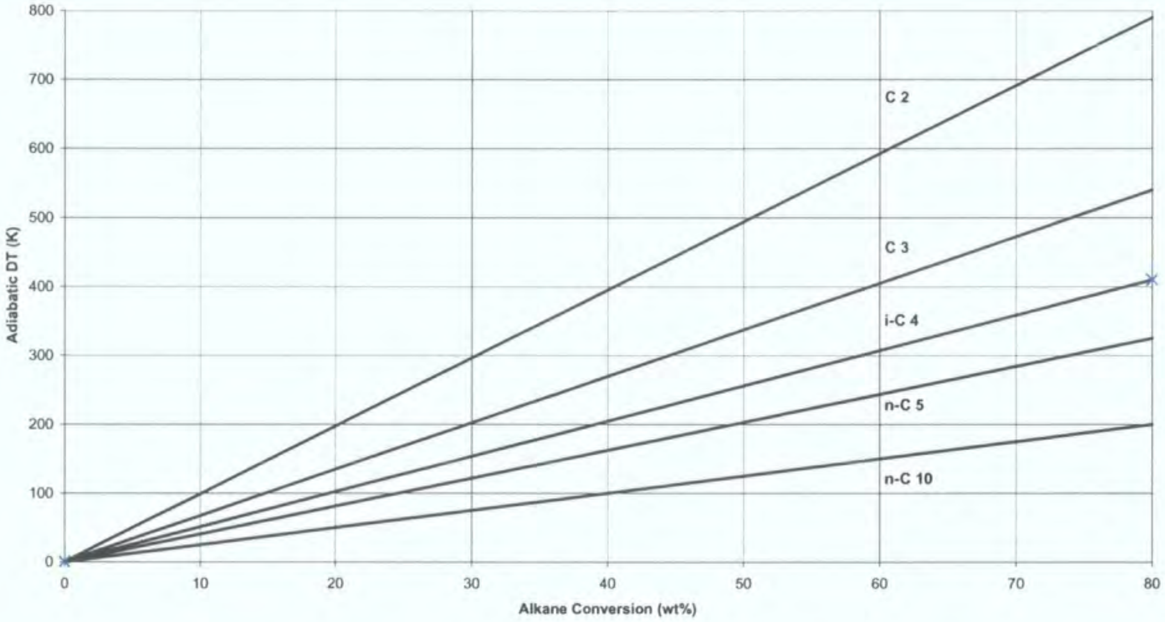


Figure 1.5 Theoretical Temperature Decrease That Must Be Overcome To Dehydrogenate Alkanes

The highly endothermic nature of the dehydrogenation forces the use of high over-temperatures in the reactor that promote cracking reactions and lead to coke and carbon deposition on the catalyst surface. Over-temperatures are where the catalyst and reacting gas are heated to above the theoretical reaction temperature to overcome heat and mass transfer limits that occur in real catalytic reactors. The carbon generated by the over-temperature is removed in an oxidative regeneration stage. Figure 1.6 summaries the dehydrogenation of iso-butane, which is typical for alkanes in general.

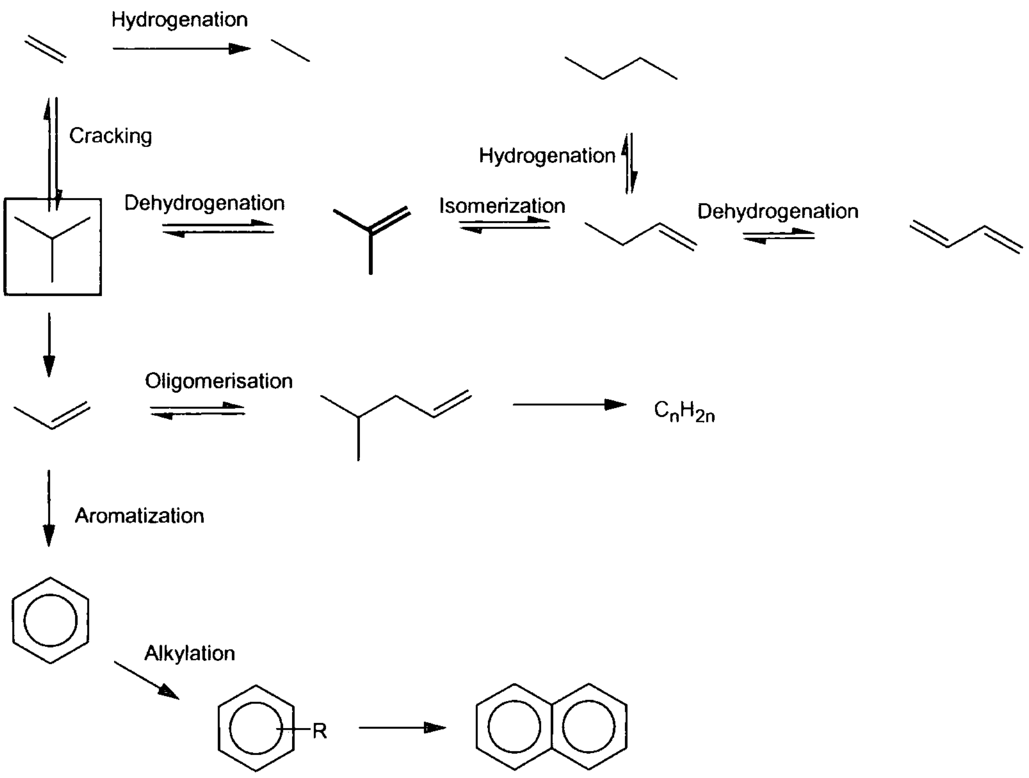


Figure 1.6 Reaction Network For Iso-Butane Dehydrogenation

Catalysts for alkane dehydrogenation are based on the platinum group metals[20] (with the addition of a number of promoters such as tin, alkali metals (Na, K) supported on zinc or magnesium aluminate), chromite based catalysts supported on Zr or alumina and nickel sulphide catalysts.

For the dehydrogenation of iso-butane the following relations have been shown for the range of platinum metal catalysts[21]

Activity: Pt < Pt-Cu = Pt-Se < Pt-Ge, Pt-Pb < Pt-In < Pt-Sn

Selectivity Pt < Pt-Cu = Pt-Se < Pt-Ge < Pt-Pb = Pt-In < Pt-Sn

Stability Pt < Pt-Cu < Pt-Se < Pt-Ge = Pt-Pb < Pt-In < Pt-Sn

Propane dehydrogenation gave broadly similar results[22]. The platinum–tin catalysts are believed to be active due to the promoting effect of tin, reducing the amount of coking on the catalyst surface. It is unclear as to how the tin effects the reduction in coke formation, but there several possibilities. The first is that tin is present in small amounts as an alloy[23, 24, 25, 26], but mainly as Sn^{2+}, and alters the surface properties of the Pt crystals, by donation of electrons to the 5d band in Pt [27, 28], thereby preventing the adsorption of coke precursors. Secondly, there is evidence of an 'ensemble effect' where the tin effectively dilutes the Pt such that the average Pt cluster size is too small to catalyse coke formation[29,30]. Another suggestion[30] is that tin segregates platinum atoms at low co-ordination sites such as at the corners of platinum crystallites, reducing the activity of these sites, which are thought to promote coking. Commercial use of the Pt Pt/Sn catalysts is exemplified in the UOP Olefex[31] process where a catalyst consisting of 1% Pt, 4% Sn and 4% alkali metals on gamma alumina is used to dehydrogenate C_3 and C_4 alkanes. Typical reaction conditions are 850K, 500 kPa at a feed rate of LHSV 4 hr^{-1}.

Chromium-oxide based catalysts are used for the dehydrogenation of low molecular weight alkanes in particular. The exact nature of the active catalyst is still under debate[32,33], but it is believed that Cr^{3+} is the active species, either by itself or with Cr^{2+} [34]. The Cr^{3+} ion is inserted into the alumina or zirconia framework, and the insertion is stabilised by the addition of alkali metal promoters caesium, rubidium and potassium[35].The Cr catalyst is used commercially to dehydrogenate C_3 and C_4 alkanes using a catalyst that contains 20% Cr_2O_3 and 2% alkali metals on gamma alumina.

Alumina supported nickel sulphide catalysts have been investigated as potential dehydrogenation catalysts[36]. Nickel catalysts of this type are highly selective but as a consequence are much less active than the more conventional Pt/Sn and Cr catalysts.

An interesting point is that Ni metal or the oxide is inactive for alkane dehydrogenation. Selectivity and activity to dehydrogenation increase proportionally to the degree of sulphidation[36].

The mechanism[33,34] for dehydrogenation on Cr catalysts is believed to be the formation of an O-H bond at the catalyst surface, followed by cleavage of the C-H bond. The mechanism[26] on Pt/Sn catalysts is the formation of a Pt-H bond followed by C-H cleavage.

1.5.2 Alcohol dehydrogenation

Dehydrogenation of primary and secondary alcohols to aldehydes and ketones respectively is an industrially important reaction. Examples of these reactions are ethanol to ethanal[37] , 2-propanol to propanone[38], 2-butanol to butanone[39], cyclohexanol to cyclohexanone[40] and methanol to formaldehyde[41] . A range of catalysts are used in these industrial processes - copper[37], silver[44], zinc, zinc oxide[39] and zinc oxide/chromium oxide[40]. The dehydrogenation of tertiary alcohols does not occur without rearrangement during the reaction. In most cases the tertiary alcohol dehydrates to form water and an alkene[42]. It should be noted that for reactions of alcohols there are two main reaction pathways; dehydration and dehydrogenation[43] and in this study the aim of an efficient catalyst is to remove dehydration as far as possible. Dehydration occurs mainly on oxide catalysts but also on oxide supports such as alumina or silica, and so the choice of support can be critical.

The dehydrogenation reaction is endothermic and strongly equilibrium limited. Conversion of the alcohol to carbonyl compounds is dependent on temperature and the structure of the parent alcohol. Figure 1.7 shown below[42] shows the calculated equilibrium conversion plotted against temperature for a range of alcohols. The effect of structure is illustrated in the difference in the temperature required for 50% conversion of 1-propanol (540K) and 2-propanol (450K). Secondary alcohols are transformed to the ketones at lower temperatures than the corresponding primary alcohols are converted to aldehydes. Methanol and ethanol are both more resistant to dehydrogenation than the higher alcohols, with methanol being the most difficult. Figure 1.7 shown below is calculated[42] from group contribution methods and does not take reactions other than the first dehydrogenation into account. The principal difference in the dehydrogenation of primary and secondary alcohols is the capability of primary alcohols to form esters. There has been some debate as to the mechanism of this reaction, some researchers favouring a Tischenko type mechanism while others favour a hemi-acetal intermediate.

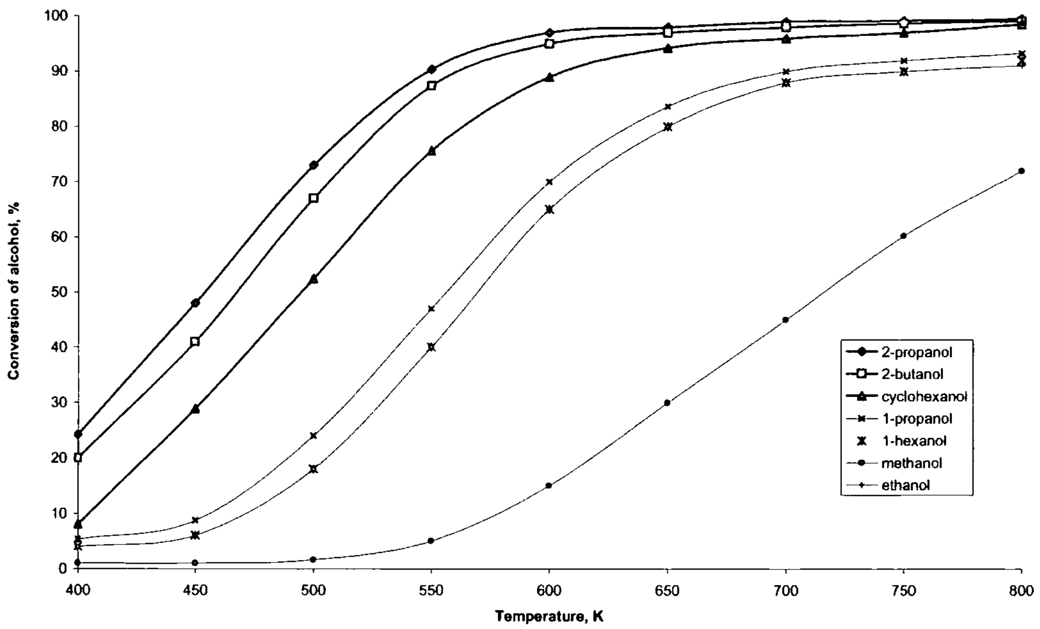


Figure 1.7 Equilibrium Conversion Of Alcohols To Aldehydes And Ketones vs. Temperature

A classic study of alcohol dehydrogenation was carried out by Palmer and Constable[45] using polycrystalline copper formed by the reduction of copper oxide support on fireclay. Ethanol and propanol were dehydrogenated, with reaction being followed by the evolution of hydrogen; no other products of dehydrogenation were followed. The study looked at the effect of temperature on activity of the catalyst, with a conclusion that there were periodic variations in catalyst activity against activation temperature. Peaks of activity were detected at 235, 275 and 380°C . The maximum activity was noted at 235°C. Above 420°C there was an unexplained change in the nature of the catalyst that subsequently increased activity at all temperatures used. The activation energy for ethanol decomposition was found to be dependent on the temperature used for catalyst activation. This result has been in part replicated in unpublished work by Waugh and Tabatabaei[46] as part of the DPT ethyl ethanoate program. Table 1.2 shows the results obtained from the dehydrogenation of a range of alcohols over alumina supported metals[47,48] . It can be readily seen that copper has the lowest activation energy for all alcohol dehydrogenations.

	Fe	Co	Ni	Cu	Ag
Methanol	22.1	17.6	21.2	14.1	30.8
Ethanol	17	13.4	15.3	9.8	22.8
2-propanol	15.8	9.9	12.2	6.4	13.7
1-butanol	16.1	12	13.7	8.7	17.1
2-butanol	14.8	9.7	12.6	7.2	14.7

Table 1.2 Activation energy of alcohols for a range of transition metal catalysts

The kinetics and selectivity of dehydrogenation and dehydration of alcohols are generally studied using 2-propanol for simplicity. Secondary alcohols cannot form esters and do not decompose by decarbonylation[49] at the temperatures needed for dehydrogenation. The decomposition of alcohols over heterogeneous catalysts results in both dehydrogenation and dehydration,[43] and 2-propanol cannot skeletally rearrange during dehydration in the way that is possible for higher alcohols. Furthermore, as a symmetrical alcohol there is no possibility of the different alkyl groups causing differences in dehydrogenation activity during initial adsorption.

The reaction of 2-propanol over ZnO catalysts is regarded as a test reaction for determining the nature of oxide surfaces, with the ratio of 9:1 of dehydrogenation to propanone over dehydration to propene at 150°C being obtained under standard conditions. Tamaru[50] showed by using deuterated 2-propanol that the mechanism for dehydrogenation was 2-propanol adsorption as an alkoxy species, followed by the removal of an alpha hydrogen . Further work by Waugh and Bowker[51] showed that at the temperature described by Tamaru the removal of the alpha hydrogen was correct, but that at higher temperatures the abstraction of a beta-hydrogen, having an activation energy of 1Kcal mol^{-1} more, resulted in propene formation. Waugh found that with ethanol the major product was ethene rather than ethanal.

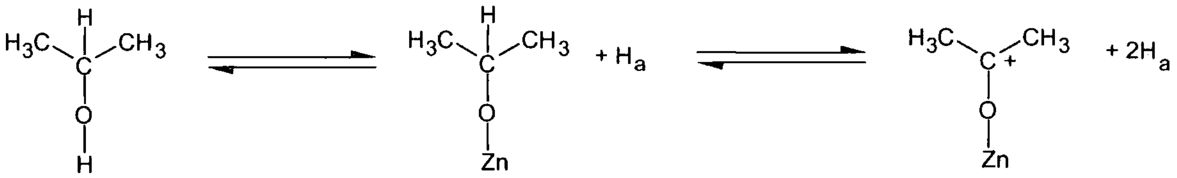


Figure 1.8 Proposed Mechanism For 2-Propanol Adsorption on to ZnO Surface

Zinc oxide catalysts are commonly doped with a promoter or co-catalyst such as Cr_2O_3. Dowden et al[52] studied Cr/Zn catalysts that had been sintered at up to 1000°C to separate the two phases (Zn rich and Cr rich) to try to separate the functions of the possible phases (Zn only, Cr only, Cr rich, Zn rich). They found that the ZnO rich phases were semi-conductors and showed a high selectivity to dehydrogenation of alcohols in comparison to dehydration. Conversely, the Cr rich phases were insulators and showed high selectivities to dehydration over dehydrogenation. This result conforms to the general principle of semi-conductors favouring dehydrogenation and insulators dehydration.

Germain et al[53] showed that the activity of a Cr/Zn catalyst was at a maximum at circa 40% Cr content, but that in contrast to the case of Cu, the energy of activation is independent of the Cr content and activity of the catalyst. Germain concluded that zinc chromite was essentially inactive and that the activity of the catalyst was proportional to the free surface area of zinc oxide. A further study by Kraus[54] on the effect of the addition of Cr^{3+} on ZnO dehydrogenation catalysts concluded that a composite catalyst made up of 54% Cr_2O_3 gave a catalyst of higher activity than either Cr_2O_3 or ZnO alone. The study used 2-propanol as the probe molecule. There was a sharp maximum in catalyst activity and selectivity at this concentration. Kraus demonstrated that the active site was not zinc chromite, as was previously suspected, but that chromia had the effect of increasing the surface area of the ZnO phase hence increasing the activity of the catalyst

Zeolites have been studied as possible dehydrogenation and dehydration catalysts. Bezouhanova[55, 56] and Yashima[57] studied the dehydrogenation of cyclic and linear alcohols over alkali-metal exchanged ZSM-5 and found that the selectivity of dehydrogenation over dehydration for cyclic compounds was a function of the ratio of silica to alumina, and the alkali metal content. Un-exchanged catalysts showed high activity but poor selectivity to dehydrogenation. A typical result was circa 80% conversion at 6% selectivity to ketone – the remainder of the converted alcohol formed alkenes and ethers by dehydration. The highest selectivity to dehydrogenation over dehydration was found in Na exchanged zeolites but the catalyst activity was significantly lower – the best result reported was 8.2% conversion, but 100% selectivity to ketone using Na ZSM-5 at 50-100:1 Si to Al ratio. The authors concluded that

Bronsted acids promote the dehydration, and exchanging the zeolites removes dehydration at these sites. Work by the same authors and others using linear alcohols, concluded that no dehydrogenation was taking place at low temperatures, even in exchanged zeolites. The explanation of this was that the carbonyl produced was enolised, then dehydrated. At higher temperatures some dehydrogenation was observed – it is thought that desorption of the ketone was taking place before enolisation could occur.

The effects of hetero-atoms on the dehydrogenation of alcohols over Zn/Cr catalysts have been studied. Gulkova and Kraus[58, 59] used alkali doped Zn-Cr, and found that dehydrogenation activity was dependent on the electronegativity of the alcohol substituents. They further concluded that the correct mechanism for alcohol dehydrogenation on oxide catalysts was via alpha-hydrogen cleavage rather than the beta-hydrogen mechanism. This result confirms the general view in the literature[60, 61].

Urbano et al[62] studied a $MgO-B_2O_3$ catalyst for 2-propanol dehydrogenation, and found that the activity and selectivity to propanone was proportional to the ratio of Mg to B over a range of 1:1 to 1:10. The ratio between dehydrogenation and dehydration was explained as a function of the ratio of alcohol adsorbed as the ethoxide (dehydrogenation) and as the carbanion (dehydration).

Metal based dehydrogenation catalysts have a long history. As noted above, Palmer and Constable[45] studied copper for dehydrogenation of ethanol and propanol and found that a catalyst made by reducing precipitated copper oxide was effective. Balandin[43] studied dehydrogenation of alcohols on a number of transition metal catalysts (Fe, Cu, Pt, Pd) and concluded that the mechanism of dehydrogenation was via alpha-hydrogen abstraction from adsorbed alcohols then beta-hydrogen abstraction from the alkoxide intermediate. Recent results[63,64] suggest that alcohols are adsorbed onto the copper surface as an alkoxide and that the mechanism for dehydrogenation is similar for both metals and oxides. Ethanol dehydrogenation to ethanal has been widely studied[65,66,67] with the aim of optimising the selectivity. Copper-based dehydrogenation catalysts are the most active for this reaction but it has been found that, at the conditions used by many workers, the copper catalyst loses activity over short time periods due to growth in the size of the copper crystallites. The addition of chromia to the copper catalyst was found to double the copper metal surface area of the catalyst and to retard the growth of copper crystallites. Chen[69] studied catalysts with copper to chromium ratios of 40:0 to 40:20 and showed that there was a maximum of catalyst activity and selectivity at a ratio of about 40:4. Chen confirmed the findings of Prasad[68] that the effect of chromia on the catalyst was to increase the surface area and prevent the growth in size of copper crystallites.

The dehydrogenation of alcohols to form esters has centred on methanol to methyl formate and ethanol to ethyl ethanoate. Ivannikov and Zherko[70] first reported the dehydrogenation of methanol to methyl formate. Copper and nickel metal catalysts were investigated by Chono[71] and Charles[72] for the dehydrogenation of methanol to methyl formate, and Franckaerts[73] for the dehydrogenation of ethanol to ethyl ethanoate. Wainwright[74] studied the dehydrogenation of methanol over a number of commercially available copper-chrome catalysts and concluded that the best catalysts contained copper-chromite. The reaction mechanism was assumed to be as follows:

adsorption of methanol as a methoxy species, followed by hydrogen elimination to form an adsorbed formaldehyde species. This species then reacts with gaseous formaldehyde via a Tishchenko-type mechanism to form methyl formate. Recent studies of the methanol to methyl formate[74] reaction have concentrated on supported copper catalysts, such as copper on silica, that have higher activities than bulk copper. There are suggestions that there is a lower limit for copper crystallite size below which dehydrogenation does not take place but this effect is not yet explained. Industrially, the dehydrogenation of methanol to methyl formate[75] is now an important part of the conceptual C_1 chemistry that has been proposed as an alternative source of petrochemicals from syn-gas.

Ethanol dehydrogenation to ethyl ethanoate was studied by Dogolov[76] and Lelchuck[77] who proposed that ethanal was the key intermediate in the reaction mechanism. Dogolov proposed that the reaction proceeded through an acetal intermediate while Lelchuck proposed an alternative route where ethanal adsorbed at the catalyst surface reacted with water to form acetic acid which in turn was esterified by excess ethanol.

Badhe and Mene[78] proposed a scheme where the reaction of ethanol to ethyl ethanoate was via a Tischenko type mechanism. Their kinetic study, using copper catalysts promoted by thoria and ceria, carried out in a fluidised bed, concluded that the Tischenko mechanism was correct and they put forward arguments based on the kinetics of ethyl ethanoate formation as evidence. By contrast, Takeshita[79] concluded that the reaction did not occur via the Tischenko mechanism, but via a hemi-acetal intermediate, produced by the reaction of adsorbed ethanal and ethanol. Takeshita showed that when ethanal and propanal were passed over a catalyst that was effective for the reaction of ethanol and n-propanol to form esters, there was no evidence of ester formation. This result is not surprising given the principle of microscopic reversal; the reaction mechanism for ester hydrogenolysis, which is a reversible reaction (for which alcohol dehydrogenation is the reverse reaction), has been shown to involve a hemi-acetal type intermediate. Chung et al[80] studied higher oxygenate formation from ethanol over Co/ZnO catalysts and showed by ^{13}C tracing that the reaction mechanism for ethyl ethanoate formation was via an ethanal and an ethoxide intermediate. Studies by other groups have demonstrated that the reaction mechanism below (Figure 1.9) is correct in all essentials.

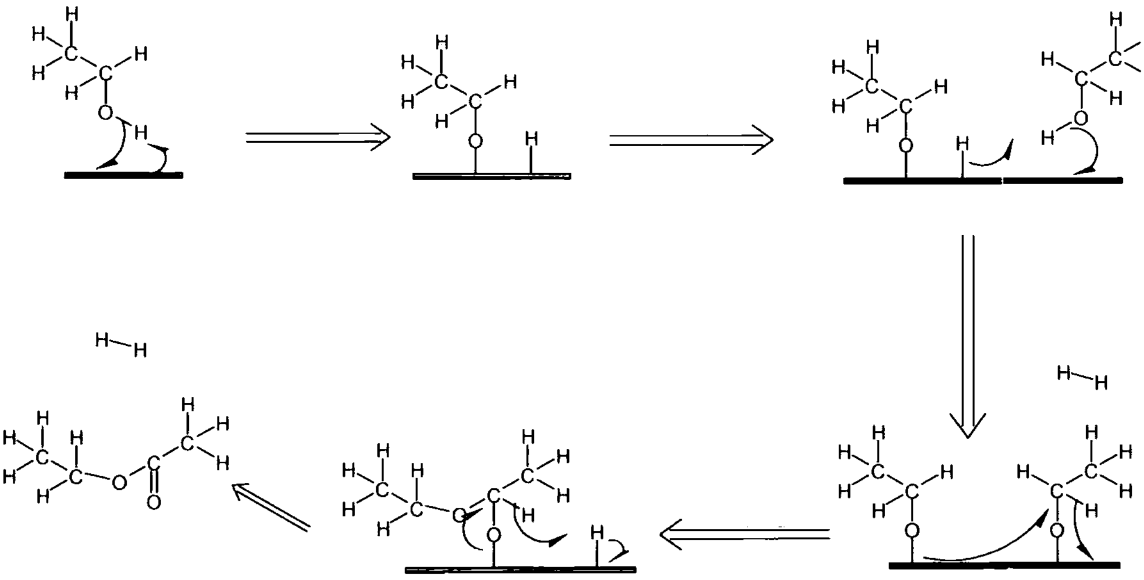


Figure 1.9 Proposed Alcohol Dehydrogenation Reaction Mechanism

The study of the dehydrogenation of alcohols to esters by Takeshita[79] reported ketones as side products, yields increasing with the chain length of the alcohol, and being of the form of 2_{m-1} – i.e. propanone from ethanol, diethyl ketone from propanol.

Other recent studies have concentrated on developing a commercial process for the dehydrogenation of ethanol to ethyl ethanoate[81]. Takezawa[82] detailed the dehydrogenation of ethanol over a copper catalyst with the aim of producing ethyl ethanoate and acetic acid. Similar papers by Chashchin et al[83], Claus[84] and Yang Schuwu[85] detail copper and nickel based dehydrogenation catalysts, all using ethanol as the feed and producing ethyl ethanoate as the primary product.

1.6 Conclusions and future work

The primary object of this short review of the dehydrogenation literature was to confirm that it is possible to synthesise ethyl ethanoate from ethanol by dehydrogenation. The reaction is well known and is actually regarded as a problem when dehydrogenating ethanol to ethanal. The literature on alcohol dehydrogenation, and ethanol dehydrogenation to ethyl ethanoate in particular, has a strong academic but a very weak industrial focus. What little work had been reported covering ethanol dehydrogenation to ethyl ethanoate did not seem to lead to an industrially viable process, due to the low yield and selectivity to ethyl ethanoate – the only exception was that reported by Inui[81] where the focus was on a potential industrial process. Even there, the catalyst employed was untried and experimental . There was no information in any paper reviewed concerning catalyst life over an extended period, or of an operating envelope, in terms of operating pressure, operating temperature and feed flows.

Heterogeneous copper based catalysts were predominant in both the industrial and academic literature, with chromium promoted catalysts being regarded as the most viable due to activity gains, thought in part to be due to copper-chromite reducing the rate of copper crystallite sintering. This mirrors the experience of DPT and others in the field of ester hydrogenolysis where chromium promoted copper catalysts dominate. Most of the research work reported concerns the synthesis of aldehydes and ketones from alcohols, and the formation of esters is a secondary effect. It has been assumed that conditions and catalysts that favour alcohol dehydrogenation to aldehydes and ketones will also be effective for ethyl ethanoate; this assumption may or may not be valid. Industrial experience over many years has shown that while classes of catalyst may promote a given reaction, in this example copper based catalysts for dehydrogenation, details of the physical state and chemical composition of catalysts are vital for the selectivity of the reaction and catalyst life.

In order to progress development of the dehydrogenation of ethanol to ethyl ethanoate a number of industrially available, proven, copper-based catalysts will be evaluated in a purpose built dehydrogenation reactor, constructed to be capable of testing these catalysts over a wide range of temperature, pressure and feed flows. The focus of the initial screening will be to provide a base from which the development of an optimised catalyst can start. It is thought unlikely that the catalysts available, which will have been optimised for their stated application, will be ideal for ethanol dehydrogenation and so there is wide scope for catalyst development.

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Chapter 2

Ethanol to Ethyl Ethanoate Dehydrogenation Catalyst Screening

2 Introduction

This chapter deals with work carried out to determine practical reaction conditions for the dehydrogenation of ethanol to ethyl ethanoate, and whether there was a commercially available catalyst that would be sufficiently active and selective. The literature available for ethanol dehydrogenation indicates that copper-based catalysts were likely to be the most effective, and so a range of copper based catalyst precursors were selected from the commercial literature for testing. The physical and chemical specifications of the catalysts were chosen to give a wide range so that from the preliminary screening a good idea of the direction that development work should take would be apparent.

The reaction was carried out in a purpose-built tubular reactor, consisting of a down-flow vapour phase reaction section that contained the dehydrogenation catalysts in a fixed bed. A charge of 100cm^3 of catalyst precursor was used for all test work. Analysis of the reaction products was performed by gas chromatography. Initial reaction conditions were chosen to reflect both the literature precedents and experience at DPT for related hydrogenation reactions. A reaction scheme is proposed in section 2.1.

2.1 Proposed Reaction Scheme

The following reaction are based on the published data on the dehydrogenation of ethanol on copper catalysts. The designation (S) represents a catalytic site.

The first part of the reaction is the adsorption of ethanol[1,2,3] as an ethoxide species on the copper component of the catalyst. This ethoxide can dehydrogenate further to form an aldehydic species, releasing hydrogen. The aldehydic species can desorb from the catalyst as ethanal

$CH_3CH_2OH + 2(S) \leftrightarrow CH_3CH_2O(S) + H(S)$

$CH_3CH_2O(S) + (S) \leftrightarrow CH_3CHO(S) + H(S)$

$CH_3CHO(S) \leftrightarrow CH_3CHO + (S)$

$H(S)+H(S) \leftrightarrow H_2 + 2(S)$

.

The aldehydic species, or intermediate with a similar structure, can react with an ethoxide to produce an adsorbed hemi-acetal species. This species can dehydrogenate yet further to form ethyl ethanoate.

$CH_3CHO(S) + CH_3CH_2O(S) \leftrightarrow CH_3CH(OH)OCH_2CH_3(S) + (S)$

$CH_3CH(OH)OCH_2CH_3(S) + 2(S) \leftrightarrow CH_3COOCH_2CH_3(S) + 2H(S)$

$CH_3COOCH_2CH_3(S) \leftrightarrow CH_3COOCH_2CH_3 + (S)$

$2H(S) \leftrightarrow H_2 + 2(S)$

If water is present, then the possible formation of a gem-diol intermediate (see below) could intercept the normal ethyl ethanoate formation mechanism and lead to reduced catalyst activity.

$CH_3CHO(S) + H_2O(S) \leftrightarrow CH_3CH(OH)_2(S) + (S)$

Two ethoxide species can react to form diethyl ether and oxide. This reaction can take place on the copper crystallites but also on the surface of the catalyst support or promoters. A diethyl ether precursor, vinyl ether, can be formed by the decomposition of ethanal diethyl acetal.

$2\ CH_3CH_2O(S) \leftrightarrow CH_3CHOCH_2CH_3(S) + O(S)$

$CH_3CHO(S) + 2CH_3CH_2O(S) \leftrightarrow CH_3CH(OCH_2CH_3)_2(S) + H_2O(S) + (S)$
$CH_3CH(OCH_2CH_3)_2(S) \leftrightarrow CH_3CH_2OCH{:}CH_2(S) + CH_3CH_2OH$

Two acyl species can react to form aldol products[4]. Two mechanisms are possible – a normal aldol reaction that ultimately forms butanal, and an aldol reaction where the product is butanone. The aldol products can be hydrogenated to form the respective alcohols, 2-butanol for butanone and n-butanol for butanal. Other side reactions include the formation of propanone and 2-propanol[5] from ethanol via the aldol type mechanism

2.2 Reactor Choice, Catalyst Loading and Catalyst Activation

Prior to any dehydrogenation test work commencing, a review of the possible reactor designs commonly used was carried out within DPT by the author and chemical engineering colleagues. The review took account of the dehydrogenation work reported in chapter 1.

The review considered the various reactor types that could be used. There are two main types of catalytic reactor that are commonly used in industry: **batch**, where the reaction takes place in a sealed reactor and where the product is contained within the reactor, and **continuous** where the reactor has a flow of reactants through it at all times. The characteristics of the two reactor types are very different. In batch reactors the composition of the reaction mixture changes with time, and is best suited for reactions that are zero or first order. Within continuous reactors the composition of the reaction mixture is invariant with time but varies with position in the reactor. Detailed treatments of the types of reactor are adequately covered by Thomas and Thomas[6] and by Wijngaarden, Knonberg and Westerterp[7]

Each reactor type has benefits and disadvantages which limits suitability for a particular type of reaction. Examination of the reported reaction conditions – 250C, pressure of below 350kPa – dictated that the reaction would take place in the vapour phase so batch reactors were ruled out due to their low capacity. The dehydrogenation reaction of ethanol to ethyl acetate is an endothermic reaction and so heat transfer was another consideration. Where there is a high heat flux, multi-tubular reactors or fluidised beds are effective, but these types of reactor are rarely used in the laboratory due to size considerations. The remaining options – Berty type continuous reactors and tubular plug flow reactors were both considered but Berty reactors are not used in industry, rather as a research tool to simulate tubular or multi-tubular reactors. The remaining option of a tubular type reactor fitted well with the stated aim of using a commercially available catalyst. The conclusion of the brief review was that for the laboratory evaluation a fixed bed of catalyst, with down flow of process fluids to guard against possible flooding of the beds if low volatility by-products were made during the reaction, would be the most efficient option. A small fixed bed plug flow reactor was built for the test work according to the sketch shown in figure 2.1.

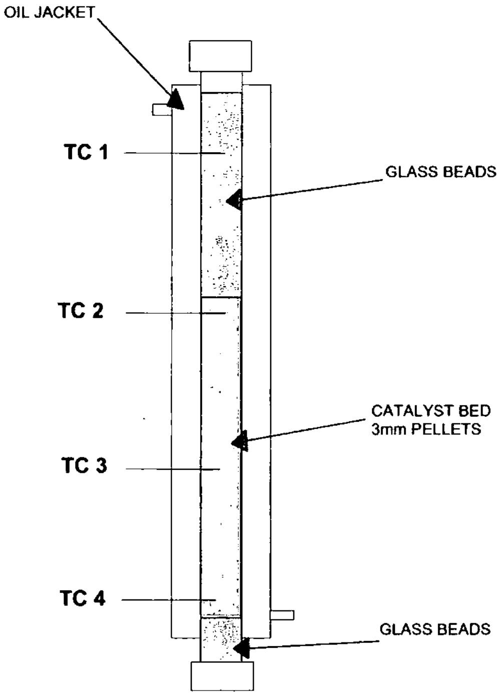

Figure 2.1 Dehydrogenation Test Reactor

The dehydrogenation apparatus consists of an 18.75mm external diameter, 13.5mm internal diameter, 316 stainless steel reactor of length 30 cm. The catalyst was packed into the reactor as shown, supported by a layer of 6mm diameter glass beads that were in turn supported on a stainless steel mesh. A further layer of 6mm glass beads was loaded onto the top of the catalyst to mix and distribute the feed. The reactor was heated by use of circulated hot oil from a temperature controlled oil bath. Ethanol was fed to the reactor from a 'constametric' high pressure HPLC pump, via a 2m length of 1mm stainless steel capillary tubing suspended in an oil bath. The effluent from the reactor was collected by condensation in a water-jacketed stainless steel catch-pot. Hydrogen was fed to the reactor via a 'Brookes' thermal mass flow controller. Reactor pressure was monitored by a dial type pressure gauge – control of reactor pressure was via a back-pressure regulator sited on the catch-pot. The temperature of the reactor was monitored by 4 thermocouples sited in pockets inside the reactor at points shown in figure 2.1 (TC1-4).

2.3 Reactor Test Protocol

In a typical test run, the reactor temperature was set by adjusting the reactor to the desired temperature by altering the temperature of the circulating hot oil. The reactor temperature was controlled by the reading from thermocouple 4 (reactor exit). The ethanol feed was adjusted to the desired delivery rate by setting the constametric pump to the approximate flow setting, then checking the actual flow by liquid displacement from a calibrated burette attached to the feed pump. Hydrogen flow was then set at the desired rate and the reactor allowed to stabilise for at least 1 hour. The condensed reactor effluent was collected and weighed at regular intervals, between 1 and 3 hours, and analysed by gas-liquid chromatography (GC). A copy of the method used is given in Appendix 2 – analytical methods. The results from the GC analysis were used to calculate conversion of ethanol and selectivity to ethyl ethanoate and other products. The initial aim of the test work was to produce ethyl ethanoate at a selectivity of >90% at an ethanol conversion of >30%.

The reactor was sized according to internal DPT protocols for reactions over heterogeneous catalysts. One prime directive of DPT research and development protocols is that where possible heterogeneous catalysts should be used in the same physical form, in terms of size and shape, as would be used in a commercial reactor. Heterogeneous catalysts that are used for fixed beds are normally supplied as tablets (3mmx3mm, 6mmx3mm, 6mmx6mm) rings, trilobe tablets or extrudates . The reason for using this type of catalyst, and not a powder or granule, is that the activity and selectivity of a catalyst supplied in a pellet form will be different from the same catalyst in a powder due to heat transfer between the catalyst and the reacting gas and transport of feed and products through the catalyst pellet[8]. While differences in activity can be allowed for, for example by increasing the amount of catalyst relative to the amount of feed, the differences in selectivity are more difficult to compensate for. There are several particular difficulties; one is where a highly reactive intermediate reacts further to yield the desired product. There will be a difference in the reactivity of the catalyst between the powder and pellet forms, and the fate of the highly reactive intermediate may be different. If the intermediate has a short lifetime in the reactor then a lower concentration of by-products may be formed which would give an optimistic view of the activity of the catalyst. Another difficulty may be that of transport; reactions commonly happen only in a portion of the catalyst pellet[8] – the feed material diffuses into the pellet, reacts then diffuses out. Catalyst pellets are sized such that the diameter of the pellet is close to twice that of the diffusion path ensuring that as much as possible of the active constituent of the pellet is used. Where the diffusion path length of a molecule is small, or where the reaction yields products that diffuse more slowly than the feed materials (i.e. dimethyl maleate [feed] and 1,4 butanediol [product]), the physical size of the individual catalyst particle has a large effect on the products that emerge. It is most likely that a powder catalyst will have a higher activity than a pelletised catalyst and often the powder catalyst also has higher selectivity, but the converse case can also be true in circumstances where a reaction intermediate does not decompose to form by-products.

The practical upshot of using a commercially acceptable catalyst design is that it places constraints on the type and size of reactors that can be used as research and development tools for industrial processes. The minimum size reactor required to accurately model a full sized commercial reactor, of 10,000 to 30,000 litres volume, is a contentious issue and the subject of much research among chemical engineers. The DPT approach is to design reactors such that the hydrodynamic flow of reactants over the catalyst is within one order of magnitude of that that would be used in a commercial reactor[9].

Practically, this limits the size of a catalyst bed that uses a 3x3mm tablet catalyst in a tube of 12-25mm diameter, to 100cm^3 of catalyst as the lower limit.

2.4 Engelhard Catalyst Ex1808T

In order to gain a baseline from which to develop the dehydrogenation catalyst a commercially available copper-chromium hydrogenation catalyst was chosen for the first set of dehydrogenation test work. This catalyst, termed Ex1808T by the manufacturer Engelhard, has uses in ester hydrogenation and dehydrogenation of ethanol to ethanal, and was therefore thought to be likely to be an effective dehydrogenation catalyst for the ethanol to ethyl ethanoate reaction. Ex1808T is an industry standard copper chromite catalyst of the approximate composition shown below.

Copper (as CuO)	38%
Chromium (as Cr_2O_3)	54%
Silica (as SiO_2)	5%
Carbon	3%

Copper is present in the catalyst in two forms[10] – copper chromite ($CuCr_2O_4$) and copper oxide (CuO) . When used in hydrogenation, the catalyst precursor is treated in a flow of hydrogen, diluted in an inert carrier such as nitrogen, to reduce copper oxide to copper metal in the form of small crystallites of between 10 and 400 microns diameter. It is this copper that is the active catalytic species[11]. Copper chromite is not reduced at the conditions used to reduce copper oxide. The exact method of activation influences the size distribution of the crystallites, which in turn influences the activity of the catalyst. Crystallite size is affected by the temperature used for activation and the concentration of hydrogen in the activating gas. Work performed by Webb[12] on behalf of DPT showed that the optimum temperature for activating the catalyst was 430°K at a hydrogen concentration of 0.5 mol% in nitrogen.

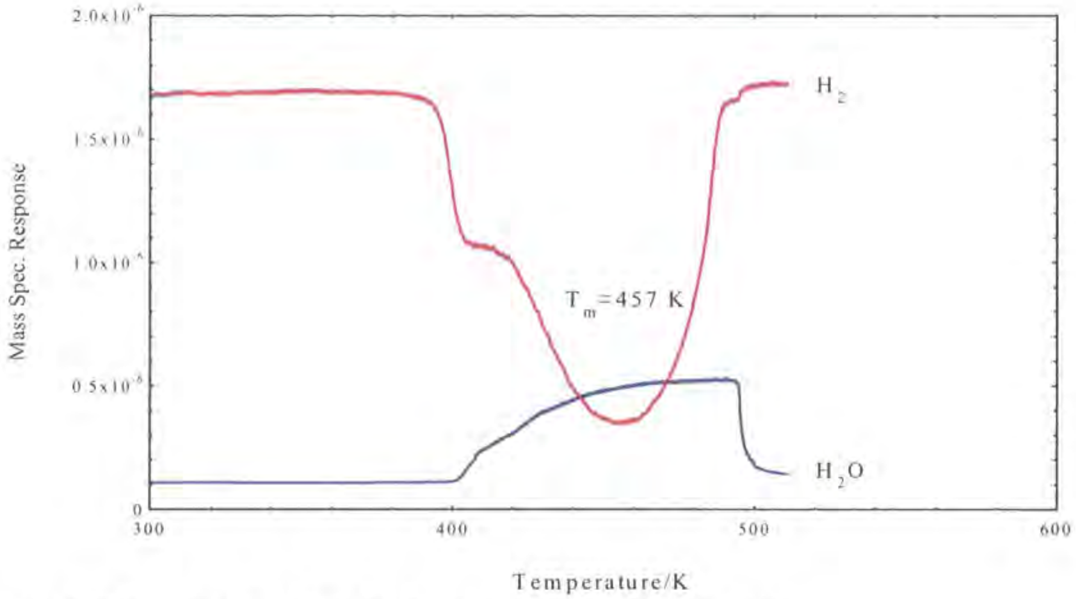

Figure 2.2 – Typical TPR of Copper Chromite Catalyst

Figure 2.2 is a schematic of a temperature programmed reduction[13] (TPR) plot of a typical copper-chromite catalyst showing the two characteristic peaks where copper oxide is reduced to copper metal. The use of dilute hydrogen is important as the reduction of copper oxide is an exothermic reaction. If the concentration of hydrogen in the activating gas is raised above a critical level, then the heat released during the activation cannot be adequately removed by either conduction through the catalyst or into the activating gas. This leads to local 'hot spots' considerably higher in temperature than the bulk reactor or pellet temperature. This local heating leads to sintering of the copper crystallites which reduces the activity of the catalyst. A typical activation procedure is detailed in appendix 1.

A charge of 100cm^3 of the catalyst was loaded into the reactor as shown in figure 2.1. The reactor was sealed and pressure tested with nitrogen at 4000 kPa. The catalyst was activated according to the procedure in appendix 1 prior to use. Figure 2.3 shows the activation of this catalyst.

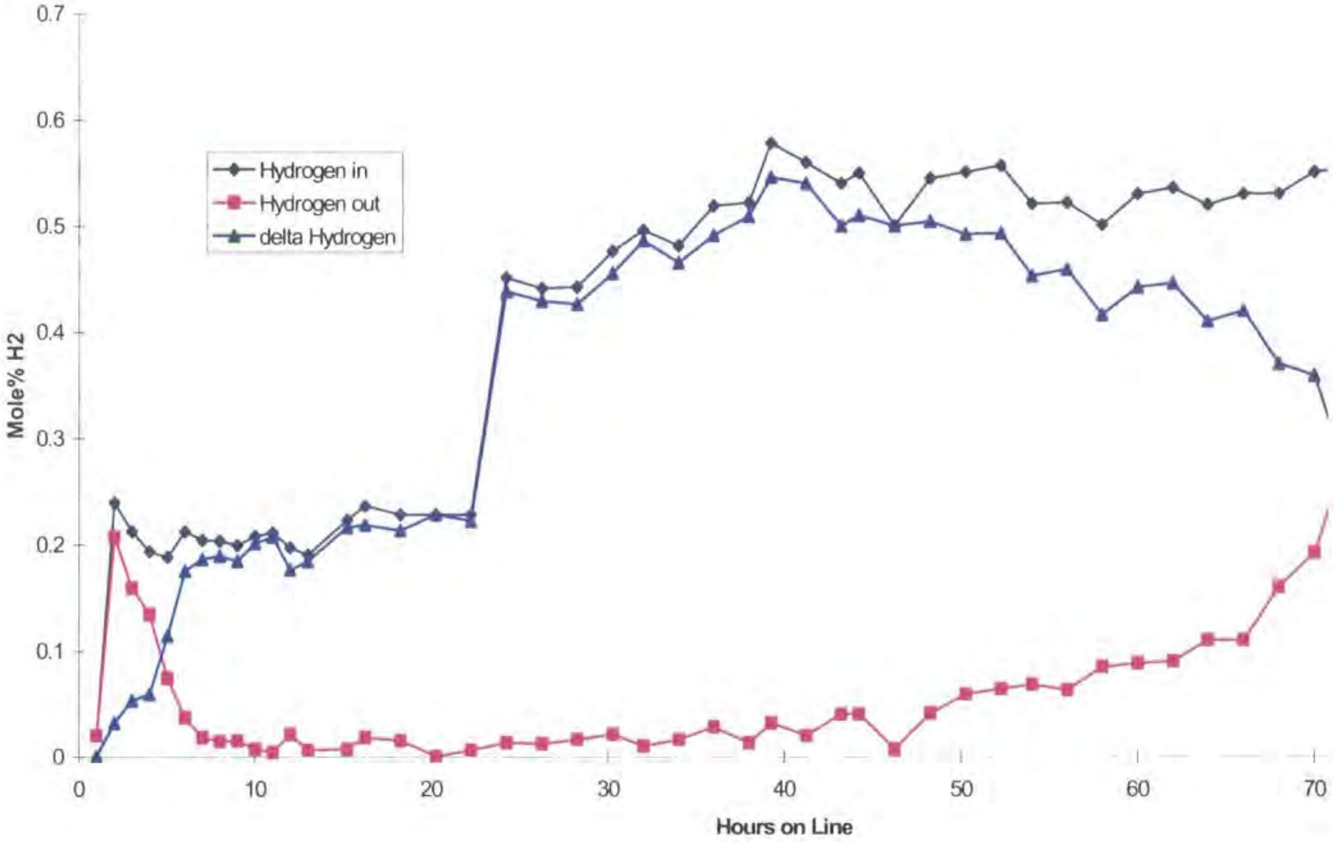

Figure 2.3 Activation of Ex1808T Catalyst

The first dehydrogenation test used conditions that were thought likely from previous experience and reports in the literature[1,14,15] to suit ethanol conversion to ethyl ethanoate. The reactor temperature was adjusted to 200°C and the pressure set at 690 kPa. Ethanol was fed to the reactor at a rate of 30cm^{3}hr^{-1} – a LHSV of 0.3 calculated according to the equation below.

LHSV = Feed Rate (cm^3)/ catalyst Volume (cm^3)

The ethanol vapour, containing a small amount of hydrogen added before the reactor (circa 2-10 Standard Litres per Hour (SLPH)), was passed over the catalyst for a total of 6 hours. Samples of the condensed reactor effluent were taken at 2 hour intervals. After 6 hours of operation an analysis of the product showed that ethyl ethanoate was being formed, but in very small amounts. A GC analysis of the product showed the following major constituents:

Ethanal	0.091
Ethanol	97.75
Methanol	0.058
Ethyl Ethanoate	1.893
2-Butanol	0.013

Figure 2.4 is a typical chromatogram of the product from this reaction, showing the peaks corresponding to those components listed above. Table 5.1 details data from this catalyst.

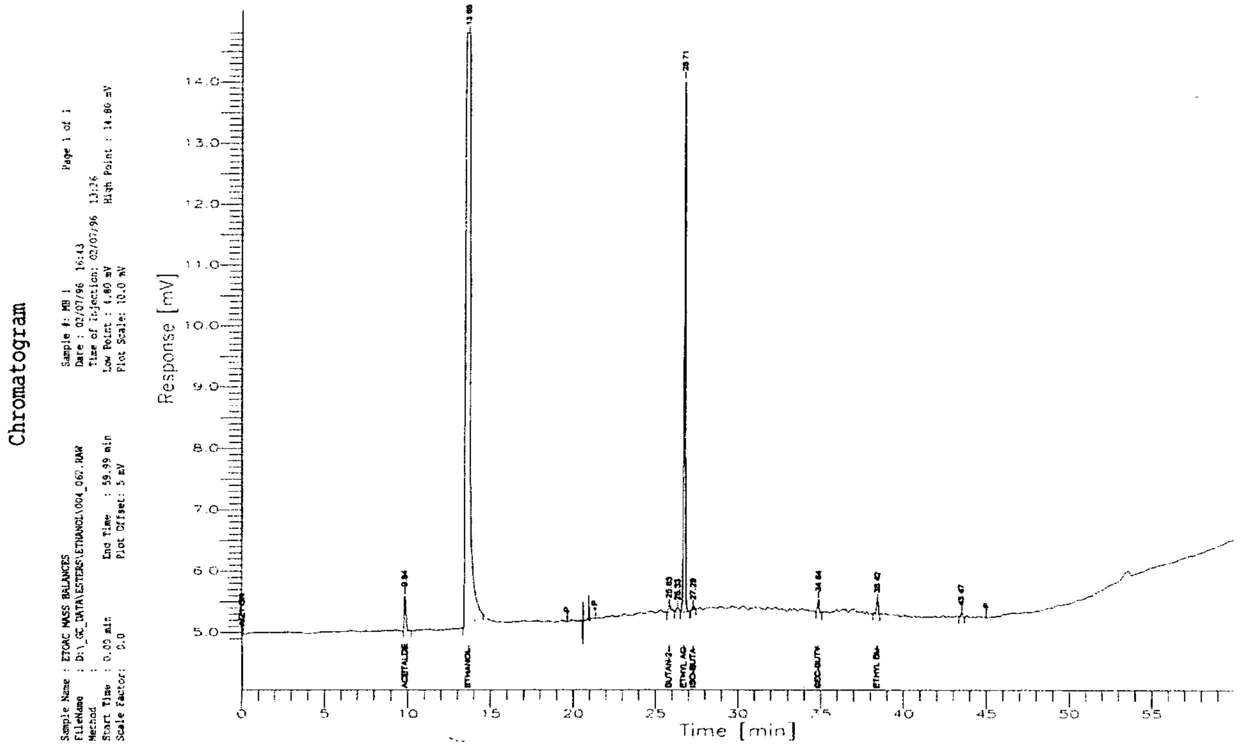

Figure 2.4 – Typical Chromatogram from Run 1

The molar conversion of ethanol and selectivity to ethyl ethanoate was calculated according to the scheme set out in appendix 3. Conversion of ethanol was calculated as 2.18 mol% and selectivity to ethyl ethanoate as 95.2 mol% - a total yield of 2.08% - obviously not a suitable figure for a commercial process.

The reactor temperature was then increased to circa 250°C (exit temperature) and the process repeated. The reactor was allowed to run until the product analysis was consistent – see, run 2 for details (p 72). This run gave a higher ethanol conversion – 69.5% - but a lower selectivity to ethyl ethanoate – 56.9% (overall yield 39.5%). It was noted that as well as the products observed in test 1, there was a forest of unidentified peaks in the gas chromatogram. Figure 2.5 is a typical chromatogram taken from this run.

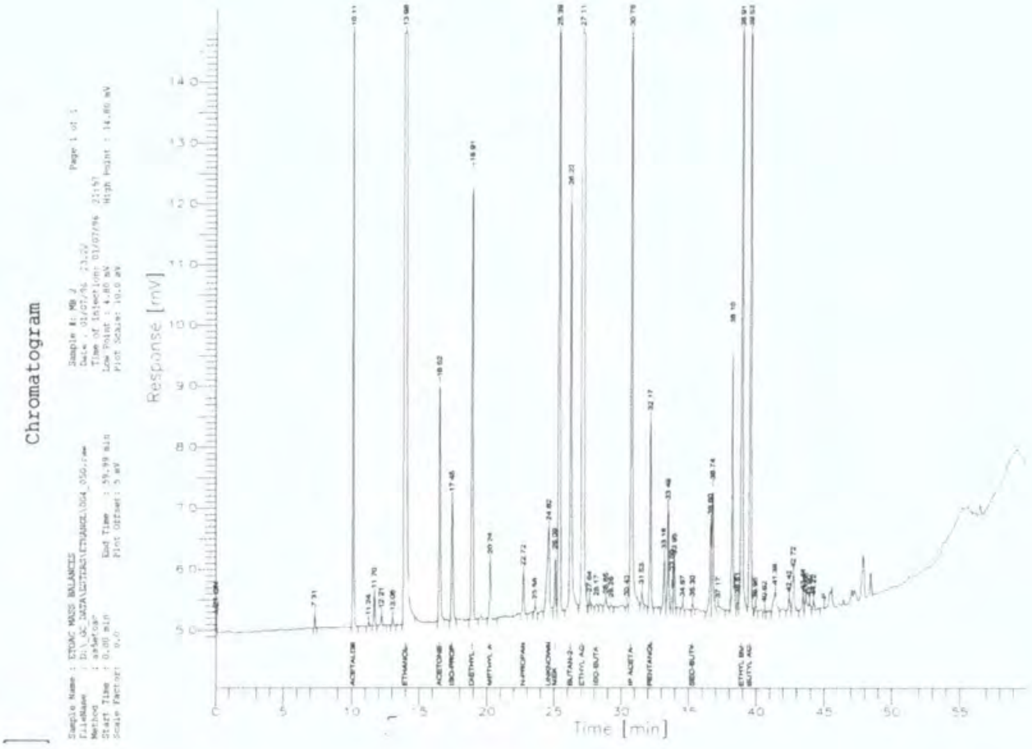

Figure 2.5 Typical Chromatogram from Run 2

When compared to figure 2.4 the difference in ethanol conversion and selectivity to ethyl ethanoate can be clearly seen.

Conditions were then changed to try to increase selectivity to ethyl ethanoate whilst keeping the high ethanol conversion. Examination of the proposed reaction mechanism (section 2.1) indicates that if the equilibrium concentration of ethanal could be reduced then the amount of by-product made would also be reduced. This was achieved by increasing the reactor pressure to 1400 kPa while keeping the other process conditions the same as for run 2. It should be noted that the increase in pressure increases the residence time of ethanol over the catalyst – doubling the pressure in effect doubles the contact time of the feed over the reactor. This is important in two ways; if the reaction has not reached equilibrium then increasing residence time will increase conversion. If the reaction has reached equilibrium then increasing residence time may decrease selectivity if the reactions that produce by-products have not reached equilibrium.

The increase in pressure resulted in a reduction of conversion from 69.5% to 58.1% whilst increasing selectivity form 56.9 to 63.3%. These raw results in themselves do not show the whole story – some of the by-products decreased in line with the overall change in selectivity, some more and some less than the average. The concentration of the main by-product (1-butanol) assumed to have derived directly from ethanal decreased further than the overall decrease in selectivity; 5.9% to 4.9% (a relative decrease of 16%), while the concentration of the by-product that was assumed to have been derived from the feed (diethyl ether) increased (3.02% to 4.91%). Butanone and 2-butanol – both assumed to derive from ethanal but via a more complex mechanism than the simple aldol mechanism for 1-butanol – decreased in selectivity, but less than the average decrease.

The next test (run 4) was carried out to investigate the effect of temperature. The pressure of operation was reduced back to 680kPa and the temperature reduced to 220°C. The results from this run – reduced conversion of 34.6 mol%, but increased selectivity of 87.4 mol% – demonstrated a dependence of selectivity on temperature. The data from these initial five runs are shown in figure 2.6. The trend of both selectivity and conversion is marked in respect of temperature – conversion increases and selectivity decreases as temperature is raised.

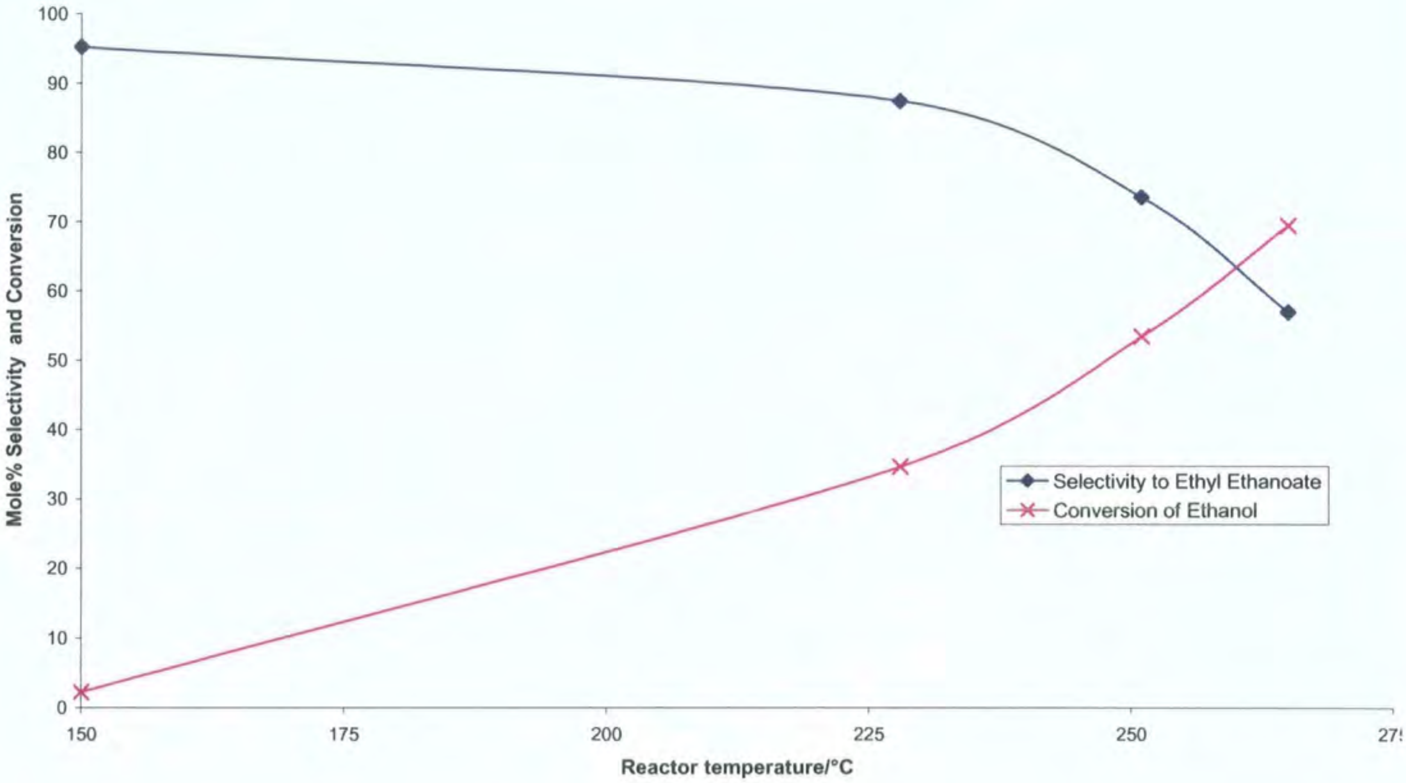

Figure 2.6 Effect Of Temperature On Conversion And Selectivity

Figure 2.7 shows the effect of temperature on yield – Mole% conversion of ethanol x mole% selectivity to ethyl ethanoate – and a more complicated picture emerges. There appears to be a linear dependence of temperature on yield up to 250°C, after which yield does not increase. The major products, other than ethyl ethanoate and other esters, show a more or less exponential relationship with temperature, with increasing temperature increasing the concentration of the by-products, indicating that they fit with the normal Arrhenius rate equation. Figure 2.8 shows log plots for a number of these compounds. The conclusions reached from this observation are discussed in section 2.9.

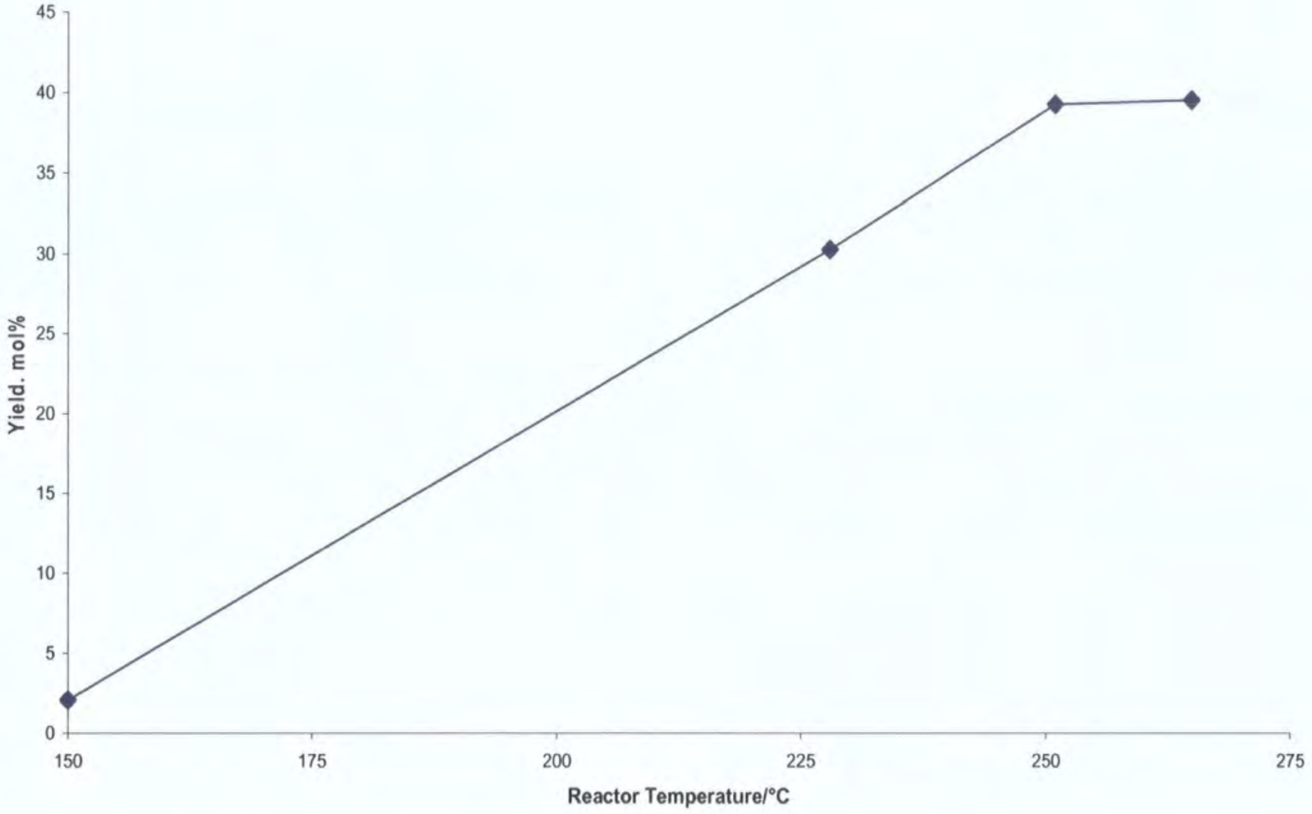

Figure 2.7 Yield Vs Reaction Temperature

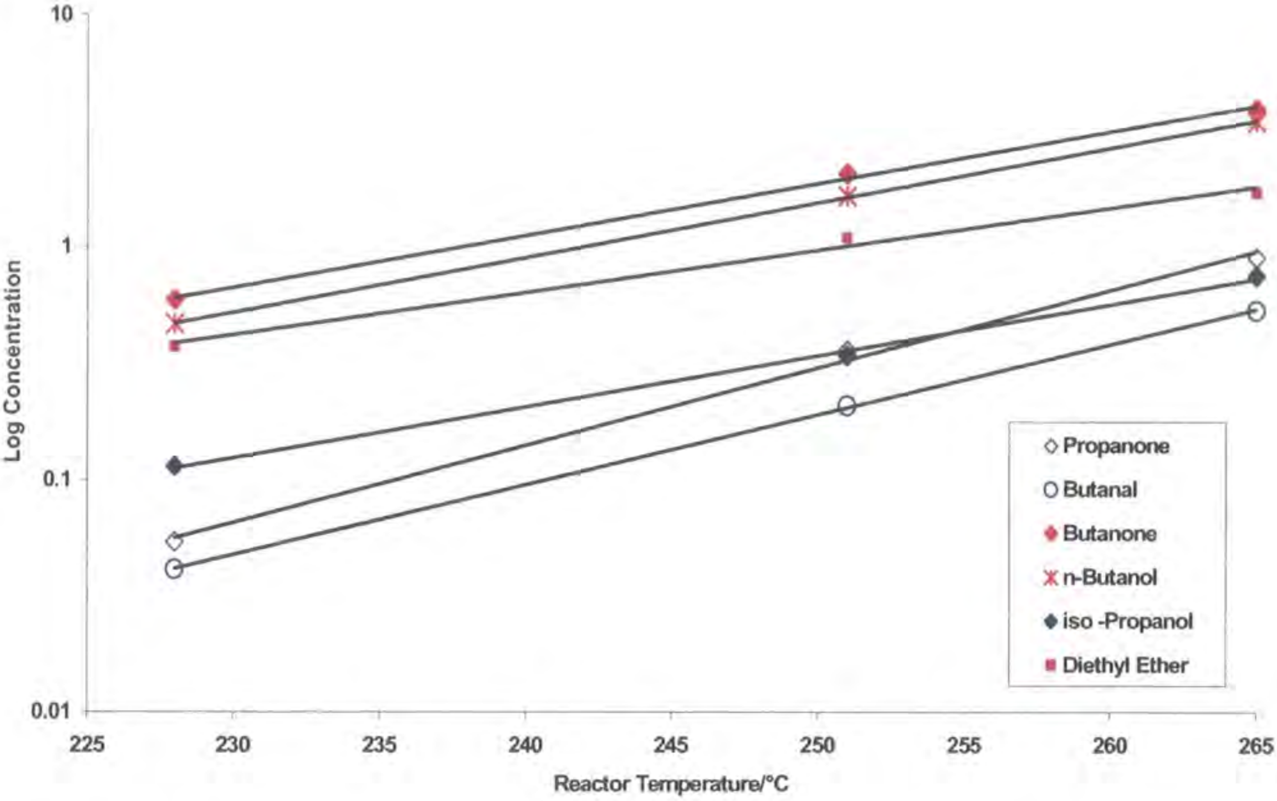

Figure 2.8 Log Concentration Of By-Products Against Reactor Temperature

2.5 Copper Manganese Alumina Catalyst T4489

The next catalyst chosen for inclusion into the screening test work was a Copper-Manganese-Alumina type, termed T4489, supplied by Sud-Chemie. The catalyst became available as it was under development as an alternative to catalysts in ester hydrogenolysis and was therefore seen as a likely candidate for alcohol dehydrogenation. The catalyst was loaded to the reactor and activated according to the procedure in appendix 1. The catalyst was tested for ethanol dehydrogenation in a similar fashion to the catalyst ex1808T, see section 2.4 above. The results are shown in table 2.2 (p 73) (runs 8-15) and are discussed below.

Test 8 was carried out at a low temperature, 160°C, in order to check the activity of the catalyst. The T4489 catalyst was known, by experience of use at DPT, to have a relatively high activity for ester hydrogenation compared to copper-chrome and so it was possible that even at low temperatures the conversion of ethanol would be high. The result indicated that while the activity of the catalyst was higher (3.5% conversion cf 2.2% for copper-chrome) the difference was not significant. What was significant was that even at low conversion the molar selectivity to ethyl ethanoate was low – 74% cf 95% for the copper-chrome catalyst.

Reaction conditions were then scanned through a range similar to that used for the copper-chrome catalyst with similar results – at all conditions the selectivity to ethyl ethanoate was significantly lower. An interesting observation was whilst the catalyst produced by-products of a similar nature, there was a wide variation in the relative concentration of these by-products. In particular, the concentrations of propanone, 1-propanol, butanone, 2-butanol and 1-butanol in the product were high compared to the Copper-chrome catalyst; in contrast, diethyl ether concentrations were relatively low. This result indicates that aldol promoting sites (basic) were more important than ether producing sites (acidic) for by-product formation. Figure 2.10 plots conversion of ethanol and selectivity to ethyl ethanoate against reaction temperature. The general shape of the plot is similar to that observed for the previous catalyst – ex1808T. Figure 2.11 plots conversion of ethanol against selectivity to ethyl ethanoate showing the dependence of selectivity on conversion of ethanol.

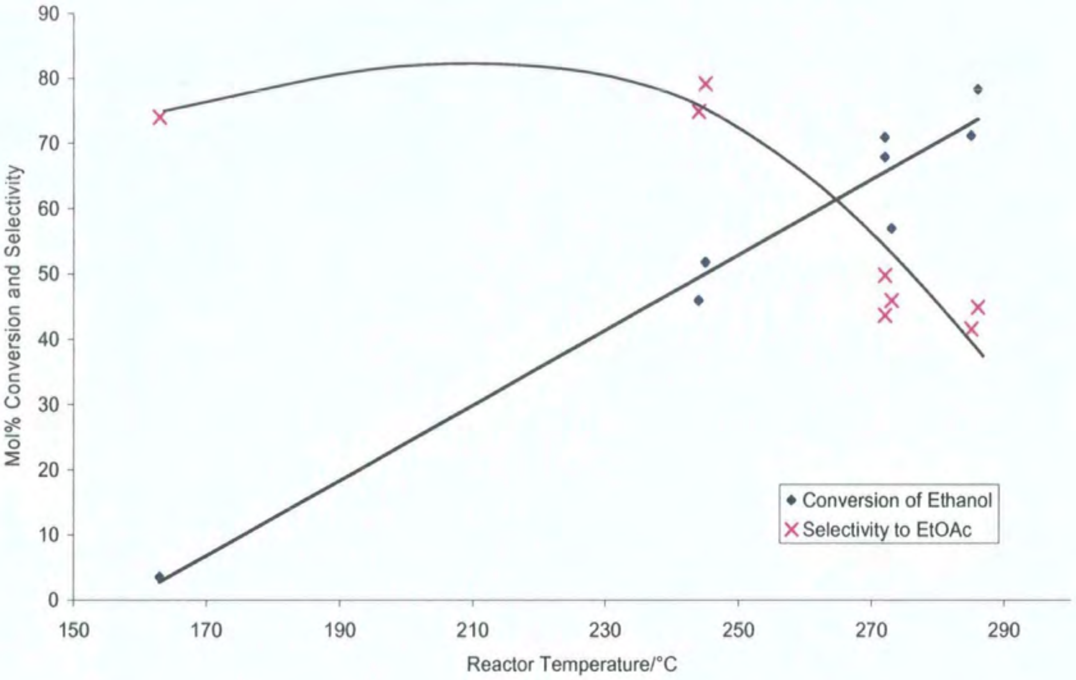

Figure 2.10 Ethanol Conversion And Selectivity To Ethyl Ethanoate Against Reactor Temperature

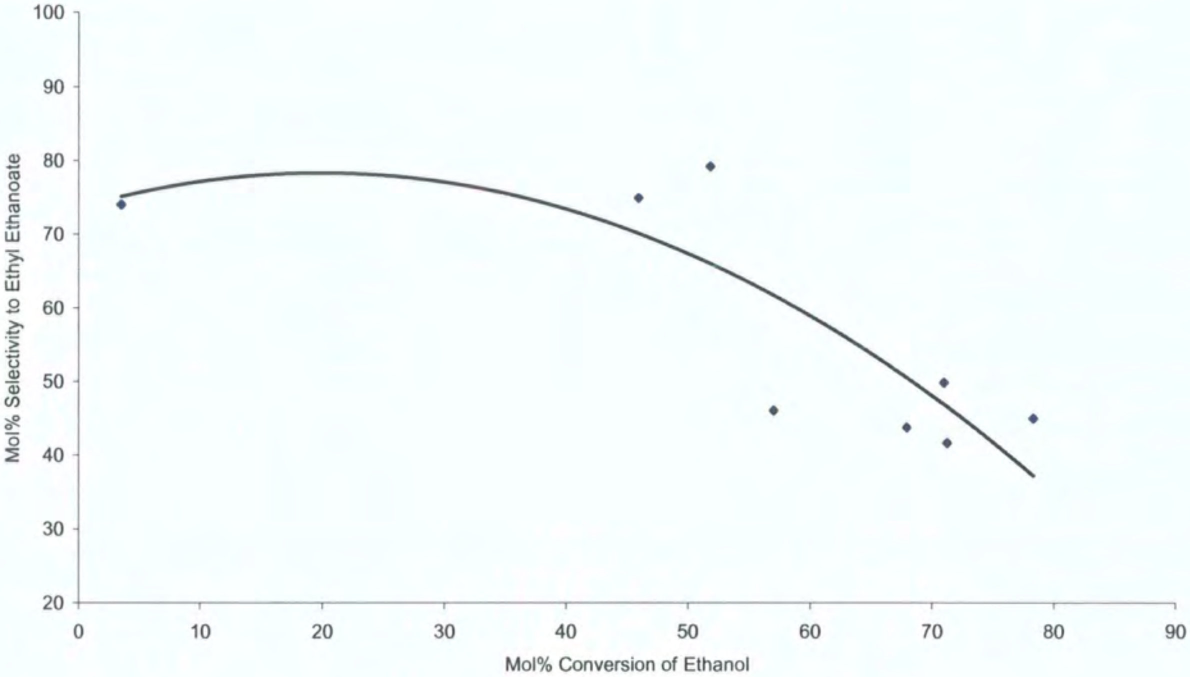

Figure 2.11 Ethanol Conversion Against Selectivity To Ethyl Ethanoate

2.6 Copper on Silica Catalyst

The next catalyst chosen for the screening was a copper on silica experimental catalyst supplied by ICI. The catalyst has a copper content of 20% supported on a high surface area silica, BET (Brunauer, Emmett and Teller)[16] area of $200m^2g^{-1}$. The catalyst had been originally used for the liquid phase hydrogenolysis of fatty acid esters to fatty alcohols but had shown poor activity but relatively high selectivity. It was this property that suggested it could be useful as a dehydrogenation catalyst.

The catalyst was loaded to the reactor and activated according to the method shown in Appendix 1. Following activation the catalyst was screened in a similar fashion to the other catalysts but due to the expected low activity of the catalyst the low temperature run was omitted. The results are shown in Table 2.3 (p 74) and graphically in figures 2.12 - ethanol conversion and selectivity to ethyl ethanoate with temperature, and 2.13 – selectivity to ethyl ethanoate plotted against ethanol conversion.

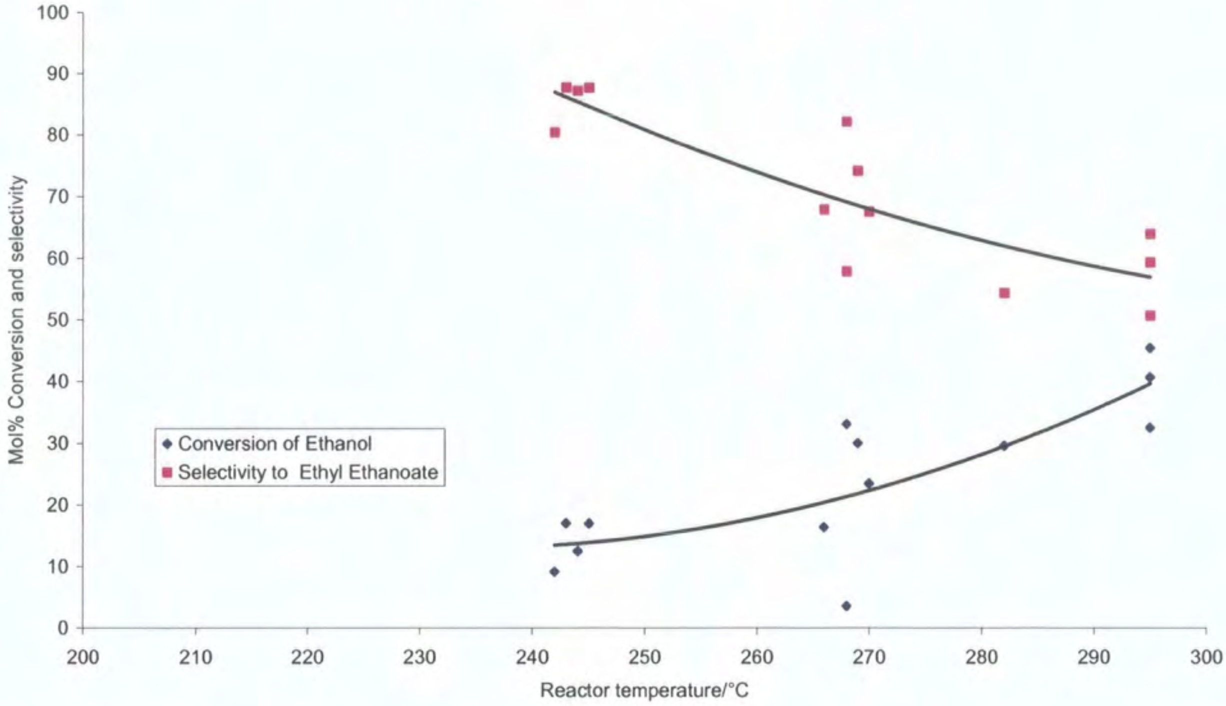

Figure 2.12 Conversion And Selectivity Against Reactor Temperature

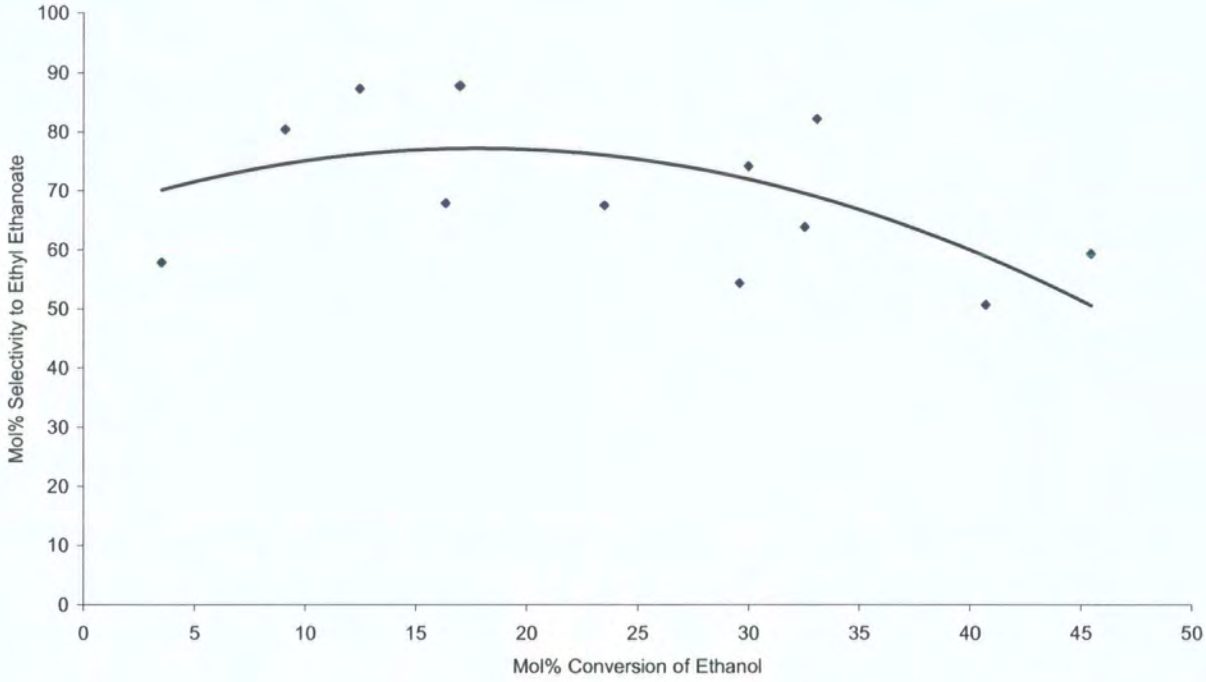

Figure 2.13 Selectivity To Ethyl Ethanoate Against Conversion Of Ethanol

The results using this catalyst show a marked difference from the previous two catalysts tested. The overall activity is low, as expected for the results from studies of ester hydrogenolysis, but overall selectivity is also low. The calculated yield of ethyl ethanoate was the lowest for any tested. The spectrum of by-products was similar to the T4489 catalyst, and was low in diethyl ether in particular. The by-product spectrum is dominated by C_4 compounds that are assumed to be formed from acetaldehyde via an aldol mechanism The catalyst shows a very marked dependence on temperature for by-product formation, and coupled with low activity the catalyst was deemed not to be a suitable candidate for the present project and the test work was discontinued.

2.7 Raney Copper Catalyst

It was clear that the catalyst support and/or promoters (Cr, Al-Mn and Si) were having a disproportionate detrimental effect on the selectivity and conversion of ethanol to ethyl ethanoate. Copper was clearly capable of performing the required reaction but the by-products, even at low conversion, were at too high a level for commercial viability. A Raney[17] copper catalyst, manufactured by Degussa, was used in an attempt to discount the effect of support materials by effectively removing them.

Raney copper is formed by first making a copper-aluminium alloy, of varying composition according to the required physical properties of the final catalyst. The alloy is treated with an aqueous base, such as NaOH, which leaches aluminium leaving a finely divided but connected copper sponge. The catalyst has a lower metal surface area than a precipitated catalyst but it has a well defined pore structure and is extremely robust.

Given the probability that the catalyst would be less active than the precipitated type due to its low surface area, the initial runs were carried out at higher temperatures than for the other catalysts. The conditions of temperature, pressure and feed flow rates were scanned, and the results are collected in Table 2.4 (p 75). At first sight, the results obtained using the Raney catalyst were poor. Selectivity to ethyl ethanoate was low, even at low conversion of ethanol. A more detailed examination of the by-product spectrum indicated that at moderate conversion of ethanol the main by-product was diethyl ether, and other by-products were at a lower level than observed when using other catalysts. This observation suggested that if the cause of the ether formation could be determined then a selective catalyst should be achievable. Investigation of the catalyst revealed that it contained significant levels of aluminium, possibly acting as the source of ether formation. Contact with the catalyst manufacturer confirmed the presence of residual aluminium which could be reduced by several means but could not be entirely eliminated. It was decided at this point that this would not be a worthwhile use of time and effort and so the Raney copper catalyst was removed from the candidate list. The data from these runs are recorded in Table 4 (p 75) and graphically in figures 2.14 and 2.15.

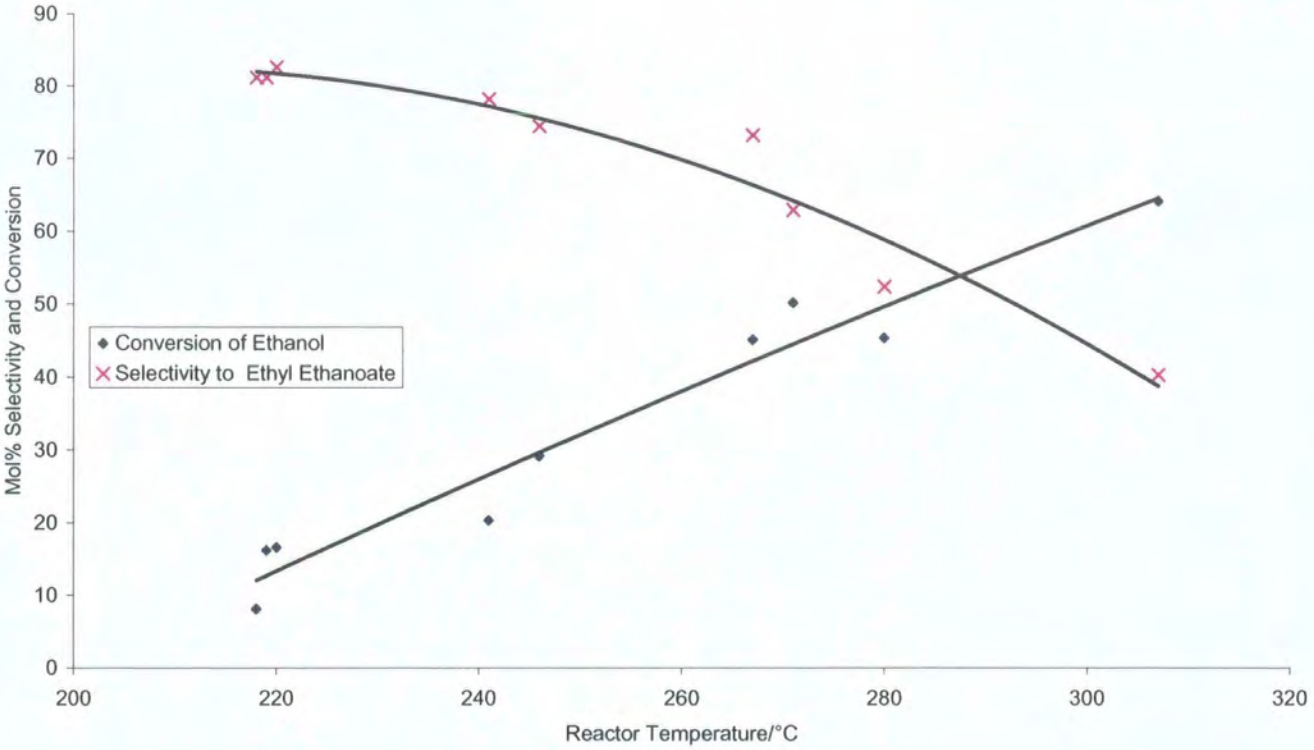

Figure 2.14 Selectivity And Conversion Against Reactor Temperature

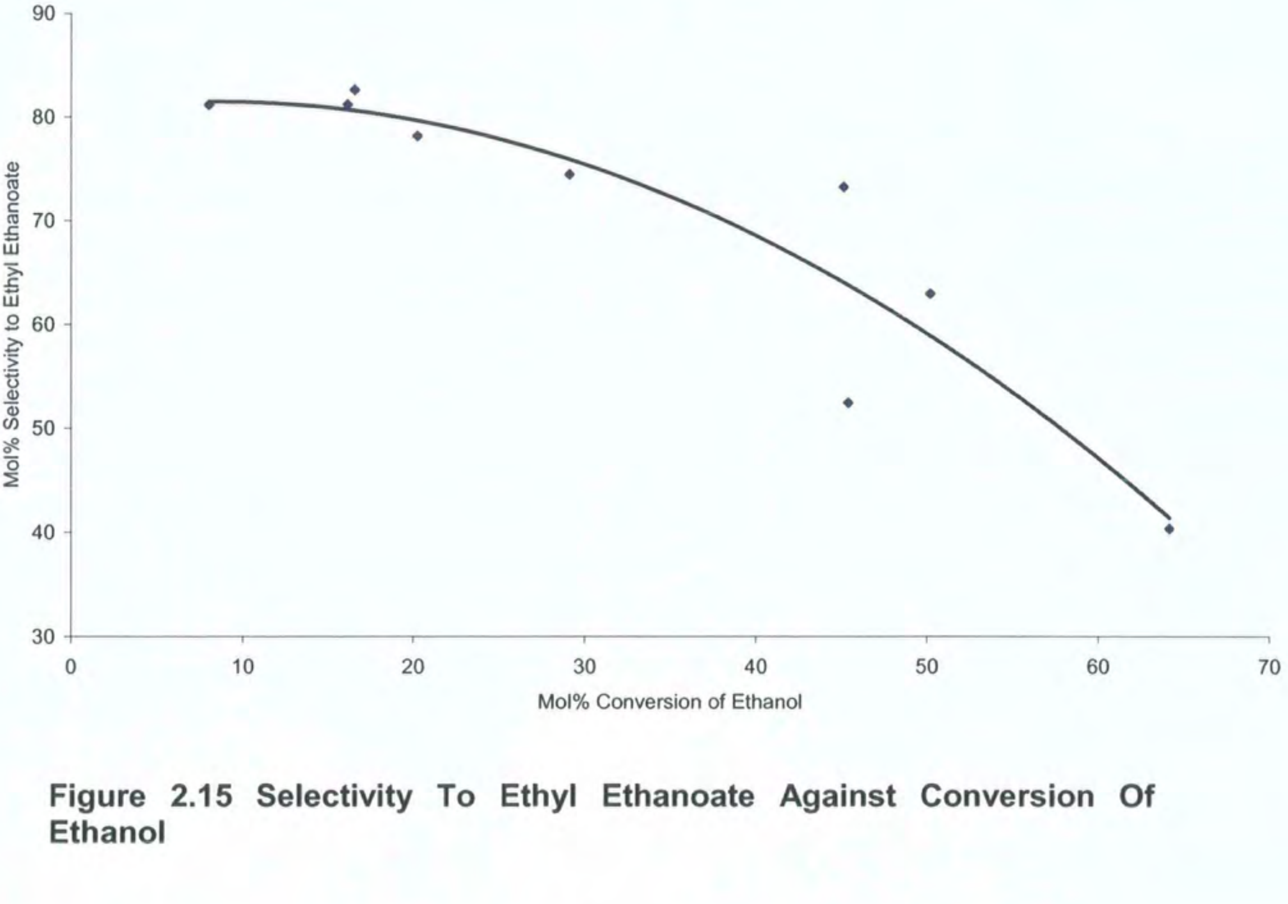

Figure 2.15 Selectivity To Ethyl Ethanoate Against Conversion Of Ethanol

2.8 Copper Oxide Catalyst – E408Tu

The results afforded by the previous catalysts tested indicated that the promoter and catalyst supports were having a negative effect on the selectivity to dehydrogenation. The Raney copper catalyst suggested that the approach of testing a 'copper-only' could be the best option. A search of the catalyst company literature resulted in the catalyst designated 'E408Tu' which contained 92% copper oxide and 8% alumina binder. The catalyst was supplied in the form of 3x3mm cylindrical tablets. The catalyst was not recommended by the manufacturers as a hydrogenation or dehydrogenation catalyst.

A 100cm^3 charge of the Engelhard catalyst was loaded into the reactor and activated as detailed in Appendix 1. Indicators for the activation of the catalyst appeared to be identical to the activation of the copper chromium and copper manganese alumina catalysts previously tested, with the exception of the activation took longer, possibly due to the increased copper content.

Following the activation the catalyst was heated to 250°C and the reactor pressure set at 690kPa. Hydrogen flow was set at 10 SLPH and the ethanol feed started at 30cm^{3}hr^{-1} (LSHV 0.3). Since the initial results from this run were not very encouraging – selectivity to ethyl ethanoate was 67.3% (see run 38, table 2.5 (p 76)) at a conversion of 47.5%, the feed rate was increased to 50cm^{3}hr^{-1} at otherwise identical conditions. The results from this run became more encouraging; selectivity to ethyl ethanoate increased to 82.4% while conversion remained relatively stable at 49.9%.

The feed rate was increased again to 100cm^{3}hr^{-1} (see run 40, table 2.5 (p 76)) and again the selectivity to ethyl ethanoate increased, stabilising at 86.4%, while conversion remained almost unchanged at 50.4%. It appeared that the activity of this catalyst was high – an increase in feed from LHSV 0.3 to 1.0 resulted in a small increase in conversion and a large increase in selectivity (67.3% to 86.4%). The feed rate to the reactor was increased again, to 200cm^{3}hr^{-1} (LHSV 2.0 – see run 41, Table 2.5 (p 76)). At this condition the conversion was seen to decrease to 41.2% while the selectivity increased marginally to 87.9%.

Having found the limit of catalyst activity at 250°C, the ethanol feed rate was reduced to 100cm^{3}hr^{-1}, and the reactor temperature lowered to 225°C. Ethanol conversion at these conditions fell to 35.0% but the selectivity to ethyl ethanoate increased to 93.4%, clearly the best result of any catalyst. In order to increase conversion the feed rate was decreased to 50cm^{3}hr^{-1}. The results from this run (run 43, table 2.5 (p 76)) – an increase in conversion to 39.6% and a marginal decrease in selectivity to 93.3% indicated that the effect of feed rate on selectivity was not the same at 225°C and 250°C. At the higher reactor temperature, selectivity increased with increasing feed rate while conversion of ethanol remained relatively unchanged. At 225°C selectivity remained unchanged while conversion of ethanol decreased with increasing ethanol feed rate.

The effect of pressure on the activity and selectivity was then tested. Runs were carried out at 1380kPa (run 44) and 345kPa (run 45). The effect of increasing pressure was to increase the maximum selectivity observed to 94.8% but to reduce ethanol conversion at this selectivity to 33.7%. Conversely decreasing pressure increased conversion to 42.7% but decreased selectivity to 91.6%. The increase in selectivity with pressure was then tested at 250°C to test whether the effect of pressure or temperature was the dominant factor in selectivity.

The next run (run 46, Table 2.5, p.76) was carried out at 250°C and at 1380 kPa. The results – conversion of 43.4% and selectivity of 91.4% should be compared to the result of run 40 which returned an ethanol conversion of 50.4%, and selectivity to ethyl ethanoate of 86.4%. Clearly, increasing the reactor pressure has a beneficial effect on selectivity but a negative effect on conversion.

Runs 47, 48 and 49 were carried out to test the effect of increasing the hydrogen concentration in the reactor. The pressure in the reactor is generated by the ethanol feed, hydrogen feed and products of dehydrogenation. Increasing the reactor pressure while keeping the ethanol and hydrogen feed rates constant does not increase the partial pressures of either but does raise the total pressure. Further tests - runs 47, 48 and 49 - were carried out to test whether the determining factor in selectivity with pressure was due to the partial pressure of hydrogen or the total hydrogen pressure. The results from these runs indicate that, at a reactor temperature of 250°C, a change in hydrogen partial pressure at both 1380 kPa and 345 kPa has little or no effect on selectivity. Runs 46 and 47, both performed at 1380 kPa but at hydrogen flows of 10 and 50 SLPH respectively gave selectivities of 91.6 and 91.2% respectively. Runs 48 and 49, performed at 345 kPa and at hydrogen flows of 50 and 10 SLPH respectively gave selectivities of 87.2 and 86.2%. When the effect of hydrogen flow is compared for conversion of ethanol, at 1385 kPa the effect is small – conversion of ethanol fell from 43.4% to 43.0% when the hydrogen flow was increased, but at 345 kPa the effect was marked, with a fall in conversion from 49.3% to 40.1%. When runs 49 and 40 are compared – both runs were carried out at 250°C and with 10 SLPH hydrogen and $100cm^3hr^{-1}$ of ethanol but at different pressures, 345 kPa and 690 kPa, the effect of pressure on selectivity and conversion at 250°C reactor temperature appears to be negligible. Comparing this observation to the results obtained from runs 42 to 45, which were performed at a lower temperature, it appears that the effect of pressure on the reaction is highly dependent on the reaction temperature employed.

A possible explanation is that there are a number of physically or chemically different sites that catalyse the formation of by-products. At high temperature, all of these sites are active and the rate of by-product formation is determined by desorption from these sites. At lower temperatures not all sites are active or not fully covered. Hence, at high temperature increasing the ethanol feed rate increases selectivity to ethyl ethanoate – more ethyl ethanoate is produced while the rate of by-product formation remains constant. A final run was carried out at 200°C – run 50, Table 2.5 (p 76). The ethanol feed rate was reduced to 50cm^{3}hr^{-1} in anticipation of a loss in activity similar to that seen when the temperature was reduced from 250 to 225°C. The results from this run – an ethanol conversion of 24.5% and selectivity to ethyl ethanoate of 97.5% completes the picture of the domination of temperature on both selectivity and conversion. The results from these runs are collected in Table 2.5 (p 76) and graphically in figures 2.16, 2.17 and 2.18.

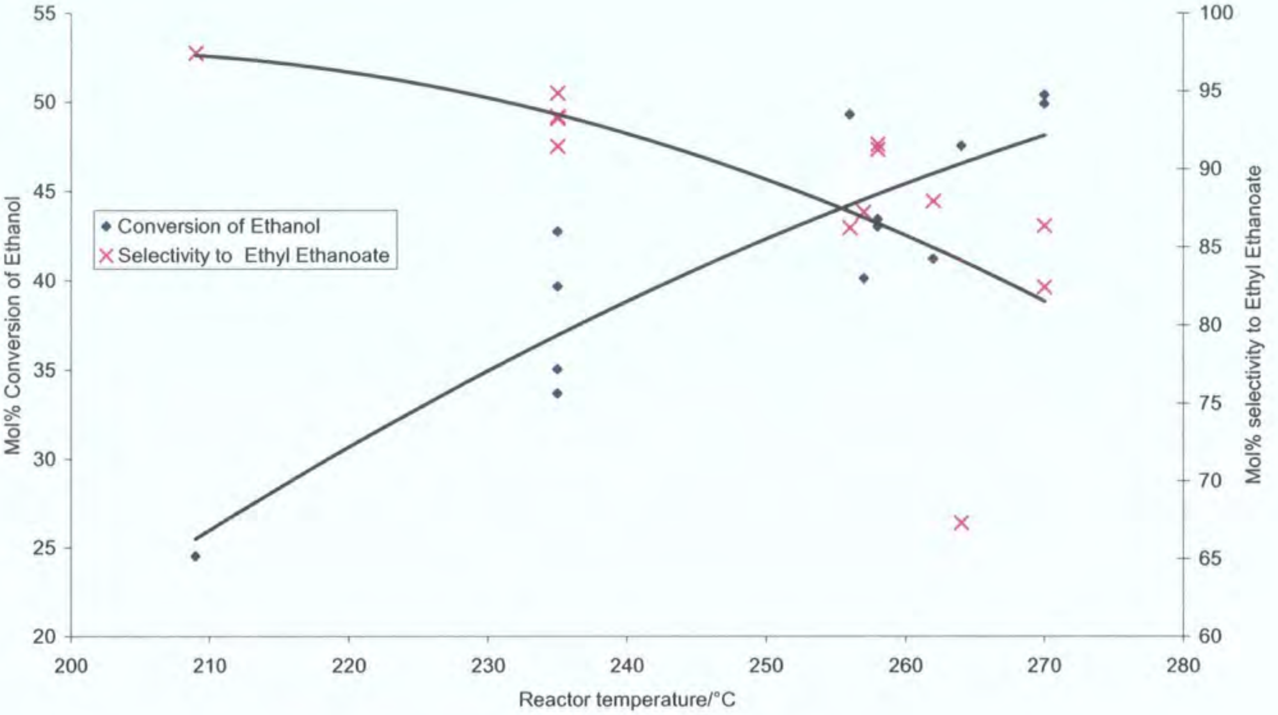

Figure 2.16 Conversion And Selectivity Against Reactor Temperature

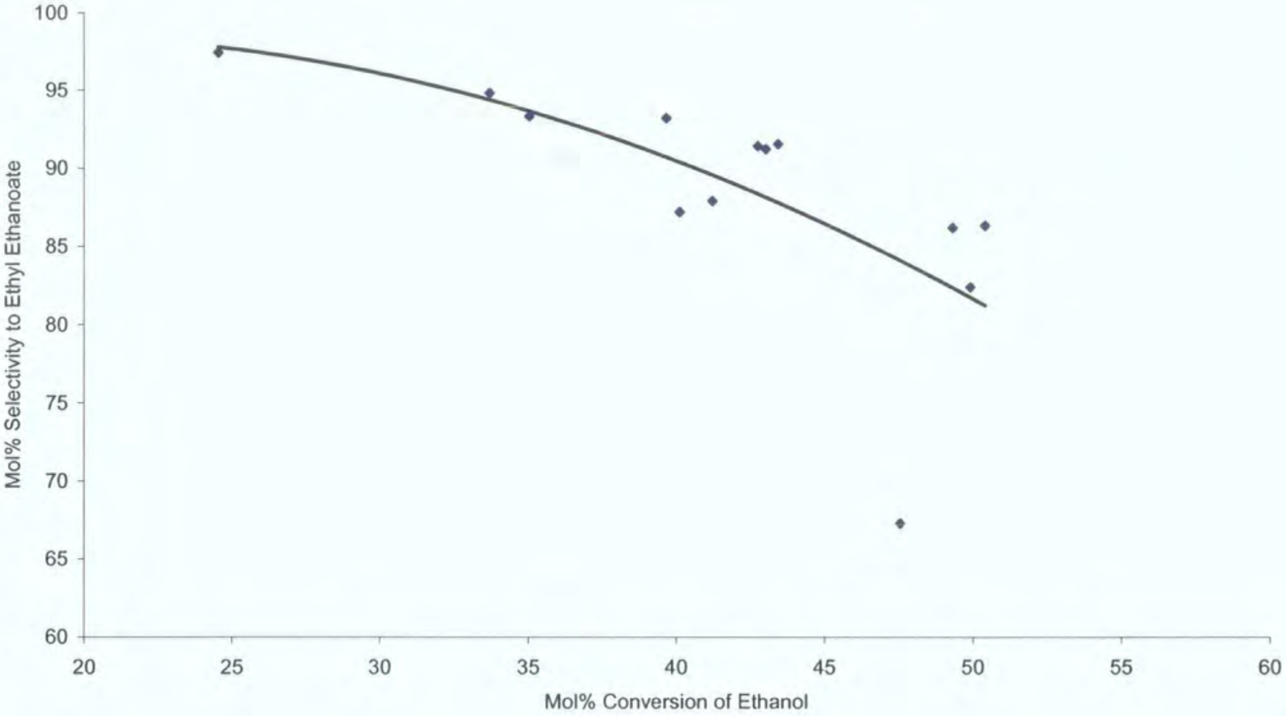

Figure 2.17 Selectivity To Ethyl Ethanoate Vs Ethanol Conversion

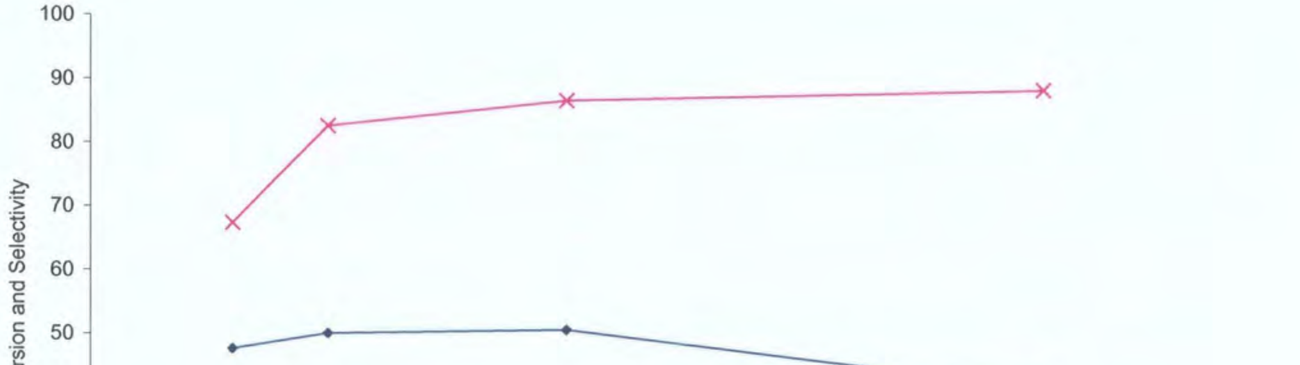

Figure 2.18 Conversion And Selectivity Against Ethanol Feed Rate

2.9 Discussion of preliminary test work

The test work that has been reported in this chapter shows that ethyl ethanoate can be selectively synthesised by the dehydrogenation of ethanol over copper metal catalysts. Five catalysts have been evaluated, 50 individual runs have been performed. All of the catalysts that were tested had activity to the target reaction, ethanol dehydrogenation to ethyl ethanoate, but there was a wide range of selectivity to the desired product. With the exception of one catalyst - Raney copper - , the catalysts contained copper in the form of copper oxide and so was activated *in situ* by reduction with hydrogen diluted in a stream of nitrogen at 160°C prior to use. All catalysts were in the form of 3x3mm cylindrical pellets, commercially produced. The dehydrogenation reactions were carried out in the vapour phase, in a fixed bed reactor using a charge of 100cm^3 of the catalysts. The most selective and active catalyst is an unpromoted copper oxide containing catalyst, sourced from Engelhard, termed E408Tu. The addition of promoters to copper oxide appears to have a negative effect on the selectivity of the reaction, in two ways: by promoting dehydration and aldol reactions. There is evidence in the literature that insulating oxides[18] promote the formation of dehydration products in preference to dehydrogenation products, and these products have been observed in the dehydrogenation products collected. The catalyst that exhibits high selectivity to ethers (Raney Copper) is suspected of containing large numbers of the sites that promote dehydration reactions but few of the sites that promote aldol reactions.

Some of the other by-products that have been identified appear to be associated with aldol reaction of acetaldehyde. They are 4-carbon species such as butanone, 1-butanol and 2-butanol. The difference in the selectivity of these side products for the differing catalysts leads to the conclusion that the promoters (Cr, Mn) cause these products to be formed. The proposed reaction mechanism for these by-products, detailed in section 2.1, is plausible given that the by-products are suspected as being based on an aldehydic intermediate (adsorbed ethanal) and the by-products are at highest concentration at conditions where ethanal is also high. The reaction of ethanol to ethyl ethanoate seems to be highly temperature dependent. Below about 200°C there appears to be little or no activity although the selectivity for ethyl ethanoate can be high. Above 250°C the reactions that form by-products appear to dominate, giving a temperature window of about 200-250°C. Increasing the reactor pressure seems to have a positive effect on the selectivity to ethyl ethanoate while having a negative effect on conversion of ethanol. Overall, the benefits of pressure in increased selectivity offsets the loss in yield. At a pressure of 1400kPa and at a temperature of 225°C, ethyl ethanoate can be synthesised at circa 95% selectivity at an ethanol conversion of 34%. This result has met the initial target of producing ethyl ethanoate at a selectivity of >90%

The catalyst screening has identified a commercially available copper containing catalyst that has acceptable performance in terms of activity and selectivity for the conversion of ethanol to ethyl ethanoate. Initial results obtained using the screening apparatus suggest that there is scope for improving the performance of the catalyst, especially in terms of the overall conversion. Given that this catalyst is unlikely to be the optimum possible for the reaction, there is scope for improvements in both the selectivity and activity. The poor selectivity of the Copper-chrome catalyst for converting ethanol into ethyl ethanoate and indeed ethanal is puzzling as catalysts of this type are used for the industrial dehydrogenation of ethanol and other alcohols to the respective aldehydes and ketones. In the published work details of the side reactions that take place during dehydrogenation are not given, and except for propanone and butanone none of the by-products identified in this work have been identified. This is surprising, especially as the results of the present study show that increasing the temperature and decreasing the pressure both increase selectivity to these by-products. At the quoted reaction temperature for ethanol dehydrogenation (275-300°C, atmospheric pressure)[14] the by-products would be expected to dominate.

The very poor selectivity exhibited by the manganese containing catalysts was unexpected as they are highly selective in the reverse hydrogenation reaction. Typically, for the hydrogenation of dialkyl maleates to 1,4 butanediol – a molecule that is prone to dehydration to form 1-butanol and the cyclic ether tetrahydrofuran – a manganese containing catalyst is more selective to butanediol and less selective to THF and 1-butanol. The Mn containing catalyst tested for this work for the dehydrogenation of ethanol to ethyl ethanoate was non-selective for ether formation, but other by-products especially alcohols and ketones formed by aldolisation reactions accounted for up to 58% of the products. The reason for this puzzling behaviour is not known.

The high activity of the Copper oxide only catalyst precursor is also surprising in the light of previous work reported in the literature. Most studies[19] have found that the activity of unpromoted copper oxide is low compared to promoted copper oxide, with the unpromoted catalyst precursor having only half the activity of the promoted analogue. It may be that this difference in activity is masked by the reaction being equilibrium limited, or one or more of the by-products inhibiting the catalysts. As the product of a dehydrogenation reaction is more strongly adsorbed than the feed material there may be 'self poisoning' where ethyl ethanoate is being held on the catalyst surface and is inhibiting reaction. Regardless of the catalyst, selectivity or conversion, the maximum amount of ethyl ethanoate that is observed in the product does not exceed 40-42 mol%. In addition, the ethyl ethanoate yield appears to reach a maximum at about 40% and does not increase even with an increase in overall conversion. This is perhaps an indication of the ethyl ethanoate reaction occurring on one site, which becomes inhibited at high ethyl ethanoate concentration, and that the side reactions occur on other sites which do not become inhibited by adsorption of ethyl ethanoate .

The results from this work are encouraging, sufficiently so to lead to the best catalyst, E408Tu, to be installed into a new reactor for more detailed testing. The test work will be designed to determine the effect of pressure, temperature feed rate and feed type on the selectivity to ethyl ethanoate. The long term stability of the catalyst will be tested by operating over an extended period of circa 1000 hours. This work is detailed in chapter 3.

Table 2.1 Engelhard Experimental Cu/Cr Catalyst Dehydrogenation Results

Run Number	1	2	3	4	5	6	7
Rx In, °C	150	265	262	228	251	279	225
Rx Out, °C	150	245	254	214	237	258	214
LHSV, hr^{-1}	0.3	0.3	0.3	0.3	0.3	0.3	0.5
Pressure. KPa	680	680	1360	680	680	340	340
Wt% Analysis							
Ethanal	0.091	1.786	1.278	0.842	1.438	3.036	1.854
Methanol	0.058	0.130	0.108	0.021	0.038	0.151	0.046
Diethyl Ether	0.000	1.711	2.299	0.373	1.096	1.233	0.286
Ethanol	97.745	31.805	42.935	66.355	47.841	29.728	69.563
Propanone	0.000	0.899	0.562	0.054	0.359	1.359	0.117
2 –Propanol	0.000	0.749	0.741	0.114	0.341	0.680	0.107
Di 2-Propyl Ether	0.000	0.022	0.008	0.000	0.000	0.016	0.000
Butanal	0.000	0.532	0.468	0.041	0.208	0.598	0.071
Ethyl ethanoate	1.893	38.396	35.285	28.545	37.542	39.289	22.716
Butane	0.000	3.912	2.347	0.591	2.058	5.198	1.346
2-butanol	0.013	1.888	2.084	0.914	1.409	1.381	0.925
2-Propyl Ethanoate	0.000	0.128	0.131	0.008	0.036	0.071	0.014
1-Butanol	0.000	3.443	2.344	0.466	1.649	3.442	0.837
2-pentanol	0.000	0.744	0.265	0.013	0.121	0.709	0.016
Sec- Butyl Ethanoate	0.000	0.449	0.418	0.085	0.206	0.294	0.049
Ethyl butanoate	0.000	2.447	1.272	0.266	1.390	2.867	0.419
2-butyl ethanoate	0.000	2.737	1.442	0.202	1.088	1.113	0.320
Di 1-Butyl Ether	0.000	0.000	0.055	0.000	0.013	0.000	0.000
Water	0.200	3.610	3.410	0.810	1.880	3.550	0.960
Others	0.000	4.067	2.283	0.257	1.029	4.941	0.294
Mole% Conversion of Ethanol	2.175	69.468	58.119	34.554	53.423	71.496	31.429
Selectivity Ethanal Free							
Selectivity to Ethyl ethanoate	95.211	56.939	63.334	87.379	73.541	57.534	79.306
Selectivity to Propanone	0.000	2.023	1.531	0.251	1.067	3.019	0.620
Selectivity to Butane	0.000	7.090	5.149	2.211	4.927	9.303	5.743
Selectivity to 2-propanol	0.000	1.629	1.951	0.512	0.980	1.460	0.548
Selectivity to 2-butanol	0.778	3.330	4.448	3.327	3.282	2.405	3.840
Selectivity to 1-Butanol	0.000	5.915	4.891	1.654	3.736	5.739	3.264
Selectivity to Diethyl Ether	0.000	3.017	4.907	1.358	2.553	2.147	1.187
Selectivity to All Others	4.011	20.056	13.789	3.309	9.913	18.391	5.492

Table 2.2 T4489 Cu/Mn/Alumina Catalyst Dehydrogenation Results

Run Number	8	9	10	11	12	13	14	15
Rx In, °C	163	272	273	245	244	272	285	286
Rx Out, °C	145	248	248	225	225	249	274	274
LHSV, hr^{-1}	0.3	0.3	0.3	0.5	0.5	0.3	0.5	0.5
Pressure, kPa	680	680	1360	680	340	340	680	340
H2 Flow, SLPH	1.5	3.2	4.1	0.6	2	3.3	0.1	2.5
TOL, hr	17	26	38	51	61	74.5	93	111
Ethanal	0.032	0.468	0.321	0.435	0.947	0.660	1.416	1.351
Methanol	0.000	0.140	0.214	0.059	0.086	0.213	0.295	0.279
Diethyl Ether	0.000	0.099	0.594	0.260	0.105	0.390	0.694	0.480
Ethanol	96.466	35.626	46.214	49.863	55.938	31.812	31.750	24.066
Propanone	0.000	3.777	1.583	0.425	0.797	3.946	4.797	6.085
2-Propanol	0.000	5.838	4.946	1.007	0.933	4.322	4.190	3.577
Butanal	0.000	0.326	0.492	0.060	0.058	0.383	0.457	0.443
Ethyl ethanoate	2.459	31.377	26.822	40.307	33.419	36.773	30.716	36.817
Butane	0.000	3.501	1.886	1.370	2.258	4.350	4.912	6.839
2-butanol	0.000	4.439	4.972	2.561	2.099	3.730	3.435	2.732
2-Propyl Ethanoate	0.000	1.101	0.939	0.083	0.035	0.718	0.897	0.636
1-Butanol	0.000	3.116	2.470	0.728	0.845	3.277	4.526	4.426
2-pentanol	0.000	1.170	1.269	0.105	0.077	0.943	1.410	1.047
2-butyl Ethanoate	0.000	0.817	0.875	0.219	0.086	0.689	0.742	0.607
Ethyl butanoate	0.000	1.046	0.763	0.502	0.443	1.279	1.483	1.727
2-butyl ethanoate	0.000	1.392	0.941	0.502	0.472	1.642	1.761	2.205
2-Hexanone	0.000	0.031	0.041	0.009	0.067	0.388	0.447	0.338
2-hexanol	0.000	0.132	0.167	0.024	0.015	0.126	0.137	0.106
Di 1-Butyl Ether	0.000	0.198	0.214	0.014	0.000	0.161	0.242	0.161
1-Hexanol	0.000	0.000	0.034	0.000	0.000	0.031	0.053	0.052
2-Heptanone	0.000	0.129	0.160	0.000	0.000	0.142	0.233	0.230
Di Propanone Alcohol	0.000	0.105	0.130	0.000	0.000	0.102	0.145	0.052
1-Heptanol	0.000	0.048	0.059	0.000	0.000	0.054	0.079	0.072
2-Octanone	0.000	0.011	0.011	0.000	0.000	0.015	0.023	0.021
2-Ethyl Hexanol	0.000	0.080	0.000	0.000	0.000	0.000	0.000	0.000
1-Octanol	0.000	0.027	0.009	0.000	0.000	0.007	0.000	0.008
Water	0.180	0.810	2.080	0.890	0.800	1.960	2.460	2.490
Others	0.863	4.196	1.794	0.577	0.520	1.887	2.674	3.117
Conversion of Ethanol	3.507	67.954	57.019	51.836	45.988	70.994	71.247	78.349
Selectivity to EtOAc	74.022	43.705	45.989	79.194	74.913	49.816	41.601	44.927
Selectivity to Propanone	0.000	7.982	4.118	1.267	2.711	8.111	9.857	11.266
Selectivity to Butane	0.000	5.960	3.952	3.290	6.186	7.202	8.131	10.200
Selectivity to IPA	0.000	11.927	12.438	2.902	3.067	8.587	8.323	6.402
Selectivity to 2-butanol	0.000	7.353	10.138	5.984	5.595	6.009	5.532	3.965
Selectivity to 1-Butanol	0.000	5.128	5.009	1.687	2.206	5.232	7.152	6.319
Selectivity to DEE	0.000	0.164	1.211	0.607	0.280	0.628	1.118	0.697
Selectivity to all Others	25.978	17.781	17.144	5.070	5.041	14.413	18.286	16.225

Table 2.3 ICI Cu On Silica Catalyst Dehydrogenation Results

Run Number	16	17	18	19	20	21	22	23	24	25	26	27	28
Rx In, °C	269	295	268	244	242	270	282	295	295	268	245	243	266
Rx Out, °C	250	275	251	225	225	250	275	274	275	251	225	225	250
LHSV, hr^{-1}	0.3	0.3	0.3	0.5	0.5	0.3	0.5	0.5	0.3	0.5	0.3	0.3	0.5
Pressure, kPa	680	680	1360	680	340	340	340	680	340	680	680	340	340
H2 Flow, slph	8.3	10	10	10	9.9	9.9	9.9	9.9	9.9	9.9	9.9	10.1	10
TOL, hr	16.5	34	49	64	75	88	100.5	112	123	135	147	159	169
Wt% Analysis													
Ethanal	0.954	1.308	0.409	0.677	1.382	1.597	4.424	2.125	2.482	0.091	0.438	0.431	2.641
Methanol	0.083	0.194	0.064	0.015	0.022	0.111	0.161	0.131	0.241	0.058	0.024	0.024	0.092
Diethyl Ether	0.000	0.011	0.000	0.000	0.000	0.009	0.009	0.000	0.000	0.000	0.000	0.000	0.000
Ethanol	71.428	57.188	68.224	87.600	91.247	77.813	72.468	68.657	62.372	96.470	83.664	83.652	84.590
Propanone	0.413	1.901	0.214	0.033	0.051	0.578	1.286	0.929	2.704	0.000	0.052	0.052	0.282
2-Propanol	0.685	2.066	0.754	0.078	0.056	0.587	0.563	0.811	1.727	0.000	0.179	0.179	0.193
Di 2-Propyl Ether	0.000	0.014	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Butanal	0.033	0.116	0.018	0.000	0.000	0.039	0.171	0.080	0.179	0.000	0.000	0.000	0.036
Ethyl ethanoate	21.016	26.269	26.196	9.821	5.919	14.335	13.450	18.905	19.511	1.893	13.963	14.026	8.943
Butanone	1.215	2.713	0.582	0.229	0.337	1.311	2.429	2.024	3.165	0.000	0.236	0.237	1.009
2-butanol	1.586	2.383	1.648	0.424	0.295	1.051	0.856	1.447	1.596	0.013	0.626	0.623	0.551
2-Propyl Ethanoate	0.012	0.050	0.024	0.000	0.000	0.000	0.000	0.010	0.026	0.000	0.000	0.000	0.000
2-Pentanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Butanol	1.088	2.648	0.603	0.190	0.233	1.078	2.177	1.956	3.190	0.000	0.234	0.232	0.817
2-pentanol	0.035	0.176	0.033	0.000	0.000	0.021	0.168	0.048	0.080	0.000	0.000	0.000	0.000
2-butyl Ethanoate	0.025	0.053	0.053	0.000	0.000	0.009	0.009	0.019	0.022	0.000	0.000	0.000	0.000
Ethyl butanoate	0.139	0.414	0.119	0.000	0.016	0.102	0.154	0.209	0.388	0.050	0.028	0.028	0.044
2-butyl ethanoate	0.280	0.815	0.206	0.000	0.035	0.197	0.307	0.438	0.794	0.000	0.047	0.047	0.083
2-Hexanone	0.026	0.048	0.018	0.000	0.000	0.015	0.020	0.015	0.025	0.000	0.000	0.000	0.022
2-hexanol	0.000	0.017	0.008	0.000	0.000	0.000	0.019	0.014	0.011	0.000	0.000	0.000	0.000
Di 1-Butyl Ether	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Hexanol	0.000	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.011	0.000	0.000	0.000	0.000
Water	0.720	1.130	0.600	0.690	0.250	0.730	0.670	1.770	0.850	0.200	0.320	0.280	0.380
Others	0.262	0.447	0.227	0.243	0.157	0.417	0.659	0.412	0.626	1.225	0.189	0.189	0.317
Conversion of Ethanol	30.014	45.468	33.112	12.469	9.108	23.476	29.614	32.570	40.715	3.514	16.974	17.020	16.351
Selectivity to EtOAc	74.140	59.297	82.128	87.227	80.382	67.501	54.365	63.879	50.689	57.888	87.691	87.766	67.878
Selectivity to Propanone	2.211	6.511	1.018	0.445	1.051	4.129	7.887	4.763	10.659	0.000	0.495	0.494	3.248
Selectivity to Butanone	5.239	7.485	2.230	2.486	5.594	7.545	12.000	8.359	10.050	0.000	1.812	1.813	9.360
Selectivity to IPA	3.544	6.840	3.467	1.016	1.115	4.054	3.338	4.019	6.581	0.000	1.649	1.643	2.149
Selectivity to 2-butanol	6.654	6.397	6.144	4.478	4.764	5.885	4.115	5.814	4.931	0.473	4.675	4.636	4.973
Selectivity to 1-Butanol	4.416	6.904	2.220	1.893	3.168	5.614	8.877	7.333	9.259	0.000	1.701	1.681	6.143
Selectivity to DEE	0.000	0.030	0.000	0.000	0.000	0.050	0.043	0.000	0.000	0.000	0.000	0.000	0.000
Selectivity to all Others	3.797	6.536	2.793	2.455	3.926	5.221	9.377	5.834	7.832	41.639	1.977	1.969	6.249

Table 2.4 Degussa Raney Copper Catalyst Dehydrogenation Results

Run Number	29	30	31	32	33	34	35	36	37
Rx In, °C	267	271	307	280	246	241	220	219	218
Rx Out, °C	247	250	275	250	225	225	200	200	200
LHSV, hr^{-1}	0.6	0.3	0.3	0.3	0.5	1	0.3	0.3	0.3
Pressure, kPa	680	680	680	1360	680	680	680	340	340
H2 Flow, SLPH	10	10	10	10	10	10	10	10	50
TOL, hr	11.5	23	38	49	58	68.5	88.0	99.0	106.5
Wt% Analysis									
Ethanal	0.420	0.313	1.332	0.195	0.231	0.429	0.105	0.147	0.059
Methanol	0.052	0.083	0.254	0.066	0.018	0.012	0.000	0.000	0.000
Diethyl Ether	2.939	5.709	8.294	10.251	2.927	1.135	1.414	1.012	0.521
Ethanol	55.791	50.120	34.292	54.173	71.496	80.041	83.828	84.203	91.887
Propanone	0.131	0.160	0.649	0.058	0.022	0.018	0.000	0.000	0.000
2-Propanol	0.401	0.697	1.341	0.551	0.135	0.064	0.032	0.039	0.017
Di 2-Propyl Ether	0.000	0.012	0.066	0.008	0.000	0.000	0.000	0.000	0.000
n –Butanal	0.102	0.222	0.338	0.204	0.037	0.015	0.000	0.008	0.000
Ethyl ethanoate	31.871	30.243	23.123	22.503	20.757	14.883	13.068	12.477	6.212
Butanone	0.984	0.970	1.909	0.400	0.300	0.324	0.057	0.113	0.029
2-butanol	2.132	2.662	2.399	1.973	1.247	0.860	0.419	0.590	0.269
2-Propyl Ethanoate	0.029	0.067	1.094	0.326	0.000	0.000	0.000	0.001	0.000
2-Pentanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1- Butanol	0.912	1.218	3.014	1.143	0.519	0.447	0.116	0.186	0.056
2-pentanol	0.085	0.120	1.177	0.146	0.024	0.010	0.000	0.000	0.000
2-butyl Ethanoate	0.149	0.247	0.219	0.180	0.052	0.020	0.000	0.000	0.000
Ethyl butanoate	0.517	0.585	1.700	0.410	0.208	0.129	0.039	0.060	0.012
2-butyl ethanoate	0.480	0.637	1.828	0.433	0.154	0.099	0.020	0.036	0.000
2- Hexanone	0.023	0.037	0.057	0.029	0.010	0.000	0.000	0.000	0.000
2-hexanol	0.035	0.058	0.026	0.035	0.014	0.000	0.000	0.000	0.000
Di 1-Butyl Ether	0.008	0.022	0.078	0.016	0.000	0.000	0.000	0.000	0.000
1-Hexanol	0.000	0.012	0.202	0.010	0.000	0.000	0.000	0.000	0.000
2-Heptanone	0.000	0.027	0.000	0.017	0.000	0.000	0.000	0.000	0.000
Di Propanone Alcohol	0.012	0.027	0.079	0.019	0.000	0.000	0.000	0.000	0.000
1-Heptanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Octanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Octanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	2.160	4.390	12.820	6.040	1.530	1.110	0.650	0.680	0.580
Others	0.767	1.362	3.709	0.814	0.319	0.404	0.252	0.449	0.360
Conversion of Ethanol	45.153	50.222	64.154	45.422	29.132	20.274	16.571	16.151	8.064
Selectivity to EtOAc	73.246	62.934	40.303	52.418	74.447	78.166	82.600	81.195	81.191
Selectivity to Propanone	0.457	0.505	1.716	0.205	0.120	0.143	0.000	0.000	0.000
Selectivity to Butanone	2.764	2.467	4.067	1.139	1.315	2.080	0.437	0.901	0.461
Selectivity to IPA	1.352	2.127	3.428	1.882	0.710	0.493	0.295	0.370	0.324
Selectivity to 2-butanol	5.827	6.587	4.972	5.465	5.319	5.371	3.151	4.568	4.175
Selectivity to 1-Butanol	2.469	2.995	6.105	3.152	2.195	2.730	0.868	1.425	0.859
Selectivity to DEE	8.032	14.128	17.191	28.396	12.484	7.089	10.626	7.829	8.103
Selectivity to all Others	5.854	8.257	22.218	7.343	3.410	3.927	2.022	3.712	4.887

Table 2.5 E408 Tu Copper Oxide/Alumina Catalyst Dehydrogenation Results

Run Number	38	39	40	41	42	43	44	45	46	47	48	49	50
Rx In, °C	264	270	270	262	235	235	235	235	258	258	257	256	209
Rx Out, °C	250	250	250	250	225	225	225	225	250	250	250	250	200
LHSV, hr^{-1}	0.3	0.5	1	2	1	0.5	0.5	0.5	1	1	1	1	0.5
Pressure, kPa	680	680	680	680	680	680	1360	340	1360	1360	340	340	680
H2 Flow, SLPH	10	10	10	10	10	10	10	10	10	50	50	10	10
Wt% Analysis													
Ethanal	0.183	0.355	0.532	1.011	0.321	0.170	0.100	0.250	0.313	0.261	0.698	0.904	0.098
Methanol	0.170	0.029	0.057	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Diethyl Ether	0.119	0.029	0.049	0.018	0.000	0.040	0.050	0.027	0.078	0.029	0.000	0.034	0.000
Ethanol	54.424	51.934	51.347	59.993	65.946	61.380	67.244	58.351	57.673	58.101	61.157	52.041	76.057
Propanone	0.358	0.258	0.210	0.226	0.027	0.027	0.000	0.060	0.064	0.032	0.183	0.282	0.000
2-Propanol	1.828	0.886	0.540	0.283	0.101	0.175	0.130	0.223	0.237	0.066	0.321	0.334	0.030
Di 2-Propyl Ether	0.000	0.077	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.221	0.000	0.000	0.000
1- Butanal	0.392	0.021	0.078	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.030	0.000
Ethyl ethanoate	31.616	40.479	42.624	34.457	31.442	35.801	30.882	37.856	38.490	38.030	33.547	40.946	22.936
Butanone	1.048	0.876	1.039	1.147	0.282	0.218	0.090	0.450	0.404	0.469	1.016	1.610	0.037
2-butanol	3.928	2.517	1.839	1.211	0.886	1.155	0.867	1.410	1.334	1.428	1.392	1.536	0.338
2-Propyl Ethanoate	0.319	0.051	0.077	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Pentanone	0.109	0.000	0.018	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Butanol	0.800	0.506	0.295	0.226	0.085	0.122	0.090	0.148	0.178	0.156	0.216	0.265	0.027
2-pentanol	0.387	0.000	0.060	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-butyl Ethanoate	0.677	0.000	0.317	0.048	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethyl butanoate	0.295	0.000	0.199	0.210	0.078	0.114	0.060	0.178	0.156	0.176	0.205	0.330	0.016
2-butyl ethanoate	0.422	0.000	0.216	0.138	0.048	0.064	0.040	0.090	0.106	0.091	0.116	0.209	0.020
2-Hexanone	0.312	0.000	0.068	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-hexanol	0.118	0.000	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Di 1-Butyl Ether	0.071	0.000	0.012	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1-Hexanol	0.055	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Heptanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	1.460	0.000	0.000	0.640	0.380	0.470	0.380	0.570	0.550	0.610	0.500	0.650	0.400
Others	0.908	1.983	0.393	0.393	0.404	0.264	0.070	0.387	0.418	0.331	0.648	0.830	0.043
Conversion of Ethanol	47.537	49.896	50.394	41.196	35.023	39.646	33.678	42.734	43.427	43.011	40.101	49.297	24.525
Selectivity to EtOAc	67.286	82.416	86.349	87.925	93.358	93.238	94.843	91.438	91.570	91.237	87.218	86.215	97.426
Selectivity to Propanone	1.155	0.795	0.645	0.873	0.121	0.106	0.000	0.219	0.230	0.116	0.722	0.901	0.000
Selectivity to Butanone	2.727	2.179	2.573	3.576	1.024	0.694	0.337	1.330	1.174	1.376	3.228	4.144	0.191
Selectivity to IPA	5.706	2.646	1.604	1.060	0.441	0.669	0.583	0.789	0.826	0.231	1.225	1.031	0.186
Selectivity to 2-butanol	9.941	6.094	4.430	3.675	3.128	3.576	3.165	4.050	3.773	4.074	4.304	3.846	1.706
Selectivity to 1-Butanol	2.017	1.216	0.703	0.667	0.299	0.377	0.326	0.423	0.500	0.443	0.656	0.652	0.135
Selectivity to DEE	0.302	0.069	0.118	0.054	0.000	0.123	0.182	0.077	0.219	0.082	0.000	0.085	0.000
Selectivity to all Others	10.865	4.585	3.577	2.170	1.629	1.217	0.563	1.675	1.708	2.441	2.647	3.126	0.356

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Chapter 3

Life Testing of E408Tu Catalyst

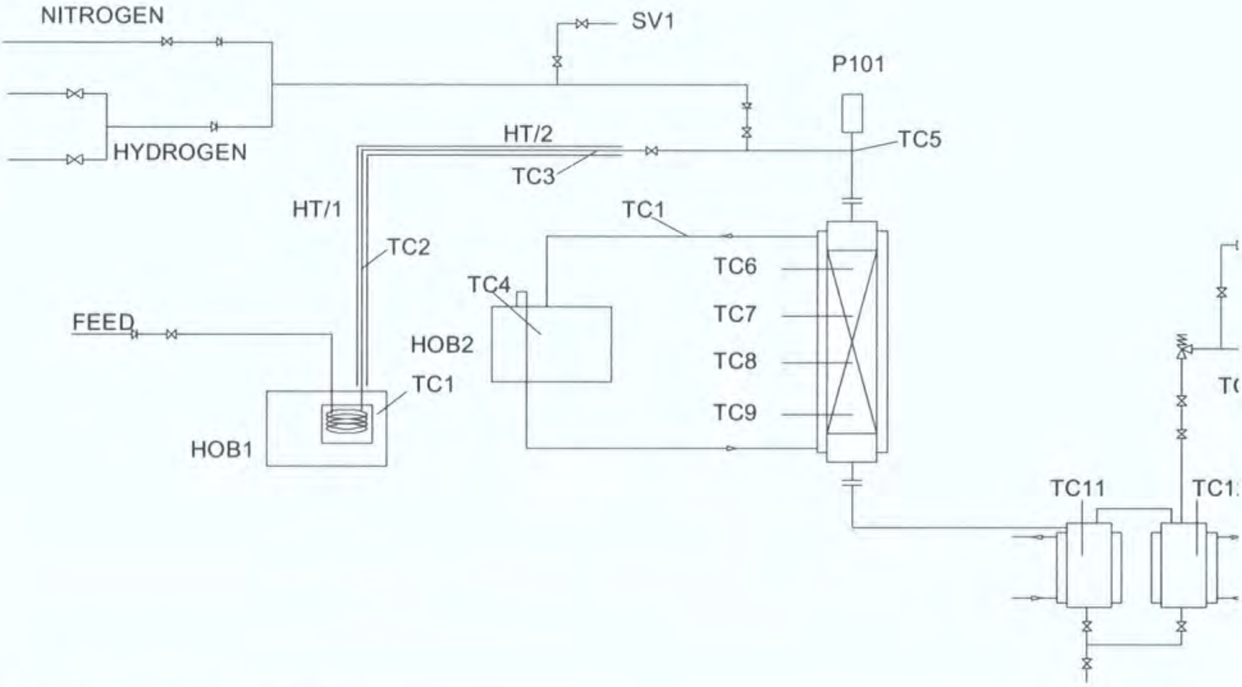
3 Introduction

The work reported in the previous chapter showed that, of all the catalysts tested, E408Tu performed best in terms of conversion of ethanol and selectivity to ethyl ethanoate. It was decided to conduct a more detailed examination of its performance over an extended time period using pure ethanol and an industrial grade ethanol feedstock supplied by Sasol. The latter ethanol feed, containing 4% 2-propyl alcohol and several other minor components, was sourced from the Sasol Fischer Tropsch process. This ethanol product was used as an additive to gasoline for automotive fuels and as a feed for ethanol purification. The economic reason for using the impure ethanol was the reported selling price of the impure ethanol, or 'Ethylol', of $220 /tonne, compared to $1280 /tonne for ethyl ethanoate and $600/tonne for high purity (perfume grade) ethanol. The presence of these impurities in the ethanol feed would have an effect on the overall process which would have to be assessed against the obvious improvement in economics compared to using pure ethanol.

For this work, a new dehydrogenation reactor was built, similar in principle to the reactor used for the preliminary test-work but with better controls. The work examined the effects of pressure, temperature and feed flow rates on selectivity to ethyl ethanoate and conversion of ethanol over an extended period of operation (circa 6 weeks). A simple empirical model was generated for use in building a first pass chemical engineering simulation of the ethanol to ethyl ethanoate flowsheet.

3.1 Charging Of Reactor And Catalyst Activation

The reactor used for the initial screening exercise was a fairly crude model in which temperature and pressure could not be accurately controlled to the required +/- 1°C and 5kPa. The new reactor had more accurate instruments and a more effective heating and pressure control system. Pressure indication was via a Brookes type electronic pressure transducer. Temperature control was via a hot oil bath, and temperature indication was by a bank of 4 thermocouples positioned in the catalyst bed. Feed was preheated by passing it through a separate hot oil bath. A diagram of the reactor is given as Figure 3.1.



TC= Temperature controller
HT = Heating Tape
HOB = Hot Oil Bath

Figure 3.1 Ethyl Ethanoate Reactor Diagram Showing Major Equipment Items

The reactor was charged with 152g, 100cm^3, of E408Tu which was then activated according to the method given in appendix 1. Figure 3.2 below shows the detailed activation of the catalyst in terms of hydrogen in to the reactor and hydrogen out of the reactor.

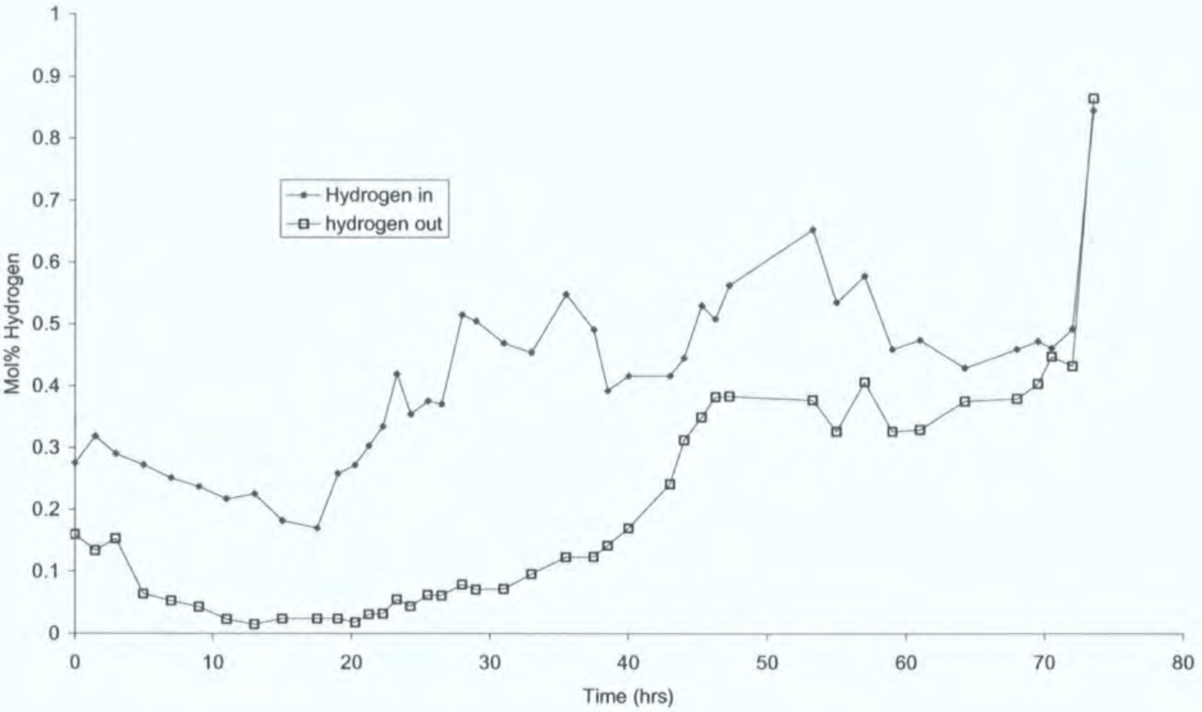


Figure 3.2 Activation Of E408Tu Catalyst Showing Hydrogen In And Out

The concentration of the hydrogen feed changed due to control problems with the mass flow controllers for both hydrogen and nitrogen feeds, but the principle of the reduction procedure was followed. The hydrogen concentration at the inlet to the reactor was held at approximately 0.5 mol% until the reactor exit concentration was equal to the inlet concentration. Following the activation the catalyst was prepared for reaction by holding at 250°C under a pure hydrogen atmosphere for 24 hours.

3.2 Dehydrogenation Testwork – Catalyst Screening

The first reaction carried out using the catalyst was performed at 340kPa, at 250°C using a pure ethanol feed at a rate of $0.50hr^{-1}$ ($50cm^3hr^{-1}$). The product from the reaction was a green colour, probably from the reaction of acetic acid in the product with copper oxide dust that had been deposited in the catchpots during the activation process. Over the course of 7 hours the green colour of the product became less intense until at 7 hours online no colour was observed in the product. The results from this first run are shown in Table 3.1 (p 116) as run 101/40/96. High conversion of ethanol was noted – 62.6%, but at low selectivity to ethyl ethanoate (80%). Unfortunately, there was no exactly comparable test performed during the screening of catalysts – the closest comparison is run 45 (Table 2.5, p 76) which was performed at a lower temperature (235°C). The major by-products formed were ketones (propanone, butanone), alcohols (2-propanol, 2-butanol, 1-butanol) and esters (methyl ethanoate, ethyl butanoate, butyl ethanoate), with diethyl ether present at low concentrations (500ppm). The by-product spectrum and relative concentrations were similar to those observed in run 45, albeit the selectivity here to ethyl ethanoate was higher (91.5%). Given the known high dependence of selectivity on temperature the results of this first run were not surprising with hindsight.

The feed was then turned off and the catalyst held at operating pressure and temperature overnight. The reactor was restarted at a higher reactor pressure (680kPa of hydrogen) leaving all other reaction conditions identical to the previous run. The results, 101/41/96 in Table 3.1 (p 116), show the conversion of ethanol and selectivity to ethyl ethanoate stabilised at 58.8% and 84.5% respectively after 5 hours online. Only a relatively small improvement in selectivity with increasing reactor pressure was observed, so the reaction temperature was reduced to 225°C for the next test - run 101/42/96. Again, the conditions used could not be compared directly to any of the screening tests performed using this catalyst, but the selectivity to ethyl ethanoate (90.7%) and conversion of ethanol (47.9%) observed compare well to those observed from run 43 (Table 2.5 (p75), 93.6% and 39.6%) which was performed using a higher rate of hydrogen feed. Initial screening showed that at any given temperature and pressure an increase in hydrogen feed rate resulted in a loss of conversion and an increase in selectivity which is confirmed here. After a total of 18 hours online the hydrogen feed rate was increased from 1 SLPH to 10 SLPH. There was an immediate increase in selectivity to 92.4% and a co-incident decrease in conversion to 40.4%. In order to determine the effect of hydrogen flow rate on conversion and selectivity the next run (101/44/96) was performed at a hydrogen flow of 5 SLPH, all other conditions being identical to 101/43/96. The results, conversion of ethanol of 44.05% and selectivity to ethyl ethanoate of 92.5% are shown in Table 3.1 (p 116) and graphically in Figure 3.3 below.

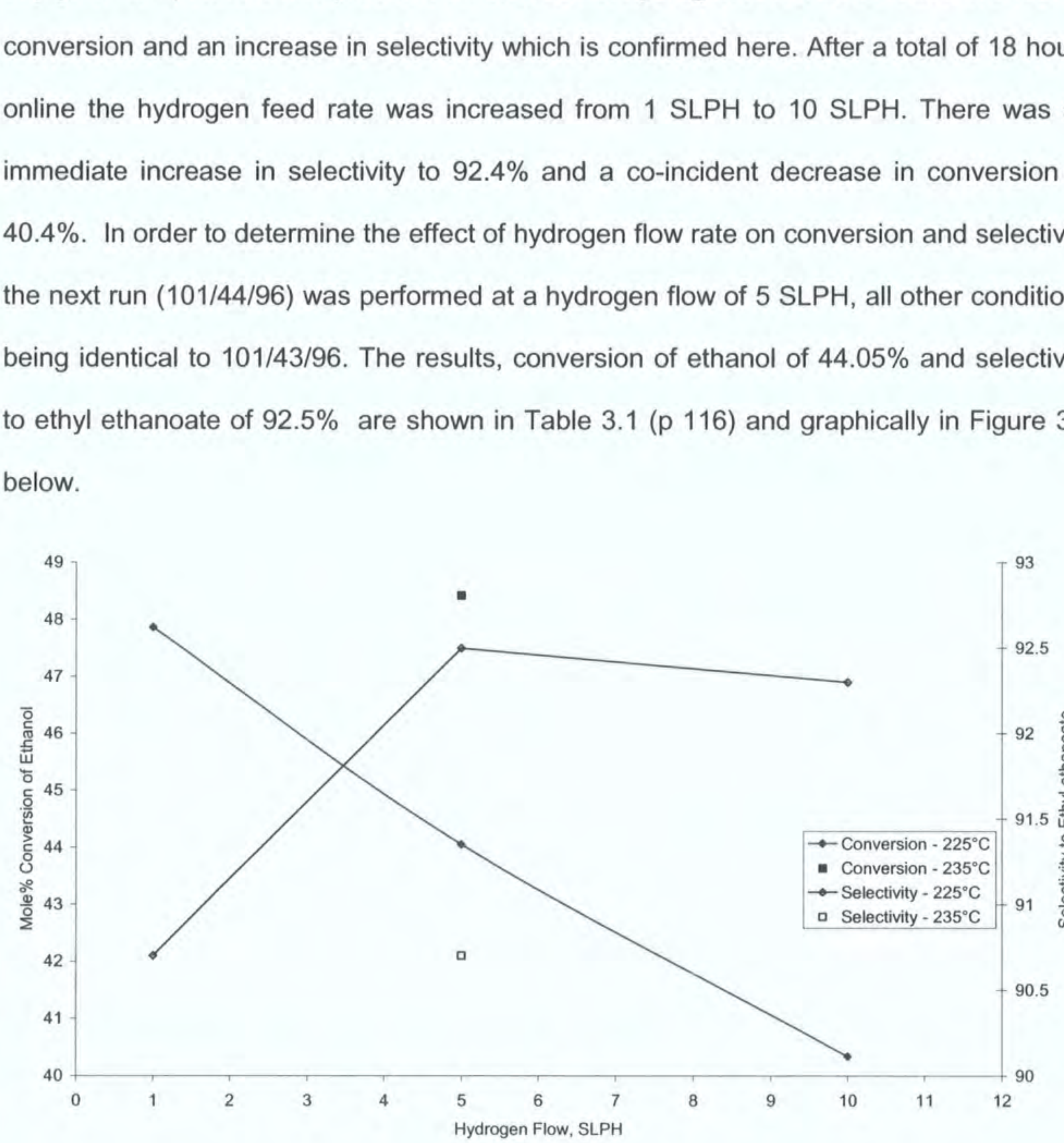


Figure 3.3 Effect Of Hydrogen Feed Rate On Dehydrogenation Reaction at 225 and 235°C

The Figure shows that there is the expected direct relationship between hydrogen feed rate on conversion of ethanol, but that the effect of hydrogen rate on selectivity is more complex. There is an increase in selectivity between 1 and 5 SLPH hydrogen, but the exact position of the maximum selectivity is not known. Above 5 SLPH there is a fall in selectivity but again it is not known where the maximum selectivity lies.

The temperature of operation was increased to 235°C (run 101/45/96) to check the effect on conversion and selectivity. The effect of the temperature increase was to reduce selectivity to 90.7% while increasing conversion to 48.4%. The results from this run are shown in Figure 3.3 and Table 3.1 (p 116).

The results obtained to this point were encouraging, allowing the testwork to progress to the next stage – using commercially available ethanol feeds in place of pure ethanol.

3.3 Dehydrogenation testwork – Wet ethanol feed

To date dehydrogenation had been carried out using pure, anhydrous ethanol to simplify interpretation of the results. The aim of the development was to produce a catalyst and reactor that would produce ethyl ethanoate from commercially available and economically attractive feeds – pure anhydrous ethanol is not economically attractive, but there are several low cost ethanol feeds that are available. The first is azeotropic ethanol containing 92 mol% ethanol and 8 mol% water, produced mainly by fermentation. Removal of water requires either a membrane separation or azeotrope breaking distillation step which adds both capital cost and processing costs to the price of the ethanol product. The ability to use wet ethanol would also have implications in the recycling of ethanol in the ethanol dehydrogenation process. Once the ethyl ethanoate is separated from the crude dehydrogenation product, unreacted ethanol would be recycled. The dehydrogenation product contains water, and after several cycles this would build up to azeotropic levels in the recovered ethanol. It was expected from the proposed reaction mechanism for ethanol dehydrogenation that water would have a detrimental effect on catalyst activity. Water is also known to cause sintering of copper crystallites, causing a long term decrease in catalyst activity and possibly a consequential decline in selectivity.

In order to test the effect of water the feed to the dehydrogenation reactor was changed to 92 mol% ethanol, 8 mol% water for run 101/46/96 using the same process conditions as for run 101/45/96. There was an immediate fall in ethanol conversion from 48.4% to 32.2%, though the selectivity was unchanged at circa 91%. The dependence of conversion on the LHSV is given in Chapter 2, Figure 2.27. A conservative extrapolation of this chart indicates that a drop in conversion from 48.5% to 32% would require an increase in feed rate of at least 3 times, which is equivalent to a 300% reduction in activity. Such a large drop in activity cannot be countered by increasing temperature as the selectivity to ethyl ethanoate falls off more quickly than activity increases, reducing the overall yield. It was therefore decided that the use of wet ethanol would not form part of the development programme.

3.4 Dehydrogenation – Sasol ethanol ('Ethylol') feed

The second and more important source of ethanol is that produced from Fischer Tropsch synthesis. Sasol synthetic fuels was contacted at an early stage in the ethanol dehydrogenation project with a view to co-developing the dehydrogenation process. Sasol joined the dehydrogenation project in July 1996 and contributed an authentic ethanol feed to the programme. The project aims shifted to developing a dehydrogenation process that could produce ethyl ethanoate at >99.8% purity from this feed material. The Sasol ethanol feed was analysed by GLC-MS, with the following typical composition:

Component	Wt%
Diethyl Ether	0.122
Ethanol	94.974
Propanone	0.022
2--Propanol	3.948
di-2-propyl ether	0.141
n-butanal	0.006
Ethyl ethanoate	0.035
Ethyl butyl ether	0.112
Di n-propyl ether	0.029
1,1 diethoxyethane	0.070
2-pentanol	0.006
2-butyl ethanoate	0.037
ethyl butanoate	0.069
Water	0.220
Unidentified Components	0.209

A series of 6 drums were analysed and found to be close to this typical analysis. The feed was changed for run 101/47/96, all other process conditions remaining identical to the previous two runs. After 10.5 hours the conversion and selectivity had stabilised at 46.4% and 89.2% respectively. The product from the dehydrogenation reaction contained a number of components, in particular 2-propyl ethanoate, 2-pentanol and 2-pentanone, not observed when using ethanol feed. All three compounds were believed to originate from 2-propanol – 2-propyl ethanoate by either transesterification of ethyl ethanoate with 2-propanol or via the cross dehydrogenation of ethanol and 2-propanol, 2-pentanol and 2-penanone via aldol condensation of ethanal and propanone. The full reaction product analyses are shown in Table 3.1 (p 116) as runs 101/45/96 and 101/47/96. The results from run 101/47/96 showed that, while there was a small loss in activity and selectivity, the addition of 2-propanol to the feed did not make the process uneconomic. A series of tests were then performed to determine the effect of reactor temperature, reaction pressure, ethanol feed rate and hydrogen feed rate on dehydrogenation when using Sasol 'ethylol'. The results of the tests are listed in Table 3.2 (p 117) and a description of the changes between tests in Table 3.5 below. A description of these runs and a discussion of the results are given below.

Run Number	Pressure kPa	Temp °C	Ethanol LHSV	Hydrogen SLPH	Conversion	Selectivity
101/48/96	340	225	1.0	1.0	32.33	82.43
101/49/96	680	225	1.0	1.0	33.06	86.05
101/50/96	680	225	2.0	1.0	22.68	83.195
101/51/96	680	225	0.5	1.0	42.36	87.27
101/52/96	680	225	0.5	5.0	39.42	89.35
101/53/96	680	225	0.5	5.0	40.04	89.3
101/54/96	680	225	0.5	1.0	44.14	87.37
101/55/96	680	225	0.5	2.0	43.87	84.87
101/56/96	680	235	0.5	2.0	50.29	88.29
101/57/96	680	235	0.75	2.0	42.80	87.50
101/58-61/96	680	235	1.0	2.0	40.78	85.85

Table 3.5 Scanning Tests Using E408Tu Catalyst

Due to time and resources limits, a complete scan of all possible combinations was not possible, so a limited screening of the main effects, performed on an *ad-hoc* basis from the results obtained, was carried out.

Runs 101/48/96 and 101/49/96 demonstrate the effect of varying the pressure from 340 to 680 kPa. As noted in previous work an increase in pressure generally leads to an increase in selectivity, and this is confirmed by these two runs. Runs 101/49/96, 101/50/96 and 101/51/96 were performed to determine the effect of ethanol feed rate on selectivity and conversion. In common with the work carried out using pure ethanol, conversion is reduced as the feed rate increases. Selectivity differs from that observed with pure ethanol – in this case selectivity declines as LHSV is increased. Figure 3.4 below illustrates the difference observed between pure ethanol feed and the ethylol feed:

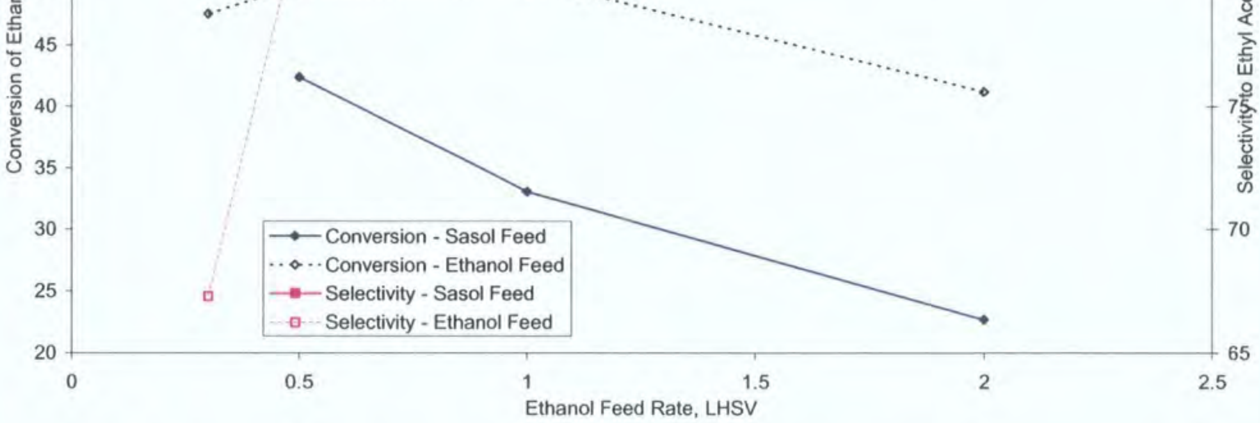


Figure 3.4 Comparison of Ethanol and Ethylol Feeds, Selectivity and Conversion Obtained

There are some differences between the sets of data for pure and Sasol ethylol. Note that the work carried out on the pure ethanol was performed at 250°C and the work on ethylol at 225°C, but the principle of a difference in the effect of increasing LHSV on selectivity holds. The likely explanation of the difference arises from the 2-propanol content of the ethylol feed, which dehydrogenates to form propanone which reacts further to form a wider range of by-products than would be the case when there is no 2-propanol in the feed. The fall in conversion with LHSV is more pronounced with the ethylol feed. This is thought to be due to the competing dehydrogenation reactions taking place. Ethanol and 2-propanol dehydrogenate at the same catalyst site, with the relative rates of reaction dependent on the heat of reaction. 2-propanol, being a secondary alcohol, dehydrogenates more readily and appears to reduce the number of sites available for ethanol dehydrogenation. Runs 101/51/96 to 101/55/96 were performed to determine the effect of hydrogen concentration over a narrow range of 1 to 5 SLPH. The result, a small decrease in conversion and increase in selectivity with increasing hydrogen feed rate, was as expected from previous tests. Figure 3.5 below plots hydrogen feed rate versus selectivity and conversion.

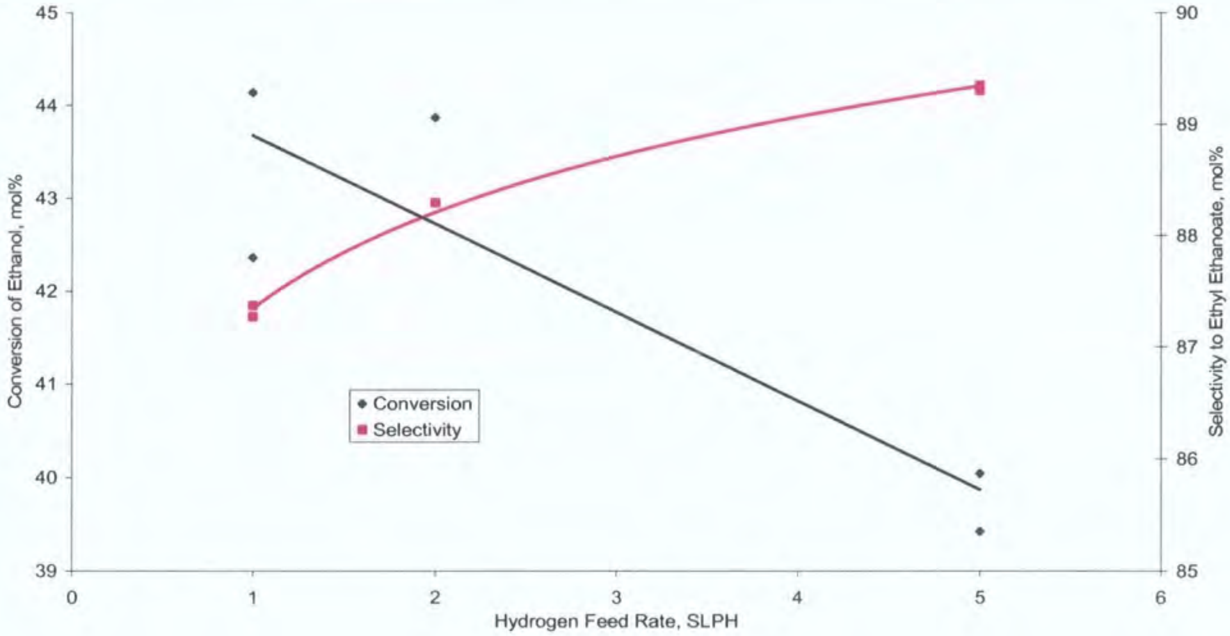


Figure 3.5 Selectivity And Conversion Versus Hydrogen Flow Rate

The picture for selectivity and conversion versus hydrogen feed rate is less clear cut due perhaps to variable reaction conditions, but the general trend is for an increase in selectivity with increasing flow, at the expense of conversion. The general trend is similar to that shown in Figure 3.3 where a similar scanning exercise was performed using pure ethanol. Runs 101/56/96, 101/57/96 and 101/58/96 show the effect of LHSV on conversion and selectivity at 235°C. The results from these runs are plotted in Figure 3.6 below:

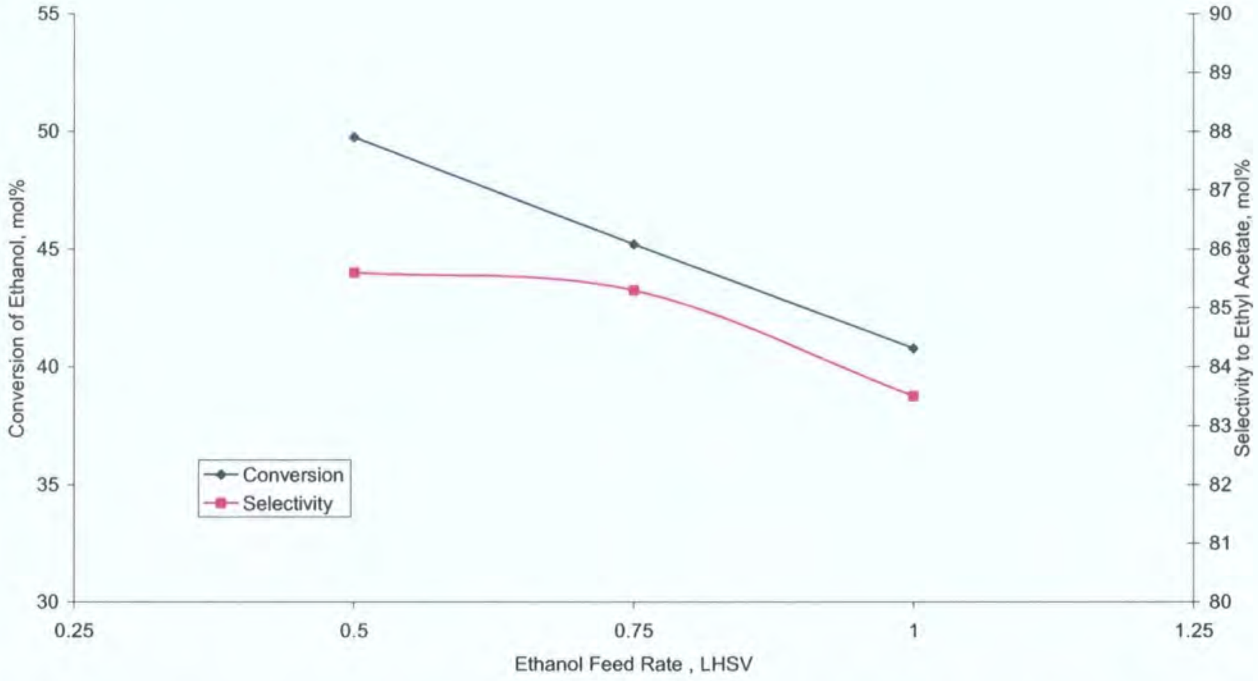


Figure 3.6 Effect of LHSV on Ethanol Conversion and Selectivity to Ethyl ethanoate

This pattern of falling selectivity and conversion with increasing feed rate is similar to that observed at both 250 and 225°C using the E408Tu catalyst and the Sasol ethylol feed.

At this stage in the project the process parameters that affect conversion and selectivity had been identified and a more structured approach to modelling the dehydrogenation reaction was adopted.

3.5 Modelling of Dehydrogenation Reaction

In order to generate data for a mathematical model of the dehydrogenation reaction for inclusion into a chemical engineering simulation of a proposed commercial unit, a series of tests based on a full factorial matrix were proposed. These tests were designed to cover the expected range of process condition of temperature, pressure and ethanol feed rate. A full factorial model, based on two reaction temperatures (225 and 245°C), two reaction pressures (340 and 680kPa) and four LHSV (0.25, 0.5, 1, 2) was generated so that every possible combination was covered – 16 tests in all (2x2x4). The tests were so arranged as to give the maximum amount of randomisation whilst also being practical to perform. Of the three parameters studied, the most difficult to vary was reactor pressure, so all the tests to be performed at 340 kPa were performed first followed by the tests at 680 kPa. The next most difficult was temperature, so the tests were arranged as far as possible to minimise temperature changes. The most convenient parameter to change was the feed rate, and so this was varied from test to test. The full test series is shown below in Table 3.6.

Run Number	DPT Run Number	Reactor Temp °C	Feed LHSV, hr^{-1}	Pressure, kPa
1	62	225	1.0	340
2	63	225	0.25	340
3	64	225	0.5	340
4	65	225	2.0	340
5	66	245	1.0	340
6	67	245	0.25	340
7	68	245	0.5	340
8	69	245	2.0	340
9	70	245	1.0	680
10	71	245	0.25	680
11	72	245	0.5	680
12	73	245	2.0	680
13	74	225	1.0	680
14	75	225	0.25	680
15	76	225	0.5	680
16	77	225	2.0	680

Table 3.6 Proposed Modelling Testwork For Dehydrogenation Reaction

The tests were performed as a continuation of the previous testwork, using the E408Tu catalyst which had been operating continuously, or 'ageing', for over 300 hours prior to the commencement of the testwork. This is an important point as it is known within DPT that over the first 200 to 250 hours copper catalysts undergo relatively rapid deactivation. After about 300 hours the rate of deactivation slows to manageable levels. The results obtained from the runs listed in Table 3.6 above are given in Table 3.3 (p 118). The tests were all carried out over a period of 246 hours at a constant hydrogen to ethanol ratio of 1:50 – that is, 0.02 moles of hydrogen per mole of ethanol. The results have been amalgamated and are shown in the Figures and tables below, along with a brief explanation of the significance of each set of results.

Figure 3.7 shows the effect of pressure and temperature on ethanol conversion over a range of feed rates. The data are taken from the factorial model and work carried out at 235°C earlier in the test sequence. The chart clearly shows that temperature has the greater effect on conversion – the results at the same temperatures but different pressures fall very closely together. The conclusion from these data, is that in any model that is generated the temperature term will have a greater effect than the pressure term. Another way to look at the data is to plot conversion against temperature for each of the LHSV's studied – see Figure 3.8. It can be seen that there is a near linear dependence of conversion on reaction temperature in the range of LHSV and pressure studied.

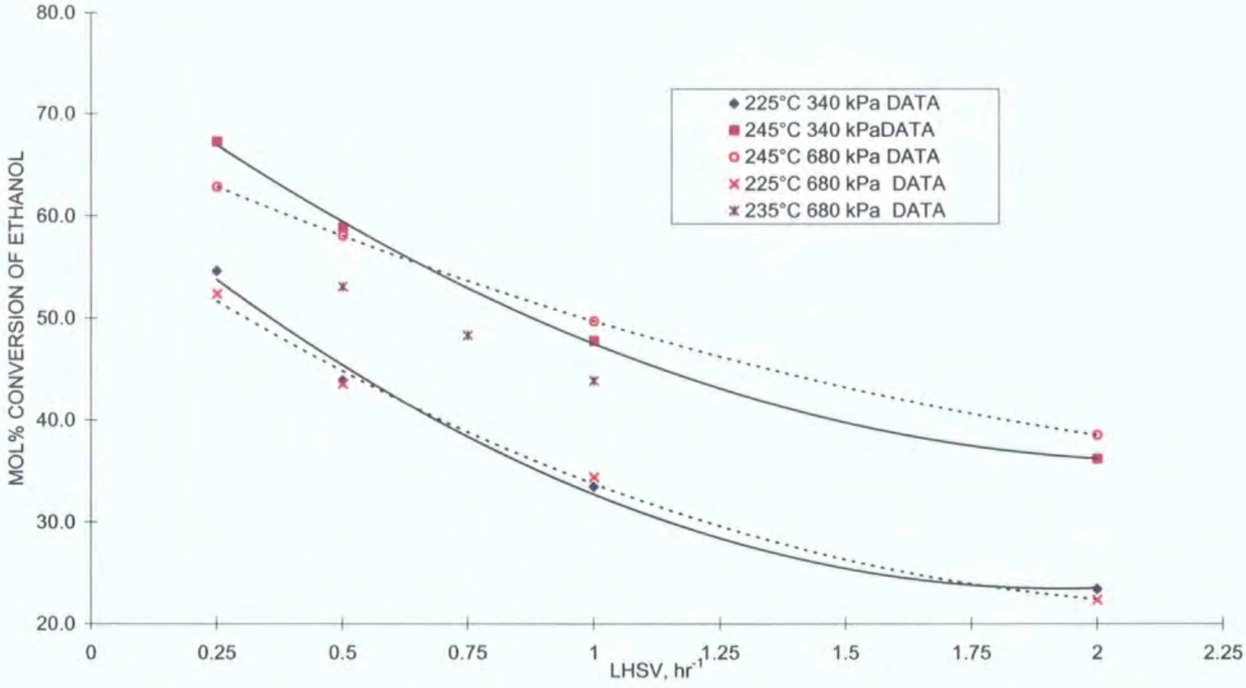


Figure 3.7 Dependence Of Conversion On LHSV At Different Pressures And Temperatures

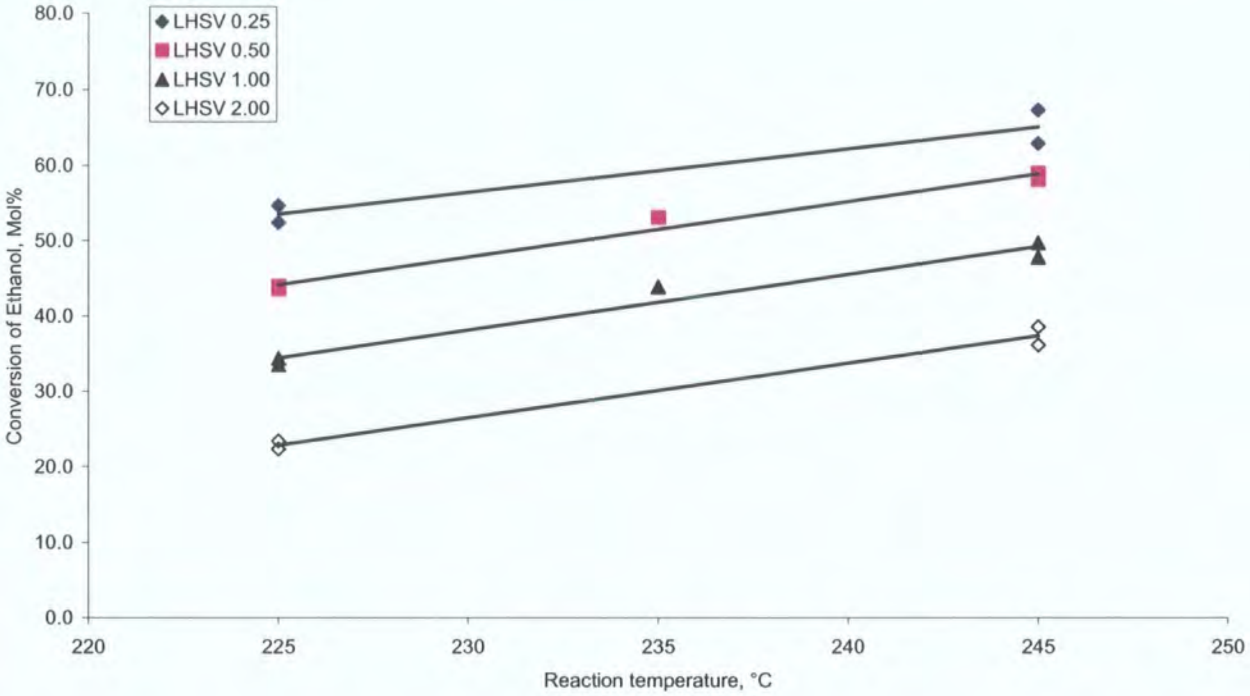


Figure 3.8 Dependence Of Conversion On Reaction Temperature At Different Ethanol Feed Rates

Conversion of ethanol is only a single consideration in determining the optimum reaction conditions; selectivity is at least as important; as selectivity determines the yield of ethyl ethanoate per mole of ethanol. Figure 3.9 plots selectivity to ethyl ethanoate against conversion of ethanol for the range of temperatures and pressures.

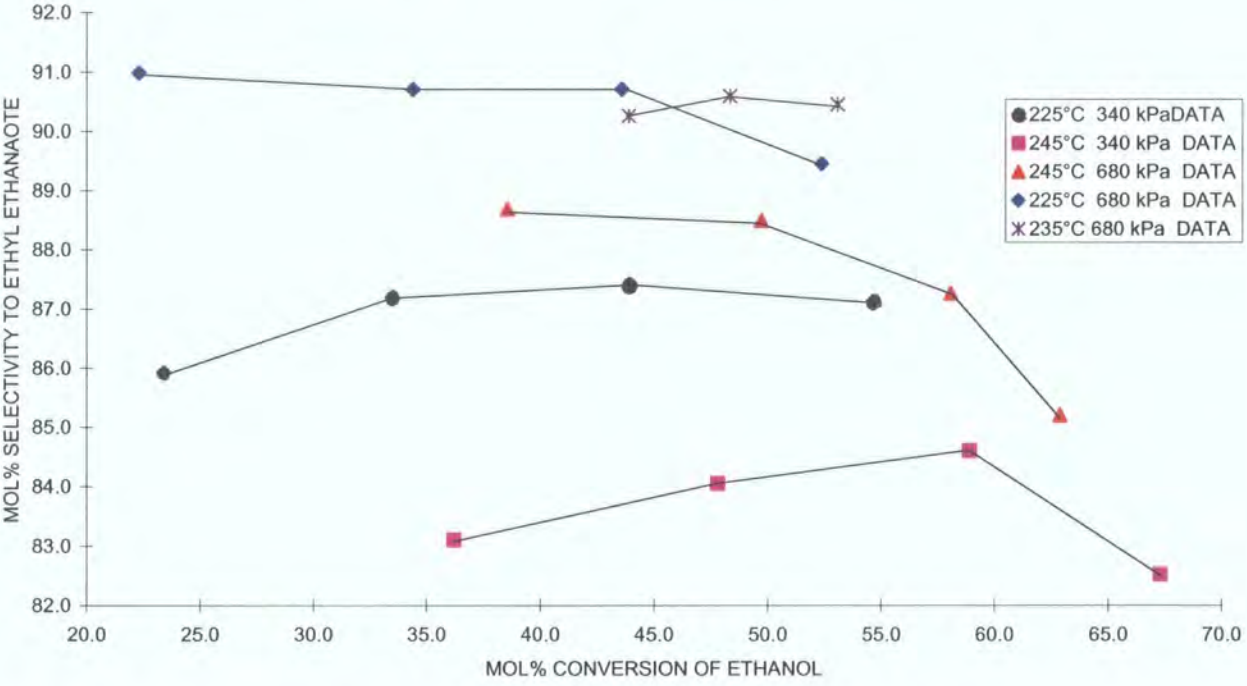


Figure 3.9 Conversion Versus Selectivity At Different Temperatures And Pressures

The results are clear – higher pressure and lower temperature favour the formation of ethyl ethanoate over other by-products. It is also clear from the chart that above 50 mol% conversion of ethanol there is a decline in selectivity to ethyl ethanoate in all of the conditions studied. The result from the run at 340kPa and 245°C is exceptional in that the selectivity appears to reach a maximum at 55-60% conversion, but selectivity is low at all conversions. When the data are plotted as selectivity to ethyl ethanoate versus LHSV the usual rise in selectivity versus ethanol feed rate is observed at 680kPa, but there is a fall in selectivity at the lower pressure of 340 kPa.

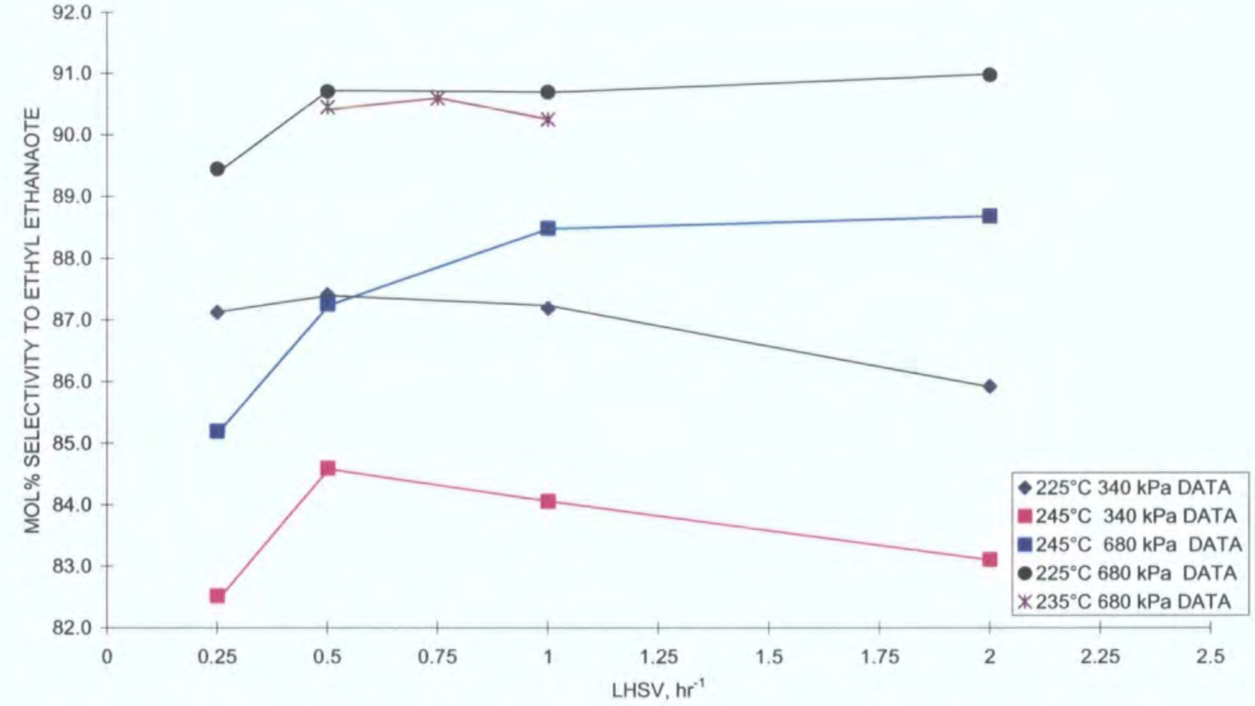


Figure 3.10 Selectivity Versus LHSV

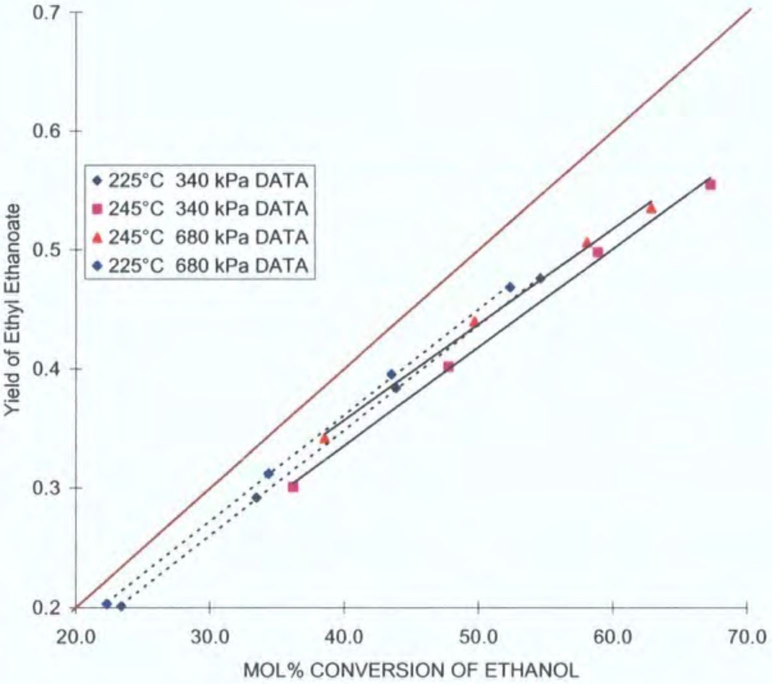


Figure 3.11 Conversion Of Ethanol Versus Yield Of Ethyl Ethanoate

In order to try to understand the reasons for this behaviour the results were plotted again in a different fashion. A valuable experiment would be to determine the concentration of each component at various points through the catalyst bed. This cannot easily be achieved from a single experiment but the results from the LHSV scans can be used to simulate different points within the reactor. The way that this is achieved is to calculate the residence time of the ethanol feed at different feed rates. Residence time is calculated as:

$$\text{Residence Time(s)} = \frac{\text{Feed Volume(l)}}{\text{Bed Volume(l)}}$$

Feed volume is in turn calculated from the equation:

$$\text{Feed Volume(l)} = \frac{\text{Moles ethanol}}{[\text{Temp(k)}/273][101.3/(\text{Pressure (kPa)} + 101.3)][22.414]}$$

The residence time is proportional to feed rate so the slowest feed rate (and highest residence time) is taken to be equivalent to the time taken for the feed to pass through the full bed length. The other feed rates are then proportioned to this and the equivalent bed position for each feed rate determined. In this case, lowest LHSV used was 0.25, so for example, the data collected at a LHSV of 0.5 would be equivalent to that that would be obtained at a point half way through the bed (position = 0.25/0.50). Similarly, a LHSV of 1 and 2 become equivalent to positions at ¼ and $^{1}/_{8}$th bed length. Of course, this is a rough approximation as the RT actually varies with conversion but it is sufficient to produce a simple model of the processes that are occurring within the reactor. Figures 3.12 to 3.15 plot the concentration of some of the major by-products as a function of position in the catalyst bed. It is interesting to note that while ethanal and propanone decrease in concentration through the bed in all cases, butanone and 2-propanol increase. The rationale for the increase in 2-propanol and decrease in propanone is the increased concentration of hydrogen in the reaction mixture (due to the dehydrogenation reaction) hence a shift of equilibrium to the alcohol. This implies that the equilibrium is reached very quickly.

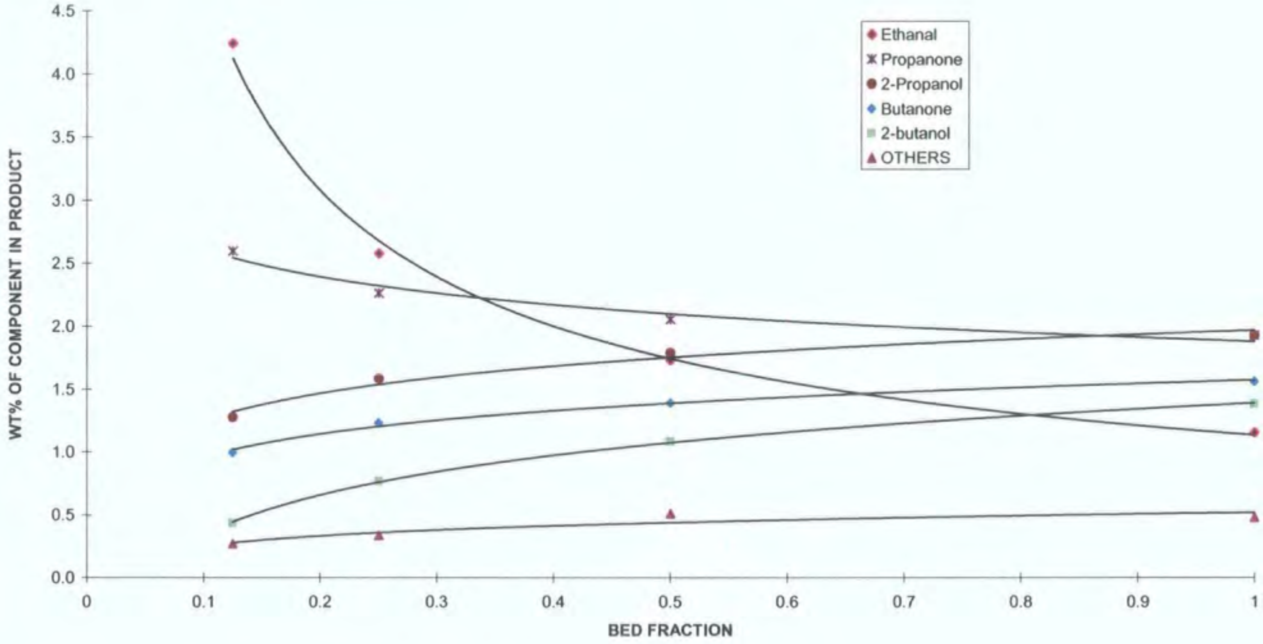


Figure 3.12 Composition Versus Bed Fraction 340 kPa, 225°C

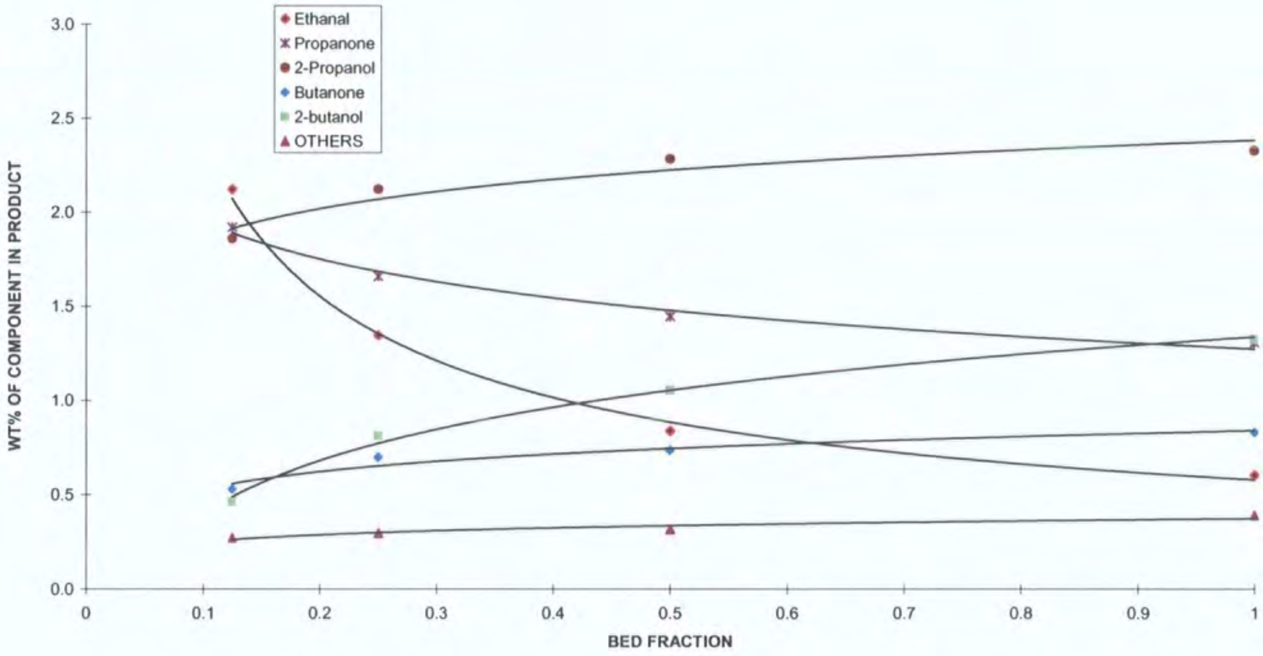


Figure 3.13 Composition Versus Bed Fraction 680 kPa, 225°C

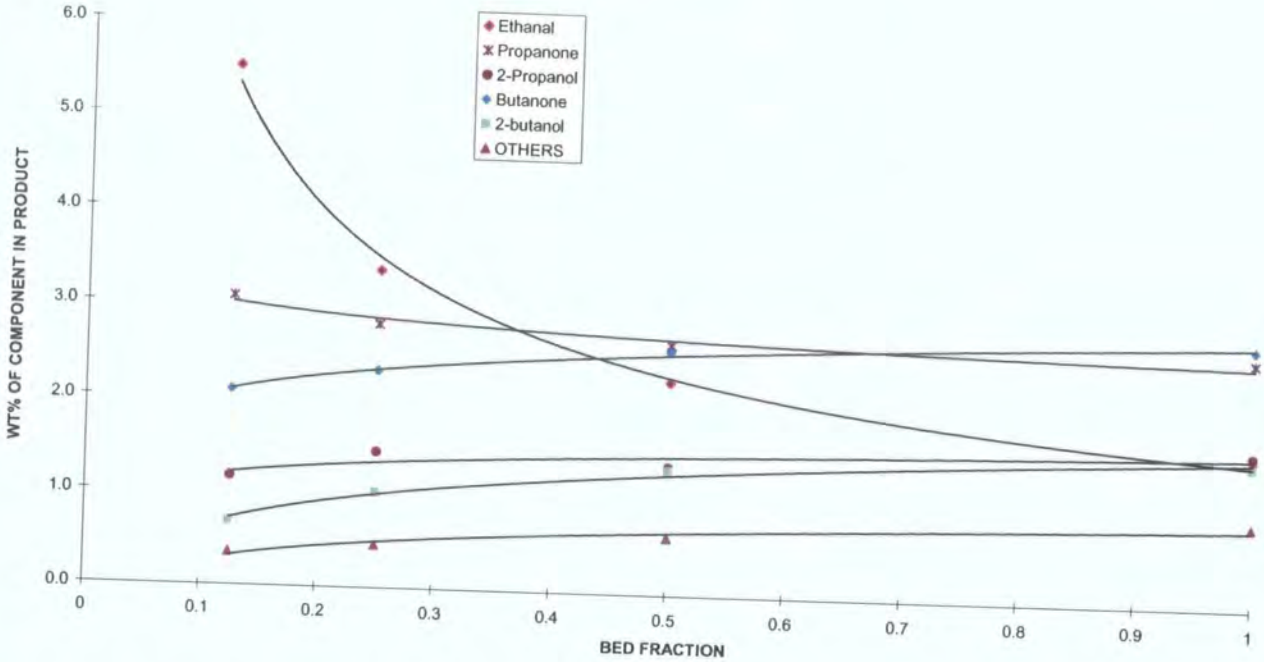


Figure 3.14 Composition Versus Bed Fraction 340 kPa, 245°C

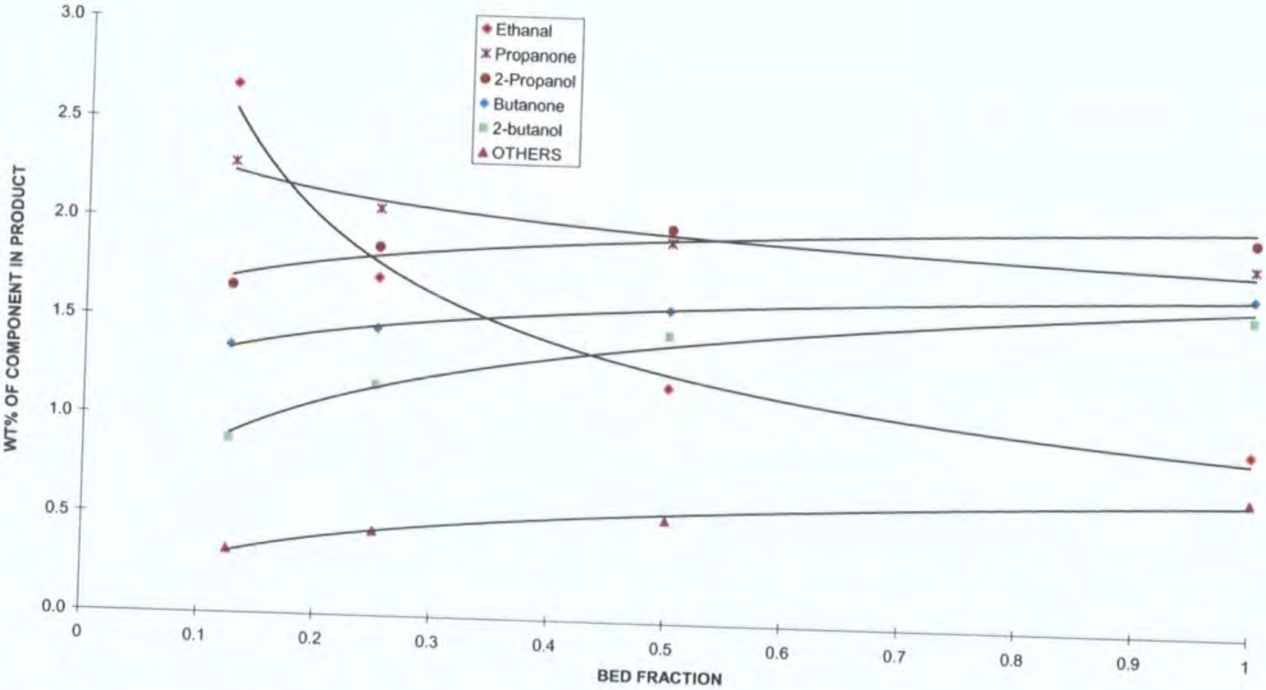


Figure 3.15 Composition Versus Bed Fraction 680 kPa, 245°C

The largest effect is in the concentration of ethanal through the catalyst bed. Figure 3.16 below is a plot of the ethanal concentration through the bed for each of the test runs for the modelling testwork. There is an unambiguous effect of both pressure and temperature on ethanal concentration – high temperatures and low pressures favour ethanal. This is unsurprising, given that the dehydrogenation of ethanol is an exothermic reaction. Figure 3.16 shows that both pressure and temperature have the expected effect on ethanal concentration. The shapes of the curves reflect the large effect that pressure has on ethanal concentration, particularly at the front of the reactor. It is interesting to note that a logarithmic fit of the data points is poor, while a power fit (shown) is acceptable. The rate of by-product concentration through the reactor is proportional to ethanal concentration which implies that at least some of the by-products (butanone, 2-butanol) are formed from ethanal.

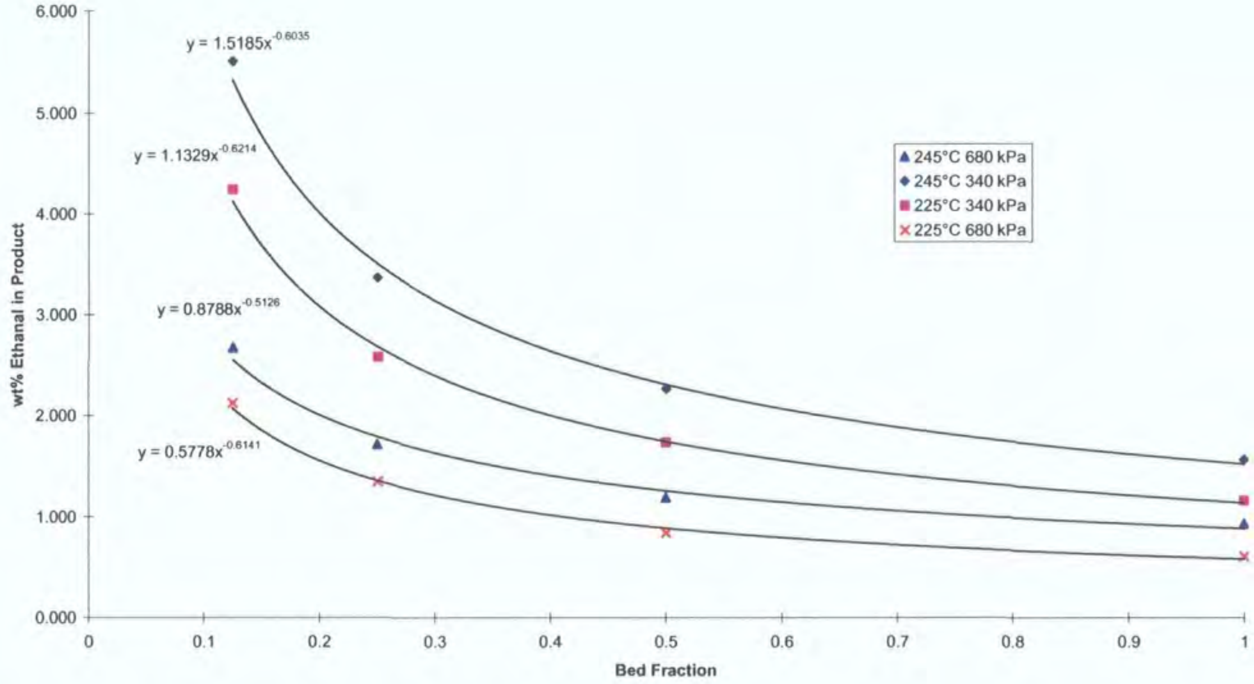


Figure 3.16 Plot Of Ethanal Content in Product Against Bed Fraction

Figures 3.17 to 3.20 show similar plots of ethanol and ethyl ethanoate concentrations versus bed fraction. The plots show the expected increase in ethyl ethanoate and decrease in ethanol concentrations versus bed fraction. Logarithmic trend lines are plotted with the data. The fit for the tests at 225°C are reasonably good, but those for the 245°C data are less precise. A rationalisation of this difference is that the reactions produce side products that are not equilibrium limited (unlike the ethyl ethanoate producing reaction) and this distorts the plot at the higher temperatures as more by-products are formed (i.e. the selectivity is lower).

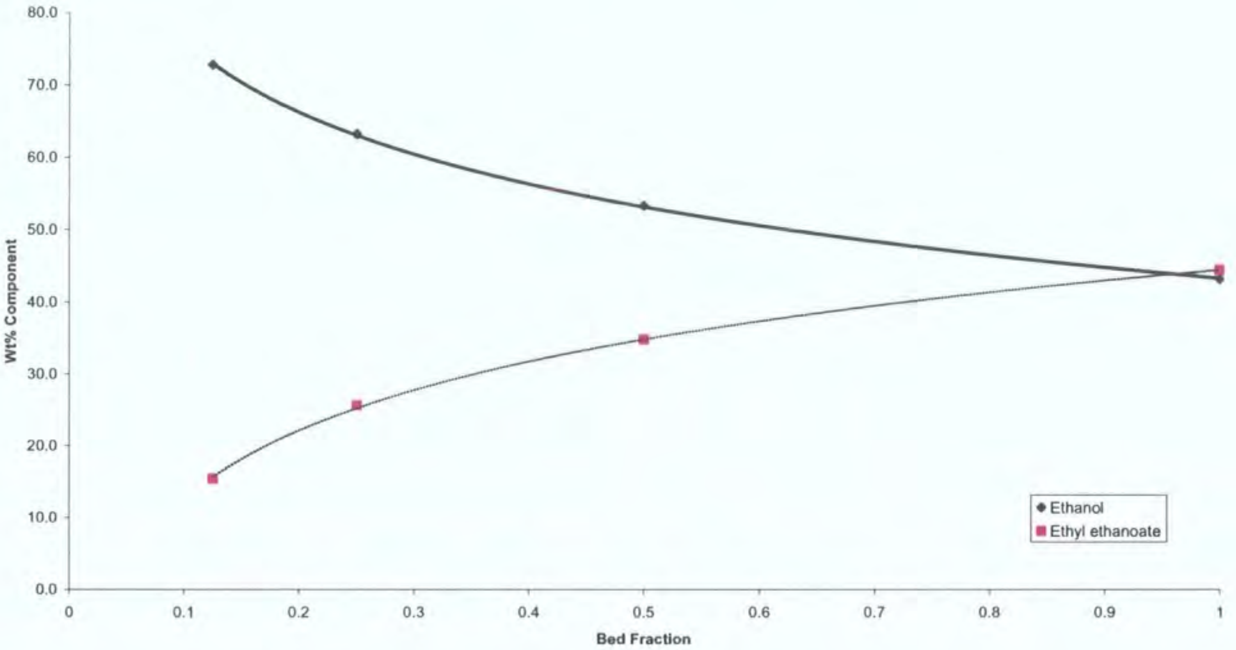


Figure 3.17 Ethanol And Ethyl Ethanoate V Bed Fraction 340 kPa, 225°C

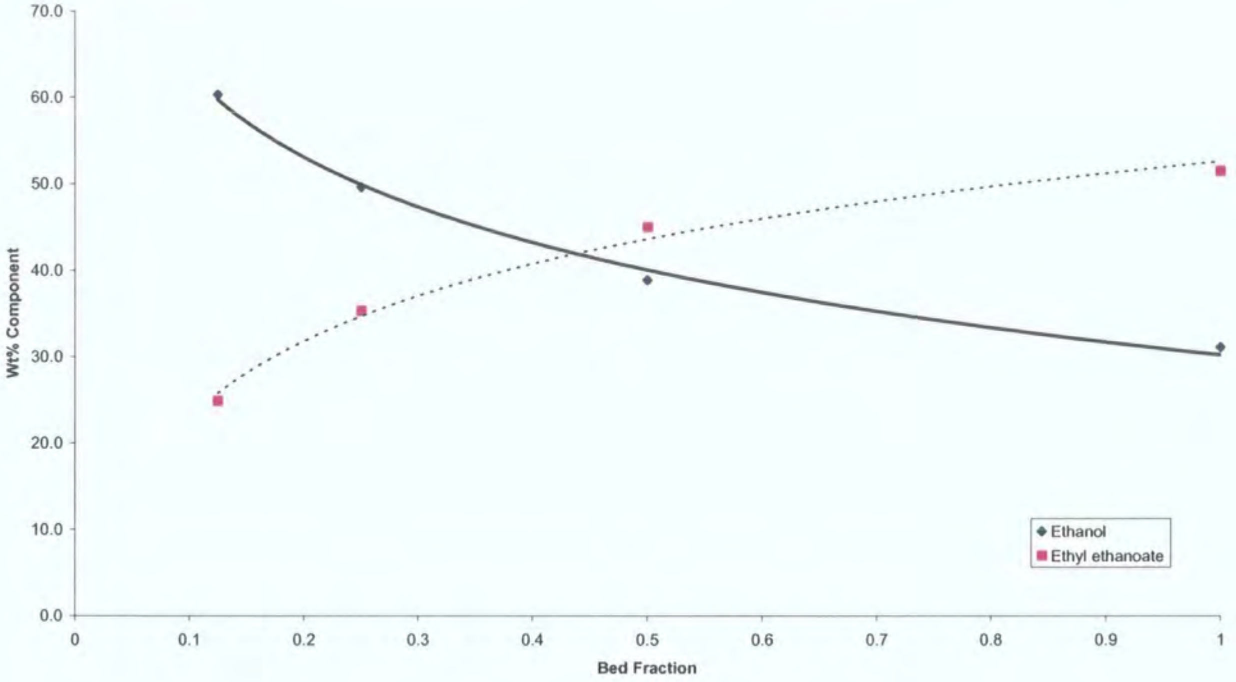


Figure 3.18 Ethanol And Ethyl Ethanoate V Bed Fraction 340 kPa, 245°C

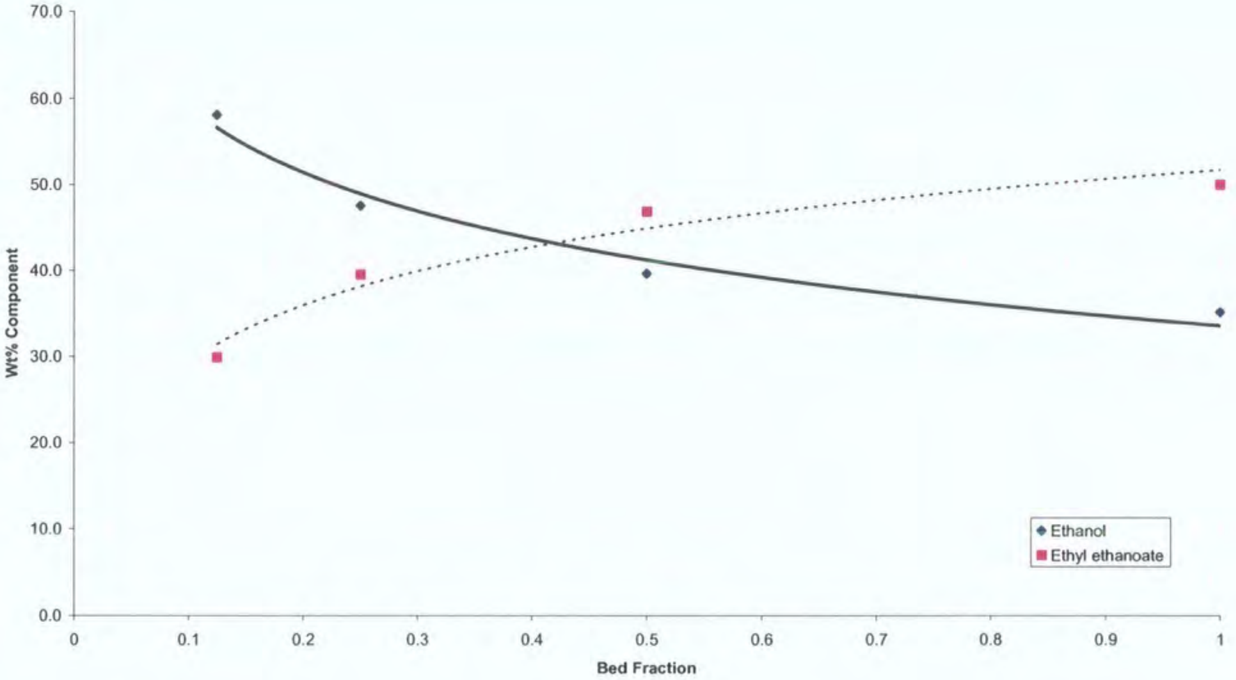


Figure 3.19 Ethanol And Ethyl Ethanoate V Bed Fraction 680 KPa, 245°C

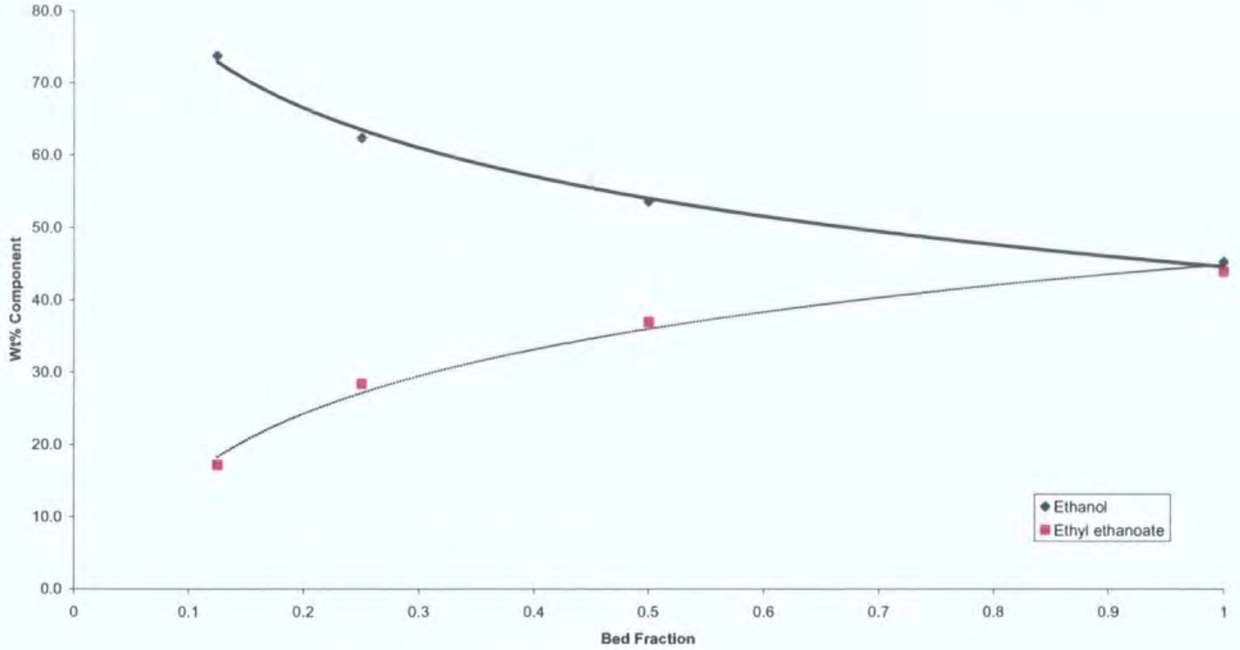


Figure 3.20 Ethanol and Ethyl ethanoate v Bed fraction 680 kPa, 225°C

The data collected for the modelling runs was processed through a linear regression modelling tool and a simple model for selectivity and conversion generated. The model had the general form:

Value = Constant + (temperature x factor 1) + (LHSV x factor 2) + (Pressure x Factor 3) + (hydrogen flow x factor 4)

The factors and constants for selectivity and conversion were found to be:

	Data Modelled	
	Conversion Data	Selectivity Data
Constant	-107.1	139.2
Factor 1	0.7160	-0.2204
Factor 2	-14.86	-0.2588
Factor 3	-0.0212	0.0149
Factor 4	-0.3945	0.0889

The actual values calculated from this model are listed in Table 3.7 below (p.105).

While this is a crude model and one that lacks theoretical basis it demonstrated the relative effects of the factors that had been altered during the testwork. From the relative values of each factor some general principles can be obtained:

Temperature has a positive effect on conversion but a negative effect on selectivity. Ethanol feed rate has a negative effect on conversion and selectivity, and conversion is affected more than selectivity. Pressure has a negative effect on conversion but a positive effect on selectivity, as does hydrogen feed flow. Figures 3.21 and 3.22 are plots of the observed (from the experimental work) and predicted (from the model described) ethanol conversion and selectivity to ethyl ethanoate. The fit for ethanol conversion is good, following the 45° line (the line where observed and predicted values are in exact agreement) closely. The fit for selectivity is less convincing, with the plotted points appearing to separate into two distinct sets. The plotted 45° line passes through the data but is not a good fit. More work was required to develop a better model for selectivity so an extended testwork plan was developed to include a wider range of reaction pressures and hydrogen flows.

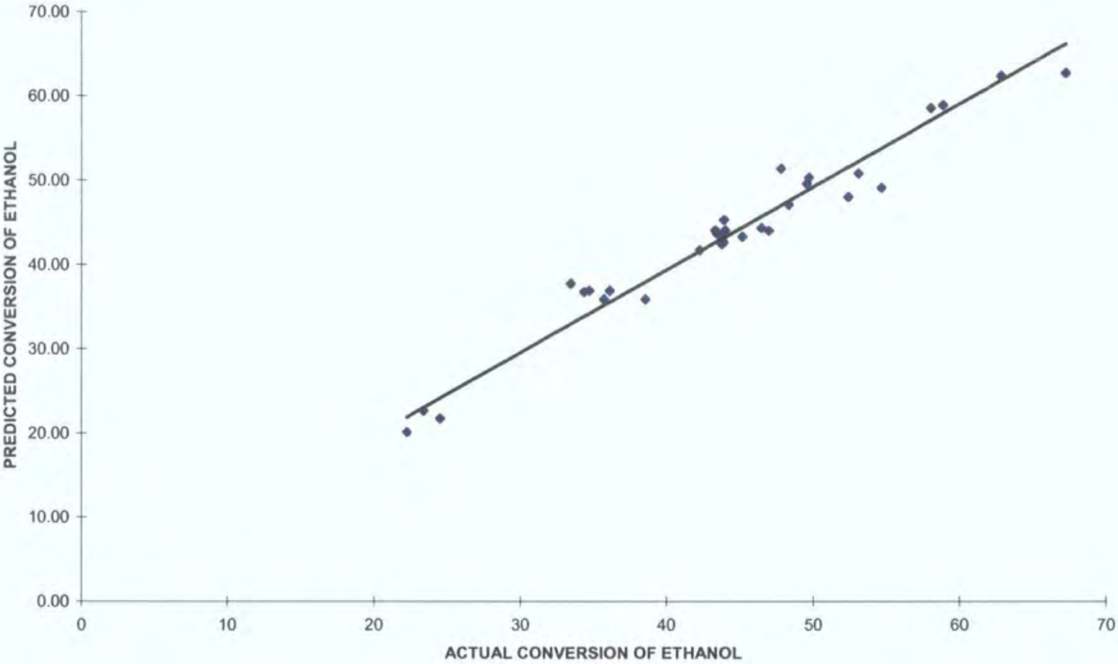


Figure 3.21 – Observed Versus Predicted Ethanol Conversion, First Pass Model

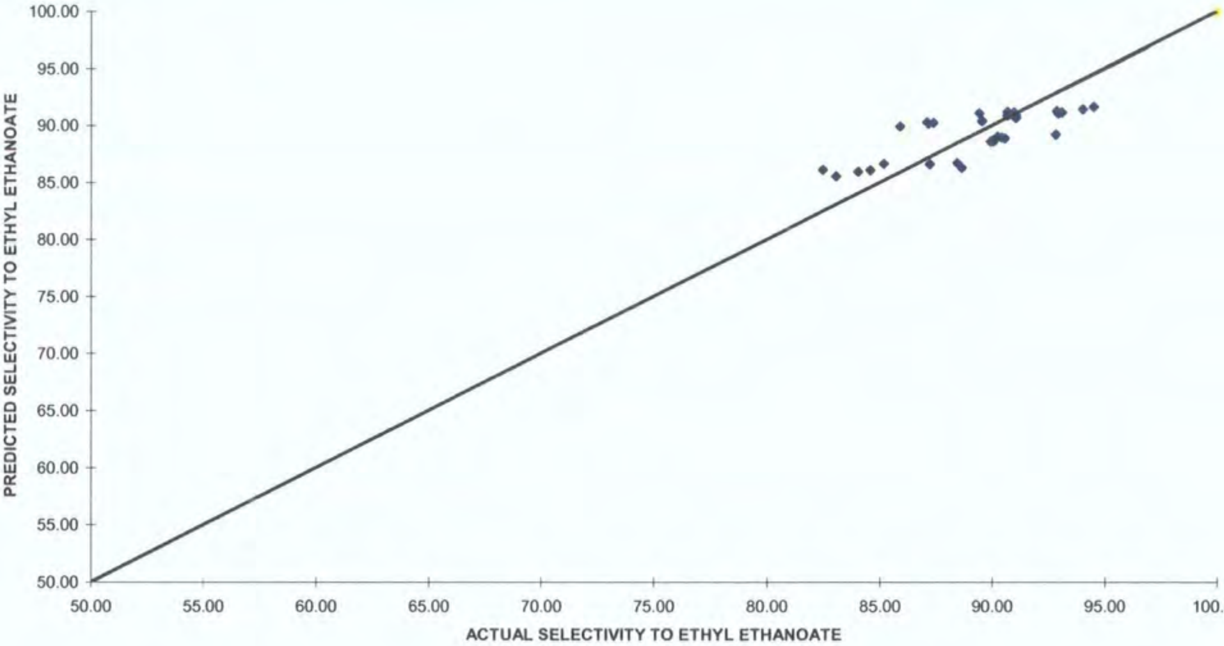


Figure 3.22 Observed Versus Predicted Selectivity To Ethyl Ethanoate, First Pass Model

					ACTUAL VALUES		COMPUTED VALUES	
RUN NUMBER	TEMP °C	LHSV Hr^{-1}	PRESS kPa	H2 FLOW SLPH	CONV Mol%	SEL Mol%	CONV Mol%	SEL Mol%
47	235	0.50	680	5.00	49.56	92.86	49.61	89.20
48	224	1.00	340	1.00	34.74	89.57	36.94	90.40
49	224	1.00	680	1.00	35.73	93.13	35.88	91.14
50	225	2.00	680	1.00	24.54	91.08	21.73	90.66
51	224	0.50	680	1.00	45.15	92.90	43.31	91.27
52	224	0.50	680	5.00	42.26	94.53	41.73	91.63
53	225	0.50	680	5.00	43.77	94.05	42.45	91.41
54	225	0.50	680	1.00	46.94	92.97	44.03	91.05
55	226	0.50	680	2.00	46.45	91.07	44.35	90.92
56	235	0.50	680	2.00	53.08	90.45	50.79	88.94
57	235	0.75	680	2.00	48.32	90.59	47.08	88.87
58	234	1.00	680	2.00	43.87	90.26	42.65	89.03
59	236	1.00	680	2.00	43.97	90.07	44.08	88.59
60	236	1.00	680	2.00	43.31	89.95	44.08	88.59
61	235	1.00	680	1.00	43.41	90.06	43.76	88.72
62	225	1.00	340	0.75	33.48	87.19	37.73	90.17
63	225	0.25	340	0.24	54.64	87.12	49.10	90.31
64	225	0.50	340	0.40	43.90	87.42	45.32	90.26
65	225	2.00	340	1.50	23.39	85.92	22.63	89.94
66	244	1.00	340	0.76	47.78	84.06	51.35	85.97
67	244	0.25	340	0.20	67.27	82.52	62.72	86.12
68	244	0.50	340	0.40	58.88	84.60	58.91	86.08
69	245	2.00	340	1.50	36.12	83.10	36.91	85.56
70	244	1.00	680	0.76	49.71	88.49	50.32	86.70
71	245	0.25	680	0.20	62.85	85.20	62.36	86.65
72	245	0.50	680	0.40	58.06	87.26	58.56	86.61
73	245	2.00	680	1.50	38.54	88.69	35.88	86.29
74	225	1.00	680	0.76	34.38	90.71	36.73	90.87
75	225	0.25	680	0.20	52.39	89.45	48.02	91.08
76	224	0.50	680	0.40	43.56	90.71	43.57	91.20
77	223	2.00	680	1.50	22.23	90.98	20.10	91.15

Table 3.7 Values used for First Pass Model

The additional tests, numbers 101/78-96/96, designed to investigate the highest temperatures and pressures are listed in Table 3.4 (p 119). They were carried out using the same ethylol feed from Sasol as the earlier tests. The tests were performed over a period of 357 hours (circa 2 weeks continuous running). At the end of the tests the catalyst had been online for a total of 927.5 hours. The range of pressures (170 to 4600 kPa) and hydrogen flows (0.75 to 54 SLPH) investigated was much wider than the previous work and included two conditions where the ethanol feed would be in the liquid phase instead of the vapour phase (runs 95 and 96). The temperature of operation was restricted to 225°C as this seemed to give the best results in terms of selectivity and conversion. The ethanol feed rate was also restricted to a fairly narrow range as the effect of LHSV has been well established in earlier work. The results of these tests were used to obtain predictions of selectivity and conversion generated by the simple model built on the results of the earlier runs. The resultant charts (Figures 3.23 and 3.24 below) show the data plotted along with the earlier data. The original co-efficients or factors generated were used to model this new data set – the predicted and actual figures are given in Table 3.7 The resultant fit of conversion remained good indicating the validity of the model in that respect. The fit for selectivity remained relatively poor with a very similar overall shape but the closeness of fit seemed to be slightly improved. An overall picture of ethyl ethanoate yield, generated by multiplying conversion and selectivity, was produced and is shown graphically in Figure 3.25. The predicted results agree well with the actual results, sufficiently so to use as a first pass engineering tool to predict catalyst performance under a range of conditions. The model can only be used within the boundaries of the testwork carried out, and for the catalyst and reactor system used to gather the data. This type of model is of limited value when attempting to move outside of established conditions.

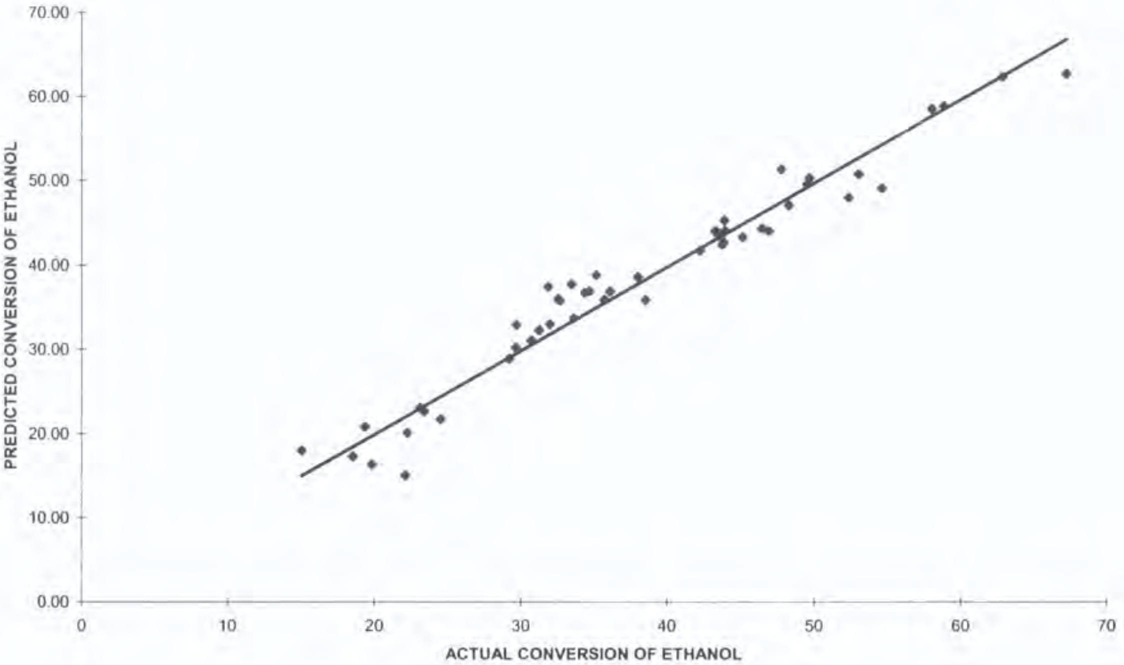


Figure 3.23 Observed vs. Predicted Conversion of Ethanol

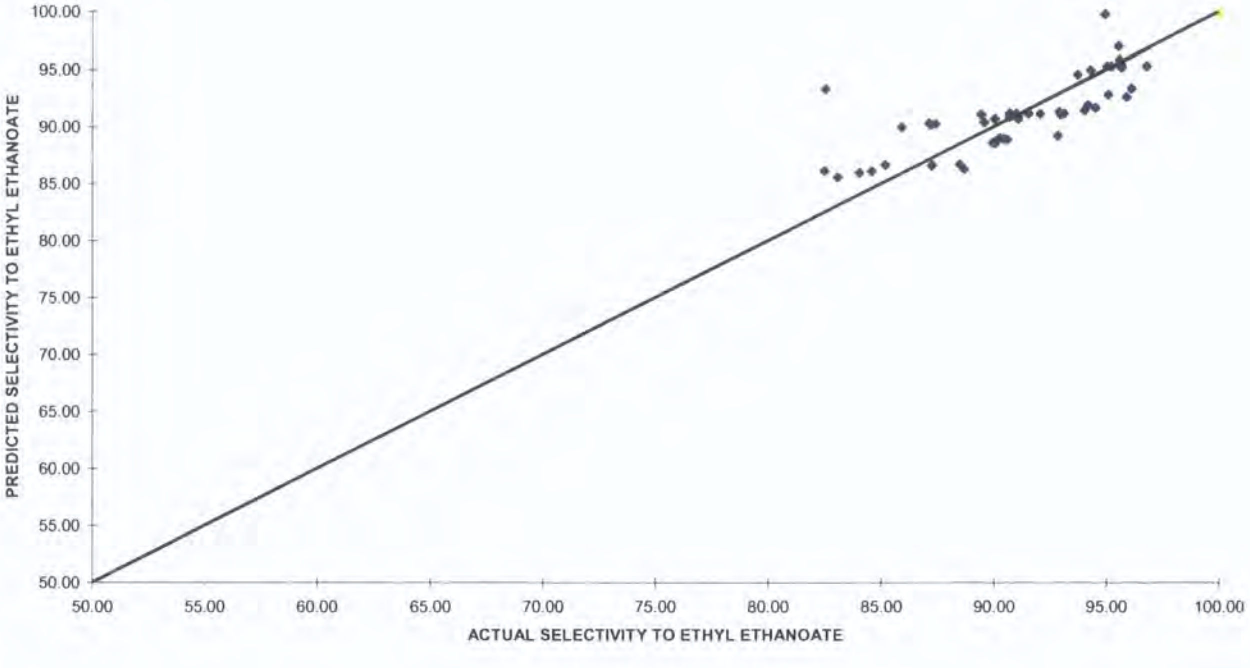


Figure 3.24 Observed Versus Predicted Ethanol Conversion, Second Pass Model

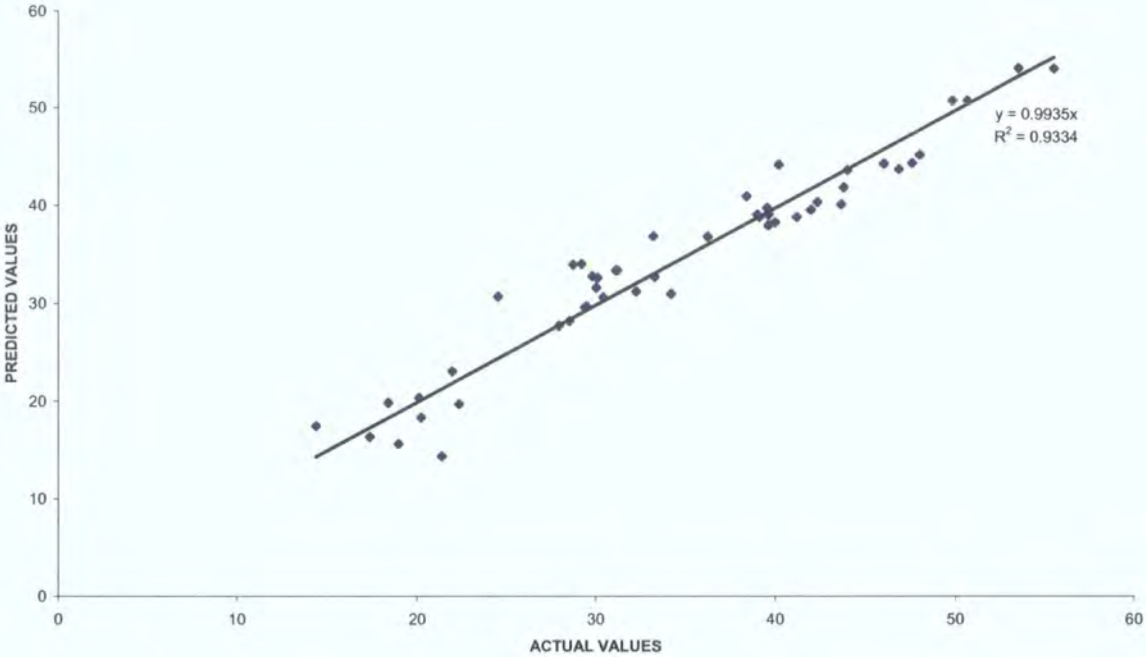


Figure 3.25 Actual Vs Predicted Yield Of Ethyl Ethanoate – Second Pass Model

					ACTUAL VALUES		COMPUTED VALUES	
RUN NUMBER 101/XX/96	TEMP	LHSV	PRESS	H2 FLOW	CONV	SEL	CONV	SEL
78	225	1.00	680	3.00	32.68	92.07	35.81	91.10
79	224	1.00	1370	3.00	31.98	95.10	32.98	92.81
80	225	1.00	1370	3.00	33.62	95.92	33.71	92.57
84	225	1.00	1370	12.00	29.65	96.13	30.23	93.33
82	225	1.00	680	12.00	31.26	94.20	32.28	91.89
83	226	1.00	680	54.20	19.83	95.67	16.37	95.40
84	227	0.75	680	54.00	19.36	95.04	20.84	95.26
85	226	0.75	1370	54.00	15.06	95.56	17.98	96.98
87	225	1.00	170	54.00	18.55	93.74	17.28	94.52
88	224	1.00	1680	0.77	29.69	82.56	32.90	93.28
89	224	1.00	680	0.76	32.54	91.54	35.97	91.12
90	223	1.00	2750	0.76	29.21	95.61	28.91	95.80
91	226	0.50	2750	0.40	38.04	95.23	38.64	95.24
92	225	2.00	2750	1.50	22.10	96.81	15.06	95.26
93	226	1.00	2750	0.75	30.71	95.69	31.07	95.14
94	226	1.00	680	0.75	31.88	90.05	37.41	90.68
95	224	1.00	4600	3.00	23.13	94.95	23.10	99.75
96	246	1.00	4600	3.00	35.19	94.33	38.85	94.90

Table 3.8 Further modelling testwork – Proposed Test Schedule

In addition to the simple model, some further observations can be made when using the data shown above. In particular, the effect of pressure on selectivity and activity can be seen clearly when a single condition of feed flow and temperature is used. Figure 3.26 below is constructed from data from runs 101/62, 80, 88, 89, 90 and 95/96 and shows the very strong effect of pressure on the optimum yield of ethyl ethanoate. There is a clear maximum in conversion at circa 1360 kPa which coincides with maximum selectivity. Hence, the likely operating conditions for a commercial unit would be at or around 1360 kPa and 225°C.

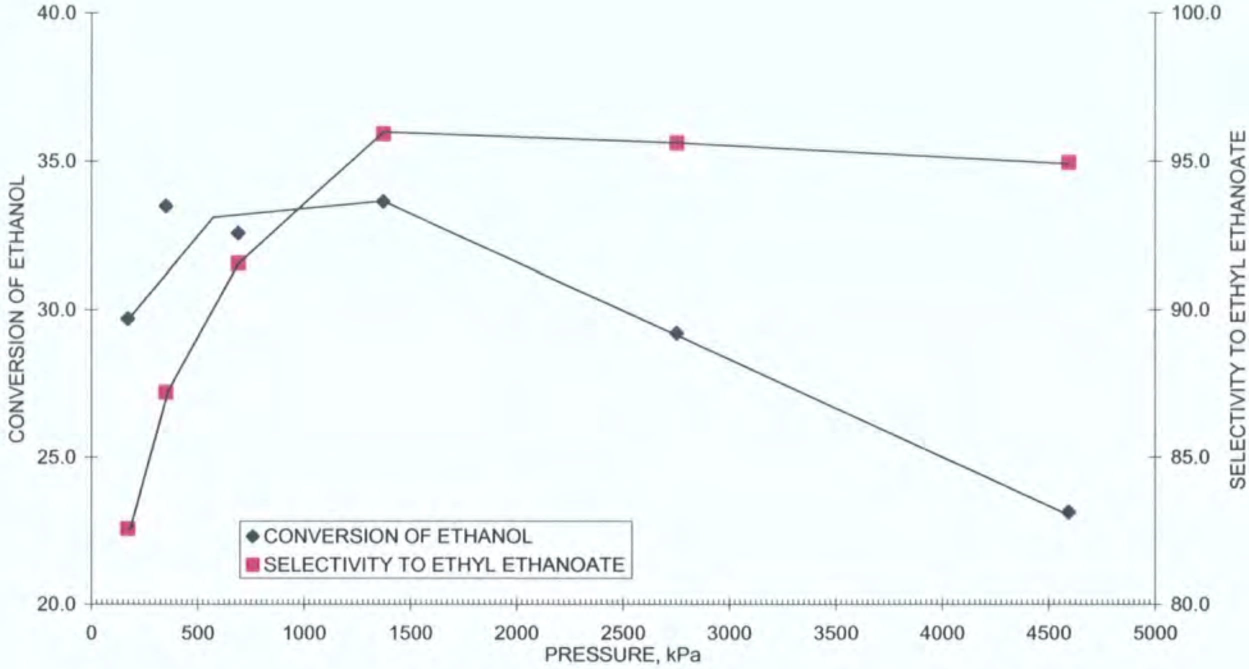


Figure 3.26 Conversion And Pressure Effect At 225°C And 680 kPa

Following this testwork the catalyst was discharged from the reactor to assess its physical and chemical state. To enable this to be carried out safely the reactor was depressurised to atmospheric pressure and purged of hydrogen at 100°C under a flow of nitrogen until analysis of the exit gas showed <0.1 mol% hydrogen. The reactor and catalyst were then cooled to ambient temperature while flowing nitrogen over the catalyst. The catalyst was then discharged into a beaker containing solid CO_2. The catalyst at the bottom of the reactor was mechanically very weak and had started to crumble. Crush strengths were taken of fresh un-reduced catalyst and catalyst taken from the top, middle and bottom of the catalyst bed. The results of the analysis is shown below.

Sample	Crush Strength NM
Fresh	25
Bed Top	3.6
Bed Middle	2.5
Bed Bottom	<1

The poor crushing strength of the catalyst (a minimum of 5-10 NM is required to withstand the weight of a large fixed bed) placed doubt on the ability of the catalyst to be used as a commercial dehydrogenation catalyst.

3.6 Conclusion and discussion

The circa 1000 hours of continuous operation of the ethanol dehydrogenation reactor has generated a wealth of data. On the general point of whether the work has shown that the process is viable, the answer is 'yes'. The targets in terms of selectivity to ethyl ethanoate and catalyst activity have been met. The use of an impure ethanol source, Ethylol, that contains a large proportion of 2-propanol did not change the process from one that was viable when using pure ethanol. The negative change in selectivity and catalyst activity observed could be counteracted by changes in reaction conditions and in general the high conversion and selectivity observed when using pure ethanol could be duplicated. The inability to use wet ethanol, due to a large loss in activity, was extremely disappointing. The proposed mechanism whereby water inhibits the ethyl ethanoate reaction catalyst (see chapter 2) would suggest that there is little prospect that a change in the catalyst composition would result in acceptable activity. It was for this reason that the work on water rich ethanol feeds was discontinued after only one test.

The fact that water is a product of the side reactions that occur during ethanol dehydrogenation suggests that if the selectivity of the catalyst can be increased then the activity will consequently increase. This may explain the relatively high activity of the catalyst observed when the reactor pressure was increased from 680 kPa (see Figure 3.26 and data in Table 3.5) to 1360 kPa. It would be expected that, due to the increase in pressure and hence partial pressure of hydrogen, the conversion to ethyl ethanoate would reduce as a direct function. In fact the conversion of ethanol increases to a maximum at the same pressure as selectivity is also at a maximum. This may be coincidental but it is more likely that the increase in selectivity is causing or allowing an increase in activity.

Once selectivity reaches a maximum then the effect of pressure on the reaction becomes apparent. In other words, the activity observed at pressures below 1360 kPa is lower than would be expected due to suppression or inhibition of the catalyst activity due to water produced in the side reactions. If the conversions observed at 1360, 2720 and 4600 kPa, 225°C,an ethanol feed rate of LHSV 1.0, and a selectivity to ethyl ethanoate of 95-96% , are projected to zero pressure then the predicted conversion of ethanol is in the region of 38-40%. The observed values are 30% at 25 kPa and 33% at 680 kPa. From this we can conclude that activity and selectivity are linked by more than one factor. There are two ways in which selectivity and activity can be linked – in the first case, where by-products are made from the feed material, there is no apparent relationship between activity and selectivity. Factors such as reaction temperature and residence time in the reactor are the key variables. The second case, when by-products are made from the product or some intermediate, there is a direct link between selectivity and conversion. In this case the reverse seems to be true, namely conversion can in some cases be linked with selectivity. Hence any future catalyst developments would be focussed on selectivity rather than activity alone.

The main effect of the impurities in the ethylol are to increase certain by-products that are formed from aldol reactions of propanone and ethanal. The formation of one such by-product, 2 pentanone (and 2-pentanol which is formed from 2-pentanone) increases as the propanone concentration of the crude dehydrogenation product increases. Two runs, 101/44/96 and 101/53/96 (tables 3.1 and 3.2) illustrate this point well. The two runs were carried out at identical reaction conditions but run 101/44/96 was performed using pure ethanol and 101/53/96 using ethylol.

	44	53
Rx Temperature, °C	225	226
LHSV, h^{-1}	0.5	0.5
Pressure, kPa	680	680
Time on line, h	31.5	144.5
H2 flow, SLPH	5	5
Ethanal	0.672	0.716
Methanol	0.025	0.023
Diethyl ether	*0.056*	*0.180*
Ethanol	55.714	55.916
Propanone	**0.081**	**1.479**
2-propanol	**0.159**	**2.690**
Di 2-propyl ether	**0.000**	**0.200**
Ethyl Ethanoate	40.340	33.989
Butanone	0.643	0.608
2- butanol	1.045	0.973
2 propyl ethanoate	**0.028**	**0.548**
2-pentanone	**0.031**	**0.337**
1-butanol	0.132	0.205
2- pentanol	**0.015**	**0.392**
2-butyl ethanoate	0.210	0.186
Ethyl butyrate	0.099	0.110
Butyl ethanoate	0.089	0.086
Hexane	0.041	0.033
2- hexanol	0.015	0.010
Water	0.510	0.760
Others	*0.097*	*0.467*
Selectivity ethanal free		
Ethyl ethanoate	92.553	88.758
Propanone	0.210	4.364
Butanone	1.802	1.940
2-propanol	0.402	-3.967
2- butanol	2.850	3.024
1-Butanol	0.361	0.637
Diethyl ether	0.152	0.113
Di 2-propyl ether	0.000	0.677

Table 3.8 Comparison Of Runs 101/44/96 And 101/53/96

The Table above shows that, with the exception of those components highlighted in bold, the composition of the dehydrogenation products were similar. Those components highlighted in italics are influenced by components appearing in the feed. The by-products that have increased are all associated with either aldol reactions (propanone + ethanal to form pentanol and pentanone) or transesterification (ethyl ethanoate + 2-propanol to form 2-propyl ethanoate).

Most of the other by-products, with the exception of ethers (diethyl ether, di 2-propyl ether) are made from a reaction intermediate, a bound aldehydic species relating to ethanal. The reaction profiles shown in figures 3.12 to 3.26 indicate that most of the by-products are formed at the front of the reactor, in the first 25% of the catalyst. This is the same portion of the bed where there is the most acetaldehyde and least ethyl ethanoate. At least 50% of the ethyl ethanoate formation also takes place in this portion of the bed, indicating that the reaction mechanism that forms ethanal also forms ethyl ethanoate. This confirms the proposed reaction mechanism shown in chapter 2.

The general conclusion from the modelling work was that to achieve high selectivity and conversion, higher pressures than those suggested by thermodynamics were the most efficient option. Thermodynamically, low pressures and high temperature would be expected to produce most dehydrogenation product, but these conditions produced high concentrations of ethanal and aldol products. Higher pressure (up to 680 kPa) actually increased the yield of ethyl ethanoate and increased overall conversion. The model itself, while being very simple and empirical, does predict the conversion and selectivity of the reaction quite well. It therefore achieved its aim of being a design tool for the initial engineering studies. A more detailed and theoretically relevant model is discussed in chapter 5.

The only disappointing aspect of the modelling work was the poor state of the catalyst when discharged from the reactor. It is possible that the products of the dehydrogenation reaction could have degraded the catalyst structure, but as there was no apparent leaching of copper during the dehydrogenation reaction apart from the first few hours this explanation is unlikely. More probable is that the catalyst lost strength due to activation at the stage where copper oxide precursor was converted to copper metal. The low level of alumina binder present (8%) seems to be unable to provide sufficient strength to the reduced catalyst. The low physical strength would preclude the use of the catalyst in a commercial reactor, and unless another fabrication of the catalyst could be found it would be unlikely that the process as envisaged could be progressed any further. What is required is another form of the copper catalyst, of similar activity and selectivity but having an increased physical strength and resistance to degradation by the reaction products and by the activation process. In Chapter 5, the development of the commercial dehydrogenation catalyst is described, starting from commercially available copper-chrome formulations that were subsequently altered to optimise performance.

The next step in the development of an industrial process is to separate the ethyl ethanoate product from the crude dehydrogenation mixture efficiently and at high purity (>99.8%). Chapter 4 deals with the issues of modelling distillation columns by the use of a Vapour Liquid Equilibrium still, and the removal of reactive and close-boiling components from the crude dehydrogenation product by selective hydrogenation in the liquid phase.

Table 3.1 Dehydrogenation Results – E408Tu Pure Ethanol Feed

Run No: 101/XX/96	40	41	42	43	44	45	46
Feed type	ethanol						Wet EtOH
Rx in, °C	250	250	225	225	225	235	235
LHSV, hr^{-1}	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Pressure, kPa	340	680	680	680	680	680	680
Tol. H	7	11.5	18	25	31.5	37	42
H2 flow in, SLPH	10	1	1	10	5	5	5
Ethanal	1.495	1.060	0.752	0.650	0.672	0.802	1.278
Methanol	0.129	0.083	0.035	0.030	0.025	0.028	0.010
Diethyl ether	0.051	0.109	0.047	0.038	0.056	0.051	0.030
Ethanol	37.229	40.945	52.130	59.345	55.714	51.402	65.049
Propanone	0.786	0.467	0.125	0.071	0.081	0.153	0.075
2-propanol	0.486	0.457	0.201	0.143	0.159	0.234	0.091
Di 2- propyl ether	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N butanal	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethyl ethanoate	48.536	48.513	42.815	37.058	40.340	43.259	28.026
Butanone	3.825	2.244	0.987	0.572	0.643	0.989	0.415
2- butanol	2.001	1.958	1.354	0.967	1.045	1.293	0.430
2- propyl ethanoate	0.101	0.124	0.035	0.024	0.028	0.050	0.003
2-pentanone	0.364	0.225	0.053	0.026	0.031	0.063	0.007
Butanol	0.552	0.409	0.215	0.119	0.132	0.182	0.313
2- pentanol	0.087	0.077	0.026	0.014	0.015	0.026	0.003
2-butyl ethanoate	0.419	0.532	0.246	0.181	0.210	0.297	0.016
Ethyl butanoate	0.646	0.402	0.188	0.074	0.099	0.145	0.083
N butyl ethanoate	0.661	0.439	0.162	0.068	0.089	0.143	0.088
2 hexanone	0.197	0.162	0.066	0.035	0.041	0.067	0.007
2- hexanol	0.033	0.036	0.021	0.013	0.015	0.023	0.000
Di n butyl ether	0.018	0.019	0.000	0.000	0.000	0.008	0.000
N hexanol	0.009	0.010	0.000	0.000	0.000	0.000	0.000
2 heptanone	0.020	0.020	0.005	0.000	0.000	0.000	0.000
Water	1.290	1.060	0.350	0.490	0.510	0.610	4.060
Others	1.066	0.650	0.187	0.083	0.097	0.178	0.016
Selectivity ethanal free							
Ethyl ethanoate	78.407	83.147	90.223	92.778	92.553	90.367	93.737
Propanone	1.444	0.911	0.299	0.201	0.210	0.364	0.285
Butanone	7.552	4.701	2.541	1.751	1.802	2.525	1.698
2-propanol	0.863	0.862	0.467	0.395	0.402	0.537	0.335
2- butanol	3.844	3.991	3.394	2.880	2.850	3.212	1.710
Butanol	1.060	0.833	0.539	0.356	0.361	0.452	1.244
Diethyl ether	0.099	0.222	0.117	0.113	0.152	0.126	0.118
Di2-propyl ether	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 3.2 Dehydrogenation results – E408Tu Sasol ethylol feed

Run No: 101/XX/96	47	48	49	50	51	52	53	54	55	57	58	59	60	61
Rx in, °C	235	216	217	212	220	221	226	213	213	220	234	236	236	225
LHSV, hr^{-1}	0.5	1	1	2	0.5	0.5	0.5	0.5	0.5	0.75	1	1	1	1
Pressure, kPa	680	340	680	680	680	680	680	680	680	680	680	680	680	680
TOL, H	49	82.5	108.5	117.5	127	137.5	144.5	178	197	239	261.5	288	311.5	317.5
H2 flow in, SLPH	5	1	1	1	1	5	5	1	2	2	2	2	2	1
Ethanal	0.762	2.104	1.186	1.781	0.825	0.695	0.716	0.687	0.668	1.239	1.225	1.468	1.475	1.462
Methanol	0.032	0.045	0.025	0.025	0.022	0.021	0.023	0.028	0.173	0.050	0.040	0.052	0.049	0.052
Diethyl ether	0.202	0.146	0.160	0.146	0.176	0.178	0.180	0.215	0.211	0.159	0.188	0.153	0.152	0.153
Ethanol	50.440	64.050	63.359	73.183	54.554	57.340	55.916	52.872	53.128	48.980	56.243	53.216	53.846	53.752
Propanone	1.646	2.558	1.928	2.313	1.698	1.478	1.479	1.670	1.632	1.725	2.120	1.816	1.827	1.798
2-propanol	2.422	1.680	2.344	2.086	2.592	2.687	2.690	2.390	2.524	2.022	2.169	1.985	1.995	2.005
Di.2- propyl ether	0.203	0.195	0.201	0.197	0.201	0.202	0.200	0.203	0.201	0.139	0.207	0.140	0.139	0.139
Butanal	0.015	0.014	0.015	0.014	0.014	0.015	0.014	0.014	0.016	0.010	0.016	0.008	0.008	0.012
Ethyl ethanoate	38.397	23.785	26.234	16.600	34.630	32.953	33.989	36.129	34.973	40.605	32.532	36.128	35.872	35.703
Butanone	0.897	1.502	0.830	0.749	0.820	0.542	0.608	0.958	0.880	0.971	1.380	1.000	0.984	0.973
2- butanol	1.163	0.902	0.909	0.602	1.111	0.869	0.973	1.256	1.184	1.021	1.276	0.974	0.964	0.981
2- propyl ethanoate	0.683	0.210	0.272	0.180	0.458	0.524	0.548	0.460	0.480	0.396	0.327	0.304	0.299	0.300
2-pentanone	0.467	0.466	0.332	0.266	0.399	0.310	0.337	0.436	0.278	0.357	0.009	0.333	0.329	0.327
Butanol	0.247	0.426	0.325	0.332	0.281	0.191	0.205	0.306	0.434	0.248	0.392	0.272	0.264	0.271
2- pentanol	0.435	0.192	0.265	0.150	0.391	0.363	0.392	0.412	0.401	0.119	0.032	0.224	0.224	0.224
2-butyl ethanoate	0.278	0.101	0.110	0.078	0.177	0.167	0.186	0.193	0.193	0.297	0.325	0.101	0.099	0.097
Ethyl butanoate	0.231	0.234	0.212	0.058	0.220	0.095	0.110	0.250	0.218	0.168	0.259	0.158	0.155	0.153
Butyl ethanoate	0.146	0.139	0.098	0.056	0.134	0.072	0.086	0.167	0.133	0.159	0.181	0.150	0.147	0.126
2 hexanone	0.052	0.038	0.030	0.014	0.042	0.027	0.033	0.040	0.045	0.040	0.000	0.034	0.033	0.034
2- hexanol	0.016	0.003	0.005	0.000	0.012	0.008	0.010	0.054	0.039	0.010	0.053	0.009	0.009	0.009
Di n butyl ether	0.093	0.003	0.008	0.000	0.048	0.051	0.058	0.051	0.000	0.030	0.027	0.017	0.016	0.018
N hexanol	0.016	0.019	0.000	0.000	0.006	0.007	0.010	0.000	0.000	0.010	0.009	0.011	0.011	0.008
2 heptanone	0.014	0.003	0.000	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.011	0.006	0.004	0.000
Water	0.770	0.890	0.660	0.630	0.760	0.700	0.760	0.990	0.780	1.040	0.750	1.140	0.730	1.060
Others	0.373	0.296	0.494	0.539	0.429	0.504	0.467	0.221	1.408	0.207	0.229	0.301	0.355	0.343
Selectivity ethanal free														
Ethyl ethanoate	87.387	82.431	86.051	83.195	87.273	89.350	88.758	87.368	84.874	90.866	85.855	90.072	89.950	90.058
Propanone	4.237	10.053	7.160	13.146	4.840	4.528	4.364	4.568	4.480	4.340	6.307	5.095	5.156	5.103
Butanone	2.497	6.365	3.328	4.595	2.526	1.798	1.940	2.834	2.612	2.656	4.451	3.047	3.016	2.998
2-propanol	-4.127	-9.119	-6.233	-10.949	-4.100	-4.128	-3.967	-4.473	-4.129	-4.771	-5.199	-5.416	-5.420	-5.426
2 butanol	3.149	3.720	3.548	3.590	3.332	2.804	3.024	3.613	3.420	2.717	4.005	2.888	2.875	2.944
Butanol	0.669	1.758	1.269	1.981	0.844	0.617	0.637	0.881	1.254	0.659	1.230	0.806	0.787	0.813
Diethyl ether	0.158	0.007	0.061	0.010	0.097	0.111	0.113	0.204	0.194	0.103	0.213	0.098	0.095	0.100
Di2-propyl ether	0.599	0.876	0.855	1.281	0.657	0.710	0.677	0.636	0.632	-0.004	0.229	0.000	-0.003	-0.005

Table 3.3 E408Tu modelling testwork results – ethylol feed

Run No: 101/XX/96	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77
Rx in, °C	225	225	225	225	244	244	244	245	244	245	245	245	225	225	224	223
LHSV, hr^{-1}	1	0.25	0.5	2	1	0.25	0.5	2	1	0.25	0.5	2	1	0.25	0.5	2
Pressure, kPa	340	340	340	340	340	340	340	340	680	680	680	680	680	680	680	680
TOL. H	333	347.5	359.5	372.5	383.5	409.5	425	434	448	464	481	496	512	530	542	566.5
H2 flow in, SLPH	0.75	0.24	0.40	1.50	0.76	0.2	0.4	1.5	0.76	0.2	0.4	1.5	0.76	0.2	0.4	1.5
Ethanal	2.578	1.153	1.732	4.243	3.365	1.559	2.263	5.508	1.711	0.924	1.189	2.675	1.343	0.601	0.837	2.122
Methanol	0.063	0.060	0.061	0.054	0.120	0.094	0.106	0.129	0.071	0.066	0.066	0.077	0.039	0.037	0.036	0.032
Diethyl ether	0.133	0.177	0.146	0.120	0.141	0.197	0.155	0.128	0.161	0.28	0.205	0.138	0.14	0.239	0.171	0.126
Ethanol	63.184	43.088	53.283	72.761	49.601	31.08	38.87	60.303	47.548	35.12	39.651	58.105	62.318	45.219	53.6	73.776
Propanone	2.264	1.927	2.056	2.599	2.799	2.6127	2.658	3.068	2.059	1.865	1.926	2.28	1.657	1.301	1.444	1.918
2-propanol	1.582	1.927	1.790	1.275	1.445	1.628	1.364	1.161	1.867	1.997	1.994	1.658	2.121	2.325	2.284	1.858
Di 2- propyl ether	0.139	0.137	0.137	0.136	0.140	0.1405	0.136	0.139	0.139	0.142	0.14	0.139	0.138	0.136	0.139	0.138
Butanal	0.012	0.009	0.011	0.016	0.029	0.0189	0.0245	0.043	0.012	0.013	0.011	0.015	0.012	0.008	0.006	0.012
Ethyl ethanoate	25.605	44.313	34.742	15.419	35.311	51.421	45.001	24.874	39.521	49.951	46.863	29.837	28.374	43.862	36.915	17.171
Butanone	1.230	1.561	1.389	0.997	2.307	2.754	2.585	2.079	1.454	1.713	1.582	1.354	0.698	0.828	0.736	0.530
2- butanol	0.768	1.378	1.084	0.433	1.017	1.512	1.327	0.679	1.169	1.606	1.456	0.88	0.811	1.321	1.053	0.461
2-propyl ethanoate	0.184	0.389	0.145	0.143	0.041	0.533	0.333	0.167	0.318	0.786	0.508	0.047	0.23	0.557	0.339	0.161
2-pentanone	0.316	0.508	0.399	0.229	0.498	0.852	0.669	0.382	0.428	0.701	0.555	0.345	0.241	0.357	0.287	0.178
Butanol	0.329	0.365	0.357	0.293	0.483	0.494	0.487	0.484	0.358	0.425	0.384	0.369	0.265	0.317	0.294	0.201
2- pentanol	0.138	0.296	0.212	0.071	0.151	0.310	0.229	0.088	0.235	0.423	0.331	0.156	0.192	0.375	0.275	0.106
2- butyl ethanoate	0.058	0.181	0.099	0.042	0.087	0.333	0.172	0.055	0.123	0.439	0.241	0.069	0.064	0.217	0.107	0.044
Ethyl butanoate	0.132	0.354	0.226	0.065	0.301	0.635	0.475	0.176	0.246	0.468	0.364	0.16	0.105	0.258	0.166	0.048
Butyl ethanoate	0.123	0.336	0.215	0.049	0.278	0.682	0.498	0.159	0.251	0.516	0.384	0.158	0.095	0.245	0.151	0.035
2 hexanone	0.024	0.074	0.046	0.005	0.004	0	0.0510	0.005	0.049	0.12	0.083	0.029	0.022	0.066	0.039	0.000
2- hexanol	0.000	0.016	0.010	0.000	0.006	0.1236	0.0127	0	0.011	0.024	0.018	0	0.007	0.017	0.011	0.000
Di n butyl ether	0.006	0.038	0.013	0.003	0.009	0.061	0.0235	0.004	0.019	0.102	0.051	0.008	0.008	0.056	0.02	0.003
N hexanol	0.008	0.010	0.004	0.000	0.018	0.056	0.033	0.009	0.005	0.05	0.031	0.009	0.005	0.017	0.009	0.000
Water	0.789	1.220	1.330	0.780	1.390	1.992	1.893	0	1.813	1.57	1.44	1.141	0.82	1.24	0.76	0.810
Others	0.335	0.478	0.509	0.269	0.455	0.877	0.613	0.351	0.428	0.685	0.521	0.322	0.295	0.389	0.315	0.272
Conversion of ethanol	**33.477**	**54.635**	**43.901**	**23.393**	**47.778**	**67.269**	**58.884**	**36.214**	**49.705**	**62.851**	**58.059**	**38.539**	**34.384**	**52.388**	**43.564**	**22.320**
Selectivity ethanal free																
Selectivity to ethyl ethanoate	**87.193**	**87.124**	**87.416**	**85.922**	**84.056**	**82.516**	**84.599**	**83.103**	**88.489**	**85.200**	**87.261**	**88.688**	**90.705**	**89.449**	**90.708**	**90.983**
Selectivity to propanone	8.696	4.267	5.830	16.351	7.526	4.734	5.628	11.557	5.175	3.565	4.022	7.617	5.955	2.970	3.980	11.457
Selectivity to butanone	5.119	3.750	4.272	6.792	6.713	5.402	5.940	8.489	3.979	3.571	3.600	4.919	2.731	2.065	2.213	3.437
Selectivity to 2-propanol	-8.908	-4.396	-6.006	-16.459	-6.586	-4.115	-5.989	-11.393	-5.896	-4.248	-4.643	-8.511	-6.432	-3.644	-4.502	-12.208
2-butanol	3.110	3.222	3.245	2.867	2.878	2.886	2.968	2.698	3.113	3.258	3.224	3.111	3.087	3.206	3.080	2.912
Selectivity to n butanol	1.332	0.855	1.069	1.940	1.368	0.944	1.090	1.923	0.953	0.862	0.850	1.304	0.742	0.599	0.655	0.829
Sel to ethanoate esters	88.570	89.105	88.708	87.353	85.150	85.295	86.711	84.518	90.209	88.499	89.606	89.607	91.557	91.415	91.929	91.512
Diethyl ether	0.053	0.133	0.078	0.000	0.059	0.148	0.025	-0.068	0.043	0.274	0.133	-0.025	0.069	0.284	0.143	0.025

Table 3.4 E408Tu further modelling data – ethylol feed

Run No: 101/XX/96	78	79	80	81	82	83	84	85	87	88	89	90	91	92	93	94	95	96
Rx in, °C	225	224	225	225	225	226	227	226	225	224	224	223	226	225	226	226	224	246
LHSV, hr^{-1}	1	1	1	1	1	1	0.7	0.7	1	1	1	1	0.5	2	1	1	1	1
Pressure, kPa	680	1360	1360	1360	680	680	680	1360	170	170	680	2750	2750	2750	2750	680	4600	4600
TOL. H	587.5	599.5	616.5	661.5	686.5	706.5	724.5	740.5	781	798	813	839.5	854.5	867.5	878.5	898.5	916.5	927.5
H2 flow in, SLPH	3	3	3	12	12	54.2	54	54	54	0.77	0.76	0.76	0.4	1.5	0.75	0.75	3	3
Ethanal	1.185	0.496	0.521	0.419	0.948	0.538	0.443	0.193	1.535	5.317	1.388	0.114	0.093	0.314	0.1343	1.448	0.027	0.061
Methanol	0.032	0.019	0.02	0.016	0.027	0.022	0.026	0.020	0.043	0.087	0.034	0.013	0.015	0.015	0.0129	0.037	0.011	0.015
Diethyl ether	0.14	0.154	0.155	0.148	0.140	0.120	0.122	0.149	0.078	0.120	0.139	0.167	0.263	0.140	0.1771	0.138	0.186	0.29
Ethanol	63.938	64.604	63.043	66.811	65.290	76.145	76.592	80.676	77.364	66.77	64.05	67.236	58.851	73.987	65.81	64.682	73.012	61.556
Propanone	1.541	0.991	1.071	0.865	1.334	0.911	0.822	0.504	1.601	2.883	1.679	0.630	0.590	0.805	0.664	1.713	0.328	0.563
2-propanol	2.21	2.768	2.712	2.865	2.378	2.767	2.821	3.229	1.889	1.081	2.114	3.210	3.084	3.062	3.136	2.085	3.527	3.108
Di 2- propyl ether	0.138	0.138	0.137	0.134	0.136	0.126	0.126	0.130	0.109	0.134	0.138	0.136	0.137	0.136	0.135	0.135	0.139	0.141
Butanal	0.013	0.006	0.006	0.005	0.006	0.013	0.013	0.013	0.005	0.010	0.006	0.004	0.138	0.013	0.0049	0.008	0.005	0.006
Ethyl ethanoate	27.578	28.537	29.995	26.575	26.949	17.498	16.841	13.384	15.029	18.935	27.087	26.377	34.790	19.998	27.766	26.671	21.205	31.963
Butanone	0.555	0.221	0.235	0.138	0.353	0.129	0.131	0.050	0.445	1.655	0.661	0.074	0.101	0.087	0.0915	0.693	0.015	0.093
2- butanol	0.708	0.549	0.554	0.397	0.555	0.346	0.399	0.299	0.416	0.543	0.761	0.360	0.510	0.310	0.4111	0.761	0.175	0.504
2- propyl ethanoate	0.111	0.307	0.324	0.350	0.285	0.301	0.324	0.322	0.191	0.144	0.040	0.316	0.552	0.038	0.327	0.208	0.319	0.555
2-pentanone	0.212	0.115	0.122	0.088	0.172	0.098	0.101	0.048	0.195	0.309	0.233	0.055	0.077	0.057	0.0637	0.244	0.010	0.068
N butanol	0.212	0.15	0.149	0.085	0.116	0.055	0.053	0.025	0.091	0.410	0.274	0.203	0.191	0.174	0.221	0.352	0.433	0.269
2- pentanol	0.188	0.192	0.197	0.171	0.190	0.172	0.203	0.175	0.123	0.075	0.180	0.148	0.223	0.114	0.163	0.183	0.087	0.208
2- butyl ethanoate	0.062	0.06	0.009	0.058	0.065	0.054	0.064	0.014	0.051	0.037	0.057	0.052	0.085	0.042	0.052	0.062	0.044	0.08
Ethyl butanoate	0.075	0.045	0.048	0.025	0.046	0.074	0.018	0.011	0.032	0.115	0.093	0.030	0.048	0.069	0.035	0.123	0.075	0.072
Butyl ethanoate	0.065	0.034	0.036	0.016	0.030	0.019	0.007	0.000	0.014	0.096	0.086	0.022	0.042	0.017	0.029	0.121	0.079	0.069
2 hexanone	0.017	0.000	0.000	0.000	0.000	0.007	0.000	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0	0.02	0.000	0
2- hexanol	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0	0.004	0.000	0
Di n butyl ether	0.008	0.011	0.012	0.012	0.011	0.012	0.014	0.010	0.000	0.004	0.000	0.000	0.000	0.005	0	0.006	0.006	0.018
N hexanol	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0	0.005	0.000	0
2 heptanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0	0	0.000	0
Water	0.590	0.400	0.680	0.550	0.680	0.410	0.630	0.440	0.520	0.920	0.660	0.450	0.000	0.400	0.45	0	0.000	0
Others	0.413	0.203	-0.026	0.272	0.289	0.186	0.250	0.309	0.271	0.339	0.320	0.403	0.210	0.219	0.305	0.301	0.303	0.350
Conversion of ethanol	**32.678**	**31.977**	**33.621**	**29.653**	**31.257**	**19.828**	**19.357**	**15.057**	**18.545**	**29.690**	**32.562**	**29.208**	**38.037**	**22.100**	**30.705**	**31.897**	**23.127**	**35.189**
Selectivity ethanal free																		
Ethyl ethanoate	**92.069**	**95.098**	**95.919**	**96.132**	**94.199**	**95.670**	**95.039**	**95.558**	**93.741**	**82.560**	**91.539**	**95.610**	**95.159**	**96.810**	**95.694**	**90.046**	**94.948**	**94.328**
Propanone	5.778	3.679	3.822	3.475	5.225	5.544	5.148	3.924	11.230	14.222	6.380	2.509	1.770	4.320	2.525	6.505	1.562	1.819
Butanone	2.267	0.901	0.920	0.611	1.510	0.867	0.905	0.436	3.398	8.834	2.732	0.326	0.338	0.514	0.386	2.863	0.082	0.336
2-propanol	-6.391	-4.331	-4.353	-4.315	-6.175	-7.324	-7.222	-5.932	-14.39	-13.94	-6.953	-3.081	-2.705	-4.909	-3.208	-7.054	-2.245	-2.840
2-butanol	2.814	2.178	2.109	1.710	2.310	2.251	2.683	2.543	3.091	2.820	3.062	1.554	1.661	1.786	1.687	3.059	0.933	1.771
N butanol	0.564	0.317	0.301	0.065	0.191	-0.099	-0.114	-0.384	0.153	1.767	0.822	0.574	0.394	0.601	0.624	1.134	1.936	0.699
Diethyl ether	0.072	0.127	0.126	0.112	0.083	-0.003	0.013	0.250	-0.315	-0.001	0.077	0.203	0.466	0.118	0.235	0.072	0.352	0.597

Chapter 4

Vapour Liquid Equilibrium, Distillation and Selective Hydrogenation

4 Introduction

The testwork reported in chapters 2 and 3 was concerned with the synthesis of ethyl ethanoate from ethanol by dehydrogenation. This chapter deals with the methods and means employed to separate ethyl ethanoate from the dehydrogenation product in a commercially relevant manner and at high purity - >99.5% - such that it can compete with existing ethyl ethanoate syntheses. The chapter deals with two main areas – separation of ethyl ethanoate from the reaction mixture by distillation and the removal of two troublesome components from the dehydrogenation product by a selective hydrogenation step. The distillation section is further split into two topics – Vapour Liquid Equilibrium (VLE) measurements of the various azeotropes that were predicted from identification of the products of dehydrogenation, and the actual distillation of ethyl ethanoate from dehydrogenation product. A technique termed 'Pressure Swing Distillation' (PSD) was used to break the ethanol / ethyl ethanoate / water azeotrope. During the distillation testwork a problem was identified regarding separation of ethyl ethanoate and butanone, which have similar boiling points. Removal of butanone by distillation was determined as being impractical and so a selective hydrogenation step was introduced. Hydrogenation of carbonyl compounds in the dehydrogenation products, specifically ethanal, propanone, butanone and pentanone, was carried out using heterogeneous nickel and ruthenium catalysts.

Combinations of ethanol dehydrogenation, selective hydrogenation of butanone (and other carbonyl compounds) and pressure swing distillation are the subject of a number of patent applications[1,2,3,4] ; a copy of the main patent is attached as Appendix 4.

4.1 VLE and Distillation –Theory and practise

Distillation[5] is defined as “a process of evaporation and re-condensation used for separating liquids into various fractions according to their boiling points or boiling ranges”. A less rigorous definition is that distillation is a method of separating components from a mixture by exploiting differences in their boiling points.

Distillation is the most commonly used technique[6] for separation and purification in the chemical industry. Distillation is a highly energy intensive process and, within a typical industrial unit that uses distillation as the separation and purification technique, it accounts for circa 50% of the capital and operating costs. To be effective, a distillation unit must be well defined and this is done in part by the use of experimental VLE data. Definitive treatments of distillation and VLE are given in Perry’s Chemical Engineering Handbook[7]. A detailed explanation of distillation theory will not be explored here. All compounds exert a vapour pressure which is dependant on temperature – raising the temperature of a substance raises its vapour pressure. A substance is said to boil when its vapour pressure equals the surrounding pressure. Liquids with high vapour pressures are said to be volatile, and boil at lower temperatures than those with low vapour pressures. A liquid mixture of two or more compounds will have a total vapour pressure, and therefore boiling point, that depends on the relative concentration and vapour pressures of the components. For a mixture of two compounds (a binary mixture) the behaviour of the liquid and vapour fractions can be read from a boiling point diagram. Figure 4.1 shows an idealised mixture of two components X and Y at constant pressure.

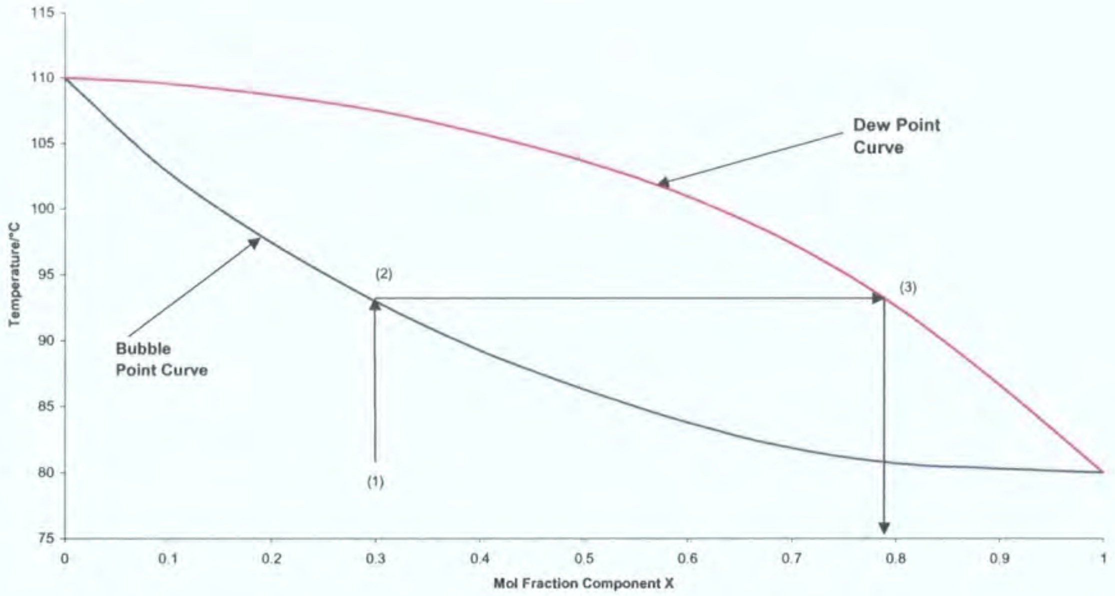


Figure 4.1 Boiling point diagram for mixture of X and Y at constant pressure

The two curves – "Bubble Point" and "Dew Point" - correspond to the temperature at which the liquid starts to boil (Bubble point) and where the saturated vapour starts to condense (Dew Point). Below the bubble point is a region where the liquid is subcooled – not at the boiling point; above the dew point curve is a region where the vapour is super-heated. The chart can be read in the following manner: Point (1) on chart 4.1 depicts a liquid below the bubble point with a molar composition of circa 0.3X and 0.7Y. As the liquid is heated its temperature rises until it meets the bubble point curve at point (2), circa 93°C, where it boils. The equilibrium vapour composition at this temperature can be read off the dew point curve – point (3). The corresponding vapour molar composition is circa 0.8X and 0.2Y, that is the vapour becomes enriched in X and distillation has begun to separate the two components. This difference in the composition of the liquid and vapour at any given temperature is the basis for distillation. The position of the two lines differs as the components change. Those compounds that have widely differing boiling points have widely spaced lines which indicates a large difference in composition between liquid and vapour, and those that have close boiling points have more closely spaced lines which indicates a smaller difference in compositions. A measure of how easily two compounds can be separated is 'Relative Volatility' α, which is defined according to equation 4.1

$\alpha_{X,Y} = (X_V/X_L)/(Y_V/Y_L)$ **eq. 4.1**

Where X_V mol fraction of X in liquid
X_L mol fraction of X in vapour
Y_V mol fraction of Y in vapour
Y_L mol fraction of Y in liquid

Components that have relative volatilities of between1.05 and 0.95 are termed hard to separate by distillation, and this leads on to the measurement of relative volatilities and VLE curves. VLE curves are an alternative way of presenting the data from VLE measurements. They are used to predict the position of azeotropes, a liquid mixture that when vaporised generates a vapour of the same composition as the liquid, and departures from ideality. Figure 4.2 shows a typical VLE curve generated from an ideal mixture, at constant pressure.

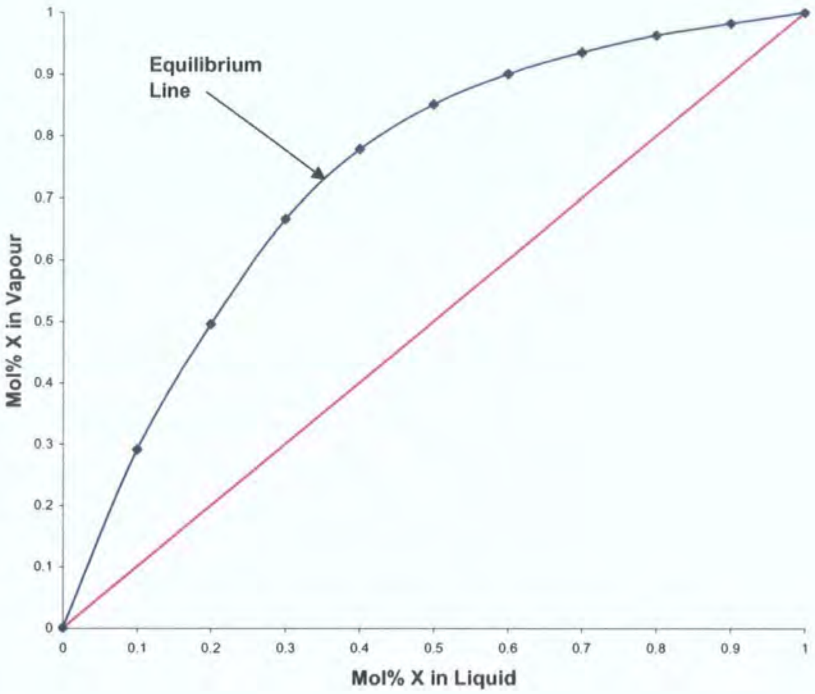


Figure 4.2 Idealised VLE curve for Component X at constant pressure

This type of VLE curve is generated from mixtures that do not form azeotropes. Where azeotropes are generated there are two types of VLE curves that are possible. Figures 4.3 and 4.4 show the curves for maximum boiling point azeotrope, where the boiling point is higher than for its components, and minimum boiling point azeotrope where the boiling point is lower than its components.

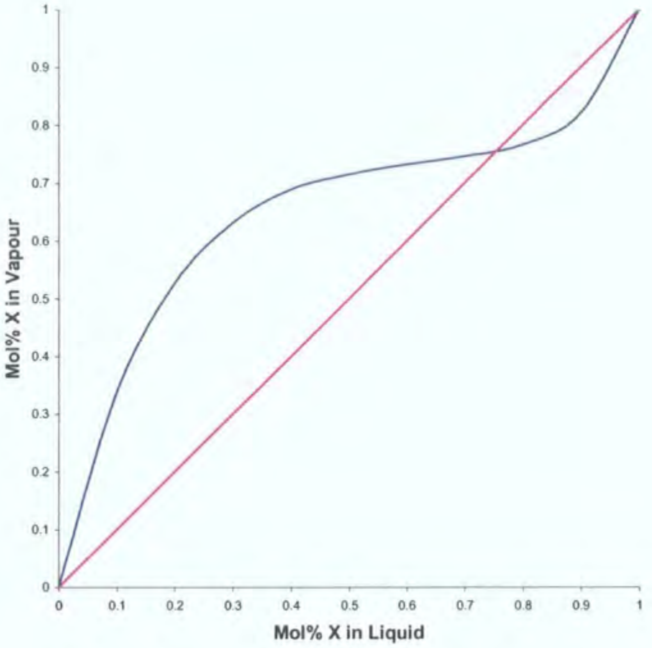


Figure 4.3 Idealised VLE curve for Minimum Boiling Point Azeotrope

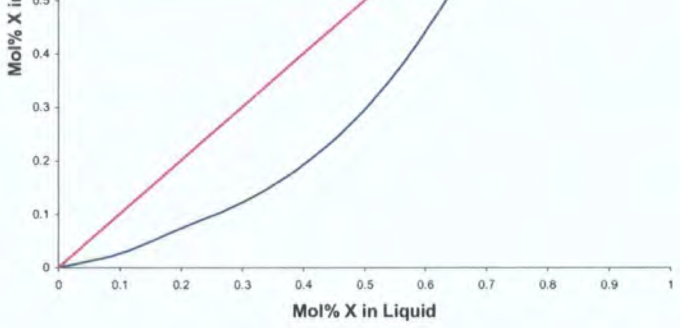


Figure 4.4 Idealised VLE curve for Maximum Boiling Point Azeotrope

The VLE curve intersects the 45° line at the azeotrope point – at the cross-over the composition of the liquid and vapour are identical. There is a third type of azeotrope, termed a 'heterogeneous azeotrope', which occurs when the feed has two immiscible phases. The VLE diagram below, figure 4.5, shows a large region where the composition of the vapour is at the azeotrope point over a wide range of liquid compositions, typical of heterogeneous azeotropes.

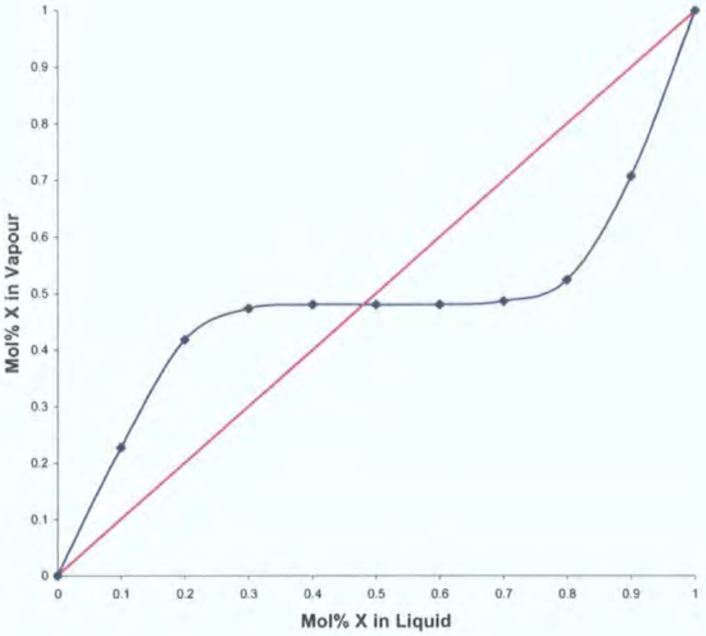


Figure 4.5 Idealised Heterogeneous Azeotrope

VLE plots can be used to construct McCabe-Thiele plots[7] that are used to design distillation columns. McCabe-Thiele plots are a graphical treatment of distillation column design. The method requires a VLE curve, and two ratios representing flows at the top and bottom of the distillation column. The first is the reflux ratio R (the ratio between the reflux flow L and distillate flow X_D, so $R = L/X_D$), and the second the ratio between the liquid rate down L_S and vapour rate up V_S the stripping section of a column. Figure 4.6 shows a distillation column and the flows used to calculate the two ratios.

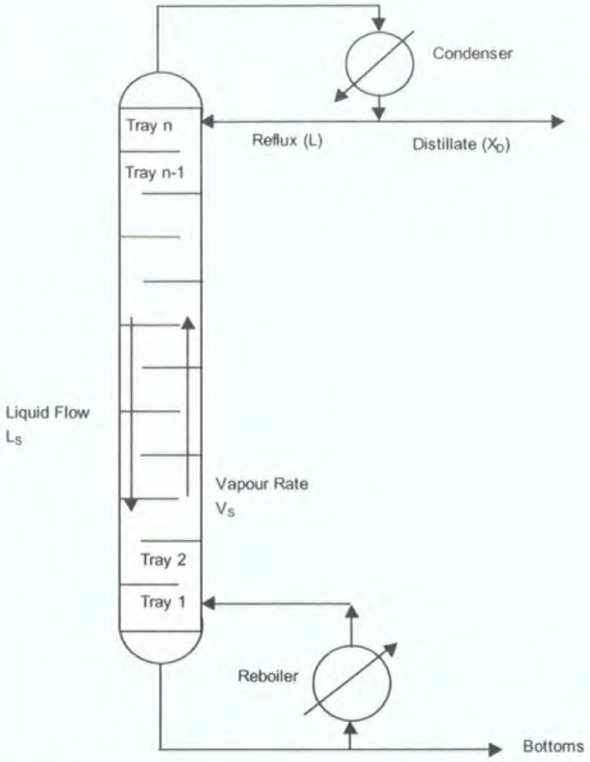


Figure 4.6 Diagram of Distillation Column Showing Flows used for Calculations

A VLE curve is constructed as in figure 4.2 and the composition that is required of the distillate X_D located on the 45° line. A line of slope R/(R+1) is plotted from the 45° line to the X axis; see figure 4.6 for a representation of this line. A second line is plotted in a similar fashion, but taken from the required composition of the bottoms product. A line of slope L_S/V_S is plotted as shown in figure 4.7

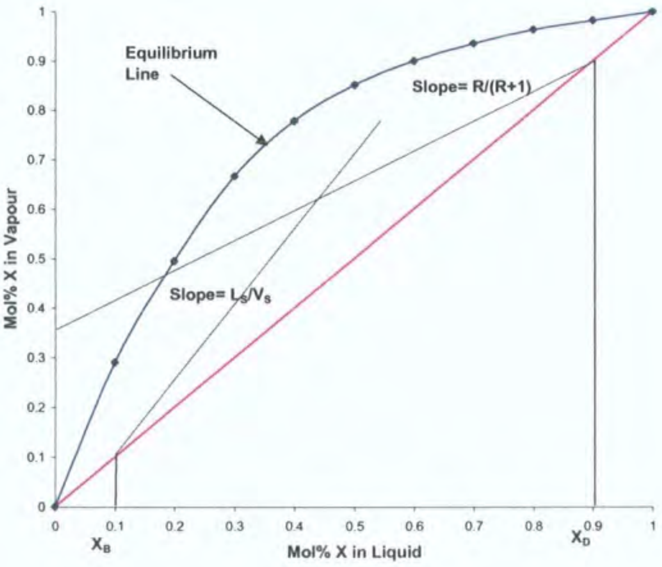


Figure 4.7 Construction of Operating Lines on an Idealised VLE Curve

The intersection of these two lines is called the operating line and is used to calculate the number of theoretical stages. Starting from the intersection of X_D and the 45° line, series of horizontal and vertical construction lines are drawn between the operating line and the equilibrium line as shown in figure 4.8.

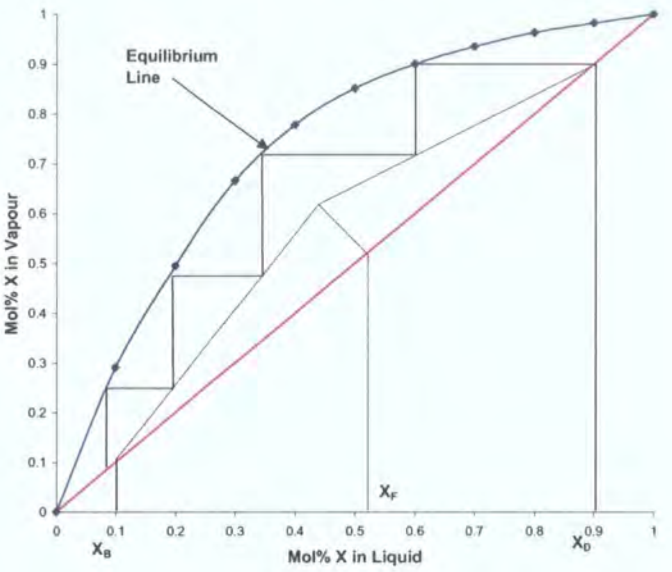


Figure 4.8 Determination of Number of Theoretical Stages

The place where the feed, if it is a distillation product, should be introduced can be found by extrapolating the position where the two operating lines meet to the 45° line. Figure 4.8 predicts that there should be 4 stages in this particular distillation column and that the feed should be introduced into stage 3. Use of this type of diagram depends on many factors, and it can only be used as an approximation. When used as a design tool the feed, overhead and bottoms compositions will be fixed but the reflux ratio, and feed and vapour flows, will be variable. Thus, McCabe-Thiele plots are used only as a guide for more detailed simulations, often carried out using a package such as Pro(II)[8] or Aspen.

VLE measurements of the composition of liquid and vapour fractions can be performed in both batch[9] and continuous[10] modes. In batch mode a mixture is heated, in a sealed apparatus, to the bubble point and allowed to equilibrate over a period of time (minutes to hours). Samples are then taken from the vapour and liquid. Continuous methods use some form of flow heater where a feed mixture is heated to its bubble point and the vapour and liquid fraction are separated. The advantage of continuous mode VLE measurement is that, for mixtures that have components that could react over time – for example a mixture of ethyl ethanoate and 2-propanol which could react to form 2-propyl ethanoate and ethanol – the shorter residence times in the heated zone minimise reaction. The DPT VLE still is constructed such that a liquid is pumped through a capillary tube embedded in an electrical heater. The residence time in the heated zone is in the region of 0.1 to 1 second depending on the feed rate. The liquid and vapour are then passed to a vapour liquid separator as shown in figure 4.9.

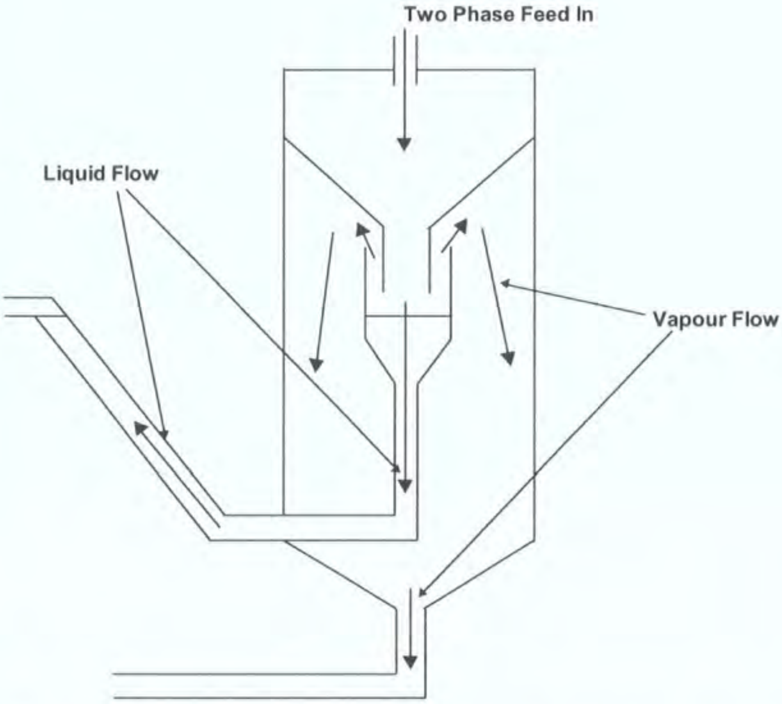


Figure 4.9 VLE Vapour Liquid Separator Details, DPT Version

In order to construct a VLE diagram a series of feeds is passed through the heater at a rate of circa 300 cm^3h^{-1} and the heater adjusted such that a liquid to vapour mass ratio of 4:1 is obtained. Thermocouples placed at the two phase feed inlet and in the vapour flow path (not illustrated in the diagram) record the liquid and vapour temperatures. The liquid and vapour fractions are cooled to ambient temperature and collected for analysis. The compositions of the feeds are adjusted so as to cover the range of 0% to 100% of a component in circa 10 tests. In this way both the boiling point curves and equilibrium lines can be plotted from a single dataset. Where an azeotrope is discovered a supplementary set of tests is carried out over a more narrow range of compositions so that the position of the azeotrope can be accurately plotted. If there is a known azeotrope only points around the azeotrope position will be tested. The DPT VLE test equipment can be configured to perform at pressures ranging from vacuum (10 Torr) to pressure (2000 kPa).

4.2 VLE of Ethyl Ethanoate, Ethanol and Other Components

In order to determine the existence of azeotropes in the ethyl ethanoate/ethanol dehydrogenation product, and to validate published data and performance of the computer simulation programme being used (Pro II), a programme of VLE testwork was performed. Three systems - ethyl ethanoate/water, ethyl ethanoate/ethanol and ethanol/water- were examined at atmospheric pressure and 1240 kPa. The usual DPT methodology of taking approximately 20 wt% of the feed as vapour, and the remainder as liquid, was used for all VLE testwork. The fractions obtained were analysed by GLC and Karl Fischer titration to determine their wt% composition. The results were converted to mol% for the construction of VLE diagrams and for inclusion into Pro(II) simulations.

4.2.1 Binary Systems At Low Pressure

The first system examined was ethanol / water. A large body of data is available for this azeotrope and so calibration and validation of the position of the azeotrope would give a degree of confidence in the results of future VLE testwork.

Four mixtures of ethanol and water, approaching the composition of the expected azeotrope, were prepared and passed through the VLE equipment. The results are shown in table 4.1 (p140) and in figure 4.10. The VLE curve passes through the 45° line at close to the expected point, at 0.82 mol fraction of ethanol in the vapour fraction. The literature VLE data for ethanol and water are plotted in figure 4.10 and the high degree of correlation confirms the suitability of using the VLE equipment for the remaining testwork.

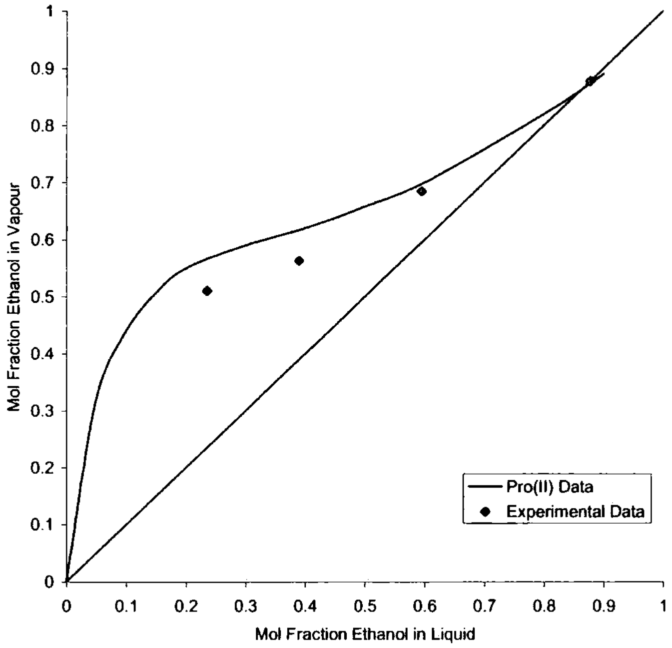


Figure 4.10 Experimental Ethanol / Water VLE Curve, Atmospheric Pressure

The next system assessed was the ethyl ethanoate / ethanol binary. The published azeotrope composition of this binary ranged from 51.9 to 57.5 mol% (mol fraction of 0.519 to 0.575) which was too wide a range to be usable for predictive work. The VLE of this system was carried out with the results shown in table 4.2 (p 140) and figure 4.11. The experimental data and an average of the literature data match fairly closely, with the experimental data predicting 52 mol% and the computer 54 mol%.

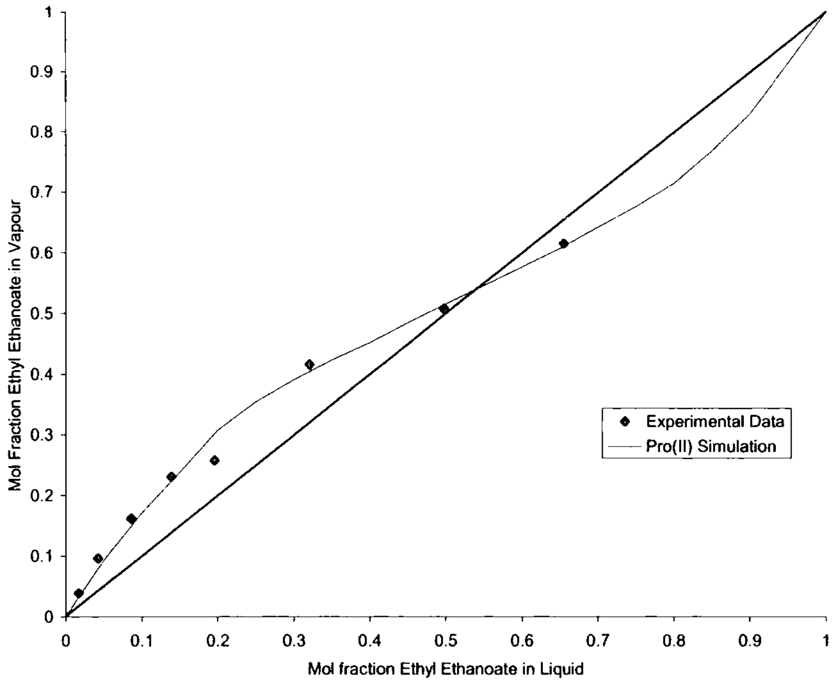


Figure 4.11 Experimental Ethyl Ethanoate / Ethanol VLE curve, Atmospheric Pressure

The last system carried out at atmospheric pressure was the ethyl ethanoate / water binary. This system proved to be the most problematic of the three owing to the immiscibility of the components. To ensure the feed to the VLE unit was homogeneous, a high efficiency Silverson laboratory mixer fitted with an emulsifier screen was employed. The feed to the VLE was continuously agitated to keep it in a homogeneous state. The results from the VLE, shown in figure 4.12 and table 4.3 (p 140), clearly shows the system is a heterogeneous azeotrope. Analysis of the products was carried out by collecting the products and then adding a known weight of ethanol to make the sample single phase – ethyl ethanoate and water are both soluble in ethanol – before analysing. The position of the azeotrope is circa 74 mol% ethyl ethanoate which contrasts to the range 68.5 to 71.5 mol% quoted in the literature.

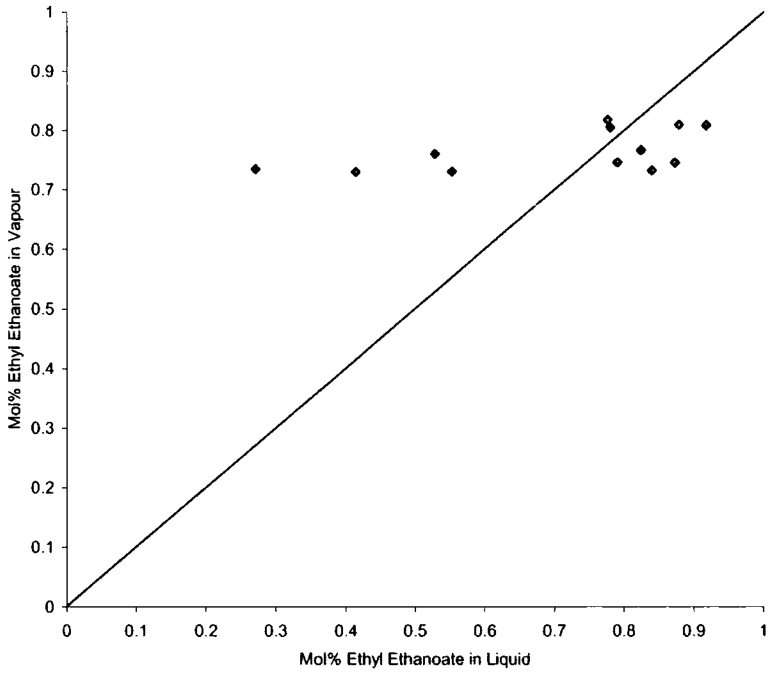


Figure 4.12 Experimental Ethyl Ethanoate/Water VLE Curve, Atmospheric Pressure

4.2.2 Binary Systems At High Pressure

A similar program to the one undertaken at atmospheric pressure was carried out at elevated pressure (1250kPa) to determine the position of azeotropes. The point of the work was to assess the difference in composition of the azeotropes of ethanol, water and ethyl ethanoate and to determine if the composition differences could lead to separation of ethyl ethanoate without the need to resort to the use of extractive distillation.

The three feed mixtures – ethyl ethanoate / ethanol, ethanol / water and ethyl ethanoate / water were tested. In the case of ethyl ethanoate / water the feed was kept as a homogenised phase by the use of a Silverson mixer. The results of the tests are shown in tables 4.4, 4.5, 4.6 (p141) and in figures 4.13, 4.14, 4.15. The results for ethanol / water at 1240 kPa shows a very poor correlation with the quoted literature composition of circa 87 mol% ethanol. The experimental position is circa 74.5 mol% ethanol. The good fit from the Pro(II) model is the result of inputting the experimental results into the program and allowing Pro(II) to generate thermodynamic data from them. The shape of the Pro(II) curve indicates that the data collected are thermodynamically valid.

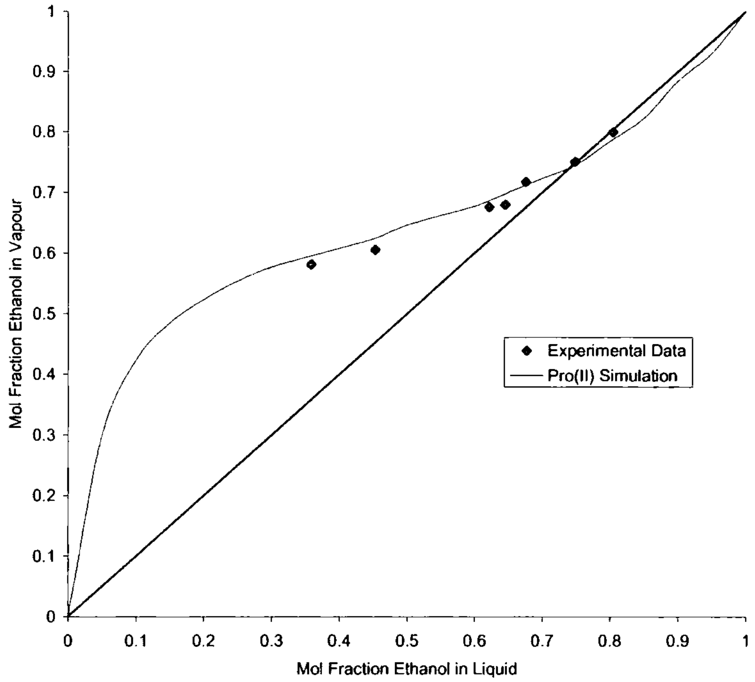


Figure 4.13 Experimental Ethanol / Water VLE Curve at 1240 kPa

Figure 4.14 plots the data from ethyl ethanoate and ethanol at 1240 kPa. The experimental data indicate that there is an azeotrope at above 90 mol% ethanol (10 mol% ethyl ethanoate). There were no good literature data to compare against and the plotted Pro(II) simulation was based on the experimental data. The position of the azeotrope should be compared to the result at atmospheric pressure where the position of the azeotrope was circa 54 mol% ethyl ethanoate. There is a large difference in composition of the two azeotropes that could be used to separate ethyl ethanoate from ethanol. If a feed of 54 mol% ethyl ethanoate, 44 mol% ethanol were fed to a column at 1240 kPa then the vapour stream would become richer in ethanol leaving the liquid stream richer in ethyl ethanoate. This result was the first indication that purification of ethyl ethanoate by distillation at two pressures – pressure swing distillation – was practically possible.

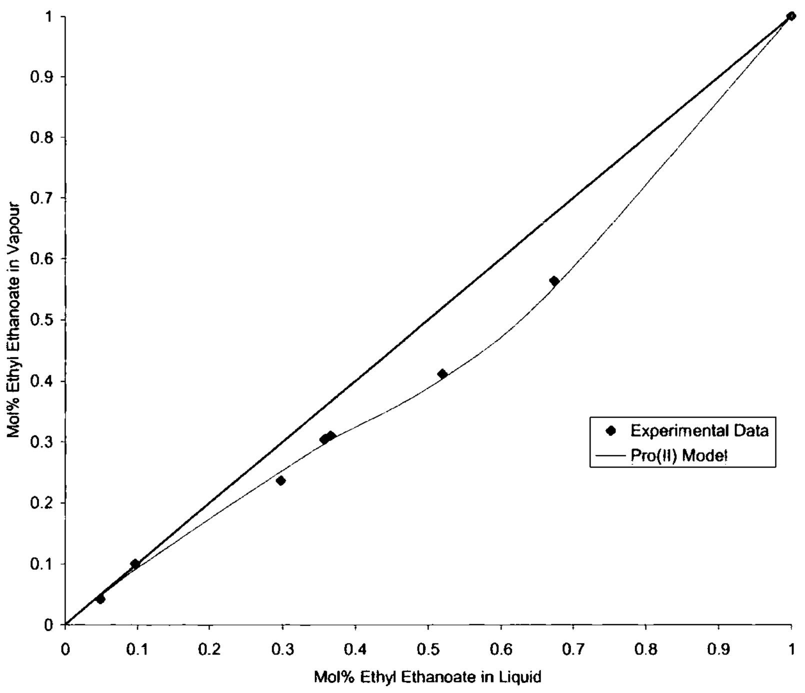


Figure 4.14 Experimental Ethyl Ethanoate / Ethanol VLE Curve 1240 kPa

The results plotted in figure 4.15 show that ethyl ethanoate and water form a heterogeneous azeotrope at 1240 kPa, with a composition of circa 54 mol% ethyl ethanoate. The concentration of ethyl ethanoate in the vapour is decreased in comparison to the composition at atmospheric pressure, in common with the ethyl ethanoate / ethanol system, so the effect of increasing pressure in this system would be to enrich the liquid phase in ethyl ethanoate and to aid separation. Water in the distillation product at atmospheric pressure would therefore not be expected to cause problems at higher pressure. The consistency of the data is relatively poor in comparison to the data from the other systems, but this can be attributed to the fact that the liquid and vapour streams are two phase and difficult to analyse.

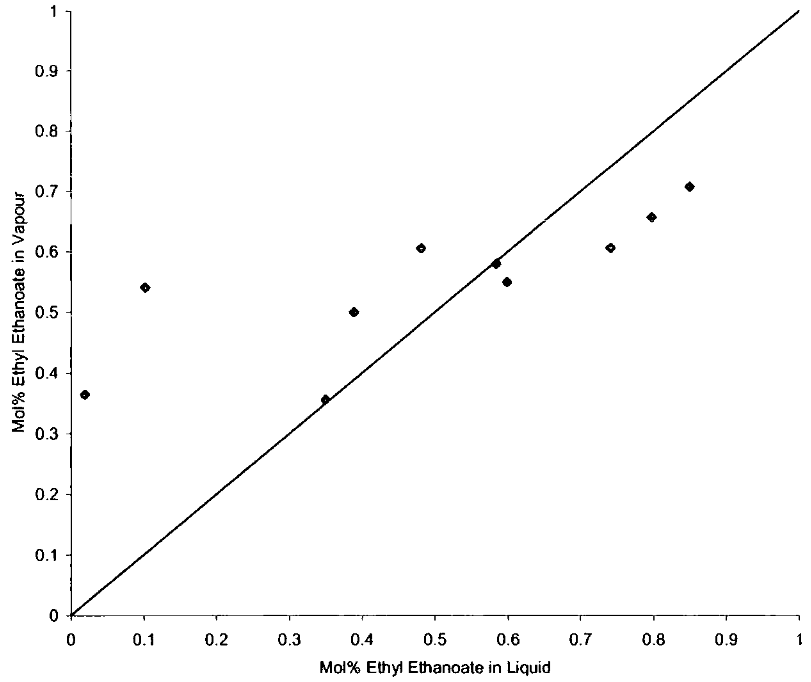


Figure 4.15 Experimental Ethyl Ethanoate / Water VLE Curve, 1240 kPa

4.2.3 Ternary System Ethyl Ethanoate / Ethanol / Water

Following the binary testwork a number of tests were carried out on the ternary system of ethyl ethanoate /ethanol / water. Again, feed compositions were examined at various pressures (atmospheric, 190 kPa, 1240 kPa). Analysis of the products from the ternary system was sometimes complicated by the formation of two phases in either the liquid or vapour streams. In this case, ethanol was not a suitable homogenisation solvent so methanol was used in its place. The results from this work are shown in tables 4.7, 4.8, 4.9 (p141) and in figures 4.18, 4.19 and 4.20. Figure 4.16 shows how these ternary diagrams should be read; note that for simplicity the internal divisions are omitted. Each side of the triangle represents 0-100 mol% (or 0-1 Mol fraction) of each component. To plot the composition of a mixture the three concentrations are located on the appropriate axis or side of the triangle. Lines are then plotted from these three points as shown in figure 4.16. The point of intersection of these lines is the position of the ternary composition. The right hand side triangle in figure 4.16 shows the position of the point X=30, Y=45, Z=25.

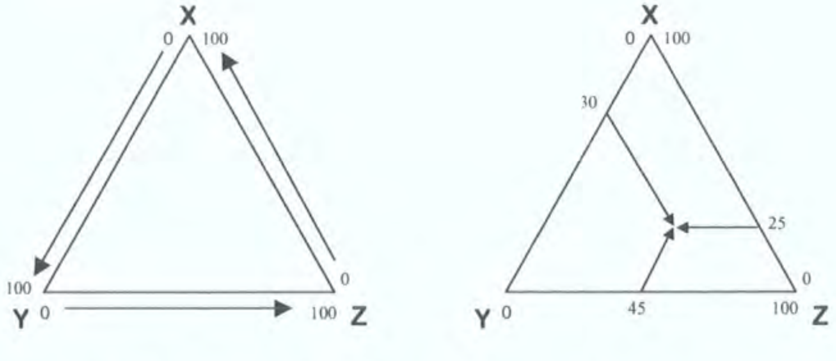


Figure 4.16 Reading Ternary Diagrams - Examples

The interpretation of ternary diagrams is dependent on whether there are azeotropes present or not. If there are no azeotropes present the plotted points tend to form a cloud or scatter plot with no discernible pattern. Where there are azeotropes there are 'distillation lines' that pass through the azeotrope composition. There are often many lines that can be plotted between these points – figure 4.17 shows an idealised diagram where there are two azeotropes. The lines are significant – if a mixture has a composition close to one of these lines, then during distillation the composition of the vapour will tend to move towards it. Once the composition of the vapour is the same as that indicated by the line, it will not then move away but will follow the line to one of the azeotrope positions, indicated by the point where the lines congregate.

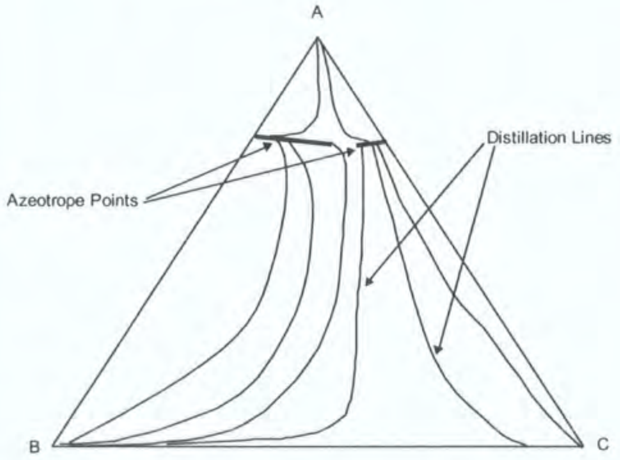


Figure 4.17 Idealised Ternary Diagram Showing Distillation Lines

Literature and experimental data predicted a ternary azeotrope of composition ethyl ethanoate 60 mol%, ethanol 12 mol%, water 28 mol% but when the information was fed to Pro(II) it indicated that a ternary would not form, but that the two lower boiling binary azeotropes (76 mol% ethyl ethanoate, 24 mol% water and 55 mol% ethyl ethanoate, 46 mol% water) would form. Figure 4.18 and the data in table 4.7 (p142) show the composition of the vapour moving close to the ethyl ethanoate / ethanol azeotrope even when there is sufficient water in the feed to produce the ternary azeotrope. There is a defined trend in the data points that appears to be moving from the ternary position to the ethanol / water binary.

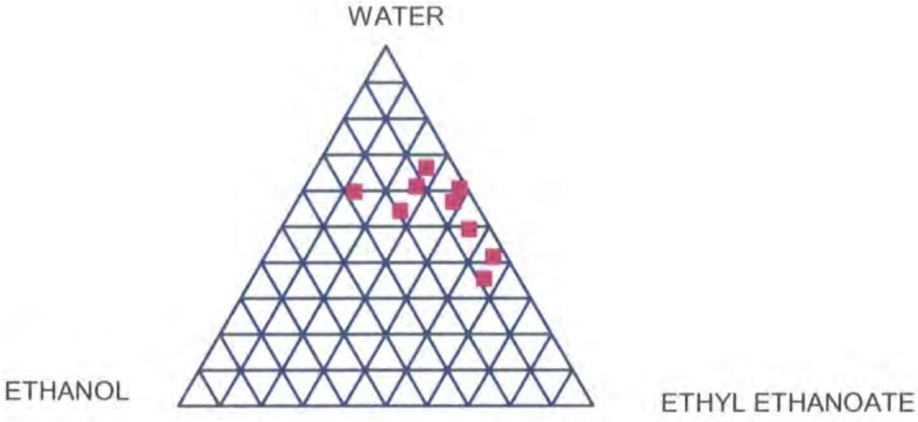


Figure 4.18 Experimental Ethanol/Ethyl Ethanoate/Water at Atmospheric Pressure

The data at 190 kPa – see figure 4.19 and table 4.8 (p142) - also show a defined trend, possibly between ethyl ethanoate and ethanol (circa 70 mol% ethyl ethanoate, 30 mol% ethanol) and a ternary azeotrope of composition 50 mol% ethyl ethanoate, 14 mol% ethanol and 36 mol% water. The results indicate that in the presence of water a ternary will be formed and so it was thought unlikely that pure ethyl ethanoate could be produced. The vapour had a relatively low concentration of ethanol and so would not be expected to be useful in removing ethanol from ethyl ethanoate-ethanol mixtures. No further work was carried out at this pressure.

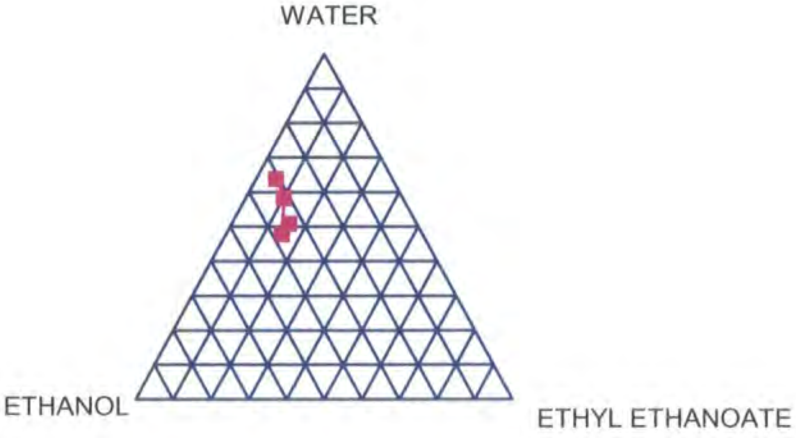


Figure 4.19 Experimental Ethanol/Ethyl Ethanoate/Water at 190 kPa

The data collected at 1240 kPa, as shown in figure 4.20 and table 4.9 (p142), demonstrate that the concentration of ethyl ethanoate in the vapour fraction can be reduced from the proposed ternary azeotrope composition. There is a well defined trend in the compositions, moving to low ethyl ethanoate concentration in the vapour. The water concentration in the vapour remains almost constant except where the ethyl ethanoate concentration is low (circa 5%) when the composition of the vapour moves toward the ethanol / water azeotrope. The ethyl ethanoate composition of the liquid fraction (see table 4.9 (p142)) is higher than that of the vapour at all feed compositions, confirming the initial findings from the binary data work that ethyl ethanoate can be separated from a mixture containing ethanol and water.

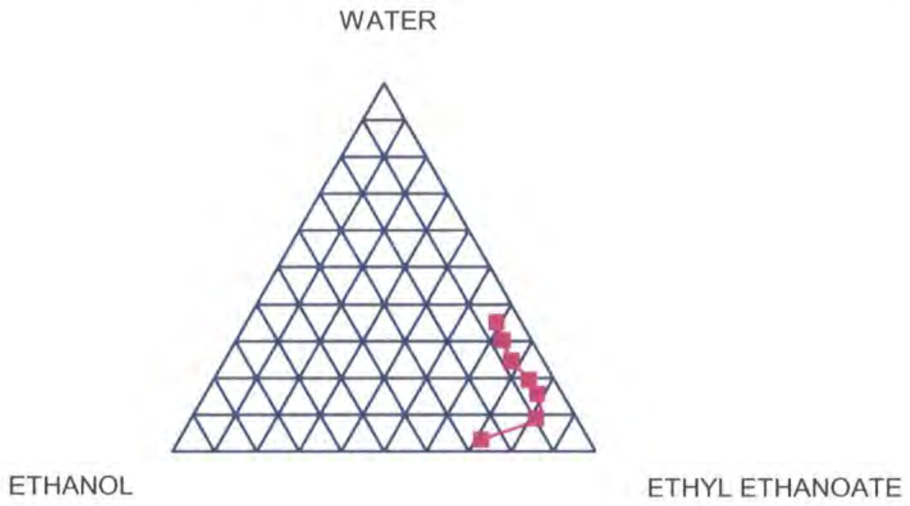


Figure 4.20 Experimental Ethanol/Ethyl Ethanoate/Water at 1240 kPa

4.2.4 Multi-component VLE

The behaviour of mixtures of many components is often different to that of ideal mixtures, and so to check reality against ideal solutions a multi-pass VLE of the product from dehydrogenation (see section 3) was carried out at atmospheric pressure.

In multi-pass VLE the liquid fraction from each run is used as the feed for the next pass. This procedure allows the tracing of components through a series of flashes that simulates a section of a real distillation column. The data from these runs is passed to Pro(II) for interpretation against the binary and ternary VLE generated in the testwork reported in section 4.2.3. Analysis of the vapour and liquid fractions from VLE was carried out by GLC and KF titration. Table 4.10 (p143) details the results of the multi-pass VLE in terms of the composition of the liquid and vapour streams from each pass. Table 4.11 (p143) details the results in terms of mol%, compared against the prediction made by Pro(II). The alpha values of each component has been calculated using ethyl ethanoate as the reference component .

The results show that the predicted and actual results for the multi-pass VLE are similar. There are no major discrepancies between the actual and predicted values for the major components. Minor components in the mixture – ethyl butanoate and 2-propyl ethanoate - do show some deviation but as the alpha values are very different to ethyl ethanoate (circa 0.2-0.3 cf 1) then these components would not be expected to interfere with purification. Low alpha values, >1, indicate a higher boiling point than the reference component, alpha values higher than 1 indicate lower boiling points. As ethyl ethanoate forms an azeotrope with ethanol, and the feed is relatively rich in ethanol compared to the azeotrope, the alpha values for all components including ethanol which has a lower boiling point compared to ethyl ethanoate, are lower than 1.

The results of the VLE testwork were used to design a distillation scheme that could be used to purify ethyl ethanoate. The distillation scheme is covered in section 4.3.

Table 4.1 Ethanol/Water at Atmospheric Pressure

	Analysis, mole%			
Temp (°C)	Liquid Fraction		Vapour Fraction	
	Ethanol	H_2O	Ethanol	H_2O
81.1	23.52	76.48	51.03	48.97
79.6	38.97	61.03	56.3	43.7
78.5	59.55	40.45	68.45	31.55

Table 4.2 Ethyl Ethanoate/Ethanol at Atmospheric Pressure

	Analysis, mole%			
Temp (°C)	Liquid Fraction		Vapour Fraction	
	Ethyl Ethanoate	Ethanol	Ethyl Ethanoate	Ethanol
NR	32.1	67.9	42.57	57.43
NR	50.15	49.85	50.79	49.21
NR	66.26	33.74	61.53	38.47

NR - not reported.

Table 4.3 Ethyl Ethanoate/Water at Atmospheric Pressure

	Analysis, mole%			
Temp (°C)	Liquid Fraction		Vapour Fraction	
	Ethyl Ethanoate	H_2O	Ethyl Ethanoate	H_2O
70.0	27.12	72.88	73.5	26.5
69.9	41.42	58.58	73.02	26.98
70.0	52.83	47.17	76.01	23.99
70.1	55.27	44.73	73	27
70.3	82.46	17.54	76.65	23.35
70.2	78.04	21.96	80.54	19.46
70.2	77.67	22.33	81.83	18.17
70.5	79.06	20.94	74.6	25.4
70.1	84	16	73.26	26.74
70.4	87.28	12.72	74.58	25.42
71.4	87.87	12.13	80.98	19.02
70.5	91.78	8.22	80.87	19.13

Table 4.4 Ethanol/Water at 1240 kPa

	Analysis, mole%			
Temp (°C)	Liquid Fraction		Vapour Fraction	
	Ethanol	H_2O	Ethanol	H_2O
160.3	80.4	19.6	79.94	20.06
160.6	74.87	25.13	75.03	24.97
161	67.59	32.41	71.71	28.29
161.1	62.19	37.81	67.51	32.49
161.1	64.55	35.45	67.9	32.1
163.7	45.26	54.74	60.45	39.55
165.9	35.87	64.13	58.06	41.94

Table 4.5 Ethyl Ethanoate/Ethanol at 1240 kPa

	Analysis, mole%			
Temp (°C)	Liquid Fraction		Vapour Fraction	
	Ethyl Ethanoate	Ethanol	Ethyl Ethanoate	Ethanol
160	4.98	95.02	4.18	95.82
160.3	9.72	90.28	10.05	89.95
161.1	29.76	70.24	23.65	76.35
161.4	35.78	64.22	30.42	69.58
161.6	36.63	63.37	31.06	68.94
164.4	51.95	48.05	41.15	58.85
167.3	67.36	32.64	56.38	43.62

Table 4.6 Ethyl Ethanoate/Water at 1240 kPa

	Analysis, mole%			
Temp (°C)	Liquid Fraction		Vapour Fraction	
	Ethyl Ethanoate	H_2O	Ethyl Ethanoate	H_2O
168.7	84.94	15.06	70.74	29.26
166.2	79.74	20.26	65.67	34.33
163.6	74.08	25.92	60.6	39.4
161.7	59.91	40.09	54.94	45.06
161	48.13	51.87	60.52	39.48
160.9	58.41	41.59	57.96	42.04
160.6	38.87	61.13	49.94	50.06
160.5	34.96	65.04	35.56	64.44
161.1	10.21	89.79	54.08	45.92
167.2	1.96	98.04	36.45	63.55

Table 4.7 Ethyl Ethanoate/Ethanol/Water at Atmospheric Pressure

	Analysis, mole%					
Temp (°C)	Liquid Fraction			Vapour Fraction		
	Ethanol	Ethyl Ethanoate	H_2O	Ethanol	Ethyl Ethanoate	H_2O
70.1	12.64	59.65	27.71	12.04	59.67	28.28
70.4	26.38	54.33	19.29	23.90	54.99	21.11
70.7	26.92	61.12	11.95	26.75	57.72	15.54
71.1	26.70	66.37	6.93	28.72	60.52	10.76
71.2	38.02	56.88	5.10	37.73	55.00	7.27
71.5	37.69	60.53	1.78	39.74	57.11	3.15
71.3	45.59	49.22	5.19	42.84	51.02	6.14
71.6	56.06	35.52	8.42	48.21	43.29	8.50
71.6	55.21	41.62	3.17	49.80	46.37	3.84

Table 4.8 Ethyl Ethanoate/Ethanol/Water at 190 kPa

	Analysis, mole%					
Temp (°C)	Liquid Fraction			Vapour Fraction		
	Ethanol	Ethyl Ethanoate	H_2O	Ethanol	Ethyl Ethanoate	H_2O
89.4	14.81	47.82	37.36	13.62	49.97	36.41
89.6	15.29	50.83	33.88	13.92	50.01	36.07
89.0	5.40	63.73	30.87	5.82	64.68	29.50
89.8	10.10	58.25	31.66	10.20	61.80	28.00

Table 4.9 Ethyl Ethanoate/Ethanol/Water at 1240 kPa

	Analysis, mole%					
Temp (°C)	Liquid Fraction			Vapour Fraction		
	Ethanol	Ethyl Ethanoate	H_2O	Ethanol	Ethyl Ethanoate	H_2O
160	71.33	3.17	25.50	71.13	4.02	24.85
159.8	81.41	9.01	9.58	77.60	10.30	12.10
159	67.80	24.50	7.70	68.55	22.38	9.07
159.5	67.82	24.73	7.45	69.11	22.61	8.27
160	62.71	30.32	6.97	65.20	26.85	7.95
159.9	62.88	30.24	6.88	65.38	26.59	8.02
159.3	58.91	35.21	5.88	62.63	30.17	7.21
159.4	74.38	19.49	6.12	74.39	18.14	7.47
89.8	78.37	15.66	5.97	77.99	15.07	6.94

Table 4.10 Multi-Component VLE Data

	Mol wt	wt% in bottoms				
		1st pass	2nd pass	3rd pass	4th pass	5th pass
Ethanol	46	60.88	63.24	65.96	67.96	69.61
2-propanol	60	3.31	3.54	3.85	4.09	4.3
Ethyl Ethanoate	88	31.24	28.44	25.23	22.54	20.21
2-butanol	74	0.74	0.84	1.01	1.15	1.28
2-propyl ethanoate	102	0.18	0.18	0.17	0.16	0.21
1-butanol	74	0.36	0.4	0.49	0.58	0.69
2-pentanol	88	0.54	0.65	0.8	0.95	1.1
Ethyl butanoate	116	0.15	0.17	0.2	0.22	0.24
Butyl ethanoate	116	0.17	0.2	0.24	0.27	0.3
	Mol wt	wt% in o/h's				
		1st pass	2nd pass	3rd pass	4th pass	5th pass
Ethanol	46	49.11	51.8	55.17	57.72	59.95
2-propanol	60	2.15	2.32	2.59	2.81	3.01
Ethyl Ethanoate	88	44.67	42.26	39.06	36.26	33.76
2-butanol	74	0.23	0.27	0.33	0.38	0.44
2-propyl ethanoate	102	0.17	0.18	0.18	0.18	0.19
1-butanol	74	0.08	0.09	0.11	0.13	0.15
2-pentanol	88	0.08	0.1	0.13	0.15	0.18
Ethyl butanoate	116	0.06	0.07	0.09	0.1	0.11
Butyl ethanoate	116	0.05	0.06	0.08	0.09	0.11

Table 4.11 Pro(II) Simulation vs. Experimental Data

	Laboratory Data					Pro(II) Simulation				
Pass Number	1	2	3	4	5	1	2	3	4	5
Mol%										
Ethanol	75.233	76.973	78.804	80.221	81.340	75.23	76.98	78.81	80.21	81.35
2-propanol	3.136	3.303	3.526	3.701	3.852	3.14	3.30	3.53	3.70	3.85
Ethyl Ethanoate	20.180	18.095	15.756	13.908	12.344	20.18	18.09	15.76	13.91	12.34
2-butanol	0.568	0.636	0.750	0.844	0.930	0.57	0.64	0.75	0.84	0.93
2-propyl ethanoate	0.100	0.099	0.092	0.085	0.111	0.10	0.10	0.09	0.09	0.11
1-butanol	0.277	0.303	0.364	0.426	0.501	0.28	0.30	0.36	0.43	0.50
2-pentanol	0.349	0.414	0.500	0.586	0.672	0.35	0.41	0.50	0.59	0.67
Ethyl butanoate	0.074	0.082	0.095	0.103	0.111	0.07	0.08	0.09	0.10	0.11
Butyl ethanoate	0.083	0.097	0.114	0.126	0.139	0.08	0.10	0.11	0.13	0.14
Temperature	73.3	74.0	74.5	74.9	75.2	74.4	74.7	75.1	75.5	75.8
Alpha Values										
Ethanol	0.56	0.55	0.54	0.54	0.52	0.59	0.57	0.55	0.54	0.53
2-propanol	0.45	0.44	0.43	0.43	0.42	0.45	0.44	0.43	0.42	0.42
Ethyl Ethanoate	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2-butanol	0.22	0.22	0.21	0.21	0.21	0.24	0.24	0.23	0.23	0.22
2-propyl ethanoate	0.66	0.67	0.68	0.69	0.54	0.65	0.65	0.65	0.65	0.65
1-butanol	0.16	0.15	0.15	0.14	0.13	0.12	0.12	0.11	0.11	0.11
2-pentanol	0.10	0.10	0.10	0.11	0.10	0.11	0.11	0.11	0.10	0.10
Ethyl butanoate	0.28	0.28	0.29	0.29	0.27	0.34	0.34	0.34	0.35	0.35
Butyl ethanoate	0.21	0.20	0.22	0.22	0.22	0.22	0.22	0.23	0.23	0.23

4.3 Distillation Of Ethyl Ethanoate From Dehydrogenation Product

4.3.1 Summary of Distillation Testwork

The separation of ethyl ethanoate from the crude dehydrogenation product was planned to be achieved by distillation. The target was to recover ethyl ethanoate at high yield (>98%) and high purity (>99.5% ethyl ethanoate). The testwork was carried out to provide a sample of ethyl ethanoate for customer testing, and to highlight any area that required further work or development. The distillation flow-scheme was developed from an evaluation carried out by DPT engineers and the author, based on the results from the VLE work and input from Pro(II), a chemical engineering development tool. Prior to distillation, the feed was subjected to a selective hydrogenation step that was used to remove aldehydes and ketones. The hydrogenation stage is described in detail in section 4.4 below (p163). The distillation scheme that was initially adopted had three main sections:

a) Light component removal at low pressure, 120 to 200 kPa, termed 'Lights Column'
b) Heavy component removal at high pressure, 720 to 930 kPa, termed 'Heavies Column'
c) A combined high and low pressure swing distillation system, set up to produce ethyl ethanoate at >99.5% purity, and an ethanol stream for recycling containing little or no ethyl ethanoate.

Two multi-purpose distillation columns were constructed to carry out these three duties - a glass column for low pressure work, and a stainless steel column for the high pressure work.

4.3.2 Lights Column Testwork (LP Column)

Due to the range of pressures at which the lights column was expected to operate, the lights removal operations were carried out in the stainless steel column. The feed to the lights column consisted of product from the partial hydrogenation reactor. Details of the testwork that produced this feed are given in Section 4.4 below (p163) This product was passed through the column at low pressure to remove low boiling components, principally DEE. Another important function of the lights column was to remove residual ethanal from the crude ethyl ethanoate stream. Ethanal is extremely reactive, and would pose a problem in the latter stages of the distillation if it was allowed to form aldolisation products such as acetaldol or crotonaldehyde. In total, 12 runs were performed within the lights column testwork. A detailed description of the distillation testwork is given below.

Run SLC/1/97 was carried out at a pressure 200 kPa, this pressure being towards the upper end of the predicted pressure range. The feed used was product from the selective hydrogenation reactor (see section 4.5) from a period of operation of 885 - 1037 hours on-line. After running at the conditions given above for 15 hours, the column temperature profile stabilised at 98°C in the overheads section and 106°C at the column bottom. A reflux ratio (see section 4.1) of approximately 80:1 was employed. At these conditions the DEE in the bottoms of the column ranged from 0.45% to 0.005%. The DEE content of the overheads settled at circa 9.7 wt%, with the ethyl ethanoate content at 57%. Small amounts of methanol were also present in the product. The results of this run can be found in Table 4.12 (p 157).

The distillation column pressure was then reduced to 120 kPa whilst maintaining the reflux rates, run SLC/2/97. After 12 hours of running the overheads temperature had fallen to 90.5°C, and the column bottoms temperature to 96.5°C. While the actual gram per hour of reflux had been maintained at the same rate as for the run SLC/1/97, the overheads take-off had increased from 2.9 to 5.9 wt% resulting in a reduction in the reflux ratio to circa 40:1. This was reflected in an increase in the methanol content of the bottoms product to 0.019 wt%. The DEE content of the overheads decreased to 7.4 wt%, while the ethyl ethanoate increased to 59.02 wt%. Over the following 3 runs, SLC/3/97 to SLC/5/97, the overheads take-off was reduced to below 1 wt%, and as low as 0.6 wt%. The actual reflux per hour remained constant at circa 1080 ghr^{-1}, which yielded an increase in the reflux ratio from 80:1 to as high as 370:1. These higher reflux conditions were maintained over the remainder of the distillation testwork. The higher reflux ratios yielded an increase in DEE content of the overheads to a maximum of 38.9%. At these levels, a large proportion of the DEE was lost to the column pressure make-up gas, and as a result the component balances for DEE through the lights column are poor. The column make-up gas was a small purge of nitrogen, used to maintain steady column pressure. The nitrogen was fed to the column at the product catchpots to avoid passing gas through the active section of the column.

A fairly typical example of the lights column separation was the final run SLC/12/97, when the overheads accounted for 0.88 wt% of the feed. DEE in the overheads levelled out at 38.9% and the ethyl ethanoate content of the overheads was at 23.0 wt%. The bottom product contained no DEE and 0.01 wt% methanol.

4.3.3 Heavies Column Testwork

The heavies column testwork was carried out in the stainless steel distillation column. The feed used was the Sasol product previously stripped of lights in the LP column. The product from the lights column was bulked into 6 containers, and given the designations shown below. The respective heavies column runs associated with the feeds are also given in this table. A total of 16 runs were performed on the heavies column.

Container Number	Lights Column Run Numbers	Heavies Column Run Numbers
1	1 - 3/97	SHC/5/97,SHC/6/97, SHC/7/97, SHC/8/97
2	4 - 5/97	SHC/10/97, SHC/11/97, SHC/12/97
3	5 - 9/97	SHC/13/97, SHC/14/97, SHC,15/97, SHC/16/97
5	10/97	SHC/4/97
7	11.97	SHC/1/97. SCH/2/97
9	12/97	SHC/3/97

The first run of the heavies column testwork was started at 930 kPa, at a feed rate of 950ghr^{-1} and a reflux rate of 1800ghr^{-1}, and a reflux ratio of approximately 2:1. Over a period of 24 hours the feed rate was decreased to 450 ghr^{-1} and the reflux reduced to 667 ghr^{-1}. The bottoms take-off rate steadied at circa 2.9 wt%. The majority of the heavy components present in the feed were removed at these conditions, but the critical components butanone and 2-propyl ethanoate were not significantly reduced in the overheads stream. In addition, two new components were produced. Both of the new components carried over into the overheads. One of the unknowns was later identified as ethyl vinyl ether. The other unknown which eluted close to butanone is still to be identified. Due to the large concentration effect on the components that appeared in the bottoms during the distillation it is not possible to identify the source of the unknowns. The low level of the unknowns, 0.023 wt% for ethyl vinyl ether and 0.050 wt% for the other unknown, makes identification difficult.

Similar conditions were used for runs SHC/2/97 to SHC/13/97 with similar results. The changing of feeds over the runs had little effect on the removal of butanone and 2-propyl ethanoate, or on the production of ethyl vinyl ether or the unknown component. Towards the end of the testwork a change in distillation pressure to 620 kPa was made in an attempt to lower the boiler temperature and therefore reduce any by-products made by thermal decomposition. The results of runs SHC/13/97 and SHC/14/97 can be compared directly as an identical feed was used for both runs, i.e. container 3, SHC/6-9/97. In general, the overheads show little difference in composition but the lower temperature reduced the concentration of ethyl vinyl ether and the unknown to 0.007 and 0.006 wt%, respectively, from 0.012 and 0.018 wt%, seen in run SHC/13/97. There was a change in the bottoms composition in that there was a greater concentration of 2-propanol and ethanol in the bottoms. The reduction in the column pressure resulted in a decrease in boiler temperature of 20°C to 212°C from 232°C.

These conditions were maintained for the remainder of the heavies column runs with similar results. These results can be found in Table 4.13 (p 159)

In general, the heavies column distillation was successful in reducing the heavies composition of the overheads product. However, a number of components that were present in the feed carried overhead into the product. 2-propyl ethanoate and butanone were not reduced significantly by the distillation, and two new components were produced - ethyl vinyl ether and the unknowns that eluted close to butanone. These compounds were found in both the bottoms and overheads, indicating that the two unknowns were due to decomposition of a reactive component or components.

4.3.4 Pressure Swing Columns

The final stage of the flow-sheeted purification of ethyl ethanoate produced from Sasol ethylol concerned the splitting of the ethanol/ethyl ethanoate/water ternary azeotrope. This was achieved by the use of two linked columns, one running at atmospheric pressure, and the other running at 1240 kPa. The linked columns worked as follows:

Overheads product from the heavies column was fed to the upper feed point of the pressure swing low pressure (PS-LP) column. The overheads, which consisted of circa 27 wt%, ethanol, 69 wt% ethyl ethanoate, 0.2 - 0.4 wt% 2-propyl ethanoate, 2% water and a number of other components was then passed to the pressure swing high pressure column (PS-HP) mid feed point. A bottoms stream of ethanol, 2-propanol and water was taken from the PS-LP column. In the PS-HP column, which was operated at 1240 kPa, the overheads stream from the PS-LP column was passed to a feed point sited in the middle of the column. The overheads from this column, which consisted of an ethyl ethanoate / ethanol azeotrope richer in ethanol than the feed from the PS-LP column, was recycled to the PS-LP column below the point where the low pressure azeotrope was formed. The difference in azeotrope concentrations resulted in excess ethyl ethanoate being removed as a bottoms product from the PS-HP column.

A total of 340 hours operation was logged with the columns coupled in one of two modes, namely close coupled - where there was a minimum inventory between the columns, and loose coupled - where a reservoir with circa 4 - 8 hours hold-up of the overhead streams was used between the columns. In both cases, careful attention to column control and operating parameters was necessary to achieve stable operation. Steady-state operation was obtained when running within the range of conditions shown below.

	Low Pressure Column	High Pressure Column
Feed rate, material ex heavies column overheads	155 - 346 g/h	
Feed rate, ex LPC overheads		128 - 187 g/h
Feed rate, ex HPC overheads	0 - 152 g/h	
Reflux rate	615 - 900 g/h	214 - 427 g/h
Reflux ratio	2.93 - 8.64	2.29 - 10.63
Pressure, kPa	0	1240
Bottoms rate	75 - 367 g/h	30 - 157.8
Overheads rate	103 - 234 g/h	39 - 185
Overheads temperature, °C	70 – 72	158 - 166
Top temperature, °C	70 – 74	162 - 197
Middle temperature, °C		164 - 179
Bottom temperature, °C	72 – 76	178 - 185

Over the 340 hours online, the highest purity ethyl ethanoate made in the pressure swing system was 99.2 wt%. The major impurity in the pure ethyl ethanoate was 2-propyl ethanoate, which accounted for up to 0.8 wt%; more typical results gave 0.4 - 0.5 wt% 2-propyl ethanoate. Other contaminants in the product ethyl ethanoate were ethanol at circa 500 ppm, di-n-propyl ether which was present in the feed, butanone and the unknown component eluting close to butanone that had been made in the heavies column. In addition, there were a number of other minor components that were present in the feed ethylol which proved difficult to separate.

The data in Table 4.14 (p 163) relate to a 24 hour period where the operation of the column was most stable, and where the purity of the ethyl ethanoate reached a peak. During the majority of the remaining testwork the purity of ethyl ethanoate was in the range 98 - 99%. At one point during the distillation work, the purity of the ethyl ethanoate rose to 99.35 wt%. This was achieved by allowing the ethyl ethanoate content of the PS-LP column bottoms to rise to a concentration of 3 - 4 wt%. Under these conditions an amount of 2-propyl ethanoate was also found in the PS-LP column bottoms. This mode of operation was not seen as sustainable, due to the loss of ethyl ethanoate, and so was discontinued.

After the 340 hours on-line, a total of 30 litres of impure ethyl ethanoate had been collected at an average purity of 98.5 wt%. The major impurities were ethanol, 2-propyl ethanoate, di-n-propyl ether and a range of unknowns that were present in the feed. Clearly, the ethyl ethanoate did not meet the target specifications laid down at the beginning of the testwork. In order to meet the specification a post-distillation on the product was required. This post-distillation is detailed in Section 4.3.5 below.

4.3.5 Post Distillation Of Ethyl Ethanoate Product

The product from the original ethyl ethanoate distillation flowsheet did not meet the specifications for ethyl ethanoate purity. In order to meet the specifications, a series of two post distillations were carried out, based on a Pro(II) model made from data from the multi-pass VLE work reported in section 4.2, indicating that the majority of the heavy components, especially 2-propyl ethanoate, could be removed by distillation at high pressure. High pressure distillation testwork had been performed to simulate the original flowsheet, but this distillation had been carried out in the presence of high concentrations of ethanol, and for this reason did not remove significant quantities of 2-propyl ethanoate.

The heavies distillation column was set up at the conditions listed below.

Column pressure, kPa	-	1240
Feed rate, ghr^{-1}	-	190
Reflux rate, ghr^{-1}	-	1050
Overheads take-off, ghr^{-1}	-	175.0
Reflux ratio	-	6:1
Bottoms take-off, ghr^{-1}	-	15.0

At these conditions the 2-propyl ethanoate present in the feed was concentrated in the bottoms product. A typical feed to this column contained 0.62 wt% 2-propyl ethanoate. After distillation the overheads contained 0.06 - 0.08 wt% 2-propyl ethanoate while the bottoms contained 4 - 7 wt%. In addition, many of the components that had carried through from the feed were also removed in the bottoms product. Table 4.15 (p 164) gives typical data from this stage of the post distillation.

The overhead product from this first post distillation did not yet meet the specification ethyl ethanoate purity of 99.5 wt%. The main contaminants were now ethanol, 2-propyl ethanoate and ethyl vinyl ether. The product also contained the di-n-propyl ether present in the feed, circa 170 ppm of butanone and 150 ppm of the unknown co-produced with ethyl vinyl ether. In order to produce 99.5% ethyl ethanoate the bulked overhead products were processed in a topping column. The column was operated at the following conditions.

Pressure - Atmospheric
Feed rate, ghr^{-1} - 220
Reflux, ghr^{-1} - 800
Bottoms, ghr^{-1} - 185
Overheads, ghr^{-1} - 35

The bulked product analysis is given in Table 4.16 (p 164). The analysis shows a purity of 99.7 wt%, ethyl ethanoate with approximately 140 ppm butanone.

4.3.6 Column Calibration

The columns used for the refining demonstration were calibrated using standard test mixtures taken from the literature. The low pressure (LP) glass column was calibrated at atmospheric pressure using a mixture of ethyl benzene / chlorobenzene. The high pressure (HP) stainless steel column was calibrated at 1240 kPa using an ethanol/methanol mixture. Calibration of the LP column was carried out using a 50:50 mol% mixture of chlorobenzene/ethyl benzene at atmospheric pressure and under total reflux. On reaching steady state conditions the temperatures of the overheads and bottoms streams were noted and samples were taken from the overheads and bottoms. These were analysed with a gas chromatograph and the separation ratio q determined from the formula:

$$\text{Separation ratio } q = \frac{x_a}{1 - x_a} \Big/ \frac{x_b}{1 - x_b}$$

Where x_a = Mol fraction of more volatile component in overheads, and x_b = mole fraction of more volatile component in bottoms. The relative volatility, alpha, was determined from literature data and the number of theoretical stages (NTS) calculated according to the Fenske equation:

$$\text{NTS} = \frac{\text{Ln } q}{\text{Ln } I}$$

A series of tests was performed using varying boil-up rates. These showed that up to 44 theoretical stages were developed, decreasing as the gas load was increased. Calibration of the HP column was carried out at 1240 kPa using a mixture of ethanol/methanol, followed the same general procedure as for the LP column. Results showed a maximum of approximately 29 theoretical stages being developed; again, this number was reduced as gas load increased. The overall results of the calibrations are consistent with performance reported by the packing supplier.

4.3.7 Summary and discussion of VLE and Distillation Testwork

Lights removal testwork was carried out over a range of pressures from 120 kPa to 200 kPa, with the aim of removing light components such as diethyl ether, while minimising ethanol and ethyl ethanoate losses. The testwork was carried out in the stainless steel column, in order that the work at 200 kPa could be performed. The bottoms product from the lights column typically contained <50 ppm of diethyl ether (DEE), while the overheads contained from 6 to 39% DEE. At high DEE concentration the percentage of feed taken as overheads was in the region of 0.5 - 0.7 wt%.

The heavies column work was carried out at elevated pressures, between 720 and 930 kPa, using the stainless steel column. These pressures were selected to effect the partial separation of a number of "heavy" components, such as 2-propyl ethanoate and butanone, that would not separate from ethyl ethanoate at atmospheric pressure. The main product from the heavies column was taken as an overheads stream, and the heavy components as a small, circa 3 - 5 wt%, bottoms stream. The high distillation pressure required high operating temperatures to volatilise the distillation feed, especially in the reboiler. These high temperatures caused a number of side reactions to occur, leading to the formation of a number of by-products, the most notable being vinyl ethyl ether and a new component that eluted between butanone and 2-butanol. This new component carried through to the final ethyl ethanoate product.

The overhead product from the heavies column was used as feed to the ethyl ethanoate pressure swing section of the refining flowsheet. This section consisted of the low and high pressure columns linked together in a pressure swing configuration. The aim of the testwork was to produce two streams of bottoms product. The first was ethyl ethanoate at >99.5% purity from the high pressure column, the second was an ethanol/2-propanol/water stream, free of ethyl ethanoate. The purity of the ethyl ethanoate product was dictated by the amount of 2-propyl ethanoate that was passed from the heavies column. The product ethyl ethanoate from the original four column distillation concept only reached a maximum of 99.1 wt% purity. In addition, the specification for butanone content was exceeded due to a number of factors that are detailed in later sections of this report. In order to produce ethyl ethanoate of the required purity, further distillation of the ethyl ethanoate product was carried out. The ethyl ethanoate was “topped and tailed”, giving a product of 99.7% ethyl ethanoate.

The topping and tailing did not significantly reduce the butanone content of the product ethyl ethanoate which remained at circa 110 ppm. Following the distillation testwork, examination of the operations and data from each column suggested an alternative distillation scheme. This scheme involved the amalgamation of the lights, heavies and LP columns into a single unit. The HP side of the pressure swing system remained unchanged. A demonstration of the concept was carried out, and the results obtained were close to those obtained from a Pro(II) simulation of the new concept. Using product from Sasol ethylol feed, a purity of 99.6 wt% ethyl ethanoate was obtained from these two columns. This compares to 99.1 wt% at a similar stage using the four column concept. Further Pro(II) studies have indicated that purities in excess of the 99.8 wt% required in the most recent specification supplied by Sasol are achievable.

Further work-up of the product from the original four column flowsheet yielded product that met the specification in all respects.

				SLC/3/97			SLC/4/97			SLC 5/97			SLC/6/97			SLC/7/97		
	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS
Ethanal	0.006	0.21	0.005	0.006	0.251	0.005	0.004	0.302	0.003	0.004	0.355	0.004	0.004	0.397	0.003	0.004	0.389	0.004
Methanol	0.038	0.562	0.019	0.038	0.527	0.007	0.034	0.777	0.006	0.035	1.531	0	0.035	1.888	0.009	0.035	2.410	0.009
Methyl formate	0.005	0.032	0	0.005	0.054	0	0.009	0.134	0.000	0.007	0.265	0.009	0.007	0.3	0	0.007	0.346	0.000
Diethyl ether	0.736	7.448	0	0.736	10.318	0	0.408	14.179	0.000	0.463	21.244	0	0.463	26.761	0	0.469	33.446	0.000
Ethanol	65.64	23.802	69.226	65.64	21.322	66.705	57.874	17.591	59.497	59.461	12.432	59.975	59.461	9.912	60.147	59.561	7.334	60.172
Propanone	0.007	0	0	0.007	0	0	0.000	0.000	0.000	0	0	0	0	0	0	0.000	5.011	0.000
2-propanol	3.16	0.295	3.41	3.16	0.332	3.255	3.058	0.592	3.127	3.087	1.277	3.133	3.087	1.564	3.141	3.103	1.993	3.131
Methyl ethanoate	0	0.028	0	0	0.037	0	0.002	0.078	0.000	0.001	0.163	0	0.001	0.197	0	0.001	0.247	0.000
Di-2-propyl ether	0.098	1.357	0	0.098	1.623	0	0.109	2.737	0.000	0.103	5.768	0	0.103	7.013	0	0.102	9.049	0.000
n-propanol	0.017	0.123	0.018	0.017	0.145	0.016	0.019	0.237	0.019	0.019	0.518	0.02	0.019	0.607	0.019	0.020	0.842	0.019
Ethyl ethanoate	26.4	59.015	23.582	26.4	53.41	23.971	34.759	50.414	33.680	32.85	44.628	33.07	32.85	35.131	32.864	32.697	26.476	32.833
Butanone	0.009	0.001	0.01	0.009	0.002	0.009	0.000	0.001	0.000	0.002	0	0	0.002	0	0.002	0.001	0.002	0.001
2-Butanol	0.625	0.05	0.674	0.625	0.059	0.649	0.652	0.099	0.675	0.728	0	0.745	0.728	0	0.747	0.743	0.002	0.752
2-propyl ethanoate	0.21	0.447	0.196	0.21	0.447	0.188	0.288	0.440	0.282	0.26	0.497	0.26	0.26	0.368	0.261	0.257	0.217	0.259
2-Pentanone	0	0.002	0.007	0	0.003	0.006	0.012	0.004	0.013	0.016	0.006	0.017	0.016	0.006	0.017	0.016	0.005	0.009
n-Butanol	0.621	0	0.673	0.621	0.003	0.027	0.319	0.003	0.340	0.438	0.006	0.451	0.438	0.005	0.448	0.446	0.004	0.451
2-Pentanol	0	0.037	0.411	0	0.041	0.4	0.48	0.045	0.49	0.468	0.061	0.48	0.468	0.048	0.481	0.473	0.027	0.486
2-Butyl Ethanoate	0	0.004	0.055	0	0.005	0.051	0.061	0.004	0.071	0.065	0.012	0.062	0.065	0.002	0.059	0.057	0.004	0.058
Ethyl butanoate	0.109	0	0.118	0.109	0	0.114	0.143	0.000	0.147	0.14	0	0.143	0.14	0	0.144	0.141	0.000	0.143
Butyl ethanoate	0.128	0.004	0.139	0.128	0	0.133	0.140	0.000	0.145	0.141	0	0.145	0.141	0	0.145	0.143	0.000	0.145
2-Hexanone	0	0	0.007	0	0	0.006	0.008	0	0.006	0.007	0	0.007	0.007	0	0.007	0.007	0	0.007
2-Hexanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Di-n-Butyl ether	0	0	0.017	0	0	0.039	0.025	0	0.026	0.021	0	0.022	0.021	0	0.021	0.021	0	0.021
n-Hexanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2-heptanone	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
n-Heptanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	1.45	5.48	1.2	1.45	9.71	3.35	1.280	9.210	1.260	1.36	5.12	1.25	1.36	8.68	1.27	1.380	8.400	1.270
Light Unknowns	0.098	0.752	0.006	0.098	0.026	0.005	0.012	0.083	0.000	0.005	0.125	0	0.005	0.143	0.002	0.005	0.150	0.002
Heavy Unknowns	0.643	0.351	0.227	0.643	1.685	1.064	0.304	3.070	0.213	0.319	5.992	0.207	0.319	6.978	0.213	0.311	3.646	0.228
Total	100	100	100	100	100	100	100.00	100.00	100.00	100	100	100	100	100	100	100.00	100.00	100.00
Weight, grams	6055	338	5378	6046.4	272.4	5561.7	6067.4	154.4	5707	5974	45.4	5805.2	6050	44.9	5799.1	6009	34.8	5801.9
Reflux, gHr-1 =	1080	Reflux Ratio=	38	1080	Reflux Ratio=	48	1080	Reflux Ratio=	84	1080	Reflux Ratio=	283	1080	Reflux Ratio=	289	1080	Reflux Ratio=	372

	SLC 8/97			SLC/9/97			SLC/10/97			SLC/11/97			SLC/12/97		
	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS
Ethanal	0.004	0.33	0.003	0.004	0.323	0.004	0.004	0.293	0.004	0.005	0.25	0.003	0.045	0.847	0.004
Methanol	0.035	2.363	0.009	0.035	2.586	0.009	0.034	2.733	0.009	0.034	2.531	0.008	0.034	2.338	0.009
Methyl formate	0.007	0.366	0	0.007	0.38	0	0.007	0.397	0.000	0.007	0.422	0	0.007	0.365	0
Diethyl ether	0.469	35.192	0.002	0.469	37.037	0	0.409	38.761	0.000	0.571	38.77	0	0.548	38.942	0
Ethanol	59.691	5.952	60.319	59.691	6.764	60.201	59.508	5.861	60.147	58.771	6.3	59.538	60.041	6.098	60.698
Propanone	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0	0	0	0
2-propanol	3.104	2.036	3.159	3.104	2.16	3.129	3.082	2.313	3.120	3.087	2.2	3.097	3.039	2.06	3.067
Methyl ethanoate	0.001	0.259	0	0.001	0.277	0	0.001	0.294	0.000	0.0032	0.29	0	0.0022	0.262	0
Di-2-propyl ether	0.102	9.354	0	0.102	9.995	0	0.103	10.680	0.000	0.103	10.173	0	0.101	9.496	0
n-propanol	0.02	0.82	0.02	0.02	0.881	0.019	0.020	0.999	0.019	0.02	0.94	0.019	0.019	0.847	0.019
Ethyl ethanoate	32.697	0.881	32.628	32.697	25.219	32.765	33.127	22.387	33.059	33.136	23.81	33.237	31.972	23.033	32.143
Butanone	0.001	0.003	0.001	0.001	0	0.001	0.005	0.003	0.005	0.024	0.003	0.017	0.028	0.002	0.028
2-Butanol	0.742	0.003	0.763	0.742	0.002	0.751	0.683	0.004	0.696	0.811	0.002	0.821	0.764	0.002	0.775
2-propyl ethanoate	0.257	0.165	0.258	0.257	0.188	0.259	0.266	0.143	0.266	0.254	0.173	0.255	0.243	0.188	0.245
2-Pentanone	0.016	0.004	0.009	0.016	0.004	0.017	0.031	0.003	0.03	0.045	0.004	0.045	0.052	0.004	0.053
n-Butanol	0.446	0.003	0.457	0.446	0.003	0.452	0.420	0.002	0.426	0.496	0.002	0.5	0.505	0.003	0.51
2-Pentanol	0.473	0.019	0.49	0.473	0.021	0.48	0.454	0.016	0.462	0.485	0.019	0.489	0.454	0.022	0.457
2-Butyl Ethanoate	0.057	0.003	0.058	0.057	0.003	0.058	0.058	0.002	0.059	0.058	0.003	0.059	0.056	0.004	0.06
Ethyl butanoate	0.141	0	0.144	0.141	0	0.142	0.134	0.000	0.136	0.155	0	0.157	0.146	0	0.149
Butyl ethanoate	0.142	0	0.146	0.142	0	0.144	0.133	0.000	0.135	0.159	0	0.16	0.15	0	0.174
2-Hexanone	0.007	0	0.007	0.007	0	0.007	0	0	0.006	0.007	0	0.008	0.006	0	0.007
2-Hexanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Di-n-Butyl ether	0.021	0	0.021	0.021	0	0.021	0.022	0	0.022	0.02	0	0.021	0.018	0	0.019
n-Hexanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2-heptanone	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
n-Heptanol	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	1.38	11.47	1.28	1.38	4.7	1.32	1.210	4.460	1.190	1.43	3.6	1.33	1.44	3.94	1.36
Light Unknowns	0.005	0.168	0.002	0.005	0.161	0.002	0.004	0.170	0.014	0.042	0.219	0.002	0.005	0.167	0.003
Heavy Unknowns	0.182	30.609	0.224	0.182	9.296	0.219	0.285	10.479	0.195	0.2768	10.289	0.234	0.3248	11.38	0.22
Total	100	100	100	100	100	100	100.00	100.00	100.00	100	100	100	100	100	100
Weight, grams	5959	52	5788.4	4902.8	32.9	4748.6	6778.7	47.6	6731.1	7446.6	84.5	7362.1	5963.1	52.4	5910.7
Reflux, gHr-1 =	1080	Reflux Ratio=	249	1080	Reflux Ratio=	323	1080	Reflux Ratio=	329	1080	Reflux Ratio=	129	1080	Reflux Ratio=	256

Table 4.13 Heavies Column Data

	SHC/1/97			SHC/2/97			SHC/3/97			SHC/4/97			SHC/5/97			SHC/6/97		
	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS
Ethanal	0.043	0.066	0.011	0.043	0.065	0.007	0.003	0.031	0.010	0.035	0.056	0.012	0.004	0.033	0.018	0.004	0.033	0.021
Methanol	0.008	0.009	0	0.008	0.009	0	0.009	0.010	0.000	0.01	0.01	0	0.008	0.009	0	0.008	0.009	0.000
Methyl formate	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0	0	0	0	0.000	0.000	0.000
Diethyl ether	0	0	0	0	0	0	0.000	0.013	0.000	0.009	0.008	0	0	0	0	0.000	0.000	0.000
Ethanol	59.085	60.842	0.517	59.085	61.099	0.463	60.885	62.301	0.692	62.196	63.671	0.873	67.331	68.572	1.903	67.331	69.117	2.306
Propanone	0	0	0	0	0.003	0	0.000	0.000	0.000	0.011	0.012	0	0	0	0	0.000	0.000	0.000
2-propanol	3.23	3.32	0.212	3.23	3.342	0.215	3.075	3.144	0.262	3.052	3.131	0.328	3.324	3.365	0.607	3.324	3.397	0.748
Methyl ethanoate	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0	0	0	0	0.000	0.000	0.000
Di-2-propyl ether	0	0	0	0	0	0	0.000	0.003	0.000	0.003	0.003	0	0.003	0	0	0.003	0.000	0.000
n-propanol	0	0	0	0	0	0	0.000	0.003	0.000	0.011	0.002	0.318	0.019	0.001	0.382	0.019	0.000	0.446
Ethyl ethanoate	33.468	33.828	15.874	33.468	33.776	17.329	32.247	32.555	16.044	31.455	31.27	14.896	25.521	26.188	10.637	25.521	25.636	8.987
Butanone	0.017	0.016	0.028	0.017	0.017	0.031	0.029	0.026	0.045	0.006	0.031	0.021	0.008	0.007	0.014	0.008	0.008	0.016
2-Butanol	0.561	0.007	20.71	0.561	0.008	19.028	0.776	0.006	20.606	0.477	0.006	21.583	0.66	0.006	22.206	0.660	0.005	22.714
2-propyl ethanoate	0.262	0.218	2.269	0.262	0.215	2.01	0.246	0.209	1.716	0.218	0.194	1.418	0.202	0.192	1.022	0.202	0.186	0.872
2-Pentanone	0.045	0.003	1.57	0.045	0.003	1.603	0.053	0.003	1.685	0.026	0.003	1.597	0.038	0.005	1.273	0.038	0.005	1.33
n-Butanol	0.213	0.013	5.405	0.213	0.015	4.842	0.513	0.017	6.869	0.277	0.012	6.61	0.621	0.017	7.841	0.621	0.018	9.219
2-Pentanol	0.385	0.005	13.359	0.385	0.004	13.057	0.466	0.005	13.581	0.317	0.005	14.299	0.413	0.003	14.958	0.413	0.002	15.207
2-Butyl Ethanoate	0.134	0.004	6.635	0.134	0.003	7.781	0.058	0.006	6.289	0.055	0.002	6.122	0.053	0.002	5.946	0.053	0.002	4.954
Ethyl butanoate	0.137	0	4.609	0.137	0.003	4.613	0.150	0.000	4.778	0.097	0	4.721	0.12	0	4.753	0.120	0.000	4.781
Butyl ethanoate	0.275	0	11.628	0.275	0	11.258	0.155	0.000	10.960	0.137	0	10.631	0.14	0	9.914	0.140	0.000	8.711
2-Hexanone	0.007	0	0.226	0.007	0	0.23	0.01	0	0.811	0.016	0	0.889	0.021	0	0.894	0.021	0	0.89
2-Hexanol	0.006	0	0.087	0.006	0.002	0.096	0.003	0	0.086	0.002	0	0.114	0.002	0	0.125	0.002	0	0.164
Di-n-Butyl ether	0.083	0	3.564	0.083	0.004	4.223	0.019	0	3.315	0.025	0	3.228	0.017	0	3.632	0.017	0	3.284
n-Hexanol	0.017	0	0.576	0.017	0	0.583	0.017	0	0.58	0.012	0	0.629	0.014	0	0.643	0.014	0	0.631
2-heptanone	0.002	0	0.055	0.002	0.01	0.06	0.002	0	0.06	0.006	0	0.075	0.002	0	0.091	0.002	0	1.449
n-Heptanol	0.014	0	0.592	0.014	0	0.551	0	0	0.62	0	0	0.582	0	0	0.736	0	0	0.956
Water	1.56	1.53	0.09	1.56	1.21	0.09	1.020	1.550	0.110	1.39	1.48	0.11	1.31	1.41	0.08	1.310	1.380	0.100
Light Unknowns	0.018	0.023	0.006	0.018	0.023	0.006	0.002	0.016	0.009	0.004	0.012	0.008	0.004	0.028	0.02	0.004	0.032	0.020
Heavy Unknowns	0.43	0.116	11.977	0.43	0.189	11.924	0.262	0.102	10.872	0.153	0.092	10.936	0.165	0.162	12.305	0.165	0.170	12.194
Total	100	100	100	100	100	100	100.00	100.00	100.00	100	100	100	100	100	100	100.00	100.00	100.00
Weight, grams	1780	1736.3	51.4	3196.4	3091.4	92	5750.85	5554.5	165.6	7268.5	7124.1	140.3	5340	5171.2	124.2	5309.9	5158.8	123.5

	Feed= EX SLC/1-3/97			Feed= EX SLC/1-3/97			Feed= EX SLC/4-5/97			Feed= EX SLC/4-5/97			Feed= EX SLC/4-5/97			Feed=EX SLC/4-5/97		
	SHC/7/97			SHC/8/97			SHC/9/97			SHC/10/97			SHC/11/97			SHC/12/97		
	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS
Ethanal	0.004	0.033	0.021	0.004	0.034	0.024	0.003	0.029	0.015	0.003	0.03	0.016	0.003	0.028	0.010	0.003	0.028	0.011
Methanol	0.008	0.009	0	0.008	0.009	0.000	0.007	0.008	0	0.007	0.008	0	0.007	0.008	0.000	0.007	0	0.01
Methyl formate	0	0	0	0.000	0.000	0.000	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0
Diethyl ether	0	0	0	0.000	0.000	0.000	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0
Ethanol	67.331	69.04	2.285	67.331	69.056	2.279	60.877	63.007	1.106	60.877	62.975	1.122	60.877	62.686	0.729	60.877	62.932	0.861
Propanone	0	0	0	0.000	0.000	0.000	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0.02
2-propanol	3.324	3.383	0.73	3.324	3.388	0.737	3.132	3.239	0.394	3.132	3.229	0.398	3.132	3.243	0.305	3.132	3.232	0.327
Methyl ethanoate	0	0	0	0.000	0.000	0.000	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0
Di-2-propyl ether	0.003	0	0	0.003	0.000	0.000	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0.041
n-propanol	0.019	0	0.449	0.019	0.001	0.455	0.018	0.004	0.385	0.018	0.004	0.39	0.018	0.004	0.368	0.018	0.003	0.365
Ethyl ethanoate	25.521	25.725	8.831	25.521	25.570	8.827	32.085	31.995	14.595	32.085	31.947	14.692	32.085	32.532	16.922	32.085	32.44	17.651
Butanone	0.008	0.007	0.016	0.008	0.007	0.015	0	0	0.008	0	0.003	0.008	0.000	0.017	0.006	0	0.017	0.006
2-Butanol	0.66	0.005	22.613	0.660	0.005	22.776	0.704	0.006	21.881	0.704	0.006	22.065	0.704	0.006	22.025	0.704	0.004	21.595
2-propyl ethanoate	0.202	0.185	0.865	0.202	0.184	0.869	0.256	0.202	1.51	0.256	0.203	1.521	0.256	0.209	1.893	0.256	0.204	1.951
2-Pentanone	0.038	0.005	1.103	0.038	0.004	1.11	0.009	0.003	0.16	0.009	0.003	1.088	0.009	0.003	0.215	0.009	0.003	0.772
n-Butanol	0.621	0.021	9.574	0.621	0.019	9.409	0.44	0.012	7.902	0.44	0.012	7.961	0.440	0.017	7.547	0.44	0.012	7.354
2-Pentanol	0.413	0.002	15.218	0.413	0.003	15.333	0.475	0.004	15.327	0.475	0.005	15.461	0.475	0.004	15.242	0.475	0.005	14.824
2-Butyl Ethanoate	0.053	0.003	4.913	0.053	0.003	4.905	0.059	0.004	4.946	0.059	0.004	4.909	0.059	0.005	4.961	0.059	0.004	4.856
Ethyl butanoate	0.12	0	4.794	0.120	0.000	4.705	0.141	0.014	4.809	0.141	0	4.847	0.141	0.000	4.756	0.141	0	4.652
Butyl ethanoate	0.14	0	8.676	0.140	0.000	8.696	0.161	0	8.99	0.161	0	9.06	0.161	0.000	9.164	0.161	0	8.99
2-Hexanone	0.021	0	0.903	0.021	0	0.29	0.025	0	0.839	0.025	0	0.234	0.025	0	0.844	0.025	0	0.307
2-Hexanol	0.002	0	0.095	0.002	0	0.102	0	0	0.106	0	0	0.084	0	0	0.085	0	0	0.074
Di-n-Butyl ether	0.017	0	3.275	0.017	0	3.244	0.022	0	2.742	0.022	0	2.728	0.022	0	2.574	0.022	0	2.567
n-Hexanol	0.014	0	0.776	0.014	0	0.789	0.02	0	0.67	0.02	0	0.647	0.02	0	0.679	0.02	0	0.423
2-heptanone	0.002	0	0.092	0.002	0	0.078	0.001	0	0.719	0.001	0	0.722	0.001	0	0.429	0.001	0	0.434
n-Heptanol	0	0	0.991	0	0	1.017	0	0	0.718	0	0	0.726	0	0	0.733	0	0	0.711
Water	1.31	1.38	0.11	1.310	1.380	0.100	1.36	1.39	0.11	1.36	1.47	0.05	1.360	1.170	0.050	1.36	1.04	0.06
Light Unknowns	0.004	0.031	0.022	0.004	0.033	0.022	0	0.014	0.013	0	0.014	0.013	0.000	0.014	0.013	0	0.014	0.013
Heavy Unknowns	0.165	0.171	13.648	0.165	0.304	14.218	0.205	0.069	12.055	0.205	0.087	11.258	0.205	0.054	10.450	0.205	0.062	11.125
Total	100	100	100	100.00	100.00	100.00	100	100	100	100	100	100	100.00	100.00	100.00	100	100	100
Weight, grams	5630.6	5428.9	130.3	4142.6	3960.8	94.3	5644.6	5455.5	152.6	5260	5126.8	150.5	5444	5276.4	157.95	4813.4	4579.7	139.1

Table 4.13 (continued)

	Feed= EX SLC/6-9/97			Feed = EX SLC/6-9/97			Feed = EX SLC/6-9/97			Feed = EX SLC/6-9/97		
Ethanal	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS	Feed	O/H's	BTMS
Methanol	0.004	0.027	0.011	0.004	0.028	0.002	0.004	0.025	0.003	0.004	0.009	0.002
Methyl formate	0.009	0.009	0	0.009	0.009	0	0.009	0.008	0.000	0.009	0	0
Diethyl ether	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0
Ethanol	0.002	0.002	0	0.002	0.002	0	0.002	0.002	0.000	0.002	0.002	0
Propanone	60.289	62.034	0.811	60.289	61.924	3.846	60.289	62.110	4.525	60.289	62.139	4.087
2-propanol	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0
Methyl ethanoate	3.134	3.221	0.311	3.134	3.156	3.846	3.134	3.175	1.901	3.134	3.187	1.728
Di-2-propyl ether	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0
n-propanol	0	0	0	0	0	0	0.000	0.000	0.000	0	0	0
Ethyl ethanoate	0.019	0.004	0.37	0.019	0	0.49	0.019	0.000	0.558	0.019	0	0.519
Butanone	32.831	32.847	18.699	32.831	32.937	17.133	32.831	32.933	18.339	32.831	32.889	17.306
2-Butanol	0.002	0.001	0.005	0.002	0.001	0.006	0.002	0.004	0.006	0.002	0.001	0.006
2-propyl ethanoate	0.749	0.006	22.664	0.749	0	27.604	0.749	0.000	23.279	0.749	0.004	27.713
2-Pentanone	0.26	0.207	1.993	0.26	0.219	1.501	0.260	0.218	1.574	0.26	0.22	1.49
n-Butanol	0.017	0.003	0.624	0.017	0.004	0.626	0.017	0.005	0.645	0.017	0.005	0.603
2-Pentanol	0.452	0.012	5.675	0.452	0.019	8.555	0.452	0.019	9.930	0.452	0.019	9.276
2-Butyl Ethanoate	0.486	0.005	15.353	0.486	0.006	13.547	0.486	0.006	14.997	0.486	0.006	13.996
Ethyl butanoate	0.06	0.004	5.008	0.06	0.004	3.423	0.06	0.006	3.07	0.06	0.005	2.885
Butyl ethanoate	0.151	0	4.82	0.151	0	4.147	0.151	0.000	4.609	0.151	0	4.319
2-Hexanone	0.167	0	9.303	0.167	0	6.79	0.167	0.000	6.837	0.167	0	6.391
2-Hexanol	0.026	0	0.862	0.026	0	0.747	0.026	0	0.832	0.026	0	0
Di-n-Butyl ether	0	0	0.074	0	0	0.079	0	0	0.039	0	0	0.04
n-Hexanol	0.022	0	2.597	0.022	0	1.926	0.022	0	0.834	0.022	0	0.77
2-heptanone	0.02	0	0.676	0.02	0	0.575	0.02	0	0.614	0.02	0	0.292
n-Heptanol	0.002	0	0	0.002	0	0.638	0.002	0	0.072	0.002	0	0.638
Water	0	0	0.533	0	0	0.257	0	0	0.275	0	0	0.257
Light inks	1.04	1.52	0.14	1.04	1.58	0.03	1.040	1.390	0.040	1.04	1.48	0.05
Heavy Unknowns	0	0.012	0.01	0	0.007	0.014	0.000	0.007	0.016	0	0.007	0.014
Total	0.258	0.086	9.461	0.258	0.104	4.218	0.258	0.092	7.005	0.258	0.027	7.618
Weight, grams										100	100	100
Reflux, gHr-1 =										3536	3395.2	112.6
	665.00	Reflux Ratio=	1.53	665.00	Reflux Ratio=	1.54	665.00	Reflux Ratio=	1.54	665.00	Reflux Ratio=	1.54

Table 4.14 Pressure Swing Column Data

	12.30 5/10/97					15.30 5/12/97					18.30 5/10/97					21.30 5/10/97				
	Feed	LP Botts	LP OHS	HP Botts	HP OHS	Feed	LP Botts	LP OHS	HP Botts	HP OHS	Feed	LP Botts	LP OHS	HP Botts	HP OHS	Feed	LP Botts	LP OHS	HP Botts	HP OHS
Ethanal	0.065	0.053	0.310	0.000	0.839	0.065	0.068	0.288	0	0.92	0.065	0.057	0.310	0.004	0.875	0.065	0.054	0.342		0.874
Methanol	0.006	0.000	0.067	0.000	0.164	0.006	0	0.071	0	0.187	0.006		0.067	0.000	0.178	0.006		0.093		0.189
Diethyl ether	0.007	0.000	0.012	0.000	0.022	0.007	0	0.01	0	0.025	0.007		0.013	0.000	0.030	0.007		0.014		0.025
Light Unk (14.95 min)	0.013	0.000	0.112	0.000	0.230	0.013	0	0.112		0.259	0.013		0.110	0.000	0.253	0.013		0.117		0.244
Ethanol	63.772	93.235	26.678	0.209	68.785	63.772	92.731	24.974	0.243	66.189	63.772	93.119	27.617	0.341	65.898	63.772	93.251	28.376	0.079	65.006
Propanone	0.014	0.000	0.012	0.000	0.027	0.014	0	0.012	0	0.028	0.014		0.013	0.000	0.032	0.014		0.004		0.03
2-Propanol	2.979	4.430	0.008	0.000	0.009	2.979	4.387	0.0018	0.005	0	2.979	4.755	0.016	0.000	0.061	2.979	4.379	0.054		0.01
Methyl Ethanoate		0.000	0.016	0.000	0.051		0	0.006	0	0.042			0.020	0.000	0.047			0.022		0.047
Di-2-propyl ether		0.000	0.000	0.000	0.000		0	0	0	0			0.000	0.000	0.004					0.003
n-Butyradehyde		0.000	0.000	0.000	0.000		0	0	0	0			0.000	0.000	0.000					
Ethyl ethanoate	31.456	0.010	69.802	98.706	24.324	31.456	0.839	71.275	98.956	25.594	31.456	0.030	68.644	98.907	26.122	31.456	0.186	67.896	99.143	26.888
Butanone	0.007	0.000	0.000	0.004	0.000	0.007	0	0	0.002	0	0.007		0.001	0.000	0.000	0.007		0.002	0.000054	0
Heavy unk (27.5 min)	0.026	0.000	0.065	0.030	0.077	0.026	0	0.061	0.028	0.069	0.026		0.054	0.028	0.064	0.026		0.047	0.029	0.063
2-Butanol	0.000	0.000	0.000	0.008	0.000	0	0	0	0.006	0	0.000		0.002	0.006	0.000	0		0	0.005	0
Heavy unk (29.22 min)	0.032	0.000	0.087	0.084	0.082	0.032	0	0.091	0.079	0.089	0.032		0.069	0.087	0.092	0.032		0.09	0.088	0.089
2-propyl ethanoate	0.187	0.000	0.402	0.587	0.137	0.187	0.14	0.271	0.443	0.153	0.187		0.417	0.397	0.149	0.187		0.419	0.411	0.151
2-Pentanone		0.000	0.000	0.000	0.000		0	0	0	0			0.000	0.000	0.000					
n-Butanol	0.011	0.011	0.023	0.051	0.000	0.011	0.017	0	0.042	0	0.011		0.000	0.044	0.000	0.011		0.028	0.045	
Water	1.410	2.260	2.310	0.080	5.230	1.41	1.79	2.67	0.05	6.42	1.410	2.039	2.510	0.060	6.170	1.41	2.13	2.38	0.06	6.35
Others	0.015	0.001	0.096	0.241	0.023	0.015	0.028	0.1572	0.146	0.025	0.015	0.000	0.137	0.126	0.025	0.015	-1.421E-14	0.116	0.139946	0.031
Weight, grams											341.8	230.6	200.7	113.0	75.5	345.8	239.8	197.6	115.5	76.3

Table 4.14 (continued)

	00.30 6/10/97				
	Feed	LP Botts	LP OHS	HP Botts	HP OHS
Ethanal	0.065	0.055	0.326		0.902
Methanol	0.006		0.084		0.200
Diethyl ether	0.007		0.011		0.026
Light Unk (14.95 min)	0.013		0.105		0.244
Ethanol	63.772	92.496	29.174	0.136	66.549
Propanone	0.014		0.012		0.030
2-Propanol	2.979	4.498	0.053		0.022
Methyl Ethanoate			0.021		0.041
Di-2-propyl ether			0.032		0.004
n-Butyradehyde					
Ethyl ethanoate	31.456	0.147	67.113	98.746	25.665
Butanone	0.007			0.004	
Heavy unk (27.5 min)	0.026		0.048	0.024	
2-Butanol	0.000			0.008	0.051
Heavy unk (29.22 min)	0.032		0.094	0.084	
2-propyl ethanoate	0.187		0.425	0.610	0.088
2-Pentanone					
n-Butanol	0.011	0.004	0.027	0.057	
Water	1.410	2.790	2.410	0.087	6.010
Others	0.015	0.010	0.065	0.244	0.168
	100.000	100.000	100.000	100.000	100.000
Weight, grams	348.1	237.5	205.2	112.2	80.6

Table 4.15 Typical High Pressure Post Distillation Analysis

	Feed	O/HD's	Bottoms
Ethanal	0.001	0.019	0.000
Methanol	0.000	0.000	0.000
methyl formate	0.000	0.000	0.000
Diethyl ether	0.000	0.023	0.000
Ethanol	0.587	0.702	0.031
Propanone	0.000	0.000	0.000
2-propanol	0.027	0.030	0.000
Methyl ethanoate	0.000	0.000	0.000
Di-2-propyl ether	0.000	0.000	0.000
n-Propanol	0.002	0.000	0.000
Ethyl ethanoate	98.204	99.080	92.442
Butanone	0.013	0.014	0.017
2-Butanol	0.015	0.000	0.143
2-propyl ethanoate	0.618	0.068	4.348
n-Butanol	0.089	0.000	0.396
Ethyl butanoate	0.001	0.000	0.004
n-Butyl ethanoate	0.000	0.000	0.000
Water	0.060	0.040	0.020
Light unks	0.025	0.000	0.000
Heavy unks	0.360	0.020	2.600
Total	100.00	100.00	100.00

Table 4.16 Typical Low Pressure Distillation Analysis

	Feed	O/H's	Bottoms
Ethanal	0.015	0.267	0.000
Methanol	0.000	0.006	0.000
methyl formate	0.000	0.000	0.000
Diethyl ether	0.000	0.455	0.000
Ethanol	0.667	13.863	0.090
Propanone	0.001	0.014	0.000
2-propanol	0.031	0.588	0.000
Methyl ethanoate	0.000	0.000	0.000
Di-2-propyl ether	0.000	0.000	0.000
n-Propanol	0.002	0.000	0.000
Ethyl ethanoate	99.022	84.474	99.716
Butanone	0.016	0.022	0.014
2-Butanol	0.000	0.000	0.000
2-propyl ethanoate	0.086	0.024	0.097
n-Butanol	0.002	0.000	0.006
Ethyl butanoate	0.000	0.000	0.000
n-Butyl ethanoate	0.000	0.000	0.000
Water	0.049	0.030	0.015
Light unks	0.014	0.138	0.005
Heavy unks	0.090	0.116	0.060
Total	100.00	100.00	100.00

4.4 Selective hydrogenation of Ketones

During the dehydrogenation of ethanol to ethyl ethanoate undesirable carbonyl compounds are produced as by-products. The main undesirable carbonyls are:

Ethanal - formed by dehydrogenation ethanol.

Propanone - mainly formed by dehydrogenation of the 2-propanol present in the feed

butanone - formed from ethanol via dehydrogenation, aldolisation and hydrogenation as detailed in section 2.1 of this report

Butanal - formed from ethanol as detailed in section 2.1 of this report.

Removal of these compounds prior to distillation is desirable for a number of reasons: (a)They are reactive and can form further by-products; (b) butanone, which cannot easily be separated from ethyl ethanoate by distillation, has a maximum allowable concentration in the final product of 50 ppm. (c) Ethanal loss represents a loss in process yield from ethanol. (d) Higher ketones cause problems in the post distillation ethanol recovery.

The most efficient, commercially attractive, means of removing carbonyls, such as aldehydes and ketones, is to hydrogenate them to their corresponding alcohols. KPT have considerable experience in hydrogenation of a range of carbonyl compounds and this expertise was used to choose catalysts for evaluation.

4.4.1 Hydrogenation of Dehydrogenation product – Introduction

The hydrogenation of aldehydes and ketones is one that is widely covered in both commercial and academic literature. The use of platinum group metals on a range of support materials[11] has been reported for many hydrogenation reactions including hydrogenation of alkenes, alkynes, aromatics such as benzene to cyclohexane, nitriles to amines.

The most commonly used catalysts for the hydrogenation of aldehydes and ketones to alcohols are reported to be palladium, nickel and ruthenium in a polar reaction medium at pressures of 100-1000 kPa and at temperatures of 20-150°C. Two common industrial processes that have an aldehyde or ketone to alcohol hydrogenation step are the production of 2-propanol from propanone[12] and the 'oxo alcohols' process[13] where butanal or 2-ethyl hexanal are hydrogenated to the respective alcohols. In these quoted cases the catalyst of choice is nickel supported on either alumina or silica. The reaction conditions tend to be higher in pressure (up to 3000 kPa) at moderate temperature (140°C in the case of propanone hydrogenation, 110°C for butanal). The reaction takes place in a fixed bed in either the vapour phase (propanone to 2-propanol) or liquid phase (oxo alcohols). In the case of oxo alcohols there may be a two bed hydrogenation system where the aldehydes are first hydrogenated at high temperature (180°C) over a bed of copper-chrome catalyst to a conversion of between 80 and 90%. This releases much of the heat of reaction at a temperature where it can be used to raise steam. The reaction will not progress much beyond 90% due to the high temperature of operation; hydrogenation is an exothermic process, the position of equilibrium being influenced by temperature. High temperatures favour the aldehyde or ketone, low temperatures the alcohol. Copper is inactive at lower temperatures, and so cannot be used to drive the reaction to the high conversions required (>99.95%) for an industrial process. A second bed containing more active nickel catalysts, that are active at the required low temperatures, is used to 'polish' the crude alcohol/aldehyde mixture.

The use of ruthenium to hydrogenate aldehydes and ketones has been restricted industrially to the production of sorbitol from the hydrogenation of glucose[14] . Typical reaction conditions are 120°C, 4000 kPa pressure with the sorbitol present as a 40% solution in water. Ruthenium based catalysts are reported as being active in ethyl ethanoate[14] and alcohol solvents and so seemed to be ideal for the hydrogenation of aldehydes and ketones in the crude ethyl ethanoate. However, the relative costs of nickel and ruthenium catalysts dictated that if possible a nickel catalyst would be used. Typically, nickel catalyst prices are in the range of $20-$40 per kg, cf. 5% ruthenium on carbon circa $70-$100 depending on the cost of ruthenium which is a traded precious metal. Copper could not be considered as it is typically used as catalyst for the hydrogenolysis of esters to alcohols; significant losses of ethyl ethanoate by hydrogenation over the aldehyde/ketone hydrogenation catalyst would severely impact on overall process economics.

4.4.2 Nickel Based Hydrogenation Catalyst Testwork

It has been determined that the major complication in the proposed flowsheet was the behaviour of butanone in boiling very close to ethyl ethanoate, causing the product ethyl ethanoate to contain concentrations of butanone that could not be tolerated commercially.

A specification for ethyl ethanoate obtained from Sastech quoted a butanone content of approximately 20 ppm. The current distillation flowsheet would not achieve this, given the expected butanone content of the dehydrogenation product of circa 0.1 wt%. A solution to the problem would be to hydrogenate the butanone to 2-butanol, which is easily separable by distillation.

Hydrogenation of carbonyls such as butanal and 2 ethyl hexanal[13] has been successfully achieved at moderate temperatures and pressures over a nickel based catalyst. However, most of this type of polishing work has been carried out in the presence of the corresponding alcohol, with little work reported in the presence of esters. A short series of tests using a commercially available nickel catalyst was carried out with the following aims:

a) To determine how readily the carbonyl species would react and

b) To determine how much ethyl ethanoate would be hydrogenated back to ethanol.

The initial testwork was carried out using a mixture of 95% ethyl ethanoate / 5% butanone. This mixture, containing only one carbonyl species, was used to simplify interpretation of the results.

A charge of 200 ml of Calsicat SR 475 nickel spheroids was charged to a fixed bed reactor, similar in construction to the dehydrogenation reactor detailed in section 2. The nickel was activated under a stream of 5% hydrogen in nitrogen at 300 kPa and 180°C. Following activation the reactor conditions were set out as those shown for run 73/96 in Table 4.17 (p183). A scan of conditions was then carried out using the 95% ethyl ethanoate/5% butanone feed. Two temperatures, two flow rates and two pressures were used giving 7 runs in all.

This initial scan showed that it was possible to hydrogenate butanone from a feed concentration of 5 wt% to a product concentration of 70 ppm (run 79/96) while losing little of the ethyl ethanoate by hydrogenation. The feed was then changed to a product from dehydrogenation which contained butanone and propanone at levels similar to those expected from the commercial reactor. The results from this test are also shown in table 1 as run 80/96, along with an analysis of the feed. The results showed similar conversion of butanone as compared to the artificial feed, but an unexpectedly high residual propanone figure. This is almost certainly due to a component eluting near to propanone being identified as propanone, a strong possibility being methyl ethanoate. The peak identified as butanal shows little indication of hydrogenation. This again is due to a non-reactive component eluting at a similar time to butanal. An estimate of the butanal content of the product yields a figure of approximately 0.006%. It would be expected that n-butanal would hydrogenate at least as well as propanone and butanone, so the figure quoted is almost certainly high. Another component of interest is 2-butyl ethanoate which appears to reduce from 0.131 to 0.010%. 2-butyl ethanoate is known to elute with another component which would appear to be either an aldehyde or ketone and the results show that this is being hydrogenated. The polishing testwork seems a promising route to removal of ketones and aldehydes with only a minor loss of ethyl ethanoate.

4.4.3 Ruthenium on Carbon Catalyst – Initial Testwork

The testwork reported in section 4.4.2 shows that a nickel catalyst, SR 275, was effective in carbonyl polishing of the dehydrogenation product, reducing the butanone content of the product to circa 70 ppm. Further work was carried out at more vigorous conditions to reduce the butanone to 10 ppm, but a problem in catalyst strength and durability was identified, leading to leaching of nickel and a loss in the integrity of the catalyst pellet. These serious problems were traced to the dehydrogenation product containing circa

2000ppm ethanoic acid which is believed to have attacked the alumina support of the SR275 catalyst. The rate of attack appeared to be temperature dependent and at temperatures where the polishing of carbonyls reached an acceptable rate the catalyst lost integrity rapidly. This nickel catalyst was therefore not a suitable commercial option for producing crude hydrogenation product with low levels of butanone.

A programme of testwork was carried out to identify a catalyst that would give low levels of butanone and other carbonyls and which would also be stable to ethanoic acid at levels present in the crude dehydrogenation product. One such catalyst, a ruthenium-on-carbon type, had been shown to be stable to acid, in an unrelated process, at temperatures far in excess of those that would be employed in the ethyl ethanoate carbonyl polishing process. A sample of this catalyst was obtained for testing.

The hydrogenation reactor was packed with 100 cm^3 of 5% ruthenium on carbon catalyst ex Engelhard, and activated in a similar fashion to the nickel catalyst reported in section 4.4.2 above. Following activation the reactor was commissioned using a synthetic feed containing ethanal, ethanol, propanone, 2-propyl alcohol, ethyl ethanoate, butanone, 2-butanol and water. Details of the feed composition and the product quality can be found in Table 4.18, as SAS/102/01/97. At the operating conditions of 100°C, 1380 kPa, LHSV 0.5 hr^{-1}, the butanone in the feed was reduced to 4 ppm. The LHSV was then increased to 0.7 hr^{-1} at otherwise identical conditions. No increase in butanone above 4 ppm was noted. The catalyst was therefore deemed to be active and suitable for use in the Sasol life test.

4.4.4 Ruthenium on Carbon Catalyst - Synthetic Feed Testwork

Following the successful commissioning of the reactor, a programme of work was performed, designed to determine the most effective range of conditions for the polishing life test. Initially nine runs were performed at a range of pressures, temperatures and LHSV's. At all times a molar hydrogen:carbonyl ratio of 10:1 was used. A table showing the conditions is given below.

Run No	Pressure kPa	Temp °C	LHSV Hr^{-1}	H_2 Flow SLPH
3	1380	100	1.00	6.0
4	1380	120	0.50	2.0
5	1380	140	0.75	4.5
6	2760	140	1.00	6.0
7	2760	120	0.75	4.5
8	2760	100	0.50	3.0
9	4100	100	0.75	4.5
10	4100	120	1.00	6.0
11	4100	140	0.75	3.0

The results from these runs are shown in Table 4.18 (p183) as runs SAS/102/03/97 - SAS/102/11/97.

The level of butanone in the product showed a marked dependence on temperature and pressure. At 140°C butanone ranged from 120 ppm at 4100 kPa to 1620 ppm at 1380 kPa. At 100°C the butanone ranged from <5 ppm to <1 ppm at 4100 kPa, depending on the LHSV employed.

The effect of temperature is easily explained. Exothermic reactions, such as that between butanone and hydrogen to form 2-butanol, are adversely affected by increased temperature, shifting the equilibrium to butanone. Conversely, lowering the reactor temperature will lead to the equilibrium shifting towards 2-butanol. The "thermodynamic temperature limit" for the butanone to 2-butanol reaction seems to be circa 120°C as maximum butanone levels of 17 ppm are permissible to meet the 50 ppm butanone specification for the ethyl ethanoate product.

While lowering the temperature shifts the equilibrium to 2- butanol, the kinetics of the reaction fall rapidly with temperature. There is a point where the kinetic curve and thermodynamic curves overlap. It is at this point that testwork is best performed. A graphical representation of these curves is shown in Figures 4.23 and 4.25 (p175).

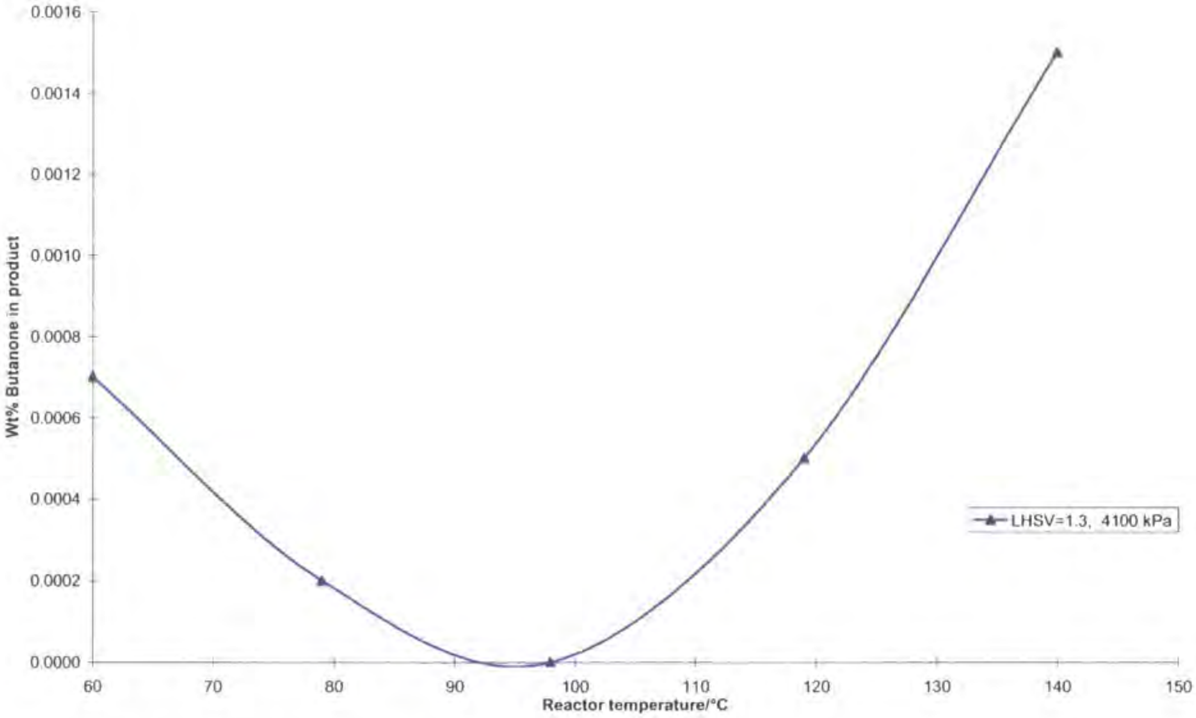


Figure 4.23 Butanone in Product Versus Temperature at 4100 kPa

An initial scan of LHSV was performed at 1.0, 1.5 and 2.0 hr^{-1} at 100°C and 4100 kPa. The results are shown in Table 4.18 (p185) as runs SAS/102/12/97 - SAS/102/13/97. There was no significant difference between any of the three runs in regard to butanone and other carbonyl content of the products suggesting equilibrium had been achieved. These runs completed the synthetic feed portion of the polishing testwork. The results indicated that the ruthenium-on-carbon catalyst was extremely active and an effective catalyst for carbonyl polishing. Immediately following the testwork based on feed derived from pure ethanol, the feed was changed to product from dehydrogenation of ethylol. The conditions chosen for the initial run were:

Rx pressure, kPa - 4100
Rx temperature, °C - 110
LHSV, hr^{-1} - 1.0
H_2 flow, SLPH - 6.0

It was expected that at these conditions there would be very little butanone remaining in the product. These conditions were held for a total of 97.5 hours. The results are shown as SAS/102/15/97 - SAS/102/18/97 in Table 4.18 (p185). The butanone content of the product was circa 2 - 5 ppm for all runs. In addition, a number of other carbonyls, such as ethanal, propanone and 2-pentanone, were also reduced to low levels.

At this point, the reactor conditions were altered to increase the butanone content of the product and to have reactor conditions that were not equilibrium limited. Any deactivation occurring while operating at equilibrium limited conditions may not be observed, and so cannot be used to determine loss in catalyst activity. Conditions need to be such that the reactor is in a kinetically controlled mode of operation. The first test was conducted at the following conditions:

Rx pressure, kPa - 2760
Rx temperature, °C - 90
LHSV, hr^{-1} - 1.00
H_2 flow, SLPH - 6

At these conditions the butanone was reduced to 1 - 2 ppm. This clearly demonstrates that thermodynamic gain, in reducing the temperature by 20°C, was greater than the kinetic loss due to the reduction in temperature, 20°C, and the thermodynamic loss due to the reduction of 1380 kPa. The pressure was therefore reduced further to 1380 kPa, similar to the operating pressure of the dehydrogenation reactor, see run SAS/102/22/97. At this condition the butanone content of the product was 2 - 5 ppm. A scan of LHSV of 1.0, 2.0 and 4.0 hr^{-1} was then carried out at 90°C and 1380 kPa. These runs are shown as SAS/102/23/97 - SAS/102/25/97. The butanone content of the product was 2.8, 36 and 175 ppm respectively. The results of these three runs are also shown graphically in Figure 4.24.

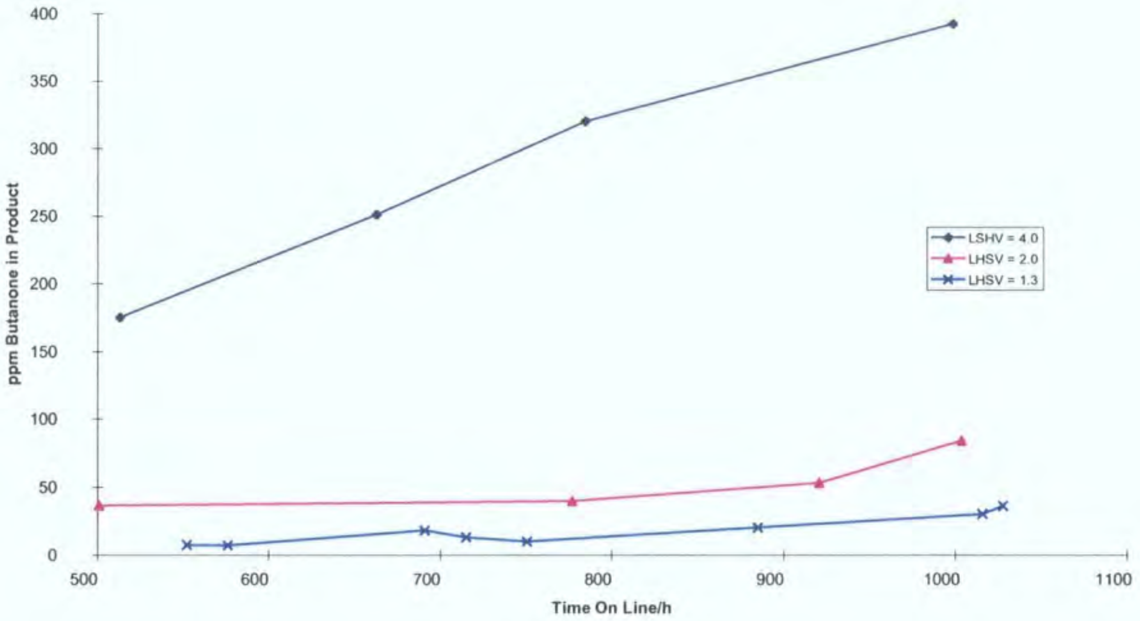


Figure 4.24 Butanone in product against Time on Line at 1300 kPa

Following this scan, it was decided to run the polishing reactor at the same volumetric rate as the dehydrogenation reactor, i.e. at an LHSV of 1.3 hr^{-1}. At these conditions the butanone content of the product was 7 ppm, within the original target of <10 ppm. A further run at these conditions was carried out with similar results, see run SAS/102/26/97 and SAS/102/27/97.

Having established the base-line kinetically controlled conditions from which the catalyst activity could be determined, further studies of the effect of temperature and LHSV on the butanone content at a pressure of 1380 kPa were carried out. These runs are recorded as SAS/102/28/97 to SAS/102/30/97. Runs 28 and 29 were carried out at 100°C and at an LHSV of 1.0 and 2.0 respectively. Run 30 was carried out at 120°C and an LHSV of 2.0 hr^{-1}. The difference between runs 29 and 30, a 10°C change in reactor temperature, resulted in a change in butanone in the product from 41 ppm to 96 ppm. This indicated that the temperature limit of the catalyst at 1380 kPa is circa 100°C.

The conditions were then changed to determine whether there had been any loss of catalyst activity during the temperature scan testwork. The conditions were:

Rx pressure, kPa - 1380
Rx temperature, °C - 90
LHSV, hr^{-1} - 4.0

This run, SAS/102/31/97, yielded 250 ppm butanone and can be compared to run SAS/102/25/97 which yielded 175 ppm butanone in the product. The results show that the catalyst showed some deactivation over the 150 hours between the two runs. The conditions were then changed back to the base-line conditions of LHSV 1.3 hr^{-1} and 90°C. The conditions were held for 87 hours over 3 runs, SAS/102/32/97 to SAS/102/34/97.

Butanone in the product stabilised at 10 ppm, compared to the previous results of 7 ppm at similar operating conditions. The two runs at LHSV 2.0 and 4.0 were then repeated. The results of these two runs, SAS/102/35/97 and SAS/102/36/97 can be found in Table 4.18 (p188). The results of the runs, 40 ppm and 320 ppm butanone, respectively, indicate that the catalyst was still losing activity at 1380 kPa. The loss was probably due to heavies build-up and blockages of the smaller pores of the catalyst. Conditions were then altered back to an LHSV of 1.3 hr^{-1} and maintained for a total of 160 hours from 785 hours on-line to 945 hours on-line. Over this period the butanone content of the product rose from 16 to 23 ppm. The results for this period of operation can be found in Table 4.18 (p188) as runs SAS/102/37/97 to SAS/102/42/97.

A short scan of 3 runs was then carried out to determine the operating temperature range of the catalyst after it had been aged. Runs at temperatures of 80°C, 70°C and 110°C were performed at an LHSV of 1.3 hr^{-1} and 1380 kPa. The results of these runs are shown in Table 4.18 (p189) as SAS/102/43/97 to SAS/102/47/97 and are also shown graphically in Figure 4.25. The activity checks at LHSV 4.0 and 2.0 hr^{-1} were then repeated. The results are shown in Table 4.18 (p189) as SAS/102/46/97 to SAS/102/47/97. The butanone in the product settled at 392 and 84 ppm respectively, indicating that the slow deactivation of the catalyst was continuing.

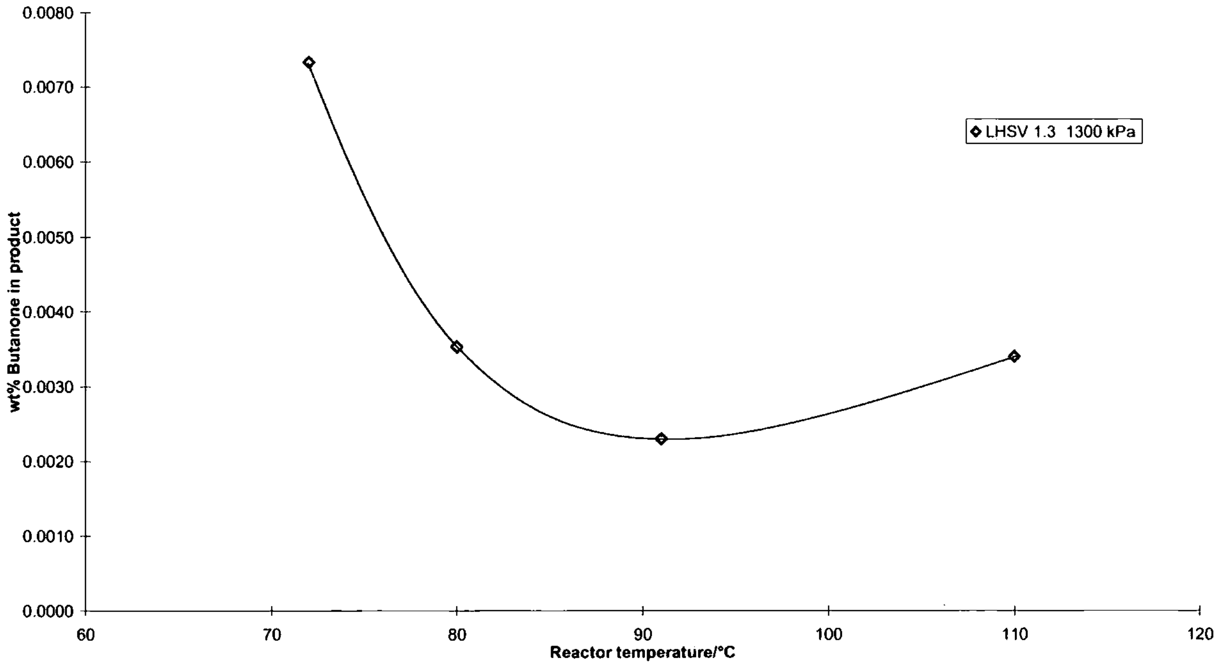


Figure 4.25 Butanone content of product at 1300 kPa

The polishing reactor was then closed down for a 48 hour period during a general weekend shut-down. Following the shut-down, the reactor was re-started at 90°C, 1380kPa and an LHSV of 1.3 hr^{-1}. The butanone content of the product settled at 36 ppm, an increase of 13 ppm over the previous period run at these conditions. The results of this run, SAS/102/48/97, can be found in Table 4.18 (p187). The butanone content in the product had now increased above 17 ppm, the maximum level which could be tolerated to achieve <50 ppm butanone in the final ethyl ethanoate product, assuming no physical separation in the distillation scheme. A change in conditions to an LHSV of 1.0 hr^{-1} was undertaken to reduce the butanone in the product to <25 ppm. The run is recorded as SAS/102/49/97 in Table 4.18 (p 189). The result of reducing the LHSV from 1.3 hr^{-1} to 1.0 hr^{-1} was to lower the butanone in the product from 14 ppm to 36 ppm, a much larger change than expected. The result can be compared directly to runs SAS/102/22/97 and SAS/102/23/97 which gave circa 3 ppm butanone in the product. Over the 574 hours between runs 23 and 49, the increase in butanone at LHSV 1.0 was 11 ppm, a modest increase and within the specification of butanone in the product. At an LHSV of 1.3 the increase was 29 ppm, which gave high butanone of 110 ppm in one product which did not meet the butanone specification <50 ppm.

The reactor pressure was then increased to 2760 kPa, run SAS/102/50/97, in order to obtain a direct comparison to run SAS/102/21/97. This resulted in a butanone content of 10 ppm in the product, which compares to 1 ppm obtained from run SAS/102/21/97. This is consistent, in terms of deactivation, with the results at 1380 kPa reported above.
The LHSV was then increased to 1.3 hr^{-1} whilst maintaining the pressure of 2760 kPa. The result of increasing the LHSV was to increase the butanone in the product from 10 ppm to 15 ppm, see run SAS/102/51/97, Table 4.18 (p190). In comparison to the large difference in butanone seen at 1380 kPa, over the same LHSV, the increase of 5 ppm at 2760 kPa is encouraging. Two further runs were carried out at 400 kPa and an LHSV of 1.3 hr^{-1}, runs SAS/102/52/97 and SAS/102/53/97. These runs were carried out at 70 and 110°C respectively and were designed to give information on the operating envelope of the aged catalyst at 2760 kPa. The results, 44 and 8 ppm respectively, show that at 2760 kPa the temperature range could be extended beyond the 100°C maximum at 1380 kPa. This has implications for the optimum pressure to be chosen for the polishing section of the ethyl ethanoate flowsheet.

The final 2 runs of the life test were carried out at 1380 kPa, 110°C and at LHSV's of 4.0 and 2.0 hr^{-1}, see runs SAS/102/54/97 and SAS/102/55/97. These runs can be directly compared to those at similar LHSV's at 90°C. The results of 246 and 68 ppm butanone can be compared to 392 and 84 ppm for runs at 90°C. Clearly, the increase in temperature in beneficial in reducing butanone content.

4.5 Discussion of Selective Hydrogenation

The results gathered from the life test indicate that the chosen catalyst, ruthenium-on-carbon, is effective over a range of LHSV's and temperatures. It is more effective at higher pressures than those used for the dehydrogenation reactor. Results have been obtained at 1380 - 4100 kPa, with the most effective polishing taking place at the higher pressures. Catalyst performance at 1380 kPa and an LHSV of 1.3 hr^{-1} is not sufficient to obtain a years life without regeneration. At higher pressures a life of one year appears achievable without regeneration by using temperature to compensate for catalyst deactivation. Figure 4.26 shows the butanone content of the product at a LHSV of 1.3 and 1.0 hr^{-1} over a range of temperatures, at 1380, 2760 and 4100 kPa.

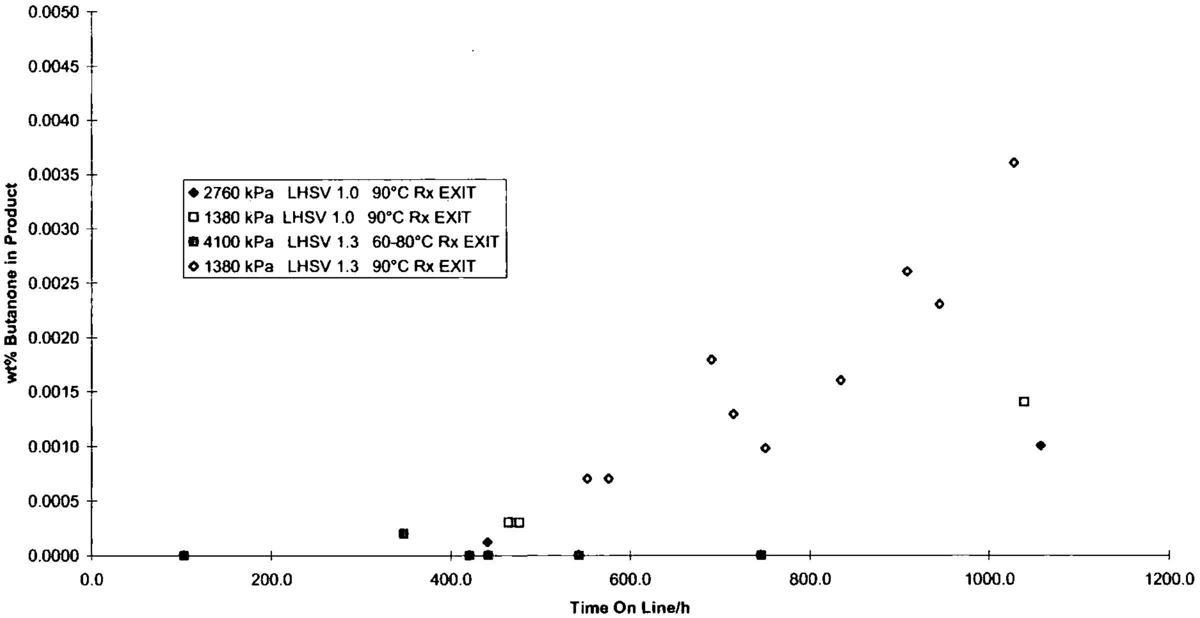


Figure 4.26 Butanone in Product against Time on Line at 1380, 2760 and 4100 kPa

The 4100 kPa data was obtained using a synthetic feed, but the results are consistent with those obtained using Sasol ethylol product. At 4100 kPa, the range of usable temperatures is from 50°C to 120°C, an increase of 40°C over the more limited range of 70 to 100°C at 1380 kPa. The higher pressure is therefore recommended for use in the ethyl ethanoate flowsheet.

Overall, it would seem advantageous to operate at the higher pressure subject to cost considerations and optimisation of the process flowsheet. The poor performance of the nickel catalyst is disappointing in terms of overall process economics as the cost of a nickel catalyst is between 0.2 and 0.33 of the same volume of ruthenium based catalysts. Nickel is a well known and trusted hydrogenation catalyst and DPT has much commercial experience in its use, while the ruthenium catalyst was relatively unknown territory. The testwork has shown that at the right process conditions- namely 4100 Pa, 5% ruthenium on carbon catalyst, 60-100°C, butanone in the product from hydrogenation could be reduced to as low as 1ppm, well below the final target of the work which was to produce ethyl ethanoate containing <50ppm of butanone. At these conditions, the loss of ethyl ethanoate to hydrogenation back to ethanol was small – less than 1% of the ester was hydrogenated. The target of selectively hydrogenating the aldehydes and ketones to low levels has been achieved. This work, linked as it was to the distillation of ethyl ethanoate from the crude dehydrogenation product, has proved that a substantially pure ethyl ethanoate stream can be synthesised from ethanol and has proved the overall process concept.

The chapters that follow are concerned with the development of a novel dehydrogenation catalyst and modelling of the dehydrogenation reaction (chapter 5) and the experience of starting the first commercial ethanol to ethyl ethanoate industrial unit at Sasol's Secunda site in South Africa (chapter 6).

Table 4.17 Hydrogenation Results – SR 275 Catalyst

Run Number	Feed	73	74	75	Feed	76	77	78	79	Feed	80
Feed Type	Synthetic Feed									Dehydrogenation Product	
Rx In		111	90	90		91	90	112	111		110
Rx Out		111	91	93		90	93	111	110		109
LHSV		0.5	0.5	1.0		0.5	1.0	1.0	0.5		0.53
Pressure		1380	1380	1380		2760	2760	2760	2760		2760
H2 Flow In		6	6	6		6	6	6	6		6
Product Analysis, wt%											
Ethanal										1.392	0.010
Methanol										0.050	0.048
Diethyl Ether										0.139	0.146
Ethanol		0.428	0.153	0.104		0.207	0.101	0.378	0.290	64.512	66.236
Propanone										1.682	0.061
2-Propanol									0.004	2.155	3.901
Di- 2-propyl Ether										0.135	0.130
Butanal										0.012	0.012
Ethyl Ethanoate	95.100	94.530	94.745	94.801	95.000	94.567	94.716	94.302	94.430	26.743	26.323
Butanone	4.900	0.013	0.151	0.560	5.000	0.131	0.370	0.069	0.007	0.672	0.007
2-Butanol		4.774	4.815	4.438		4.918	4.707	4.878	4.961	0.756	1.496
2-propyl Ethanoate			0.006	0.006		0.006	0.005	0.005	0.008	0.213	0.230
n-Butanol			0.016	0.017		0.015	0.017	0.014	0.013	0.356	0.299
2-Pentanone										0.198	0.002
2-Pentanol										0.186	0.385
2-Butyl Ethanoate		0.178	0.086	0.053		0.127	0.058	0.316	0.230	0.135	0.100
Ethyl Butanoate										0.068	0.126
n-Butyl Ethanoate		0.011	0.007				0.004			0.025	0.120
Others		0.066	0.021	0.021		0.029	0.022	0.038	0.057	0.781	0.406

Table 4.18 Carbonyl Polishing Results – 5% Ruthenium on Carbon Catalyst

Run Number SAS/102/xx/97	Feed	1	2	3	4	5	6	7
Rx In		99	98	99	119	142	142	123
Rx Out		100	100	100	119	141	141	122
LHSV		0.500	0.760	0.999	0.498	0.748	0.998	0.750
Pressure		202	210	410	209	206	409	407
TOL								
H2 Flow In		2.98	4.48	6	2.99	4.48	5.99	4.49
Feed SG		0.8236	0.8236	0.8236	0.8236	0.8236	0.8236	0.8236
Feed Wt, g		123.6	375.6	164.6	123	184.8	328.8	278.1
Product Wt, g		124.5	381.3	163.8	125.1	185.1	312.6	278.9
Mass Balance Time, hrs		3.0	6.0	2.0	3.0	3.0	4.0	4.5
Mass Balance, %		100.73	101.52	99.51	101.71	100.16	95.07	100.29
Product Analysis, wt%								
Ethanal	0.462	0.0030		0.0030	0.0040	0.0100	0.0050	0.0030
Methanol								
Methyl Formate								
Diethyl Ether								
Ethanol	54.143	55.540	54.515	54.552	54.192	53.837	53.423	54.311
Propanone	0.947	0.002	0.008	0.002	0.008	0.282	0.027	0.004
2-Propanol	1.949	3.024	2.978	2.972	2.992	2.687	2.973	2.980
Di- 2-propyl Ether								
Butanal								
Ethyl Ethanoate	40.089	40.348	39.996	40.104	40.340	40.280	40.425	40.124
Butanone	0.296	0.0004	0.0004	0.0010	0.0030	0.1540	0.0112	0.0003
2-Butanol	0.605	0.941	0.925	0.913	0.928	0.761	0.914	0.924
2-propyl Ethanoate								
2-Pentanone								
n-Butanol					0.009	0.020		0.008
Water	1.5		1.56	1.42	1.50	1.91	2.18	1.62
Others	0.009	0.142	0.018	0.033	0.024	0.059	0.042	0.026

Table 4.18 (continued)

Run Number SAS/102/xx/97	Feed	8		9	10	11	12	13		14
Feed Type										
Rx In		101		100	121	141	99	99		100
Rx Out		101		101	121	139	99	100		100
LHSV		0.497		0.750	1.019	0.501	1.002	1.502		1.995
Pressure		409		630	630	600	561	599		616
TOL							198	214		229
H2 Flow In		2.99		4.5	6	3	6	9		12
Feed SG		0.8236		0.8236	0.8236	0.8236	0.8236	0.8236		0.8302
Feed Wt (g)		122.7		61.8	503.4	165.2	330	494.8		662.4
Product Wt (g)		125.3		61.8	483.4	137.9	329.5	492.5		631.6
Mass balance time (hrs)		3.0		1.0	6.0	4.0	4.0	4.0		4.0
Mass Balance %		102.12		100.00	96.03	83.47	99.85	99.54		95.35
Product Analysis, wt%										
Ethanal	0.462	0.0030	0.235	0.0000	0.0100	0.0120	0.0080	0.0080	0.259	0.0090
Methanol										
Methyl Formate										
Diethyl Ether										
Ethanol	54.143	54.835	53.663	54.182	53.870	53.748	55.210	55.214	54.146	55.658
Propanone	0.947	0.000	0.949	0.000	0.002	0.044	0.000	0.000	0.960	0.000
2-Propanol	1.949	2.961	1.933	2.982	2.985	3.052	3.035	3.034	1.954	3.078
Di- 2-propyl Ether										
Butanal										
Ethyl Ethanoate	40.089	39.816	40.044	39.682	39.920	41.431	40.096	40.081	40.251	40.166
Butanone	0.296	0.0003	0.293	0.0001		0.0120		0.0003	0.302	0.0001
2-Butanol	0.605	0.926	0.597	0.920	0.916	0.946	0.935	0.939	0.603	0.957
2-propyl Ethanoate										
2-Pentanone										
n-Butanol		0.008	0.579	0.526	0.591	0.627	0.606	0.611		0.014
2-Pentanol										
2-Butyl Ethanoate										
Ethyl Butanoate			0.009	0.006	0.004	0.004	0.006	0.007	0.009	0.008
n-Butyl Ethanoate										0.008
2-Hexanone										
2-Hexanol										
Di-n-Butyl Ether										
n-Hexanol										
2-Heptanone										
Dipropanone Alcohol										
n-Heptanol										
2-Octanone										
2-Ethyl Hexanol										
n-Octanol										
Water	1.5	1.43	1.6	1.60	1.60				1.41	
Others	0.009	0.021	0.098	0.102	0.102	0.124	0.104	0.106	0.106	0.102

Table 4.18 (continued)

Run Number SAS/102/xx/97	Feed HOL	15		16	17	18		19	20	21
	320-365		369-437				441-509			
Rx In		110		110	110	110		110	110	90
Rx Out		110		110	110	110		110	110	91
LHSV		1.025		1.008	1.040	1.041		1.060	1.040	1.051
Pressure		602		598	598	596		399	399	402
TOL		272		301		369.5		393	417	441
H2 Flow In		6		6	5.99	5.99		5.99	5.99	5.99
Feed SG		0.8221		0.8221	0.8221	0.8221		0.8221	0.8221	0.8221
Feed Wt (g)		337.2		331.6	2052.4	2096.8		2048.7	2051.2	2074.1
Product Wt (g)		320.1		317.9	2003.5	2035.9		1948.5	1957.2	1974.5
Mass balance time (hrs)		4.0		4.0	24.0	24.5		23.5	24.0	24.0
Mass Balance %		94.93		95.87	97.62	97.10		95.11	95.42	95.20
Ethanal	0.530	0.0030	0.471	0.0040	0.0040	0.0040	0.491	0.0040	0.0040	0.0030
Methanol	0.036	0.034	0.035	0.034	0.035	0.035	0.033	0.035	0.035	0.035
Methyl Formate	0.012	0.009	0.012	0.008	0.010	0.010	0.013	0.010	0.009	0.010
Diethyl Ether	0.411	0.368	0.407	0.357	0.402	0.401	0.447	0.409	0.423	0.415
Ethanol	58.05	58.716	58.195	58.804	58.120	57.935	56.973	57.730	57.790	58.030
Propanone	0.767	0.000	0.684	0.000	0.000	0.000	0.751	0.000	0.000	0.000
2-Propanol	2.261	3.075	2.354	3.066	3.084	3.047	2.264	3.068	3.058	3.057
Di- 2-propyl Ether	0.114	0.109	0.114	0.107	0.110	0.109	0.114	0.109	0.109	0.109
Butanal	0.000	0.000	0.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethyl Ethanoate	34.17	33.877	34.214	33.531	34.398	34.373	34.611	34.550	34.770	34.590
Butanone	0.155	0.0003	0.136	0.0005	0.0002	0.0004	0.159	0.0005	0.0004	0.0001
2-Butanol	0.443	0.615	0.461	0.620	0.643	0.644	0.471	0.664	0.673	0.673
2-propyl Ethanoate	0.176	0.181	0.179	0.178	0.186	0.189	0.184	0.188	0.185	0.184
2-Pentanone	0.161	0.010	0.142	0.000	0.009	0.000	0.162	0.009	0.009	0.009
n-Butanol	0.345	0.290	0.340	0.326	0.319	0.323	0.333	0.295	0.296	0.361
2-Pentanol	0.32	0.470	0.335	0.476	0.487	0.482	0.333	0.487	0.489	0.487
2-Butyl Ethanoate	0.065	0.066	0.065	0.068	0.068	0.070	0.068	0.068	0.068	0.068
Ethyl Butanoate	0.139	0.141	0.139	0.141	0.145	0.142	0.143	0.145	0.146	0.146
n-Butyl Ethanoate	0.151	0.156	0.154	0.158	0.163	0.176	0.155	0.163	0.164	0.164
2-Hexanone	0.000		0.003			0.010	0.000		0.028	0.000
2-Hexanol	0.000		0.000				0.004			
Di-n-Butyl Ether	0.000		0.025				0.000			0.019
n-Hexanol	0.000		0.015				0.000			
2-Heptanone	0.000		0.002				0.000			
Dipropanone Alcohol	0.000		0.000				0.000			
n-Heptanol	0.000		0.001				0.000			
2-Octanone	0.000		0.000				0.000			
2-Ethyl Hexanol	0.000		0.000				0.000			
n-Octanol	0.000		0.005				0.000			
Water	1.11	1.22	0.97	1.31	1.31	1.47	1.50	1.58	1.28	1.17
Others	0.584	0.660	0.532	0.811	0.507	0.580	0.794	0.486	0.464	0.470

Table 4.18 (continued)

Run Number SAS/102/xx/97		22	23	24		25	26		27	28
Feed Type	509-581	Ex 10/1	Ex 10/1	Ex 10/1	581-663	Ex 10/1	Ex 10/1	663-748	Ex 10/1	Ex 10/1
Rx In		90	90	91		94	90		90	100
Rx Out		91	91	91		91	91		91	100
LHSV		1.094	1.026	2.007		4.069	1.317		1.311	1.015
Pressure		206	207	204		204	201		200	193
TOL		465	477	501		513.5	552.5		576.5	600.5
H2 Flow In		5.98	5.98	11.97		23.88	7.87		7.85	5.87
Feed SG		0.8221	0.8221	0.8221		0.8221	0.8221		0.8221	0.8221
Feed Wt (g)		2157.6	1012.5	3959.9		669.1	2598.3		2585.7	2003.1
Product Wt (g)		1899.2	1016.5	3950.1		654.7	2514		2430	1875.2
Mass balance time (hrs)		24.0	12.0	24.0		2.0	24.0		24.0	24.0
Mass Balance %		88.02	100.40	99.75		97.85	96.76		93.98	93.61
Ethanal	0.514	0.0040	0.0040	0.0030	0.533	0.0034	0.0030	0.560	0.0030	0.0060
Methanol	0.036	0.034	0.034	0.034	0.036	0.034	0.034	0.036	0.035	0.035
Methyl Formate	0.012	0.009	0.009	0.008	0.012	0.008	0.006	0.013	0.006	0.006
Diethyl Ether	0.485	0.428	0.432	0.443	0.511	0.424	0.409	0.537	0.419	0.408
Ethanol	57.608	58.180	58.460	58.596	57.998	59.101	59.680	58.500	59.770	59.900
Propanone	0.761	0.000	0.000	0.000	0.773	0.000	0.000	0.781	0.000	0.000
2-Propanol	2.269	3.063	3.094	3.089	2.260	3.073	3.133	2.271	3.127	3.129
Di- 2-propyl Ether	0.114	0.108	0.108	0.106	0.113	0.105	0.102	0.113	0.102	0.101
Butanal	0.010	0.000	0.000	0.000	0.011	0.000	0.000	0.011	0.000	0.000
Ethyl Ethanoate	34.535	34.250	34.000	33.980	33.974	33.414	32.810	33.557	32.780	32.620
Butanone	0.168	0.0003	0.0003	0.0036	0.173	0.0175	0.0007	0.175	0.0007	0.0011
2-Butanol	0.487	0.672	0.682	0.676	0.490	0.671	0.696	0.492	0.693	0.693
2-propyl Ethanoate	0.175	0.177	0.174	0.173	0.166	0.163	0.162	0.160	0.156	0.161
2-Pentanone	0.161	0.009	0.009	0.018	0.161	0.033	0.009	0.159	0.009	0.009
n-Butanol	0.329	0.381	0.389	0.393	0.328	0.440	0.415	0.323	0.412	0.380
2-Pentanol	0.324	0.477	0.479	0.473	0.316	0.446	0.472	0.311	0.462	0.467
2-Butyl Ethanoate	0.065	0.066	0.066	0.067	0.063	0.065	0.065	0.064	0.064	0.065
Ethyl Butanoate	0.138	0.142	0.141	0.141	0.135	0.136	0.133	0.127	0.131	0.131
n-Butyl Ethanoate	0.151	0.159	0.159	0.159	0.147	0.154	0.151	0.140	0.149	0.149
2-Hexanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Di-n-Butyl Ether	0.024	0.025	0.025	0.017	0.016	0.023	0.023	0.022	0.015	0.016
n-Hexanol	0.008		0.000	0.004	0.013	0.002	0.001	0.008	0.001	0.002
2-Heptanone	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dipropanone Alcohol	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptanol	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Octanone	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl Hexanol	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octanol	0.000		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	1.21	1.34	1.26	1.26	1.35	1.17	1.24	1.22	1.21	1.27
Others	0.416	0.476	0.475	0.356	0.421	0.517	0.455	0.420	0.455	0.451

Table 4.18 (continued)

Run Number SAS/102/xx/97	Feed	29	Feed	30	31	Feed	32	33	34	Feed	35
Feed Type	983-1071	Ex 10/1	1071-1143	Ex 10/1	Ex 10/1	1143 - 1215	Ex 10/1	Ex 10/1	Ex 10/1	1219-1287	Ex 10/1
Rx In		101		123	92		90	90	90		89
Rx Out		101		121	89		91	91	91		91
LHSV		2.001		1.996	4.007		1.297	1.312	1.307		2.011
Pressure		188		191	188		191	190	191		189
TOL		634		651	663		691	715	750.75		777
H2 Flow In		11.88		11.87	23.85		7.85	7.84	7.83		11.85
Feed SG		0.8221		0.8221	0.8221		0.8221	0.8221	0.8221		0.8221
Feed Wt (g)		740.3		656.4	658.8		426.4	2588	3813.3		661.2
Product Wt (g)		722.1		636.9	642.4		411.5	2494	3638.8		639.6
Mass balance time (hrs)		4.5		4.0	2.0		4.0	24.0	35.5		4.0
Mass Balance %		97.54		97.03	97.51		96.51	96.37	95.42		96.73
Ethanal	0.612	0.0035	0.631	0.0032	0.0037	0.638	0.0032	0.0035	0.0020	0.665	0.0040
Methanol	0.036	0.035	0.037	0.034	0.035	0.038	0.034	0.035	0.034	0.038	0.036
Methyl Formate	0.013	0.007	0.013	0.007	0.007	0.013	0.006	0.006	0.006	0.013	0.007
Diethyl Ether	0.711	0.558	0.752	0.566	0.578	0.768	0.553	0.562	0.549	0.788	0.582
Ethanol	57.709	58.690	57.269	58.697	58.570	57.540	59.040	59.100	59.382	58.760	60.100
Propanone	0.842	0.000	0.868	0.000	0.000	0.858	0.000	0.000	0.000	0.876	0.000
2-Propanol	2.217	3.094	2.178	3.083	3.027	2.162	3.114	3.109	3.136	2.170	3.139
Di- 2-propyl Ether	0.113	0.107	0.114	0.102	0.103	0.113	0.100	0.100	0.099	0.113	0.101
Butanal	0.011	0.000	0.011	0.000	0.000	0.011	0.000	0.000	0.000	0.011	0.000
Ethyl Ethanoate	34.075	33.380	34.260	33.202	33.300	33.762	32.860	32.770	32.477	32.911	31.785
Butanone	0.217	0.0041	0.233	0.0096	0.0251	0.233	0.0018	0.0013	0.0010	0.231	0.0040
2-Butanol	0.556	0.798	0.566	0.812	0.799	0.565	0.839	0.832	0.844	0.555	0.827
2-propyl Ethanoate	0.151	0.142	0.138	0.253	0.251	0.247	0.246	0.245	0.244	0.241	0.238
2-Pentanone	0.181	0.007	0.189	0.044	0.059	0.196	0.008	0.008	0.015	0.194	0.020
n-Butanol	0.339	0.456	0.367	0.430	0.540	0.368	0.500	0.498	0.505	0.378	0.525
2-Pentanol	0.320	0.482	0.321	0.480	0.463	0.312	0.499	0.495	0.507	0.305	0.481
2-Butyl Ethanoate	0.065	0.060	0.064	0.060	0.060	0.060	0.061	0.058	0.060	0.058	0.056
Ethyl Butanoate	0.142	0.142	0.154	0.154	0.158	0.153	0.157	0.156	0.158	0.147	0.151
n-Butyl Ethanoate	0.160	0.165	0.177	0.179	0.184	0.175	0.185	0.185	0.187	0.171	0.179
2-Hexanone	0.000	0.007	0.000	0.008	0.007	0.004	0.008	0.009	0.008	0.005	0.008
2-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Di-n-Butyl Ether	0.015	0.021	0.020	0.020	0.020	0.019	0.020	0.022	0.022	0.017	0.019
n-Hexanol	0.010	0.000	0.009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Heptanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dipropanone Alcohol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Octanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	1.03	1.37	1.11	1.48	1.42	1.40	1.43	1.44	1.41	0.99	1.41
Others	0.475	0.471	0.519	0.376	0.390	0.365	0.335	0.365	0.354	0.363	0.328

Table 4.18 (continued)

Run Number SAS/102/xx/97	36		37		38		39	40	41		42
Feed Type	Ex 10/1	796-868	Ex 10/1	748-796	Ex 10/1	MIXED	Ex 10/1	Ex 10/1	Ex 10/1	1290-1350	Ex 10/1
Rx In	94		90		90		90	91	94		91
Rx Out	91		91		91		91	91	91		91
LHSV	4.004		1.322		1.204		1.330	1.909	3.999		1.305
Pressure	186		187		188		188	188	193		191
TOL	785		835		885		909	921	927		945
H2 Flow In	23.85		7.84		7.73		7.77	11.78	23.79		7.78
Feed SG	0.8221		0.8221		0.8221		0.8204	0.8204	0.8108		0.8108
Feed Wt (g)	658.4		3476.6		4949		2618	1879.7	648.4		423.2
Product Wt (g)	640		3288.9		5041		2469.1	1786.3	638.8		410
Mass balance time (hrs)	2.0		32.0		50.0		24.0	12.0	2.0		4.0
Mass Balance %	97.21		94.60		101.86		94.31	95.03	98.52		96.88
Ethanal	0.0050	0.569	0.0050	0.560	0.0050	0.549	0.0033	0.0060	0.0333	0.904	0.0343
Methanol	0.035	0.037	0.034	0.037	0.035	0.038	0.035	0.035	0.035	0.043	0.039
Methyl Formate	0.007	0.012	0.005	0.012	0.005	0.013	0.006	0.007	0.007	0.011	0.005
Diethyl Ether	0.592	0.573	0.393	0.567	0.393	0.607	0.434	0.446	0.468	0.579	0.428
Ethanol	59.980	59.301	61.040	58.865	60.787	58.255	60.197	59.795	59.560	68.223	70.040
Propanone	0.000	0.789	0.000	0.784	0.000	0.782	0.000	0.000	0.000	2.282	0.000
2-Propanol	3.054	2.243	3.278	2.246	3.152	2.227	3.123	3.106	3.041	1.004	3.232
Di- 2-propyl Ether	0.101	0.112	0.095	0.112	0.097	0.112	0.097	0.100	0.101	0.003	0.098
Butanal	0.000	0.011	0.000	0.010	0.000	0.010	0.000	0.010	0.000	0.010	0.010
Ethyl Ethanoate	31.950	32.596	31.400	33.055	31.769	33.587	32.275	32.650	32.850	23.263	22.572
Butanone	0.0320	0.177	0.0016	0.175	0.0020	0.180	0.0026	0.0053	0.0272	0.170	0.0023
2-Butanol	0.788	0.480	0.699	0.483	0.694	0.496	0.712	0.713	0.684	0.371	0.567
2-propyl Ethanoate	0.238	0.245	0.242	0.252	0.247	0.261	0.254	0.260	0.259	0.186	0.185
2-Pentanone	0.058	0.168	0.017	0.168	0.008	0.170	0.017	0.029	0.055	0.022	0.021
n-Butanol	0.549	0.332	0.447	0.327	0.456	0.346	0.476	0.482	0.506	0.507	0.730
2-Pentanol	0.452	0.300	0.457	0.301	0.458	0.311	0.466	0.466	0.442	0.214	0.332
2-Butyl Ethanoate	0.055	0.053	0.058	0.058	0.057	0.060	0.059	0.060	0.061	0.005	0.046
Ethyl Butanoate	0.151	0.122	0.128	0.124	0.128	0.129	0.132	0.133	0.134	0.047	0.090
n-Butyl Ethanoate	0.177	0.141	0.149	0.142	0.150	0.147	0.153	0.155	0.153	0.006	0.107
2-Hexanone	0.007	0.005	0.007	0.005	0.007	0.005	0.007	0.008	0.007	0.009	0.019
2-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Di-n-Butyl Ether	0.017	0.018	0.019	0.019	0.020	0.024	0.020	0.024	0.022	0.024	0.013
n-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Heptanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.009	0.000
Dipropanone Alcohol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Octanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	1.40	1.4	1.23	1.37	1.20	1.34	1.20	1.20	1.26	1.41	1.17
Others	0.352	0.316	0.295	0.328	0.330	0.351	0.331	0.310	0.294	0.698	0.259

Table 4.18 (continued)

Run Number SAS/102/xx/97	43	44	45		46	47	48		49
Feed Type	Ex 10/1	Ex 10/1	Ex 10/1	1350-1422.5	Ex 10/1	Ex 10/1	Ex 10/1	923-983	Ex 10/1
Rx In	80	71	110		95	91	90		91
Rx Out	80	72	110		92	91	91		91
LHSV	1.301	1.309	1.307		3.985	2.018	1.311		1.002
Pressure	192	194	190		192	193	188		186
TOL	961	977	991		999	1004	1028		1039
H2 Flow In	7.76	7.79	7.8		23.79	11.8	7.79		5.86
Feed SG	0.8108	0.8108	0.8108		0.8133	0.8133	0.8133		0.8242
Feed Wt (g)	422	424	424		648.2	164.1	426.4		330.4
Product Wt (g)	384.1	426	417.2		636.4	158	403.3		321.7
Mass balance time (hrs)	4.0	4.0	4.0		2.0	1.0	4.0		4.0
Mass Balance %	91.02	100.38	98.40		98.18	96.28	94.58		97.37
Ethanal	0.0395	0.0376	0.0385	0.761	0.0380	0.0310	0.0375	0.608	0.0319
Methanol	0.040	0.040	0.040	0.042	0.038	0.038	0.038	0.036	0.039
Methyl Formate	0.006	0.005	0.005	0.011	0.005	0.004	0.005	0.013	0.005
Diethyl Ether	0.418	0.417	0.419	0.614	0.476	0.447	0.445	0.677	0.414
Ethanol	70.121	70.163	70.301	67.111	68.253	68.500	68.540	56.418	68.889
Propanone	0.000	0.000	0.000	0.915	0.000	0.000	0.000	0.830	0.000
2-Propanol	3.233	3.213	3.231	2.202	3.077	3.208	3.222	2.165	3.226
Di- 2-propyl Ether	0.097	0.097	0.097	0.003	0.101	0.098	0.098	0.113	0.094
Butanal	0.000	0.000	0.000	0.010	0.000	0.000	0.000	0.010	0.000
Ethyl Ethanoate	22.464	22.437	22.396	24.961	24.366	24.110	24.030	34.924	23.698
Butanone	0.0035	0.0073	0.0034	0.172	0.0392	0.0084	0.0036	0.228	0.0014
2-Butanol	0.566	0.560	0.567	0.394	0.549	0.587	0.597	0.567	0.598
2-propyl Ethanoate	0.184	0.184	0.184	0.186	0.186	0.184	0.183	0.265	0.168
2-Pentanone	0.023	0.037	0.024	0.154	0.026	0.037	0.021	0.202	0.019
n-Butanol	0.770	0.776	0.570	0.439	0.711	0.670	0.650	0.370	0.619
2-Pentanol	0.331	0.325	0.331	0.230	0.312	0.341	0.353	0.333	0.356
2-Butyl Ethanoate	0.048	0.046	0.046	0.044	0.044	0.044	0.044	0.059	0.045
Ethyl Butanoate	0.090	0.090	0.090	0.096	0.097	0.098	0.099	0.163	0.099
n-Butyl Ethanoate	0.106	0.105	0.105	0.112	0.116	0.117	0.119	0.187	0.103
2-Hexanone	0.005	0.004	0.005	0.002	0.003	0.004	0.005	0.005	0.005
2-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Di-n-Butyl Ether	0.010	0.006	0.015	0.006	0.006	0.006	0.011	0.025	0.006
n-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Heptanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dipropanone Alcohol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Octanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	1.17	1.20	1.27	1.09	1.21	1.22	1.22	1.46	1.30
Others	0.275	0.250	0.262	0.445	0.347	0.248	0.279	0.342	0.284

Table 4.18 (continued)

Run Number SAS/102/xx/97	50	51		52	53	54	55
Catalyst	5%Ru/ C	5%Ru/ C		5%Ru/ C	5%Ru/ C	5%Ru/ C	5%Ru/ C
Feed Type	Ex 10/1	Ex 10/1	261-317	Ex 10/1	Ex 10/1	Ex 10/1	Ex 10/1
Rx In	90	90		70	110	114	110
Rx Out	91	91		70	110	110	110
LHSV	1.005	1.301		1.308	1.294	3.927	1.980
Pressure	402	403		390	400	186	192
TOL	1057	1083		1097	1115	1123	1130
H2 Flow In	5.87	7.85		7.86	7.83	23.86	11.86
Feed SG	0.8242	0.8242		0.819	0.819	0.819	0.819
Feed Wt (g)	331.2	482.4		214.2	424	643.2	162.2
Product Wt (g)	316.4	468.3		210	416.7	633.7	160
Mass balance time (hrs)	4.0	4.5		2.0	4.0	2.0	1.0
Mass Balance %	95.53	97.08		98.04	98.28	98.52	98.64
Ethanal	0.0310	0.0300	0.570	0.0355	0.0336	0.0060	0.0050
Methanol	0.035	0.034	0.039	0.037	0.037	0.037	0.039
Methyl Formate	0.005	0.007	0.011	0.005	0.005	0.006	0.005
Diethyl Ether	0.470	0.493	0.335	0.258	0.245	0.259	0.003
Ethanol	59.000	58.060	64.399	65.353	65.971	65.619	65.926
Propanone	0.000	0.000	0.771	0.000	0.000	0.000	0.000
2-Propanol	3.132	3.091	2.308	3.174	3.189	3.064	3.156
Di- 2-propyl Ether	0.098	0.099	0.113	0.097	0.098	0.101	0.098
Butanal	0.000	0.000	0.008	0.000	0.006	0.011	0.006
Ethyl Ethanoate	32.98	33.78	28.292	27.725	27.263	27.514	27.257
Butanone	0.0010	0.0015	0.112	0.0045	0.0008	0.0240	0.0060
2-Butanol	0.827	0.845	0.329	0.493	0.469	0.435	0.459
2-propyl Ethanoate	0.257	0.262	0.237	0.234	0.234	0.233	0.215
2-Pentanone	0.014	0.014	0.135	0.018	0.014	0.056	0.033
n-Butanol	0.486	0.496	0.400	0.535	0.026	0.581	0.025
2-Pentanol	0.521	0.532	0.257	0.381	0.371	0.331	0.358
2-Butyl Ethanoate	0.060	0.066	0.049	0.049	0.051	0.050	0.050
Ethyl Butanoate	0.162	0.168	0.095	0.104	0.098	0.099	0.098
n-Butyl Ethanoate	0.180	0.196	0.102	0.118	0.095	0.107	0.019
2-Hexanone	0.008	0.009	0.002	0.005	0.004	0.004	0.005
2-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Di-n-Butyl Ether	0.022	0.027	0.017	0.024	0.018	0.025	0.035
n-Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Heptanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Dipropanone Alcohol	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Heptanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Octanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Ethyl Hexanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000
n-Octanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water	1.41	1.46	1.13	1.06	1.13	1.10	1.10
Others	0.301	0.330	0.289	0.290	0.642	0.338	1.102

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Chapter 5

Dehydrogenation Catalyst Optimisation

5 Introduction

Chapters 2 and 3 were concerned with the development of a dehydrogenation reactor and catalyst that could be used to produce ethyl ethanoate at commercially viable rates and purity. The catalyst chosen for life testing, E408Tu, was found to be structurally weak and therefore not an acceptable candidate for commercialisation. A further search of commercially available catalysts was carried out, and a more likely candidate was identified. The screening testwork performed in finding the new catalyst was similar to that reported in chapter 2 and is not detailed. The new catalyst, designated Cu0203T, was found to have a similar performance to E408Tu in terms of selectivity and activity, and was physically stronger even after extended operation. The optimisation of the catalyst formulation and physical properties is described in section 5.2.

Having chosen the catalyst that would be carried through to commercialisation, three modelling studies were carried out in order to validate and characterise the performance of the catalyst. These were: a life test over an extended time period (section 5.3) and an investigation into the reaction mechanism of ethanol dehydrogenation to ethyl ethanoate carried out at UMIST in collaboration with Prof. Ken Waugh (section 5.4). The result of these studies was to fully characterise the performance of the catalyst under commercial conditions and to confirm the reaction mechanism proposed in chapter 2.

5.1 Investigation of Cu0203T Catalyst

The problems of loss of physical strength encountered with the E408Tu catalyst forced a re-evaluation of the dehydrogenation section of the ethyl ethanoate process. Of the options available – changing the reactor type to accommodate the weak catalyst, reformulating the catalyst for increased strength, investigating further industrially available catalysts – the latter option was thought to be the most likely to succeed. A further review of the available catalysts identified one designated Cu0203T. The catalyst was a high density, high copper to chrome ratio type that was developed for aldehyde hydrogenation and nitrile hydration

A sample of Cu0203T was obtained from Engelhard from their existing stocks. The catalyst was charged to the dehydrogenation reactor and activated according to the method detailed in Appendix 1. A plot of the hydrogen consumption during the activation is shown as figure 5.1.

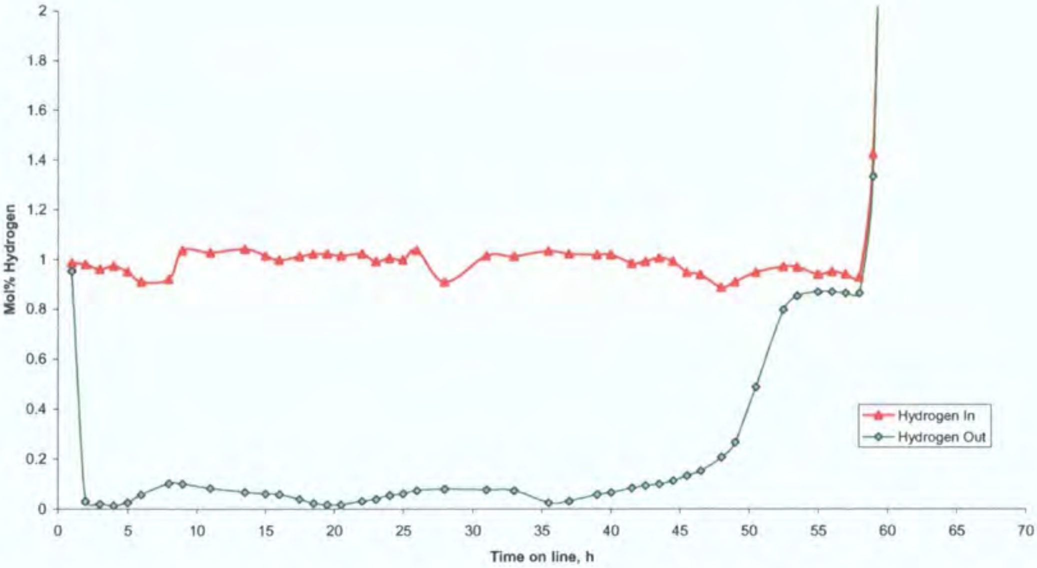

Figure 5.1 Activation Of Cu0203T Catalyst – Plot Of Hydrogen In And Out Of Reactor

Following activation, the reactor conditions were set at those shown below. A pure ethanol feed was used for all testwork using this charge of catalyst. The results of this run can be found in Table 5.1 (p229) and plotted in Figure 5.12.

Run Number	SAS/ 11/99
LHSV, hr^{-1}	0.65
Pressure, kPa	640
Temperature, °C	220
H_2 Feed in, SLPH	2
Time on Line, hours	18.5

The conversion observed at this condition, 41.8 mol%, and selectivity, 93.0 mol%, compared well with that observed when using E408Tu. See table 3.1 (p116), run 101/44/96 for a run carried out at similar conditions. A set of tests performed at a range of ethanol feed rates was then performed in order to determine the effect of feed rate on selectivity and conversion at otherwise identical process conditions. The conditions used for this scanning work are shown below. Results for these runs are plotted in Figure 5.2 and shown in table 5.1 (p229) as runs SAS/12/99 to SAS/15/99

Run Number	SAS/ 12/99	SAS/13/99	SAS/14/99	SAS/15/99
LHSV, hr^{-1}	1.5	0.5	2.0	1.0
Pressure, psig	200	200	200	200
Temperature, °C	220	220	220	220
H_2 in, SLPH	2	2	2	20
Time on Line, hours	29	45.5	55.5	68
Conv. of ethanol, mole%	31.7	42.9	27.6	34.7
Sel. to Ethyl ethanoate, mole%	90.7	92.5	88.4	91.6

The reactor conditions were then changed back to those used for run SAS/11/99 as a check of catalyst activity to determine if any gross deactivation had taken place during the scanning work. This run is shown as SAS/16/99 in table 5.1 (p229) and is plotted in figure 5.1. The fall in conversion observed in this run, from 41.8 to 41.0 mole% is small, and would not materially affect the results obtained from the LHSV scan. Following this run, the catalyst was cooled, purged of hydrogen with nitrogen at atmospheric pressure and discharged. Samples were retained for future analysis.

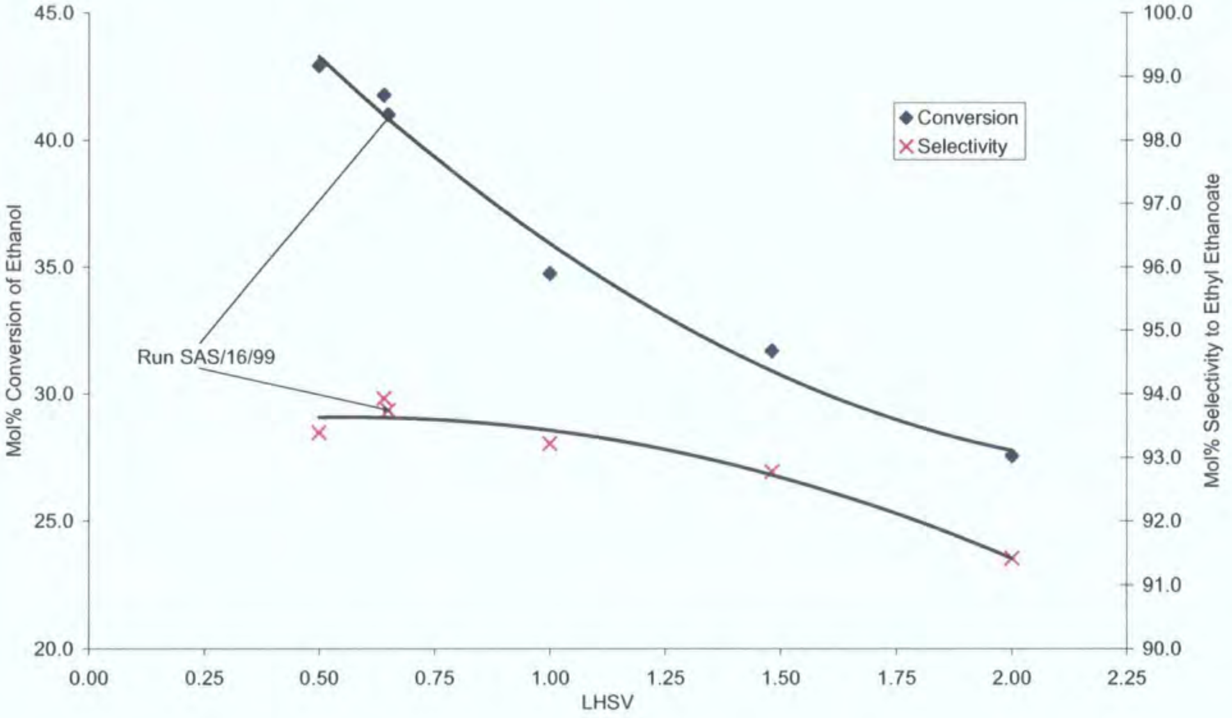

Figure 5.2. Screening Of Cu0203T Catalyst For Activity And Selectivity Against LHSV

The result of this run were encouraging, in that in comparison to data collected from the E408Tu catalyst under similar conditions, ethanol conversion over Cu0203T was similar or superior to that obtained using E408Tu. Figure 5.3 plots data obtained from E408Tu at 225°C, using ethylol feed, with the data obtained from Cu0203T. A similar comparison of selectivity was not available as extensive screening work using pure ethanol was not performed using E408Tu.

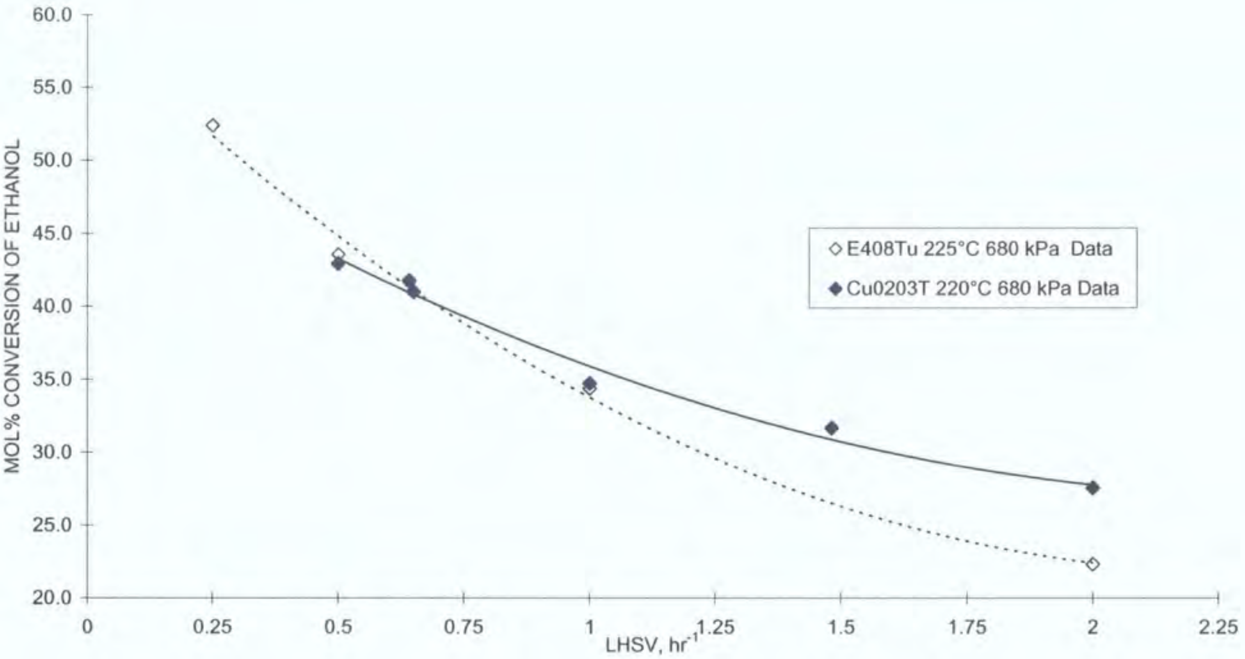

Figure 5.3 Comparison of Ethanol Conversion for E408Tu and Cu0203T

Following the success of this test, further samples of Cu0203T were obtained from Engelhard. These samples were from different commercial production batches of catalyst. The testing of a number of batches is important, as there is likely to be a variation in physical and chemical composition between batches. These variations are controlled by quality control (QC) procedures within acceptable limits for the application that the catalyst was designed for. As the commercial use of Cu0203T was not for dehydrogenation reactions, the variations in properties that would be deemed acceptable for its stated use may be too wide for the new reaction. Data supplied by Engelhard (see table 5.2, p230) with the catalyst highlighted a major variation in physical properties that was thought likely to have an effect on ethanol dehydrogenation. Of particular note is the surface area variation between different batches, which has a QC window of 12 m^2g^{-1} +/- $4m^2g^{-1}$; this range was thought to be unacceptably broad. The catalyst tested above, lot 103, had a surface area of 15 m^2g^{-1} and was found to have acceptable activity and selectivity. In order to discover what, if any effect, the variation in surface area had on ethanol dehydrogenation, lots 116 and 118 were tested separately in a similar fashion to lot 103. The results of the testwork can be found in tables 5.3 (lot 116, p229) and 5.4 (lot 118, p230) and in Figures 5.4, 5.5, 5.6 and 5.7. Figures 5.4 and 5.4 detail the activation of lots 116 (figure 5.4) and 118 (figure 5.5).

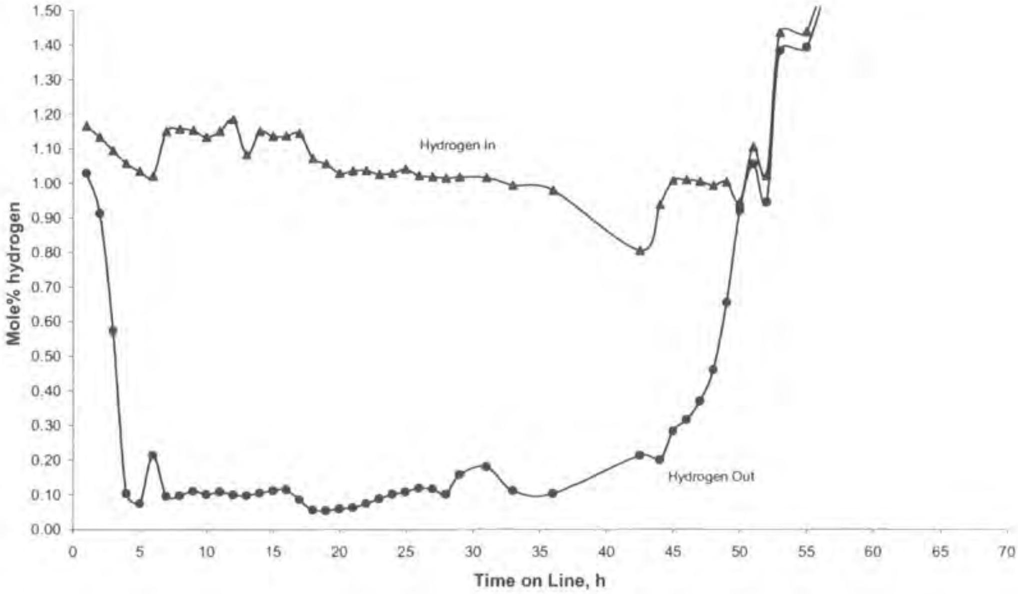

Figure 5.4 Activation of Cu0203T, Lot 116, Showing Hydrogen In and Out

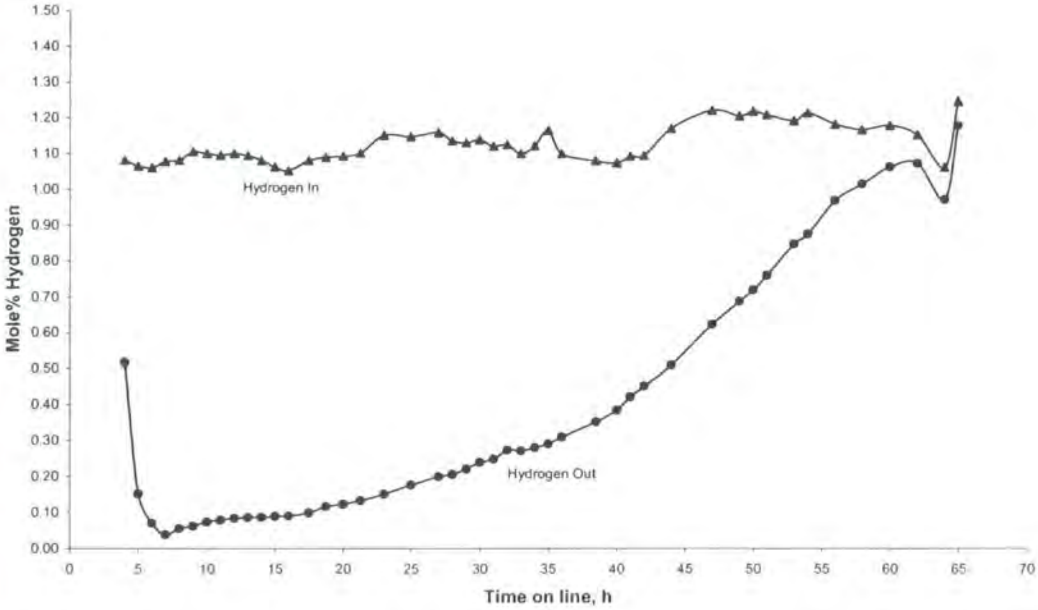

Figure 5.5 Activation of Cu0203T, Lot 118, Showing Hydrogen In and Out

The similarity of figures 5.1 and 5.4, and the difference between these figures and figure 5.5 are striking. The two catalyst samples that have relatively high surface areas show a sharp transition in the concentration of hydrogen in the reactor exit gas stream at about 45-50 hours. The exit gas hydrogen concentration for the sample with low surface area shows a gradual rise from about 7 hours online until the activation was complete after 60 hours. Summing the number of moles of hydrogen consumed during the activation gives the result of 6.2 moles of hydrogen for lot 103 and 5.9 moles for lot 118. For the weight of catalyst used for each test – 611 grams- the amount of copper contained in the catalyst (64%) equates to circa 6.16 moles [(611/(64/100))/63.5]. Given the accuracy of sampling and analysis the results suggest that in both cases all the copper is being reduced from the oxide. However, for the case of lot 118 the reduction is very slow. Given that the catalyst has a low surface area compared to other catalysts (8-15m^2g^{-1} cf 30-60 m^2g^{-1}) then the catalysts will contain a large proportion of the copper in the bulk rather than surface form. The implication of the activation work is that all of the copper in the catalyst is being activated, and that adsorption into the bulk is via surface copper. The slow activation of lot 118 suggests that the low surface area is the causative factor in slowing activation of the bulk copper.

The results from the dehydrogenation testwork on all three catalysts is shown in graphical form in figure 5.6, which plots ethanol conversion against LHSV. The difference in conversion between the catalysts is clear, with the low surface area catalyst lot 118 performing poorly in comparison to the higher surface area catalysts. At high LHSV the difference between lot 116 (11m^2g^{-1}) and 103 (15m^2g^{-1}) becomes apparent with the higher surface area giving a higher conversion. At low feed rates the conversion is almost identical, suggesting that the reaction has reached equilibrium.

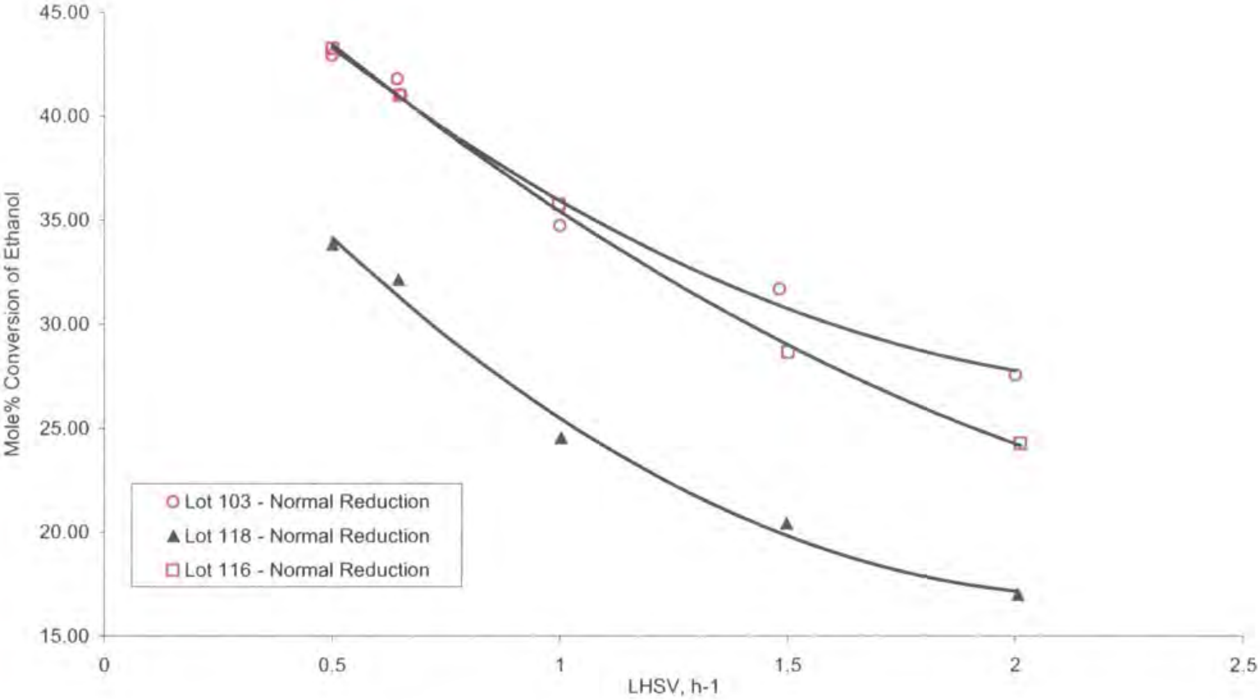

Figure 5.6 Performance of Different Surface Area Catalysts

Plotted in another way, the effect of surface area on conversion can be seen more clearly in figure 5.7. Conversion at all feed rates increases with catalyst surface area.

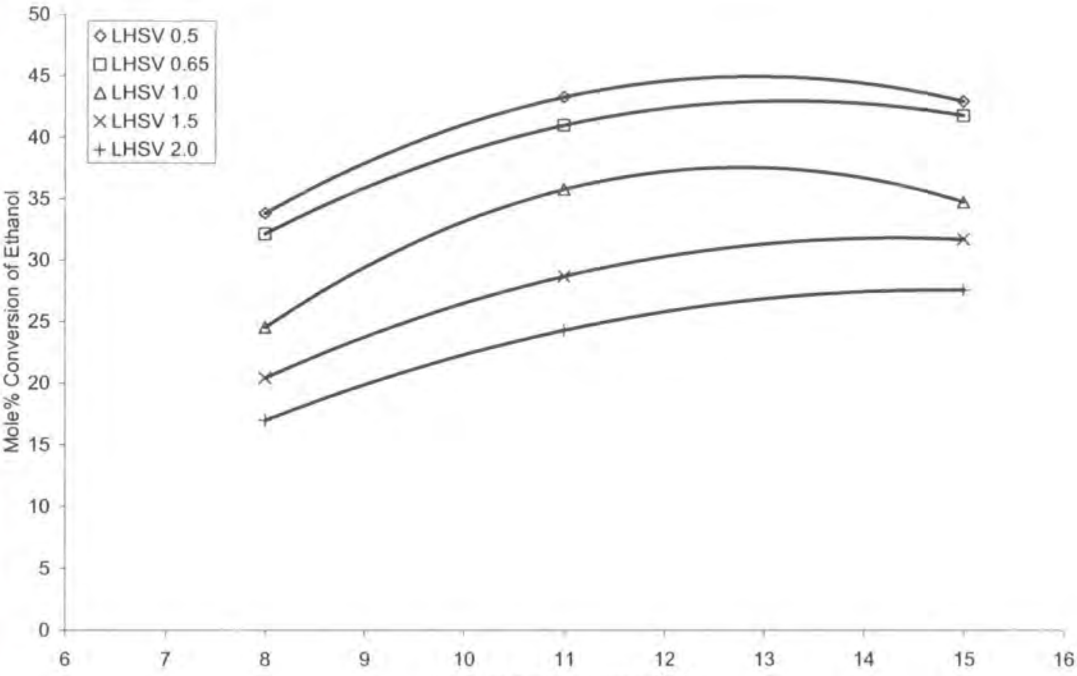

Figure 5.7 Conversion of Ethanol vs. Catalyst Surface Area

The story for selectivity is slightly different. Figure 5.8 plots selectivity against LHSV for each of the three catalysts. In this case lot 118 is again poor in comparison to the other two catalysts, but the selectivity is at a maximum for lot 116. Lot 103, which has the highest surface area, has a lower selectivity. These results, when combined, indicate that there is an optimum catalyst surface area of circa 11 m^2g^{-1} that gives acceptable conversion of ethanol and selectivity to ethyl ethanoate.

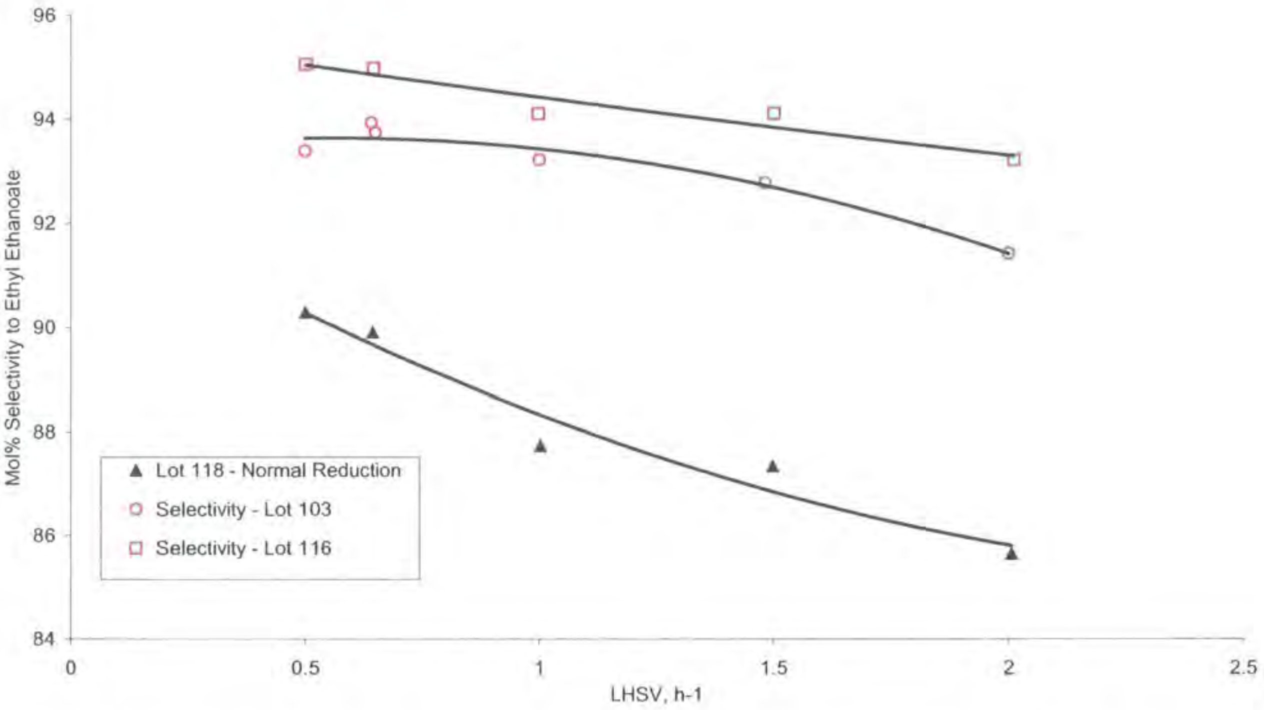

Figure 5.8 Selectivity To Ethyl Ethanoate for Catalysts of Different Surface Areas

The clear result from this testwork is that surface area is the determining factor in the activity of Cu0203T catalysts. There is a clear relationship between surface area and catalyst activity. For the purposes of commercial viability, catalysts that have surface areas below $11m^2g^{-1}$ are unacceptable in terms of both selectivity and activity.

The work carried out into Cu0203T has highlighted the effect of surface area on both activity and selectivity. The results from this work were carried onto the next stage – a life test of the catalyst over an extended period at commercially viable reaction conditions.

5.2 Life Test on Cu0203T catalyst

In order to validate the new catalyst for commercial applications a life test was performed on a fresh charge of lot 116 catalyst. The aim of the life test was to operate the catalyst at commercially realistic conditions for an extended period, during which the performance of the catalyst was monitored regularly. A life test of sorts had already been performed on the E408Tu catalyst (see chapter 3 for details), but for this charge of catalyst a more rigorous program was proposed.

The plan for this work was to run for circa 200 hours at a constant temperature, pressure and liquid feed rate ('Standard Conditions') using pure ethanol as feed, until the catalyst activity had stabilised – copper based catalysts are observed to deactivate relatively rapidly over the first 200 hours of operation and then the rate of deactivation stabilises to a lower figure. After this time, the liquid feed would be changed to ethylol and the feed rate would be scanned over a wide range and the catalyst activity and selectivity measured under these testing conditions. The catalyst would then be operated for an extended period until selectivity or activity fell below a predetermined value (38% conversion, 90% selectivity). If that occurred, then the reaction conditions would be altered to obtain the minimum values for activity and selectivity. Near the end of the life test (at least 1000 hours and preferably 1500 hours) the feed rate scan would be repeated. The results would be compared against those obtained at the start of the test to give some idea of catalyst deactivation.

The reactor was charged with 300cm^3 of lot 16 Cu0203T and activated according to the method detailed in appendix 1. Following activation the reactor was set up at the following conditions:

Temperature	220°C
Pressure	680 kPa
Feed Type	Pure Ethanol
LHSV	0.75 h^{-1}
Hydrogen Flow	2 SLPH

This condition was held for a total of 198 hours, during which time the mol% conversion of ethanol fell from 41.4% to 39.9%. The data are shown in table 5.5 (p233) as runs 1-7, and graphically in figure 5.9.

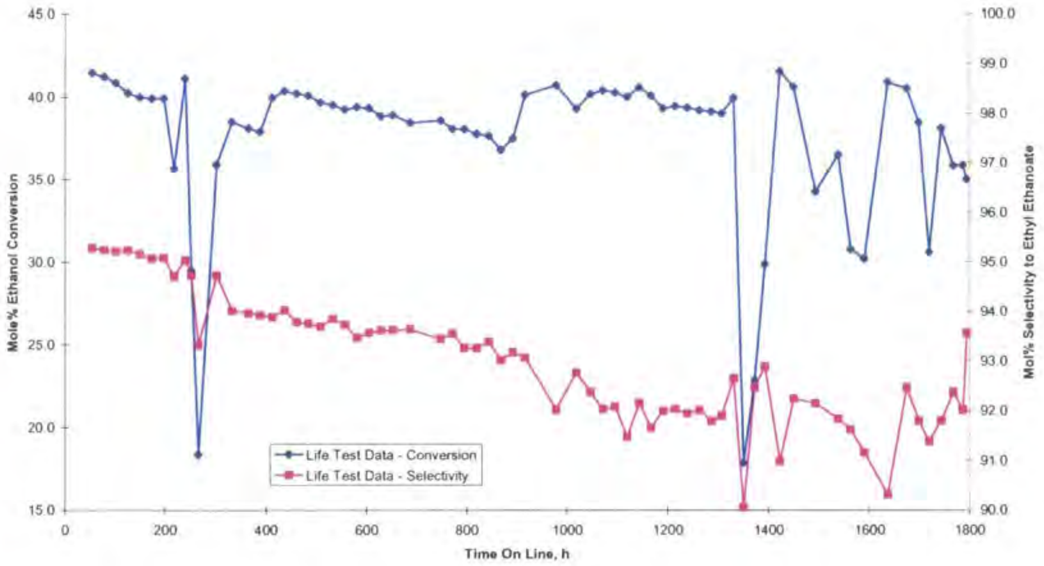

Figure 5.9 Life Test Graph Showing selectivity and Conversion

The mol% conversion of ethanol had stabilised at this point and so the feed was changed to ethylol. When the feed was changed there was a drop in conversion from 39.9 mol% to 35.7 mol%. The drop in conversion was expected, and is due to the 2-propanol content of the ethylol feed. Selectivity to ethyl ethanoate was not affected significantly – see run 8, table 5.5 (p233) for more details.

The scan of feed rates was then performed over a period of 74 hours, returning to the condition used for run 8. 4 further runs were carried out, at feed rates of 0.50, 1.00, 1.50 and 0.75; Table 5.5 (p233) details these runs as 9-12. The conversion of ethanol for these runs is plotted in figure 5.10 as 'Data from 200 Hours on line', and shows the expected fall in conversion with increasing feed rate. Comparisons of the conversion obtained from runs 8 and 12, 35.65 and 35.9 mol% respectively, indicate that there was no further catalyst deactivation over the scanning testwork. However, with the use of ethylol the ethanol conversion had fallen to below the minimum required level of 38 mol% and so the reactor temperature was increased by 5°C. This increase resulted in a rise in conversion from 35.9mol% to 38.5 mol% - see run 13, table 5.5 (p233) for details. This condition was held for 56 hours before ethanol conversion again fell to below 38 mol%. In order to increase conversion the feed rate was reduced from 0.75 h^{-1} to 0.65 h^{-1}. The result of the change was to increase ethanol conversion to 39.9 mol% while maintaining selectivity to ethyl ethanoate at circa 94 mol%. This condition was held for a total of 479 hours, to a cumulative total of 892 hours online. During this time the conversion of ethanol fell gradually to just below 37.5 mol% (runs 16 to 34 in table 5.5 (p233)) while selectivity to ethyl ethanoate fell from 94 mol% to 93.2 mol%. At this point the reaction conditions were again altered to raise ethanol conversion above the minimum required level of 38 mol%. In the first instance, the feed rate was reduced to a LHSV of 0.55 (run 35 in table 5.5 (p233)). This had the result of increasing conversion back to 40.1 mol% implying that the loss in catalyst activity was of the order of 15% (i.e. a reduction in LHSV of 0.1 is 15% of the total feed rate ((0.1/0.65)= 0.15)) . To determine by how much the reactor temperature would need to be raised to duplicate the activity gain by reducing the feed rate, the feed rate was returned to 0.65 h-1 and the reactor temperature increased slowly. At 229°C, ethanol conversion stabilised to circa 40.2 mol% and selectivity to ethyl ethanoate stabilised at circa 92 mol% (see runs 36-40 in table 5.5 (p233)). Over a period of 329 hours, to a cumulative total of 1307 hours online, conversion had fallen to 39 mol%, while selectivity to ethyl ethanoate had remained almost constant at 91.9 mol%. These data are recorded in table 5.5 (p233), runs 41-49, and in figure 5.9. The reactor temperature was then reduced to 225°C and the ethanol feed rate adjusted to give circa 40 mol% conversion. This was achieved at a feed LHSV of 0.5 – see run 50 in table 5.3. When this result is compared to that obtained from run 16 which was the first run performed at 225°C and a LHSV of 0.65 and which gave similar ethanol conversion, the loss in catalyst activity can be equated to 0.15/0.65 or 23%, over a period of 918 hours (0.025% loss per hour) .

The next three runs were performed as a scan of feed LHSV at 220°C to help determine the nature of deactivation. These three runs are recorded in table 5.5 (p233) (runs 51-53) and in figure 5.10.

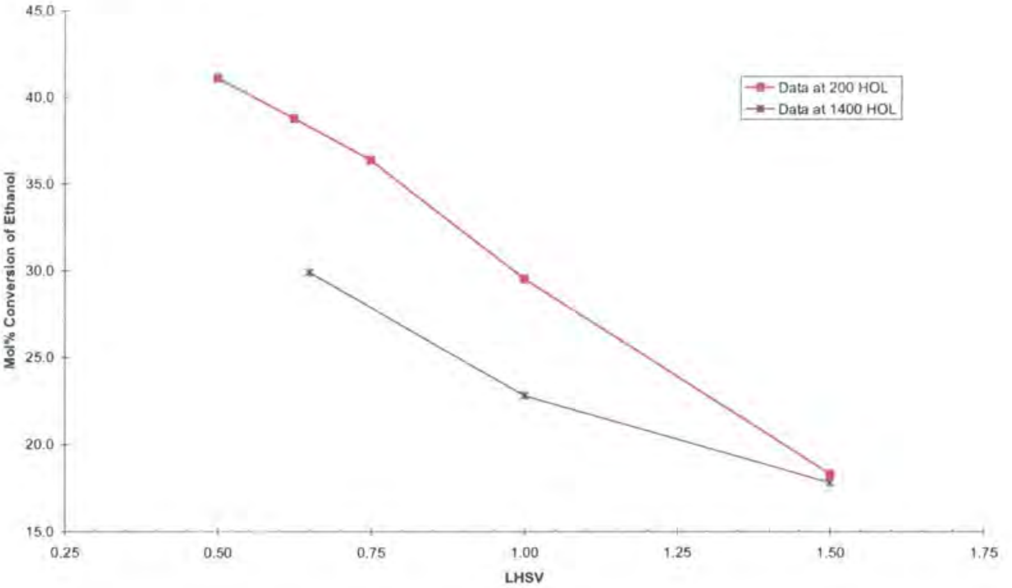

Figure 5.10 Comparison of Catalyst Activity at Start and end of Life Test

The result from the comparison of the two sets of scanning runs clearly shows the effect of time on the catalyst. The activity of the catalyst at low feed rates is low, which when taken with the results of the work reported in section 5.2 suggests that the effective surface area has been reduced,. This may be either by sintering of copper crystallites or by lay-down of poisons or heavy material on the catalyst surface. The result at LHSV 1.5 is difficult to explain satisfactorily, as it would be expected that conversion after 1400 hours should have been lower than that at 200 hours on line.

Runs 54 and 56 were carried out to test the effect of raising temperature at a LHSV of 0.65. The two temperatures used, 233 and 225°C respectively gave ethanol conversions of 41.5 and 34.2 mol% respectively. The two results can be used with run 53 to show the effect of temperature on ethanol conversion. A rise of 5°C from 220 to 225 increased conversion from 29.9% to 34.2% - 0.86% per °C, and the rise from 225 to 233°C gave 0.9% per °C.

The feed was then changed back to pure ethylol and the reaction conditions returned to those used for run 16. The pure ethanol feed was used for 9 runs (57 to 65) during which time a scan of reaction conditions was carried out. Reaction temperature of between 220 and 234°C and feed rates of LHSV 0.39 to 0.75 were used. The data collected is listed in table 5.5 (p233) and is shown in figure 5.9 and 5.11. Figure 5.11 shows ethanol conversion when using pure ethanol only, and is taken from runs 1-7 and runs 59 and 60. The reason for these runs was that there was a concern expressed that the rate of catalyst deactivation over the first 150-200 hours could be extrapolated linearly (see figure 5.11 for an illustration of this). A linear loss in activity would mean that the catalyst would not be suitable for use in an industrial application as the life would be very much less than the required 8000 hours (1 year). When the data from runs 58 and 59 are added to the chart, at circa 1600 hours on line, it can be seen that the catalyst deactivation is not linear and appears to follow an exponential decay pattern, which was the expected result. The conversion at 1600 hours on line is : linear deactivation – 22%, observed deactivation-30%. The difference between the linear and observed deactivation becomes significant at 3000 hours on line where the linear model predict 0% conversion.

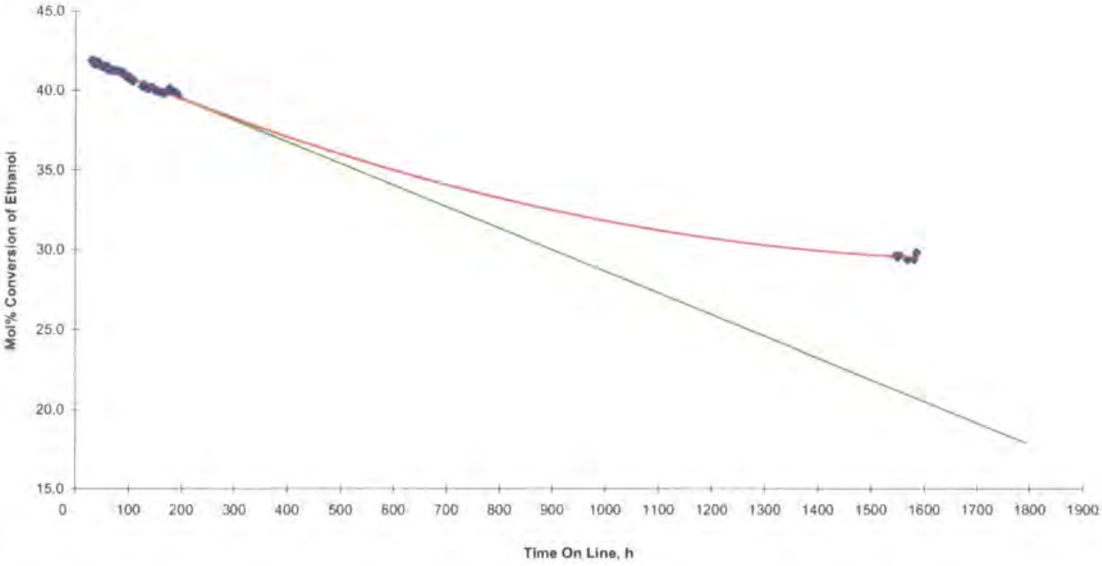

Figure 5.11 Catalyst Deactivation When Using Pure Ethanol Feed

During the work, selectivity was found to fall slowly with time, and the rate of fall was not clearly related to the reaction temperature. Figure 5.12 plots selectivity to some major by-products against time. The most striking feature is that while all of the by-products rise with time, the most noticeable change is in diethyl ether. Between 200 and 1400 hours on line there is a seemingly linear rise in selectivity which does not change with reaction temperature.

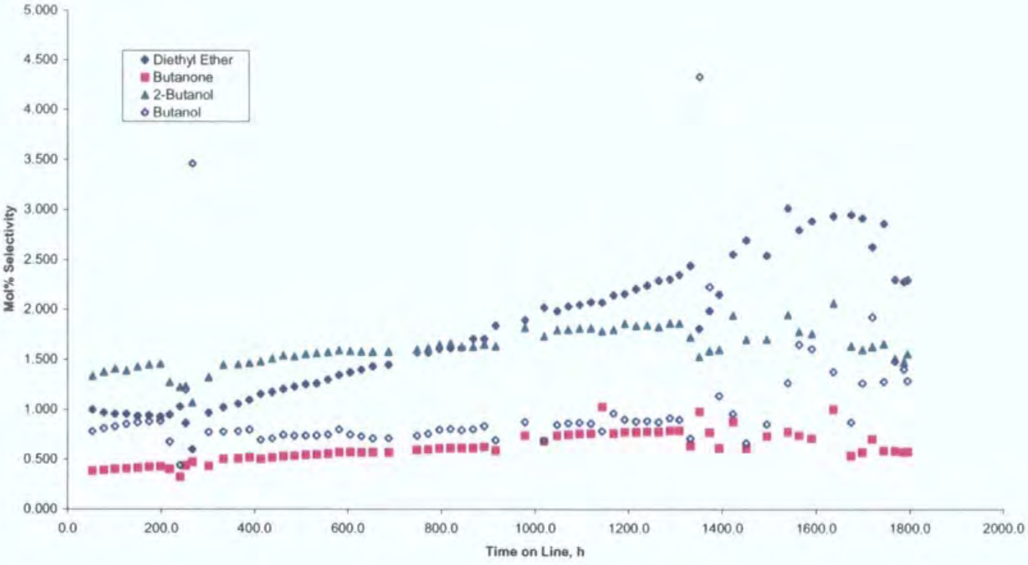

Figure 5.12 By-Product Concentration in Product During Life Test

When this data is plotted as moles of diethyl ether produced per hour, figure 5.13, a slightly different picture emerges. The linear increase in diethyl ether production is still apparent, but there is a step change in the molar production rate per hour when the reactor temperature is raised. This linear change in diethyl ether production rate suggests that there is a time dependant increase in the number of ether producing sites on the catalyst.

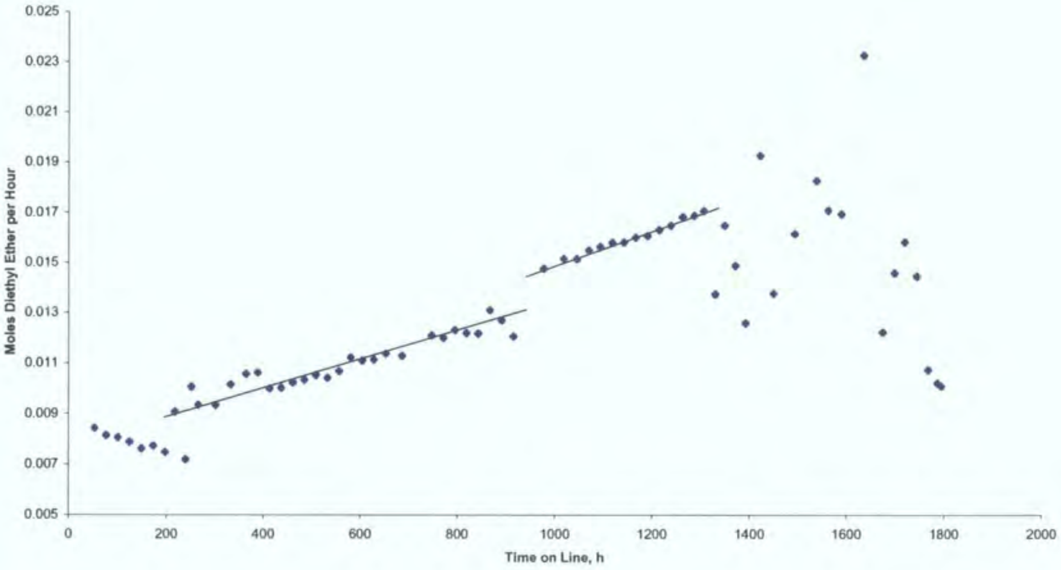

Figure 5.13 Diethyl Ether Production During Life Test

The sites that produce diethyl ether are suggested as being acidic or metal oxides[1]. No analysis of the catalyst has been performed to identify which site is likely to be responsible for diethyl ether synthesis.

The life test was terminated at this point and was judged successful. The catalyst had been used for over 1600 hours and was still capable of producing ethyl ethanoate at the required rate and at the required selectivity. The catalyst had operated well within the temperature operating envelope – 220 to 240°C - that had been determined from work carried out in chapters 2 and 3. Sufficient information had been gathered to enable a confident prediction of catalyst life.

The reactor was cooled to room temperature and the catalyst purged with nitrogen to remove hydrogen and adsorbed organics. The catalyst was then discharged and tested for crushing strength. The average crushing strength of the fresh, unreduced catalyst had been determined at 20 N. The discharged catalyst was determined to have a crushing strength of 13-15N, well within the required minimum value of 10N for a fixed bed.

5.3 Catalyst Studies at UMIST

Two programmes of work have been carried out in collaboration with Prof. Ken Waugh at UMIST. Programme 1[2] was involved with finding why a chemically identical series of catalysts gave varying selectivity and conversion. The testwork performed at DPT was reported in section 5.2 above, finding that surface area has at least some effect on the selectivity and activity of the Cu0203T samples. A series of catalysts, samples of individual 10 tonne production runs that constituted a 100 tonne batch of catalyst made for the commercial ethyl ethanoate unit by Engelhard, was subsequently tested in the same manner as those detailed in section 5.4. Some of the results from these catalysts are detailed in section 5.4.1 but the majority of the testwork is not reported to avoid unnecessary duplication of test results. The conclusion of the study was the discovery that the poorly performing catalysts had significant quantities of graphitic carbon on the active copper surface, and that this carbon was blocking the active sites. The deposition of carbon was correlated with low total surface area and low copper surface area, but it is not known how or where in the manufacturing process the carbon was deposited on the catalyst surface.

The second programme[3] was a study of the reaction mechanism of ethanol dehydrogenation, mainly by the use of a technique termed 'Reactive Frontal Chromatography' developed and improved by Waugh. The work found that the assumed reaction mechanism (see chapter 2) was essentially correct. The counterproposal of a Tischenko-type mechanism proposed[4] was found to inconsistent with the results of the study and was therefore discounted as the reaction mechanism.

All of the experimental results, except for catalyst activity and selectivity, were produced by Prof. Ken Waugh and Dr. Javad Tabatabaei and are reproduced with their permission. The interpretation of the results of both programmes was a collaborative effort between the author and Prof. Waugh, except where referenced.

5.3.1 Programme 1: Characterisation of Cu0203T catalyst

A series of 6 catalysts were supplied to Waugh, along with the conversion and activity obtained at the 'standard' conditions detailed in section 5.2.

Catalyst Activity	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Conversion of Ethanol	42.21	41.76	40.97	39.63	35.80	41.77
Selectivity to Ethyl Ethanoate	94.45	93.93	94.98	89.37	87.34	92.89

There is a clear trend between selectivity and activity in the data above – the most active catalysts are also the most selective. Two catalysts are have particularly poor selectivity – samples 4 and 5 – and these also have poor activity.

A series of surface area measurements were then taken – the detailed results are shown below. Total surface area was determined by nitrogen adsorption at 77K in-situ in the characterisation reactor by reactive frontal chromatography. Total copper areas were obtained in-situ, also by reactive frontal chromatography. Total surface area was confirmed by ex-situ BET surface area[5] measurements, and the pore volume and pore radius by ex-situ mercury porosimetry[6].

Catalyst	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**
TSA (m^2/g)	13.8	14.1	13.6	13.0	12.6	14.0
Cu MA (m^2/g)	7.6	8.0	7.5	7.4	5.4	7.8
BET SA (m^2/g)	13.93	14.45	-	13.06	13.13	-
Pore Volume (cm^3/g)	0.119	0.149	-	0.121	0.113	-
Av. Pore Radius (nm)	13.65	15.20	-	15.95	15.31	-
TPA (m^2/g)	10.76	12.28	9.44	11.20	9.48	10.87
Av. Pore Diameter (nm)	141.1	141.1	163.6	137.4	165.0	134.4

Copper metal areas (Cu MA) were measured by reactive frontal chromatography. In this technique the catalyst is first reduced in hydrogen, and then adsorbed hydrogen is removed by temperature programmed desorption (TPD). Once all the hydrogen has been desorbed, nitrous oxide is then dosed onto the catalyst where it decomposes at the surface of the copper crystallites only, to form copper oxide and nitrogen. The amount of nitrogen produced is measured and the area deduced from this figure. The figures for TSA by reactive frontal chromatography agree well with the BET surface areas, which are taken as the industrial standard. It must be noted that there is a substantial non-copper surface area component in the catalyst. For most of the tested catalysts, the copper area is only circa 60% of the total surface area. It is unlikely that this non-copper surface is inactive, and may contribute to side reactions. The total surface area differed less than metal surface area between catalysts, and correlates to selectivity and activity. Figure 5.14 shows the relationship between copper area and selectivity and activity for the six tested catalysts.

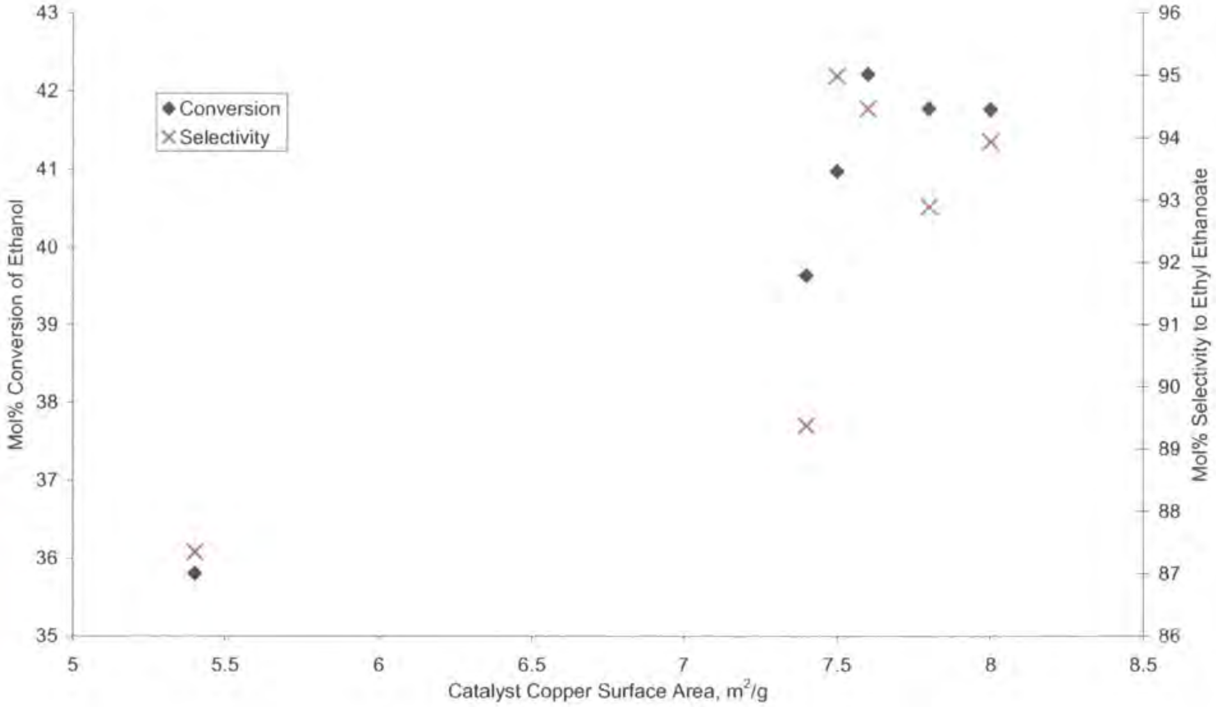

Figure 5.14 – Copper surface Area vs. Conversion and selectivity

A series of tests was then carried out on the ease of activation of each of the catalyst samples. Figure 5.15 below shows a typical temperature programmed reduction (TPD) for the catalyst samples showing the uptake of hydrogen and evolution of water.

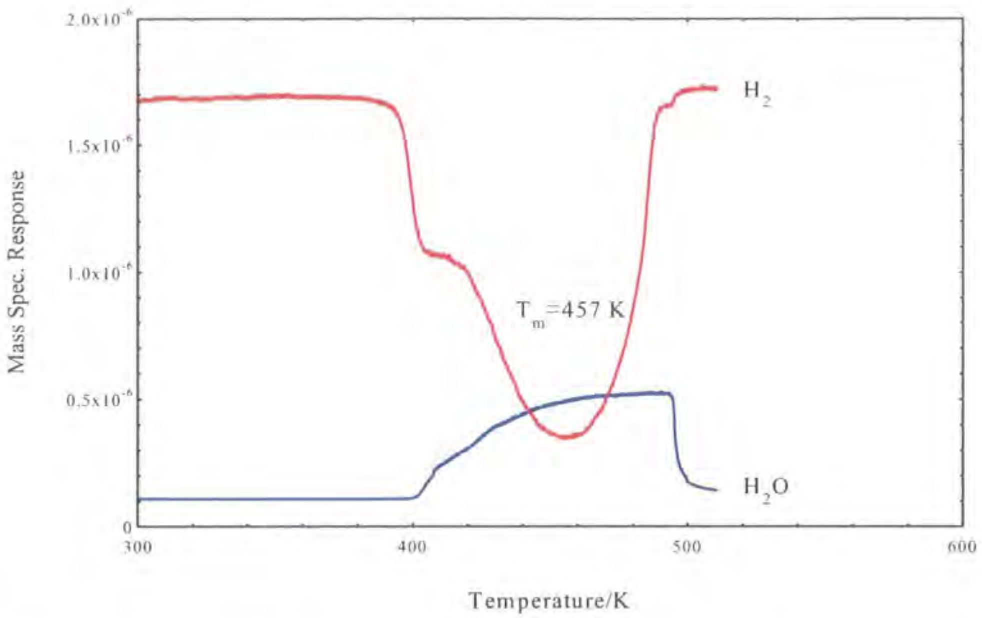

Figure 5.15 TPR of Cu0203T Catalyst Showing Water and Hydrogen

The temperature was raised at 0.5°C/min. There are three features of note in this figure: firstly, there are two peaks corresponding to hydrogen uptake, one at 410K and the other at 457K. The first is assumed to be due to surface copper activation. The second can be used to calculate the activation energy of reduction and will vary from catalyst to catalyst. The activation energy is calculated as:

$$\frac{Er}{RT_M^2} = \frac{A[H_2]_m^{-Er/RT}}{\beta}$$

Where Er is the reduction activation energy (J mol^{-1}), Tm is the temperature (K) at the maximum rate of hydrogen consumption, R is the gas constant (J K^{-1} mol^{-1}), A is a pre-exponential term and $[H_2]_m$ is the concentration of hydrogen in the gas phase (mol cm^3) at Tm, and β is the rate of heating (K s^{-1}). As the pre-exponential term is not known, the absolute value of Er cannot be calculated, but the ease of activation relates to Tm.

A list of T_m for the six catalysts tested is shown below. Note that T_m relates quite well to the activity and selectivity of the catalyst as shown in table 5.3.

Catalyst	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Peak Maximum (T_m/K)	436	438	445	452	465	434

Table 5.5 Observed Tm for Cu0203T Catalyst Samples

As all of the catalysts have identical chemical specifications the difference in activation energy is thought to be due to a physical barrier blocking the surface of the catalyst.

Two catalyst samples (sample 1 and sample 5) were compared under a SEM. Figures 5.16 and 5.17 are the resulting images at a magnification of x400. The only significant visual difference between the two samples was a large black area seen in figure 5.17 which was found to be carbon by EDAX analysis. The carbon completely obliterated the EDAX Cu signal and is therefore a candidate for the cause of the low copper surface area, and possibly low activity and selectivity. The carbon may constitute the physical barrier that is thought to increase the activation energy of reduction reported above.

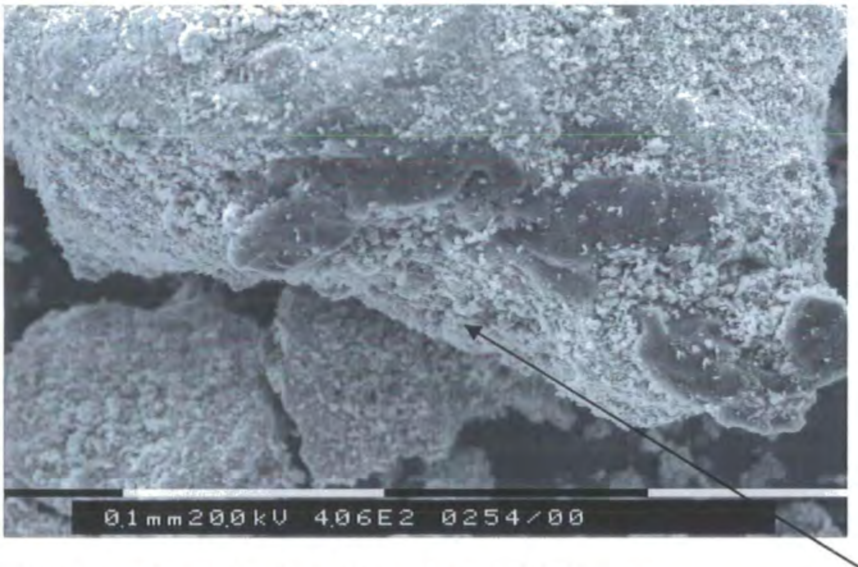

Figure 5.16 SEM of Sample 1 Cu0203T catalyst

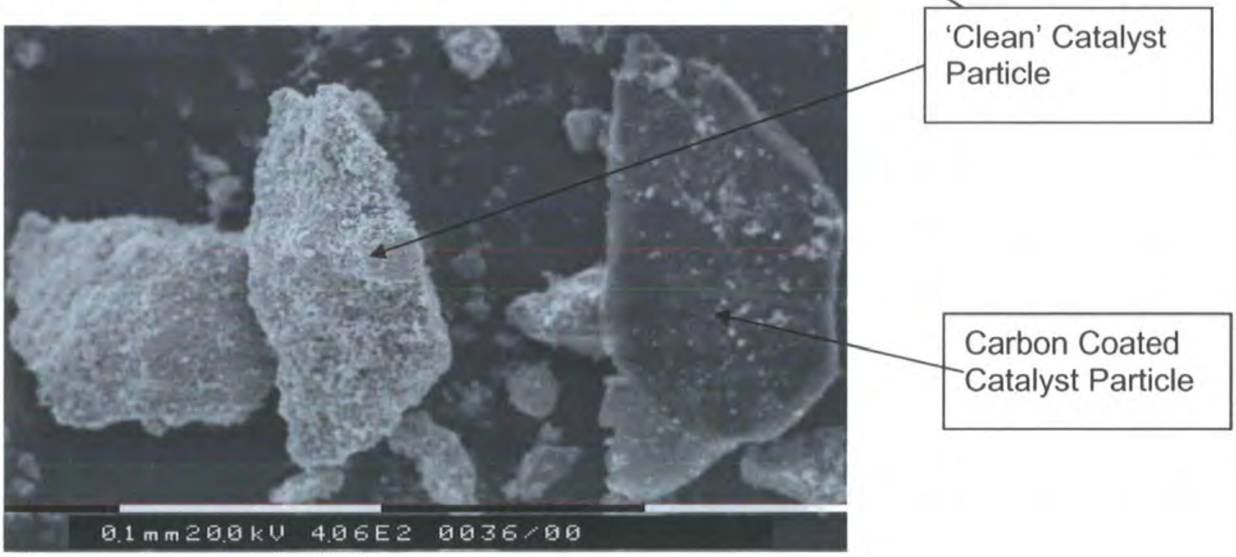

Figure 5.17 SEM of Sample 5 Cu0203T catalyst

The nature of the non copper surface area was then probed. Figure 5.18 is a plot of the desorption of hydrogen and water from the surface of catalyst samples 1 and 5. The plots were obtained by first activating the catalyst, then cooling down in a stream of hydrogen to 200K. The gas flow was then switched to He and the catalyst temperature raised to 1000K at a rate of 5K min^{-1}. Hydrogen was followed by measuring m/z = 2 and water by m/z =18.

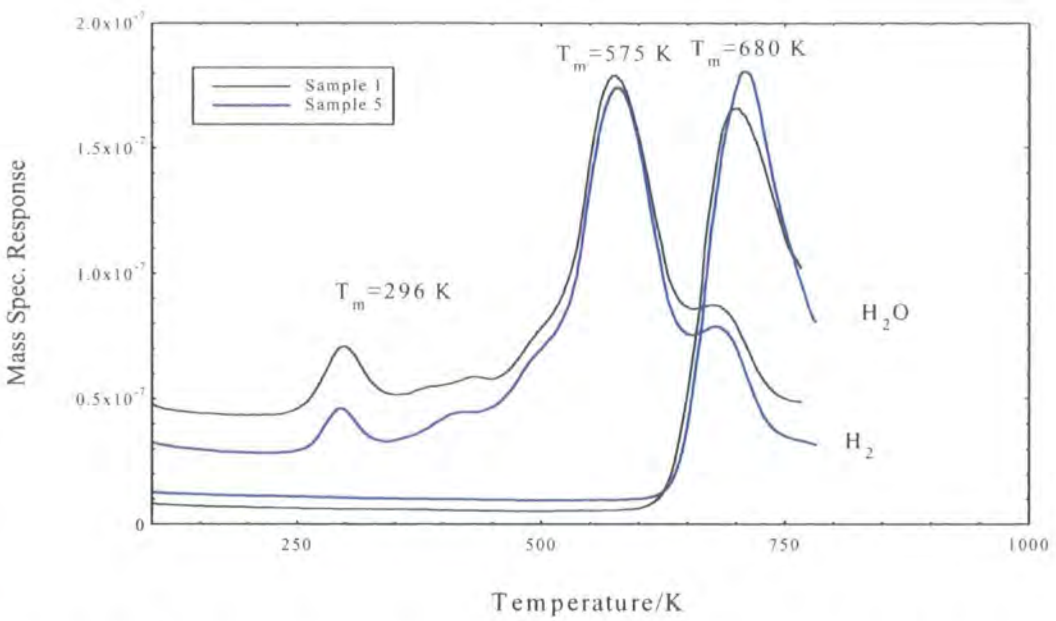

Figure 5.18 TPD of Cu0203T Catalysts Showing Desorption of Hydrogen and Water

There are four clear hydrogen desorption peaks at Tm = 296K, 410K, 575K and 616K., corresponding to four distinct desorption activation energies, and therefore four distinct sites within the catalyst. The amount of hydrogen desorbed from the two catalysts at each T_m is shown below.

Catalyst Peak	Sample 1	Sample 5
1st Peak	0.53	0.3
2nd Peak	4.8	5.7
3rd Peak	1.3	1.2
H_2O	1.45×10^{20}	1.5×10^{20}

The peak at 296K is derived from H atoms desorbing from the Cu surface, while that for 410 is for subsurface hydrogen. Hydrogen is completely desorbed from Cu above this temperature and so the peaks at 575K and 616K must derive from the non-copper surface, and are thought to be from Cr_2O_3 sites.

The water desorption from the catalyst is interesting, as the temperature of desorption (680K) is too high for it to have been adsorbed molecular water on either copper or Cr_2O_3. The suggestion is that the water comes from the reaction of two surface –OH groups:

$OH_{(a)} + OH_{(a)} = H_2O + O_{(a)} + Vo$

Where Vo is a vacant oxygen position in the surface lattice.

The normal activation and operating temperature of the ethanol dehydrogenation catalyst is only ~500K so this loss of water would not be observed. It is interesting to note that Constable[8] observed an increase in ethanol dehydrogenation activity after treating a copper catalyst at circa 680-700K. It is tempting to propose that the treatment at 680K would increase catalyst activity, and in section 5.4.2 this is explored in detail.

Examination of figure 5.18 and table 5.6 shows that there is vastly more hydrogen adsorbed on the non-copper surface than the copper surface. Assuming the commonly used figure of circa 10^{15} sites cm^{-2} for any surface, and calculating the number of molecules desorbed from the catalyst, Waugh[7] calculates that the surface coverage of H on copper is about 0.1 of a monolayer, and on Cr_2O_3 about 1 monolayer. The high energy site at 680K constitutes about 20-25% of the Cr_2O_3 sites, and so the Cr_2O_3 phase in the catalyst must be highly defected or reduced with H both on the surface and within the bulk. The copper catalyst precursor is calcined at 700K during the manufacturing process, so it is unlikely that the water derives from the manufacturing process.

The exact form of these sites was tested by the desorption of ammonia before and after desorption of hydrogen. Figure 5.19 shows the TPD of ammonia on a freshly reduced sample of the dehydrogenation catalyst.

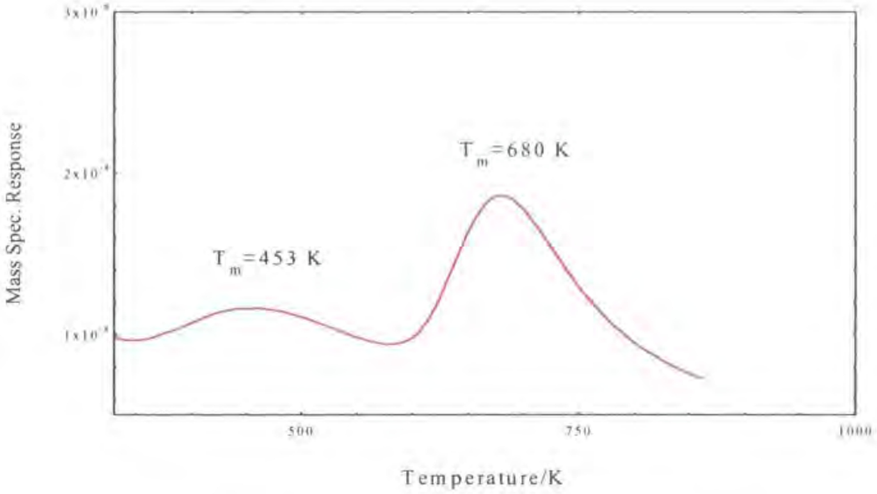

Figure 5.19 TPD of Ammonia from Cu0203T Catalyst

Two peaks appear, at 453 and 680K; the second peak coincides exactly with the water desorption peak, suggesting that they may be related. The TPD of ammonia was repeated on fresh reduced catalyst and on fresh reduced catalyst that had been subjected to TPD of hydrogen first. The results are shown in figure 5.20. It is clear that after desorption of hydrogen, subsequent TPD of ammonia does not exhibit the peak at 680K, suggesting that the ammonia is bound as an NH_4^+ species, probably on a Bronsted acid site on the Cr_2O_3 surface. An –OH defected Cr_2O_3 species is a likely candidate for this Bronsted acid. In order to ensure that the site was not associated with hydrogen bound to copper, the test was repeated on a fresh reduced catalyst that had been subjected to TPD to 600K only, desorbing H from the copper surface but not from Cr_2O_3. Figure 5.21 shows the result – the peak at 680K is still seen, indicating that it is associated with hydrogen adsorbed on Cr_2O_3 and not with hydrogen adsorbed on copper.

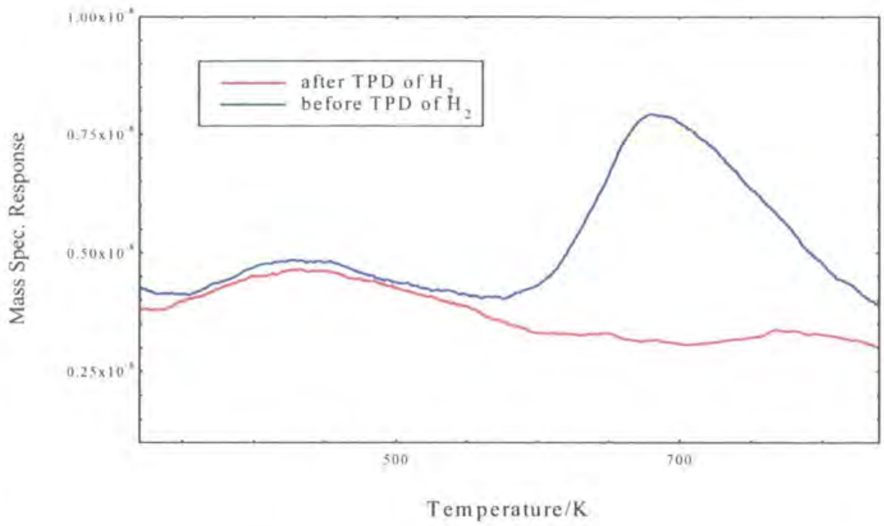

Figure 5.20 TPD of Ammonia on Cu0203T Catalyst, Before and After TPD of Hydrogen

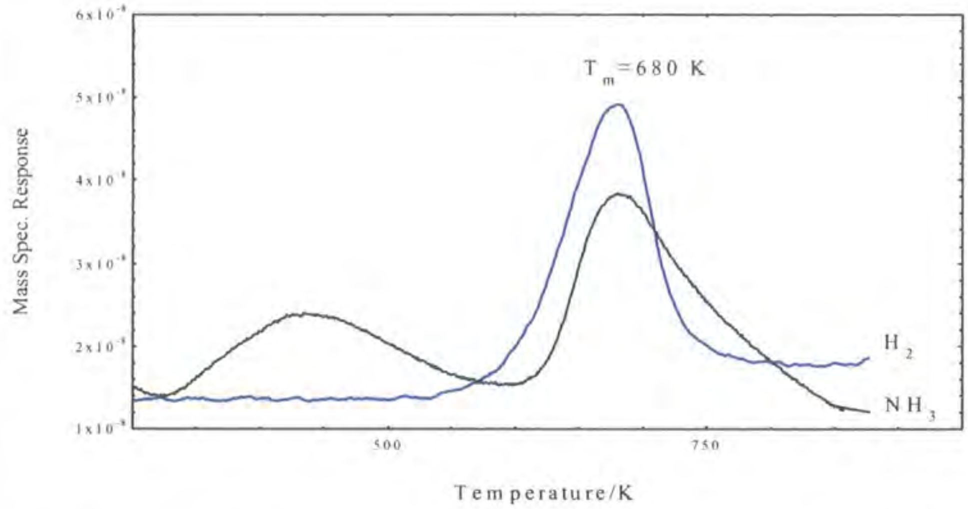

Figure 5.21 TDP of Ammonia after Hydrogen Desorption at 600K

The conclusion of this part of the characterisation work is that during normal operating temperatures (500K) there is little hydrogen adsorbed on the active copper surface but there is a large reservoir of hydrogen bound to the Cr_2O_3 surface. This hydrogen appears to partially reduce the Cr_2O_3 surface, forming Bronsted acid sites such as HCr_2O_2OH. The sites are destroyed by release of water on heating to elevated temperatures.

Constable[8] observed that on heating a copper-chrome catalyst to above 680K, an increase in activity to alcohol dehydrogenation was observed but no mechanism for the activity increase was proposed. The possible role of the Bronsted acid sites in catalyst activity is explored in section 5.4.2.

5.3.2 Mechanistic studies at UMIST

Prof. K. Waugh was commissioned to determine whether the reaction mechanism for ethyl ethanoate formation proposed in chapter 2 was plausible, and supported by data that could be gathered using the technique of reactive frontal chromatography (RFC), temperature programmed reaction spectroscopy (TPRS) and temperature programmed desorption (TPD). The results of the study by Waugh and Tabatabaei[2] support the reaction mechanism for ethyl ethanoate formation directly, and therefore indirectly support the reaction mechanism for by-product formation. The data and information used to demonstrate the mechanism for ethyl ethanoate formation are taken directly from the report; the implications for the formation of by-products are the authors interpretation of Waugh's results.

The principle of TPRS is essentially simple: a component (A) is adsorbed onto a catalyst surface (S) at low temperature. The temperature is then raised and some of the adsorbed species react to form an intermediate (BC)S which on further heating desorbed as B and C The measurements are carried out on equipment as detailed in figure 5.22 below. The identity and quantity of the desorbed species are deduced by analysis by mass spectrum.

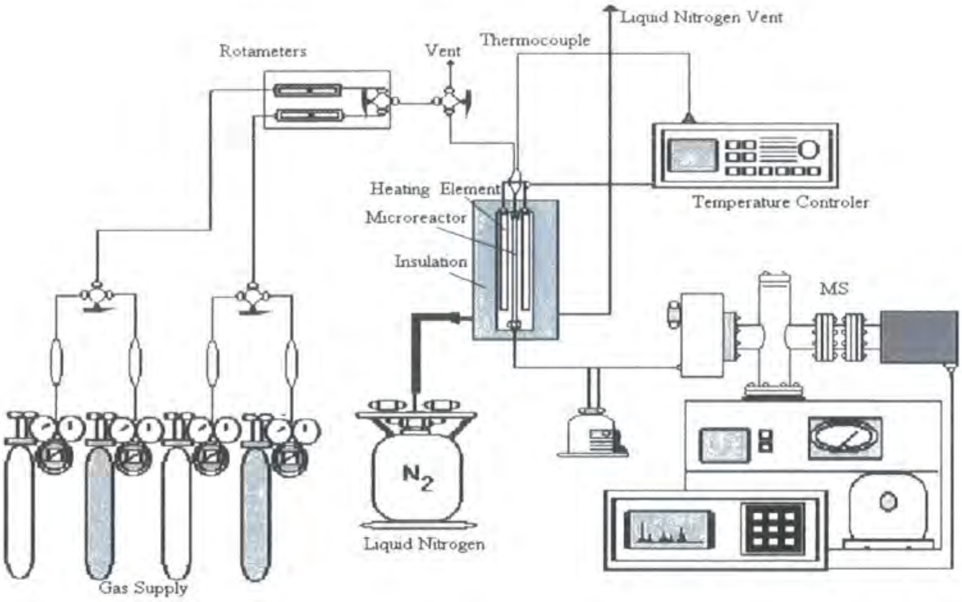

Figure 5.22: TPRS Equipment as used at UMIST

The data collected from this equipment and its interpretation are summarised in figure 5.23. Simply, the reactant A is adsorbed onto the catalyst and the temperature is raised while flowing a gas over the catalyst. Initially, some of the adsorbed A is desorbed from the catalyst – this desorption is followed by monitoring the gas flowing over the reactor for a characteristic peak in the MS signal. At some point in the temperature program there will be co-incident desorption of two or more species related to the reaction of A at the catalyst surface. The important point here is that the desorption occurs at the same temperature – this unambiguously relates the components that are desorbed. Moreover, a measure of the relative amounts of the desorbed species gives an indication of the stoichiometry of the reaction that is taking place. If the reaction is carried out isothermally – that is if the component is dosed onto the catalyst at an elevated temperature, and the desorption of the components B and C followed over time, the results can be used to calculate activation energies for the adsorption of the feed.

- Dose $A+S \xrightarrow{k_a} AS \xrightarrow{k_s} (BC)S'$
- Evacuate
- Heat $AS' \xrightarrow{k_d} A+S$

$$(BC)S' \xrightarrow{k_{dec}} B+C+S'$$

$\therefore$ Stoichiometry of B and C $\propto$ Stoichiometry of surface intermediate

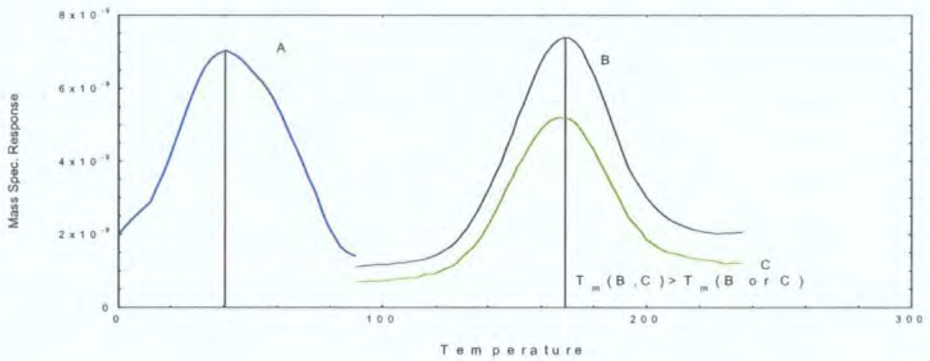

Figure 5.23 Interpretation of TPRS Data (after Waugh)

A further experiment can be carried out where the feed is passed over the catalyst continuously while the temperature is increased. The formation of the final product can be monitored and a plot of the rate of reaction vs. temperature obtained. This information can be used to calculate the activation energy of the reaction.

Waugh and Tabatabaei carried out these experiments with the following results: Figures 5.24 and 5.25 are graphical representations of the adsorption of ethanol over the DPT dehydrogenation catalysts. Figure 5.24 shows the concentration of ethanol eluting from the reactor at a range of temperatures.

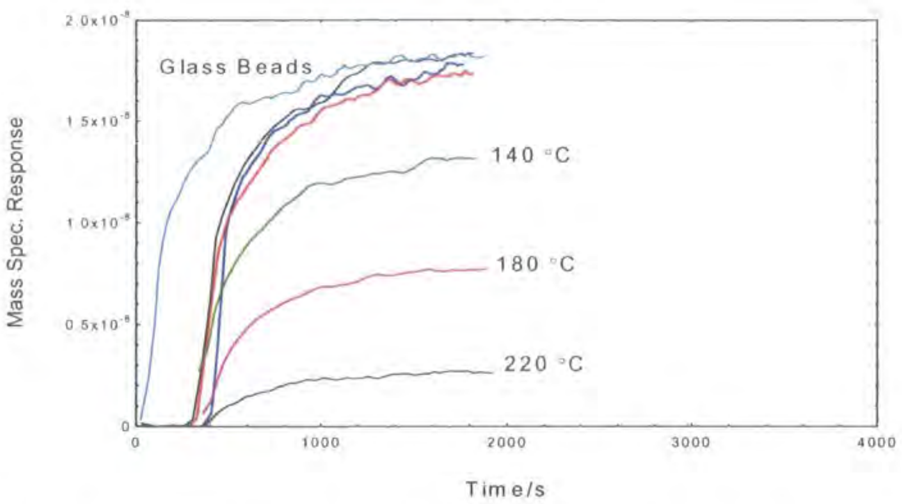

Figure 5.24 Ethanol Elution During TPRS of Cu0203T Catalyst

Figure 5.25 shows hydrogen elution during the same tests. Note that there is a spike in hydrogen production at circa 300 seconds. The data obtained from the catalyst is compared to that from glass beads, which are used as a control. The tests were carried out at 30, 70, 140, 180 and 200°C.

Note that in figure 5.24 it takes some time for ethanol to be eluted from the reactor when catalyst is loaded, as compared to when glass balls were used. Hydrogen begins to be eluted from the reactor at circa 150 seconds, while ethanol elution begins at 250 seconds. This is evidence of the formation of an ethoxy species on the catalyst surface. The temperature at which ethanol is consumed at an appreciable rate is between 100 and 140°C. At 100°C and below, the ethanol concentration at the reactor exit is similar to that observed when using glass balls- see fig 5.24.

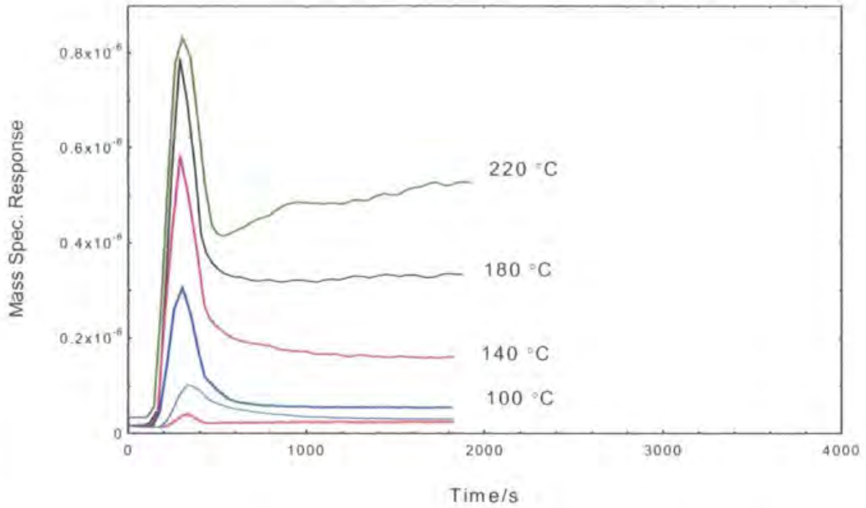

Figure 5.25 Hydrogen eluted from TPRS Tests on Cu0203T Catalyst

There is a significant peak of hydrogen desorption at 100°C (see figure 5.25) but the baseline hydrogen elution is similar to that of glass balls. This is interpreted as showing the formation of a surface ethoxy species only. The hydrogen eluted after the initial spike at 300 seconds is associated with the formation of ethyl ethanoate from this adsorbed ethoxy species. Waugh[3] calculated the activation energy of ethanol adsorption as 7.5 kcal mol^{-1}

Another important point was that the pulse of hydrogen formation did not coincide with a pulse in ethanol adsorption, and the molar amount of hydrogen generated was more than the molar amount of ethanol adsorbed. This is interpreted as being due to a second adsorbed species being formed by dehydrogenation of the adsorbed ethoxy.

$CH_3CH_2OH + Cu \leftrightarrow CH_3CH_2O(a) + H(a)$

$CH_3CH_2O(a) + Cu \leftrightarrow CH_3CHO(a) + H(a)$

$CH_3CH_2O(a) + Cu \leftrightarrow CH_3CO(a) + H(a)$

Thus ethanol forms firstly an ethoxy species, which is dehydrogenated in two steps to form an acyl species.

Waugh's initial conclusions were that this acyl species reacted with an ethoxy species to form ethyl ethanoate:

$CH_3CO(a) + CH_3CH_2O(a) \leftrightarrow CH_3CH_2OOCCH_3(g) + 2\ Cu$

This result contradicts the reaction mechanism detailed in section 2, which involves the reaction of an aldehydic species and an ethoxy species, followed by dehydrogenation.

However, further studies on the TPRS of ethyl ethanoate on the catalyst showed a slightly different pattern , where the products observed in the reactor exit were hydrogen, ethanol and ethanal. Waugh concluded that this was evidence of ethyl ethanoate decomposing at the catalyst surface, forming an ethoxy group and an aldehydic group. The bound species were then hydrogenated to form ethanol and ethanal which desorbed from the catalyst surface, and is shown as scheme (1) below . The results were also consistent with the hydrogenation of ethyl ethanoate via a hemi-acetal intermediate as shown in scheme (2).

$CH_3CH_2OOCCH_3(g) \leftrightarrow CH_3CO(a) + CH_3CH_2O(a)$ (1)

$CH_3CH_2OOCCH_3(g) + H(a) \leftrightarrow CH_2OC(OH)CH_3(a) \leftrightarrow CH_3CHO(a) + CH_3CH_2O(a)$ (2)

When Waugh dosed the catalyst with ethanal, he observed no ethyl ethanoate formation. If the scheme he proposed was true, the adsorption of ethanal onto the catalyst would be followed by dehydrogenation of some of the adsorbed ethanal to an acyl species. The released hydrogen would then hydrogenate some of the adsorbed ethanal forming ethoxy which could react with the aldehydic species forming ethyl ethanoate. The DPT scheme predicts that the adsorbed ethanal would not dehydrogenate further, and so no hydrogen would be released and therefore no ethyl ethanoate would be produced. The surface species would consist only of acyl species which do not form ethyl ethanoate, in the DPT scheme; this prediction ties in with the observations. Additionally, this result disproves the Tischenko mechanism for ethyl ethanoate formation. The DPT mechanism predicts that the reaction of two acyl species accounts for the formation of butanone and butanol. When Waugh performed the ethanal TPRS work he observed crotonaldehyde (a butanol precursor) and 2-butanol or butanone. If the major reaction of ethanal was further dehydrogenation to the bound acyl species, the formation of crotonaldehyde would not be expected.

The observation that at 680K, water is produced that is due to dehydration of hydrogen defected Cr_2O_3, was found to have a connection to a result obtained by Constable who found a rise in the activity of a copper catalyst after treatment at high temperature. A test was performed where a charge of Cu0203T catalyst was activated under hydrogen, then used to dehydrogenate ethanol at 220°C and atmospheric pressure. The reactor effluent was analysed for ethanol and ethyl ethanoate over an extended period. The result is shown graphically in figure 5.26 as the black lines.

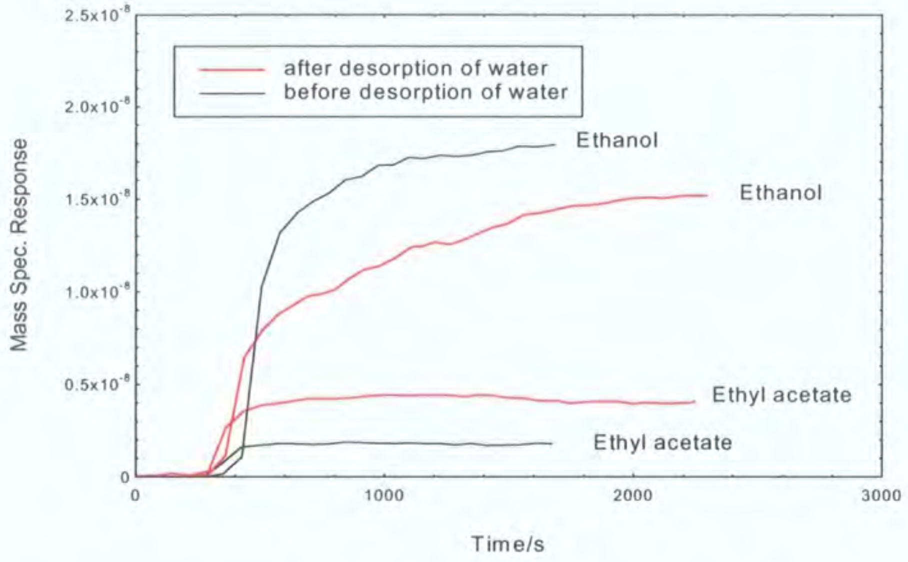

Figure 5.26 Catalyst Activity Before and After High Temperature Activation

The catalyst was then subjected to high temperature activation (to 680K) and the test repeated. The result is shown in figure 5.26 as the red lines. The result is an increase in the ethyl ethanoate and a decrease in the ethanol concentration in the exit gas for the catalyst subjected to high temperature – i.e. an increase in catalyst activity. The increase in activity was stable over a period of 40 minutes.

5.4 Conclusions

The broad conclusions for this chapter are two-fold; Firstly, a new commercially viable dehydrogenation catalyst has been found (Cu0203T), that exhibits satisfactory activity and selectivity over an extended period of operation. An investigation of some of the factors that influence the activity and selectivity have resulted in the specifications of the catalyst being altered sufficiently for it to be re-designated as a custom catalyst by Engelhard. Secondly, the reaction mechanism proposed in chapter 2 has been tested and in part validated by work performed at UMIST. Where there are differences in the interpretation of the experimental results from UMIST, the mechanism suggested by DPT seems to be more consistent. Within these two broad conclusions there are other implications of the catalyst screening and characterisation exercises. The first is that the physical properties of the catalyst are not, at first sight, those that would be expected to achieve high selectivity and activity to the desired reaction. Dehydrogenation and hydrogenation reactions tend to be carried out on high surface area catalyst. A typical copper-based catalyst would have a total surface area of $60m^2g^{-1}$ and a copper area of 30 m^2g^{-1} while Cu0203T has a total surface area of 14 m^2g^{-1} and a copper area of 7-8 m^2g^{-1}. These low areas suggest that the dehydrogenation reaction is very rapid. The discovery that below a certain surface area, catalyst activity and selectivity falls rapidly is interesting, as it suggests that there may be a way of predicting the life of a catalyst by examining the decay in surface area with time, with the break point of catalyst usefulness being 6 m^2g^{-1}. Since the catalyst retained acceptable properties at 1600 hours on line, it may be assumed that the surface area does not fall rapidly with time. The discovery of carbon deposits on the catalyst that are associated with both low surface area and poor performance has enabled the catalyst manufacturer to tighten specifications for this particular use. The carbon deposits have no appreciable effect on the catalyst's other uses.

The testwork carried out by Waugh and Tabatabaei has uncovered some interesting results that possibly explain an effect first discovered by Constable in 1924. The heating of copper-chrome catalysts to above 680K in the presence of hydrogen has been shown by our studies to increase the activity of the catalyst to the ethanol to ethyl ethanoate reaction. This is a somewhat surprising result as it is generally assumed that copper catalysts are not useful above 550K due to rapid loss of surface area and hence activity. It may well be that the low surface area of Cu0203T is relatively resistant to further loss and so the beneficial effects of the heat treatment can be observed. While the effect of heat treatment on the catalyst surface has been determined – the dehydration of H-defected Cr_2O_3 – the reason why this would increase catalyst activity is not certain. There are two possibilities; one is that the Bronsted acid sites hold ethyl ethanoate close to the catalyst surface, inhibiting the catalyst. The second is that the Bronsted acid sites hold hydrogen close to the catalyst surface, again inhibiting the reaction. Further investigation of this effect will be carried out with the aim of improving catalyst performance.

There is some disagreement between the proposed DPT and Waugh reaction mechanisms for ethyl ethanoate synthesis from ethanol but in one respect there is complete agreement – the Tischenko mechanism does not play a role in ethyl ethanoate synthesis over copper catalysts. The differences between the DPT and Waugh mechanisms lie in the sequencing of the dehydrogenation reactions that occur. There are two common steps in the mechanisms – the dehydrogenation of ethanol to an ethoxy species and the dehydrogenation of the ethoxy species to an acyl species. The mechanisms then differ – Waugh suggests a further dehydrogenation of the acyl species to an aldehydic species, followed by reaction with ethoxide to form ethyl ethanoate. DPT suggests a reaction of an acyl species with an ethoxide to form a bound hemi-acetal species, followed by dehydrogenation of this species to form ethyl ethanoate. Evidence from the formation of by-products suggests that the DPT interpretation is the correct version.

The work reported in this and other chapters has lead to the definition of an industrial process for ethyl ethanoate production from ethanol. The final chapter – Chapter 6 – describes the culmination of all this work – the construction and start-up of the World's first plant in South Africa producing ethyl ethanoate from ethanol.

Table 5.1 Catalyst Performance – Screening of Samples of Cu0203T Catalyst

Run number	11/99	12/99	13/99	14/99	15/99	16/99
Catalyst	0203T lot103	0203T lot103	0203T lot103	0203T lot103	0203T lot103	0203T lot103
Reactor Temperature, °C	221	221	221	221	221	222
LHSV, H-1	0.642	1.482	0.499	2.000	1.000	0.651
Pressure, kPa	680	680	680	680	680	680
Time On Line, H	18.5	29	45.5	55.5	68	77
Hydrogen Flow In, SLPH	2	2	2	2	2	2
Product Analysis Wt%						
Ethanal	0.411	0.677	0.405	0.897	0.583	0.446
Diethyl Ether	0.808	0.455	1.000	0.422	0.598	0.811
Ethanol	58.190	68.260	57.030	72.390	65.220	58.958
Propanone	0.006	0.007	0.006	0.008	0.006	0.007
2 Propanol	0.015	0.015	0.021	0.012	0.015	0.014
Ethyl Ethanoate	38.130	28.020	38.820	23.983	31.270	37.378
Butanone	0.216	0.165	0.138	0.189	0.164	0.164
2- Butanol	0.394	0.429	0.496	0.374	0.464	0.485
2 Propyl Ethanoate	0.014	0.007	0.015	0.006	0.009	0.013
N Butanol	0.254	0.509	0.237	0.683	0.362	0.250
2- Butyl ethanoate	0.082	0.032	0.103	0.020	0.047	0.082
Ethyl Butanoate	0.103	0.079	0.099	0.070	0.089	0.096
N Butyl Ethanoate	0.104	0.080	0.104	0.059	0.085	0.093
Conversion Of Ethanol	41.763	31.685	42.924	27.552	34.728	40.994
Selectivity To Ethyl ethanoate	93.926	92.774	93.385	91.409	93.214	93.738
Selectivity To Propanone	0.017	0.026	0.016	0.034	0.020	0.020
Selectivity To Butanone	0.650	0.668	0.406	0.879	0.598	0.501
Selectivity To 2-propanol	0.041	0.055	0.056	0.051	0.049	0.039
Selectivity To 2- Butanol	1.154	1.689	1.419	1.694	1.645	1.447
Selectivity To Butanol	0.744	2.004	0.678	3.096	1.283	0.745
Selectivity To Diethyl Ether	2.367	1.792	2.861	1.912	2.120	2.417

Table 5.2 Physical Properties of Cu0203T Catalyst

Lot Number	Specification	Lot 99	Lot 103	Lot 116	Lot 118
Copper [LOI free], %	63.5 +/- 2	64.0	64.0	64.0	64.0
Chromium [LOI free], %	11+/- 1.5	11.0	11.0	11.0	12.0
LOI 350 °C, %	2.5 max	0.2	0.3	0.2	0.2
Specific Surface Area, m^2/g	12 +/- 4	13.0	15.0	11.0	8.0
Bulk Density (Ave Packed), g/cm^3	1.95	2.00	2.00	2.20	2.20
KPT Packed Bulk Density, g/cm^3	---		2.002	2.089	2.087
Side Crush Strength, lb/in^2	20	19	18	24	19
Pore Volume, cm^3/g	0.135 +/- 0.025	0.150	0.160	0.130	0.140

Table 5.3 Lot 116 dehydrogenation Data

Run number	22/99	23/99	24/99	25/99	26/99
Catalyst	0203T lot116	0203T lot116	0203T lot116	0203T lot116	0203T lot116
Feed Type	PURE ETOH	PURE ETOH	PURE ETOH	PURE ETOH	PURE ETOH
Rx In, °C	222	219.8	222.3	221.5	222.3
Rx Out, °C	218.9	217.6	219.9	219.9	219.4
LHSV, hr^{-1}	0.647	1.500	0.501	2.011	0.998
Pressure, kPa	680	680	680	680	680
TOL, hours	14	23	45	55	62.5
H2 Flow In, SLPH	2.00	2.00	2.00	2.00	2.00
Cat Volume, cm^3	300	300	300	300	300
Feed SG	0.789	0.789	0.789	0.789	0.789
Feed Wt, g	306.2	710.2	355.5	832.8775	590.5
Product Wt, g	296.5	675.2	351.7	824.9	573.5
Mass balance time, hours	2	2	3	1.75	2.5
Mass Balance %	96.83	95.07	98.93	99.04	97.12
Product Analysis, wt%					
Ethanal	0.463	0.759	0.4135	0.937	0.664
Methanol					
Diethyl Ether	0.254	0.097	0.2888	0.062	0.202
Ethanol	58.981	71.276	56.6965	75.66	64.2
Propanone	0.005	0.005	0.0072	0.006	0.007
2-Propanol	0.016	0.012	0.0251	0.011	0.021
Butanal					
Ethyl Ethanoate	37.586	25.744	40.1884	21.55	32.66
Butananone	0.143	0.152	0.1563	0.177	0.188
2-Butanol	0.515	0.389	0.5567	0.353	0.517
2-Propyl Ethanoate	0.008	0.000	0.0084	0	0.006
2-Pentanone					
1-Butanol	0.282	0.429	0.2517	0.486	0.382
2-Pentanol					
2-Butyl Ethanoate	0.069	0.019	0.0879	0.011	0.041
Ethyl Butanoate	0.157	0.104	0.1484	0.085	0.146
Butyl Ethanoate	0.155	0.108	0.1519	0.095	0.154
Water	1.270	0.850	0.91	0.520	0.730
Others	0.096	0.057	0.109	0.047	0.082
Mole% Conversion of Ethanol	40.972	28.667	43.258	24.279	35.749
Selectivities, Ethanal free					
Ethyl Ethanoate	94.981	94.109	95.053	93.205	94.103
Propanone	0.015	0.020	0.019	0.030	0.023
Butanone	0.441	0.677	0.452	0.936	0.662
2-Propanol	0.044	0.047	0.065	0.052	0.067
2-Butanol	1.548	1.689	1.566	1.816	1.771
1-Butanol	0.848	1.866	0.708	2.500	1.309
Diethyl Ether	0.765	0.423	0.812	0.319	0.692

Table 5.4 Lot 118 Dehydrogenation Data

Run number	17/99	18/99	19/99	20/99	21/99
Catalyst	0203T lot118	0203T lot118	0203T lot118	0203T lot118	0203T lot118
Feed Type	PURE ETOH	PURE ETOH	PURE ETOH	PURE ETOH	PURE ETOH
Rx In, °C	222.1	221.6	221.1	221.9	222.8
Rx Out, °C	218.2	219.4	217.4	222.9	219.4
LHSV, hr^{-1}	0.645	1.498	0.500	2.006	1.003
Pressure, kPa	680	680	680	680	680
TOL, hours	9.5	17.5	32	45	55
H2 Flow In, SLPH	2.00	2.00	2.00	2.00	2.00
Cat Volume, cm^3	300	300	300	300	300
Feed SG	0.789	0.789	0.789	0.789	0.789
Feed Wt, g	305.2	709	236.8	949.6	474.6
Product Wt, g	299.3	705.7	231.9	919.4	461.7
Mass balance time, hours	2	2	2	2	2
Mass Balance %	98.07	99.53	97.93	96.82	97.28
Product Analysis, wt%					
Ethanal	0.636	1.135	0.523	1.470	0.944
Methanol					
Diethyl Ether	1.170	0.643	1.190	0.414	0.885
Ethanol	67.800	79.519	66.140	82.954	75.410
Propanone	0.004		0.005	0.006	0.007
2-Propanol	0.012	0.009	0.015	0.008	0.014
Butanal					
Ethyl Ethanoate	27.490	16.336	29.290	12.850	20.020
Butananone	0.138	0.150	0.143	0.168	0.178
2-Butanol	0.361	0.240	0.397	0.235	0.322
2-Propyl Ethanoate	0.032	0.016	0.029	0.012	0.025
2-Pentanone					
1-Butanol	0.456	0.660	0.409	0.730	0.583
2-Pentanol					
2-Butyl Ethanoate	0.015		0.021	0.014	0.010
Ethyl Butanoate	0.178	0.094	0.174	0.078	0.130
Butyl Ethanoate	0.189	0.119	0.182	0.100	0.159
Water	1.450	1.000	1.360	0.900	1.250
Others	0.069	0.081	0.122	0.061	0.063
Mole% Conversion of Ethanol	32.146	20.417	33.807	16.979	24.530
Selectivities, Ethanal free					
Ethyl Ethanoate	89.903	87.343	90.282	85.651	87.731
Propanone	0.015	0.000	0.018	0.044	0.035
Butanone	0.552	0.978	0.539	1.371	0.953
2-Propanol	0.043	0.051	0.051	0.058	0.067
2-Butanol	1.404	1.523	1.455	1.861	1.678
1-Butanol	1.773	4.195	1.499	5.782	3.038
Diethyl Ether	4.550	4.090	4.362	3.283	4.612

Table 5.5 Dehydrogenation Life Test on Cu0203T Catalyst

Run number	1	2	3	4	5	6	7	8	9	10
Feed Type	PURE ETHANOL							Ethylol	Ethylol	Ethylol
Reactor Exit temperature, °C	220	220	220	220	220	220	220	220	220	220
LHSV,h^{-1}	0.759	0.758	0.769	0.764	0.757	0.765	0.751	0.746	0.500	1.007
Pressure, kPa	680	680	680	680	680	680	680	680	680	680
TOL, h	54.0	78.0	102.0	126.0	150.0	174.0	198.0	218.0	240.0	252.0
H2 Flow In, SLPH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Product Analysis										
Ethanal	0.400	0.403	0.408	0.413	0.417	0.424	0.420	0.484	0.369	0.580
Methanol	0.003	0.003	0.003	0.003	0.002	0.003	0.002	0.037	0.032	0.041
Diethyl Ether	0.347	0.335	0.327	0.322	0.314	0.315	0.311	0.380	0.449	0.312
Ethanol	58.440	58.676	59.044	59.651	59.907	59.993	59.980	61.214	56.026	67.089
Propanone	0.004	0.004	0.003	0.003	0.003	0.003	0.004	0.732	0.596	0.806
2-Propanol	0.013	0.016	0.014	0.013	0.013	0.013	0.013	2.386	2.401	2.384
di 2-Propyl Ether	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.115	0.117	0.117
Butanal	0.009	0.008	0.008	0.008	0.008	0.008	0.008	0.011	0.011	0.012
Ethyl Ethanoate	39.490	39.246	38.879	38.299	38.023	37.902	37.926	32.453	37.626	26.765
Butanone	0.130	0.132	0.135	0.134	0.136	0.139	0.140	0.118	0.110	0.106
2-Butanol	0.465	0.477	0.483	0.470	0.480	0.486	0.489	0.370	0.411	0.297
2-Propyl Ethanoate	0.006	0.007	0.005	0.005	0.005	0.006	0.005	0.105	0.273	0.102
Pentanone	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.134	0.132	0.118
Butanol	0.271	0.280	0.284	0.288	0.292	0.294	0.296	0.293	0.245	0.383
2-Pentanol	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.278	0.322	0.217
2-butyl ethanoate	0.044	0.043	0.042	0.038	0.038	0.038	0.038	0.060	0.075	0.052
Ethyl Butanoate	0.154	0.151	0.147	0.141	0.140	0.139	0.139	0.124	0.113	0.084
Butyl Ethanoate	0.144	0.141	0.139	0.135	0.119	0.134	0.136	0.129	0.120	0.088
Di Butyl Ether	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.021	0.035	0.013
Water	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Unknowns	0.078	0.076	0.077	0.072	0.101	0.101	0.091	0.542	0.528	0.429
Conversion of Ethanol	41.443	41.206	40.838	40.229	39.973	39.887	39.900	35.651	41.105	29.475
Selectivity										
Ethyl Ethanoate	95.283	95.241	95.213	95.229	95.161	95.070	95.087	94.713	95.043	94.734
Propanone	0.011	0.011	0.008	0.008	0.009	0.009	0.011	2.364	1.654	3.166
Butanone	0.383	0.392	0.404	0.407	0.416	0.426	0.429	0.404	0.324	0.438
2-Propanol	0.035	0.043	0.038	0.036	0.036	0.036	0.036	-3.395	-2.896	-4.126
2-Butanol	1.334	1.377	1.407	1.390	1.429	1.450	1.458	1.271	1.224	1.235
Butanol	0.778	0.808	0.827	0.852	0.869	0.877	0.883	0.675	0.440	1.199
Diethyl Ether	0.996	0.967	0.952	0.952	0.935	0.940	0.927	0.947	1.027	0.862

Table 5.5 Dehydrogenation Life Test on Cu0203T Catalyst - Continued

Run number	11	12	13	14	15	16	17	18	19	20
Feed Type	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol
Reactor Exit temperature, °C	220	220	225	225	225	225	225	225	225	225
LHSV,h^{-1}	1.497	0.753	0.748	0.764	0.751	0.650	0.653	0.656	0.655	0.659
Pressure, kPa	680	680	680	680	680	680	680	680	680	680
TOL, h	266.3	302.0	333.0	365.0	389.0	413.0	437.0	461.0	485.0	509.0
H2 Flow In, SLPH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Product Analysis										
Ethanal	0.776	0.509	0.528	0.529	0.535	0.506	0.507	0.513	0.515	0.515
Methanol	0.048	0.036	0.037	0.035	0.035	0.036	0.035	0.035	0.035	0.036
Diethyl Ether	0.195	0.387	0.424	0.432	0.442	0.480	0.479	0.487	0.493	0.499
Ethanol	77.690	60.980	58.535	58.900	59.090	57.140	56.750	56.890	57.010	57.400
Propanone	0.961	0.754	0.773	0.781	0.788	0.763	0.757	0.762	0.768	0.773
2-Propanol	2.345	2.361	2.299	2.302	2.290	2.291	2.264	2.264	2.260	2.282
di 2-Propyl Ether	0.116	0.117	0.117	0.117	0.118	0.118	0.116	0.116	0.117	0.116
Butanal	0.012	0.012	0.010	0.011	0.011	0.011	0.011	0.011	0.011	0.011
Ethyl Ethanoate	16.240	32.660	34.763	34.390	34.200	36.060	35.470	35.200	35.110	34.870
Butanone	0.072	0.127	0.157	0.157	0.160	0.163	0.165	0.168	0.169	0.170
2-Butanol	0.160	0.387	0.453	0.450	0.452	0.482	0.483	0.490	0.486	0.490
2-Propyl Ethanoate	0.037	0.107	0.184	0.108	0.172	0.201	0.190	0.185	0.182	0.177
Pentanone	0.090	0.140	0.163	0.162	0.164	0.166	0.165	0.167	0.165	0.164
Butanol	0.604	0.322	0.339	0.338	0.342	0.323	0.323	0.333	0.330	0.329
2-Pentanol	0.123	0.285	0.313	0.312	0.307	0.330	0.324	0.321	0.318	0.316
2-butyl ethanoate	0.045	0.062	0.067	0.066	0.066	0.071	0.070	0.069	0.068	0.068
Ethyl Butanoate	0.036	0.115	0.147	0.141	0.141	0.147	0.146	0.148	0.146	0.143
Butyl Ethanoate	0.041	0.123	0.155	0.152	0.153	0.159	0.158	0.161	0.158	0.156
Di Butyl Ether	0.002	0.000	0.019	0.025	0.024	0.028	0.000	0.027	0.023	0.022
Water	0.000	0.000	0.000	0.000	0.000	0.000	1.060	1.120	1.080	0.920
Unknowns	0.404	0.512	0.485	0.581	0.499	0.509	0.509	0.513	0.536	0.529
Conversion of Ethanol	18.331	35.897	38.467	38.083	37.884	39.934	40.344	40.196	40.070	39.660
Selectivity										
Ethyl Ethanoate	93.320	94.725	94.020	93.965	93.929	93.882	94.027	93.783	93.755	93.690
Propanone	6.158	2.422	2.317	2.365	2.399	2.200	2.222	2.249	2.272	2.301
Butanone	0.472	0.433	0.503	0.508	0.521	0.503	0.519	0.531	0.536	0.542
2-Propanol	-6.950	-3.453	-3.405	-3.431	-3.485	-3.300	-3.439	-3.457	-3.476	-3.433
2-Butanol	1.068	1.322	1.445	1.450	1.465	1.481	1.511	1.541	1.532	1.554
Butanol	3.460	0.771	0.774	0.779	0.796	0.695	0.708	0.743	0.736	0.737
Diethyl Ether	0.599	0.965	1.019	1.055	1.093	1.154	1.172	1.203	1.225	1.252

Table 5.5 Dehydrogenation Life Test on Cu0203T Catalyst - Continued

Run number	21	22	23	24	25	26	27	28	29	30
Feed Type	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol
Reactor Exit temperature, °C	225	226	225	225	224	224	224	225	225	
LHSV,h^{-1}	0.651	0.657	0.668	0.656	0.651	0.656	0.651	0.651	0.652	0.658
Pressure, kPa	680	680	680	680	680	680	680	680	680	680
TOL, h	533.0	557.0	581.0	605.0	629.0	653.0	687.0	748.0	772.0	796.0
H2 Flow In, SLPH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Product Analysis										
Ethanal	0.522	0.530	0.538	0.543	0.538	0.538	0.548	0.548	0.566	0.580
Methanol	0.037	0.035	0.036	0.037	0.036	0.036	0.037	0.034	0.036	0.037
Diethyl Ether	0.500	0.508	0.525	0.529	0.535	0.542	0.542	0.581	0.575	0.584
Ethanol	57.560	57.810	57.680	57.730	58.200	58.150	58.580	58.453	58.921	58.940
Propanone	0.772	0.781	0.792	0.792	0.794	0.797	0.799	0.813	0.812	0.813
2-Propanol	2.280	2.270	2.263	2.262	2.276	2.270	2.289	2.431	2.270	2.272
di 2-Propyl Ether	0.117	0.115	0.117	0.117	0.116	0.116	0.115	0.116	0.116	0.115
Butanal	0.012	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011
Ethyl Ethanoate	34.850	34.410	34.600	34.250	34.080	33.850	33.490	33.513	33.221	32.926
Butanone	0.171	0.172	0.178	0.176	0.174	0.174	0.171	0.179	0.179	0.181
2-Butanol	0.492	0.489	0.499	0.492	0.487	0.483	0.478	0.486	0.486	0.494
2-Propyl Ethanoate	0.178	0.170	0.167	0.165	0.166	0.108	0.161	0.154	0.148	0.147
Pentanone	0.165	0.164	0.168	0.164	0.161	0.160	0.157	0.162	0.162	0.164
Butanol	0.329	0.329	0.347	0.328	0.322	0.314	0.312	0.320	0.324	0.335
2-Pentanol	0.316	0.315	0.310	0.305	0.300	0.295	0.292	0.297	0.295	0.296
2-butyl ethanoate	0.068	0.067	0.068	0.066	0.066	0.065	0.064	0.064	0.063	0.063
Ethyl Butanoate	0.143	0.139	0.142	0.137	0.132	0.128	0.125	0.127	0.127	0.130
Butyl Ethanoate	0.156	0.152	0.156	0.151	0.144	0.140	0.136	0.141	0.141	0.145
Di Butyl Ether	0.022	0.018	0.024	0.023	0.023	0.022	0.021	0.018	0.021	0.020
Water	0.840	1.000	0.830	1.180	0.910	1.200	1.150	1.210	1.060	1.240
Unknowns	0.456	0.502	0.535	0.531	0.518	0.590	0.510	0.331	0.455	0.496
Conversion of Ethanol	39.492	39.229	39.366	39.313	38.819	38.872	38.420	38.553	38.061	38.041
Selectivity										
Ethyl Ethanoate	93.853	93.730	93.468	93.573	93.616	93.624	93.636	93.443	93.551	93.262
Propanone	2.304	2.358	2.372	2.399	2.419	2.445	2.478	2.515	2.537	2.555
Butanone	0.547	0.557	0.572	0.572	0.568	0.572	0.568	0.594	0.599	0.610
2-Propanol	-3.447	-3.516	-3.508	-3.551	-3.528	-3.570	-3.551	-3.105	-3.635	-3.650
2-Butanol	1.564	1.572	1.592	1.587	1.579	1.577	1.577	1.600	1.616	1.652
Butanol	0.739	0.747	0.799	0.746	0.731	0.709	0.710	0.735	0.756	0.797
Diethyl Ether	1.258	1.298	1.342	1.371	1.398	1.430	1.446	1.571	1.567	1.606

Table 5.5 Dehydrogenation Life Test on Cu0203T Catalyst - Continued

Run number	31	32	33	34	35	36	37	38	39	40
Feed Type	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol
Reactor Exit temperature, °C	225	225	225	225	225	229	229	229	229	229
LHSV,h^{-1}	0.650	0.650	0.667	0.650	0.549	0.653	0.649	0.651	0.652	0.653
Pressure, kPa	680	680	680	680	680	680	680	680	680	680
TOL, h	820.0	844.0	868.0	892.0	916.0	978.0	1019.0	1047.0	1071.0	1095.0
H2 Flow In, SLPH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Product Analysis										
Ethanal	0.569	0.567	0.593	0.579	0.524	0.613	0.596	0.628	0.631	0.618
Methanol	0.034	0.034	0.037	0.035	0.034	0.033	0.035	0.037	0.037	0.036
Diethyl Ether	0.586	0.585	0.614	0.610	0.687	0.706	0.729	0.727	0.742	0.747
Ethanol	59.228	59.350	60.140	59.490	56.970	56.422	57.784	56.929	56.716	56.847
Propanone	0.817	0.818	0.834	0.834	0.801	0.859	0.849	0.859	0.869	0.871
2-Propanol	2.274	2.266	2.290	2.261	2.261	2.186	2.225	2.187	2.170	2.176
di 2-Propyl Ether	0.116	0.115	0.117	0.116	0.117	0.115	0.116	0.116	0.116	0.116
Butanal	0.011	0.011	0.011	0.010	0.011	0.011	0.013	0.013	0.012	0.013
Ethyl Ethanoate	32.968	32.810	32.870	32.650	34.920	34.587	33.941	34.309	34.201	34.213
Butanone	0.182	0.181	0.182	0.184	0.185	0.232	0.209	0.229	0.232	0.235
2-Butanol	0.498	0.485	0.487	0.490	0.519	0.578	0.537	0.565	0.566	0.570
2-Propyl Ethanoate	0.143	0.144	0.140	0.139	0.168	0.150	0.159	0.150	0.144	0.143
Pentanone	0.165	0.163	0.164	0.165	0.167	0.195	0.174	0.190	0.191	0.192
Butanol	0.337	0.332	0.336	0.343	0.316	0.374	0.309	0.362	0.367	0.369
2-Pentanol	0.295	0.291	0.290	0.292	0.314	0.328	0.304	0.317	0.311	0.310
2-butyl ethanoate	0.062	0.062	0.062	0.061	0.066	0.067	0.066	0.066	0.065	0.065
Ethyl Butanoate	0.129	0.126	0.126	0.128	0.133	0.163	0.125	0.154	0.158	0.159
Butyl Ethanoate	0.145	0.143	0.142	0.146	0.151	0.187	0.141	0.176	0.180	0.181
Di Butyl Ether	0.020	0.019	0.019	0.019	0.022	0.023	0.021	0.018	0.021	0.018
Water	0.920	1.010	0.000	0.960	1.080	1.530	1.141	1.440	1.640	1.530
Unknowns	0.489	0.478	0.535	0.477	0.539	0.625	0.515	0.515	0.607	0.575
Conversion of Ethanol	37.739	37.610	36.780	37.463	40.112	40.688	39.257	40.155	40.379	40.242
Selectivity										
Ethyl Ethanoate	93.258	93.387	93.014	93.172	93.065	92.019	92.766	92.368	92.032	92.083
Propanone	2.565	2.584	2.621	2.643	2.368	2.539	2.578	2.570	2.599	2.606
Butanone	0.613	0.613	0.613	0.625	0.587	0.740	0.682	0.738	0.747	0.757
2-Propanol	-3.639	-3.687	-3.591	-3.712	-3.466	-3.680	-3.663	-3.721	-3.770	-3.753
2-Butanol	1.663	1.630	1.627	1.651	1.634	1.818	1.734	1.798	1.800	1.813
Butanol	0.803	0.791	0.800	0.830	0.690	0.873	0.685	0.844	0.860	0.866
Diethyl Ether	1.611	1.618	1.706	1.707	1.838	1.895	2.022	1.985	2.032	2.049

Table 5.5 Dehydrogenation Life Test on Cu0203T Catalyst - Continued

Run number	41	42	43	44	45	46	47	48	49	50
Feed Type	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol
Reactor Exit temperature, °C	230	229	229	230	229	229	229	229	229	225
LHSV,h^{-1}	0.654	0.650	0.652	0.653	0.650	0.650	0.653	0.654	0.653	0.500
Pressure, kPa	680	680	680	680	680	680	680	680	680	680
TOL, h	1119.0	1143.0	1167.0	1191.0	1215.0	1239.0	1263.0	1287.0	1307.0	1331.0
H2 Flow In, SLPH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Product Analysis										
Ethanal	0.627	0.630	0.635	0.643	0.645	0.651	0.653	0.668	0.660	0.557
Methanol	0.035	0.035	0.037	0.036	0.037	0.038	0.038	0.080	0.037	0.037
Diethyl Ether	0.754	0.760	0.767	0.769	0.783	0.792	0.804	0.805	0.816	0.858
Ethanol	57.102	56.547	57.024	57.746	57.638	57.720	57.870	57.930	58.053	57.150
Propanone	0.870	0.888	0.869	0.874	0.880	0.884	0.888	0.885	0.886	0.820
2-Propanol	2.184	2.213	2.157	2.188	2.182	2.181	2.177	2.177	2.173	2.240
di 2-Propyl Ether	0.115	0.111	0.114	0.114	0.115	0.115	0.115	0.115	0.114	0.114
Butanal	0.011	0.012	0.014	0.014	0.013	0.011	0.011	0.012	0.012	0.011
Ethyl Ethanoate	33.920	34.569	33.577	33.596	33.541	33.420	33.330	33.100	33.010	33.930
Butanone	0.235	0.320	0.233	0.236	0.235	0.236	0.235	0.238	0.237	0.195
2-Butanol	0.569	0.567	0.558	0.575	0.567	0.567	0.560	0.569	0.566	0.534
2-Propyl Ethanoate	0.142	0.137	0.141	0.136	0.132	0.132	0.132	0.129	0.129	0.148
Pentanone	0.190	0.184	0.188	0.190	0.188	0.188	0.186	0.187	0.186	0.005
Butanol	0.366	0.345	0.394	0.374	0.368	0.368	0.364	0.375	0.369	0.316
2-Pentanol	0.318	0.309	0.324	0.318	0.312	0.311	0.305	0.307	0.305	0.304
2-butyl ethanoate	0.065	0.060	0.077	0.063	0.063	0.062	0.063	0.062	0.062	0.062
Ethyl Butanoate	0.156	0.149	0.159	0.156	0.152	0.153	0.149	0.152	0.150	0.131
Butyl Ethanoate	0.178	0.171	0.194	0.179	0.175	0.174	0.171	0.174	0.173	0.148
Di Butyl Ether	0.018	0.010	0.018	0.014	0.013	0.015	0.019	0.018	0.012	0.019
Water	1.340	1.480	1.860	1.250	1.420	1.430	1.400	1.480	1.520	1.750
Unknowns	0.787	0.465	0.658	0.502	0.534	0.551	0.529	0.536	0.520	0.666
Conversion of Ethanol	39.974	40.557	40.055	39.297	39.410	39.324	39.166	39.103	38.974	39.923
Selectivity										
Ethyl Ethanoate	91.470	92.154	91.653	91.994	92.030	91.945	92.009	91.787	91.901	92.653
Propanone	2.608	2.633	2.637	2.661	2.685	2.704	2.726	2.729	2.743	2.485
Butanone	0.759	1.027	0.761	0.774	0.772	0.778	0.777	0.790	0.790	0.635
2-Propanol	-3.736	-3.608	-3.863	-3.782	-3.808	-3.821	-3.846	-3.863	-3.891	-3.615
2-Butanol	1.814	1.786	1.800	1.861	1.839	1.844	1.827	1.865	1.862	1.723
Butanol	0.858	0.782	0.960	0.898	0.880	0.882	0.872	0.912	0.896	0.707
Diethyl Ether	2.075	2.070	2.143	2.156	2.206	2.241	2.288	2.302	2.348	2.439

Table 5.5 Dehydrogenation Life Test on Cu0203T Catalyst - Continued

Run number	51	52	53	54	55	56	57	58	59	60
Feed Type	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	Ethylol	PureEtOH	PureEtOH	PureEtOH	PureEtOH
Reactor Exit temperature, °C	221	220	219	233	224	224	225	220	221	234
LHSV,h^{-1}	1.500	1.033	0.650	0.650	0.449	0.649	0.635	0.772	0.750	0.752
Pressure, kPa	680	680	680	680	680	680	680	680	680	680
TOL, h	1350.0	1372.0	1392.5	1422.5	1450.0	1494.0	1539.0	1563.0	1590.5	1637.0
H2 Flow In, SLPH	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Product Analysis										
Ethanal	1.189	0.870	0.647	0.686	0.531	0.664	0.657	0.696	0.694	0.770
Methanol	0.049	0.044	0.040	0.036	0.036	0.038	0.004	0.000	0.000	0.005
Diethyl Ether	0.343	0.450	0.605	0.926	0.958	0.777	0.898	0.691	0.705	0.966
Ethanol	78.160	73.430	66.720	55.640	56.540	62.550	63.430	69.135	69.690	59.030
Propanone	1.191	1.002	0.852	0.916	0.804	0.877	0.006	0.005	0.006	0.010
2-Propanol	2.055	2.221	2.334	2.103	2.263	2.245	0.018	0.017	0.012	0.021
di 2-Propyl Ether	0.113	0.113	0.114	0.115	0.114	0.112	0.000	0.000	0.000	0.000
Butanal	0.012	0.011	0.011	0.010	0.011	0.011	0.008	0.005	0.006	0.012
Ethyl Ethanoate	13.980	18.960	25.572	34.720	34.650	28.910	32.550	26.935	26.500	35.350
Butanone	0.129	0.134	0.143	0.279	0.192	0.193	0.225	0.178	0.169	0.321
2-Butanol	0.203	0.277	0.374	0.627	0.541	0.453	0.581	0.440	0.430	0.680
2-Propyl Ethanoate	0.132	0.069	0.111	0.138	0.161	0.111	0.014	0.009	0.009	0.023
Pentanone	0.113	0.119	0.125	0.217	0.162	0.020	0.000	0.000	0.000	0.005
Butanol	0.663	0.482	0.361	0.405	0.308	0.323	0.377	0.408	0.393	0.453
2-Pentanol	0.112	0.157	0.218	0.335	0.313	0.152	0.003	0.003	0.002	0.004
2-butyl ethanoate	0.042	0.044	0.049	0.024	0.064	0.288	0.018	0.010	0.010	0.025
Ethyl Butanoate	0.039	0.055	0.079	0.185	0.132	0.105	0.138	0.091	0.087	0.212
Butyl Ethanoate	0.044	0.064	0.092	0.213	0.150	0.121	0.162	0.112	0.105	0.250
Di Butyl Ether	0.002	0.000	0.007	0.015	0.021	0.018	0.000	0.007	0.016	0.014
Water	1.070	1.140	1.100	1.730	1.510	1.460	0.920	1.140	0.910	1.610
Unknowns	0.356	0.355	0.441	0.679	0.531	0.547	-0.014	0.115	0.253	0.233
Conversion of Ethanol	17.837	22.809	29.863	41.510	40.564	34.246	36.487	30.775	30.170	40.852
Selectivity										
Ethyl Ethanoate	90.056	92.455	92.887	90.979	92.241	92.145	91.833	91.623	91.154	90.314
Propanone	8.595	5.453	3.439	2.671	2.374	3.108	0.019	0.019	0.023	0.029
Butanone	0.979	0.770	0.613	0.878	0.609	0.733	0.776	0.740	0.711	1.002
2-Propanol	-9.852	-6.562	-4.434	-3.864	-3.457	-4.203	0.056	0.064	0.045	0.059
2-Butanol	1.528	1.586	1.600	1.943	1.702	1.704	1.949	1.780	1.759	2.066
Butanol	4.333	2.227	1.135	0.956	0.664	0.852	1.265	1.650	1.608	1.376
Diethyl Ether	1.808	1.989	2.151	2.553	2.695	2.540	3.013	2.795	2.884	2.935

Table 5.5 Dehydrogenation Life Test on Cu0203T Catalyst - Continued

Run number	61	62	63	64	65	66	67
Feed Type	PureEtOH	PureEtOH	PureEtOH	PureEtOH	PureEtOH	synthetic	synthetic
Reactor Exit temperature, °C	220	221	221	221	221	221	221
LHSV,h^{-1}	0.391	0.500	0.754	0.503	0.502	0.501	0.502
Pressure, kPa	680	680	680	680	680	680	680
TOL, h	1675.0	1699.0	1720.0	1744.5	1768.0	1787.0	1795.0
H2 Flow In, SLPH	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Product Analysis							
Ethanal	0.472	0.545	0.719	0.540	0.608	0.585	0.566
Methanol	0.003	0.000	0.000	0.000	0.000	0.000	1.036
Diethyl Ether	0.976	0.911	0.655	0.897	0.668	0.637	0.628
Ethanol	59.389	61.450	69.281	61.796	64.058	61.182	60.813
Propanone	0.004	0.005	0.004	0.004	0.005	0.924	0.896
2-Propanol	0.016	0.014	0.011	0.015	0.013	2.585	2.354
di 2-Propyl Ether	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Butanal	0.007	0.008	0.006	0.011	0.006	0.000	0.006
Ethyl Ethanoate	36.407	34.120	27.111	34.242	31.928	30.574	30.441
Butanone	0.173	0.174	0.171	0.179	0.165	0.156	0.154
2-Butanol	0.541	0.500	0.406	0.519	0.439	0.412	0.426
2-Propyl Ethanoate	0.014	0.018	0.012	0.017	0.014	0.131	0.143
Pentanone	0.000	0.000	0.000	0.000	0.000	0.164	0.155
Butanol	0.288	0.395	0.480	0.401	0.430	0.392	0.352
2-Pentanol	0.002	0.002	0.002	0.003	0.002	0.303	0.302
2-butyl ethanoate	0.023	0.018	0.009	0.018	0.013	0.011	0.013
Ethyl Butanoate	0.126	0.171	0.123	0.169	0.162	0.142	0.133
Butyl Ethanoate	0.149	0.194	0.149	0.194	0.193	0.170	0.155
Di Butyl Ether	0.019	0.013	0.015	0.015	0.016	0.007	0.010
Water	1.200	1.280	0.710	0.810	1.160	1.450	0.970
Unknowns	0.186	0.178	0.134	0.166	0.116	0.173	0.444
Conversion of Ethanol	40.492	38.427	30.580	38.080	35.814	35.840	34.987
Selectivity							
Ethyl Ethanoate	92.468	91.795	91.379	91.794	92.373	92.012	93.555
Propanone	0.012	0.015	0.015	0.012	0.016	3.164	3.134
Butanone	0.537	0.572	0.704	0.586	0.583	0.574	0.578
2-Propanol	0.045	0.041	0.041	0.044	0.041	-4.767	-5.112
2-Butanol	1.634	1.600	1.627	1.655	1.510	1.474	1.557
Butanol	0.870	1.264	1.924	1.278	1.479	1.403	1.286
Diethyl Ether	2.948	2.915	2.625	2.860	2.298	2.280	2.295

References for Chapter 5

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Chapter 6

Plant Start-up, Conclusions and Further Work

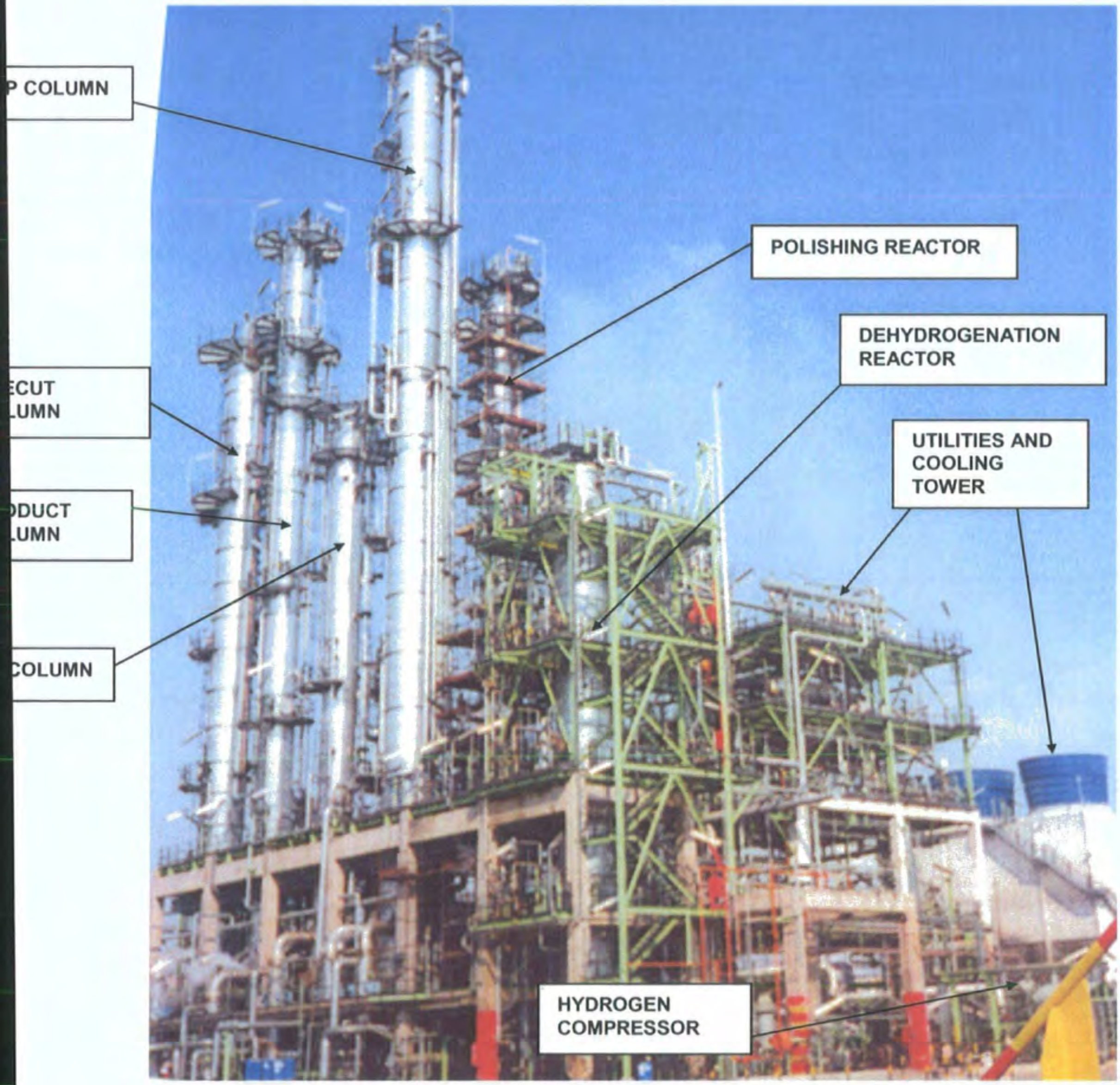
6 Introduction

The culmination of any industrial R&D is the building and operation of a commercial scale plant. DPT, unlike the majority of industrial research organisations, had no parent company to build and operate plant and so in order to make profit and to continue research, technology (in the form of licences to operate) must be sold to third parties. The ethyl ethanoate programme had been instigated with the aim of developing the technology and then selling the first licence to Sasol Pty of South Africa. In November of 1999, Sasol bought a licence to build and operate a 50,000 TPA ethanol to ethyl ethanoate unit based on the technology development described in this thesis.

By April 2001, the plant had been constructed and was ready for operation. A team of Chemical engineers and the author were assigned to the Secunda site to commission and start the world's first ethanol to ethyl ethanoate unit. Section 6.2 is a brief description of the main sections of the commercial unit, and section 6.3 a brief description of how the commissioning and start-up was achieved. Section 6.4 concludes the thesis, and lists the further work and development that have been carried out during write-up.

6.1 Description Of The Commercial Ethyl Ethanoate Unit

The huge difference in scale between a laboratory reactor and the 'real thing' is something that still surprises even experienced industrial researchers. Figure 6.1 is a picture of the ethanol to ethyl ethanoate plant. It is difficult to gauge scale within this picture without some calibration. The tallest distillation tower measures some 35m from ground level to the top. This is in contrast to the laboratory reactors and distillation columns, of which the tallest used was some 1.5 metres.



The plant pictured in figure 6.1 can be split into 4 main functional blocks: Feed Pre-treatment, Reaction, Product Purification (distillation) and Utilities. A description of each, with some pertinent dimensions and references to earlier chapters of the thesis, is given below.

6.1.1 Feed Pre-treatment: 'Precut Column'

The function of this column is to remove two troublesome components of the raw ethanol feed – ethyl butyl ether and di-n-propyl ether – before the feed is passed to the dehydrogenation reactor. These two compounds can easily be separated from ethanol but cannot be separated from ethyl ethanoate. A description of some of the work performed to prove this column is given in section 4.3.5. The capacity of the column is circa 130,000 TPA of feed. The ethers, and some other light components, are removed as an overhead stream of about 10% of the total feed. The remainder of the feed is passed to the dehydrogenation reactor. The column is *circa* 30m in height and 2m in diameter.

6.1.2 Reaction Section: Dehydrogenation Reactor.

The reactor is *circa* 25m in height, 2m in diameter and holds 104 tonnes of Cu0203T catalyst when completely full. The catalyst is separated into four beds of 26 tonnes each with re-heaters between each bed. The re-heaters are needed to keep the reactor at operating temperature – the reaction is endothermic, with a loss of 25°C seen in the first bed, 15°C in the second bed and 10°C in beds 3 and 4. By contrast, DPT reactors held between 210 and 610g of catalyst and were 0.3 to 1.5 m in length. The scale-up factor involved for this reactor is 104,000/0.61, approximately 170,000 times or 10^5. More usual scale-up factors are of the order 10^3 – 10^4. Descriptions of the testwork carried out in the laboratory reactors can be found in chapters 2, 3 and 5. Typically, the crude product from the reactor would consist of 38 wt% ethyl ethanoate, 2 wt% 2-propanol, 55 wt% ethanol and 5 wt% other components. The reactor has a throughput of 120,000 TPA feed. At 40% conversion this equates to 50,000TPA ethyl ethanoate. The reactor has a further product – 280kgh^{-1} of hydrogen which is compressed and sent to other sections of the Sasol site for use in hydrogenation and hydrotreating reactions. The hydrogen is a valuable side product for Sasol.

6.1.3 Reaction Section: Polishing Reactor

The polisher, which converts aldehydes and ketones into the respective alcohols, contains 26m^3 of 5% ruthenium on carbon catalyst, which consists of coconut carbon granules, dimensions 2 x 4 mm, containing ruthenium as a shell coating. The reactor is circa 27m tall and 1.2m in diameter, and consists of four separate catalyst beds , each containing 6.5m^3 of catalyst. The beds are separated to allow re-distribution of liquid and gas at regular intervals – trickle reactors can suffer from mal-distribution and it is common practise to include the facility to re-distribute the feed materials. A scale-up factor similar to that employed on the dehydrogenation reactor was used when designing the reactor – in this case 130,000. The reactions and testwork carried out on the laboratory reactor are detailed in chapter 4. Typically, the reactor would react ethanal, propanone, butanone and others to less than 10ppm from a total of 2 wt% (or 20,000ppm).

6.1.4 Distillation: Pressure Swing Columns – LP Side And HP Side

The LP column as pictured is the largest single equipment item on the plant. With a height of some 35m and diameter of 1.6m it is also a fairly large distillation tower. It is coupled with the HP column, height 23m diameter 1.2m, to produce ethyl ethanoate of 99.5% purity.

There are two products from the columns – 99.5% ethyl ethanoate from the HP column and an impure ethanol stream from the LP column. The 99.5% ethyl ethanoate stream is passed to the product column, while the impure ethanol stream is sent off-limits to another section of the Sasol site. Chapter 4 details the work carried out on the distillation section of the ethyl ethanoate technology.

6.1.5 Distillation: Product Column

The purity from the pressure swing columns would normally be sufficient for most commercial applications, but adding a small product column to the plant increased to purity from 99.55 to 99.95% at little extra cost. The column is 31m in height and 1.2m in diameter, and has the smallest through-put of any unit – only 50,000 TPA as unlike all other columns it only processes the almost pure ethyl ethanoate product. The Product is taken as an overhead stream and the waste product (the impurities in the 99.5% ethyl ethanoate) as a bottoms product. Typical composition of the ethyl ethanoate product is:

Ethyl Ethanoate	99.95%
Water	0.01%
Ethanol	0.02%
Ethers	0.02%

6.1.6 Utilities

There are numerous utilities used on a commercial plant. These include – cooling water and the cooling tower, steam (for heating), nitrogen and hydrogen supplies (for activation of the catalysts and operation of the reactors), instrument air (most instruments and valves are air actuated), and electricity. The utilities and instruments form a large portion of the plant build and are a major operating cost.

6.2 Starting Up The Ethanol to Ethyl Ethanoate Plant

The start-up of a commercial plant is a tricky operation that is usually performed by a team of experienced commissioning engineers and chemists. The commissioning takes place in two parts – testing of the basic systems such as valves, heaters and pumps – and the actual plant start-up where feed is introduced to the reactor and products made. Part one had been completed by an engineering team, but part two remained. When I arrived on site the catalysts had been charged to the reactors and all pressure testing completed.

The first task was to activate the dehydrogenation catalyst. Sasol are in a unique position whereby they have a large amount of oxygen free nitrogen from their oxygen plants that produce pure oxygen for coal gasification. The activation of the dehydrogenation catalyst was carried out in a flow of 15 tonnes of nitrogen per hour (5.36×10^5 mols per hour!) and a hydrogen feed flow of 11kg per hour (5.5×10^3 mols per hour) – 1 mol% hydrogen in nitrogen. The activation method used was almost exactly as that described in Appendix 1. Because of the market conditions pertaining at the time of start-up, only half the catalyst was charged to the reactor – 52 tonnes in total. It was calculated that this catalyst would consume a total of $4.4 * 10^5$ mols of hydrogen during the activation – circa 80 hours at a feed rate of 5.5×10^3 mols per hour. The actual activation took over 120 hours due to problems in controlling the hydrogen feed flow, but in all other respects the activation went as expected.

The next job was to activate the polishing catalyst. The activation had to be performed at 180°C to ensure that the catalyst was fully active. This was where the first problem occurred – the catalyst had been delivered water wet (circa 50% water). In the laboratory reactor, heat is applied to the walls of the reactor as well as the feed gases so the catalyst can be heated directly. This speeds the water removal as the gas temperature can be maintained at an elevated level. In the commercial reactor, heat is applied only to the gas feed and so the catalyst cannot be heated directly. As the gas was passed through the reactor, it evaporated the water but in the process also cooled. Thus the reactor exit temperature was never above 40°C and thus the rate of removal of water was limited to the saturation point in nitrogen at 40°C. The drying part of the activation took a total of 140 hours before the reactor could be heated to 180°C. The activation part of the process took 24 hours.

Eventually, the catalysts were activated and the feed introduced – after 6 hours online the reactors had stabilised and were starting to feed crude dehydrogenation product to the distillation section. The dehydrogenation reactor was held at a pressure of 680 kPa, at 220°C and at a feed rate of 0.5 hr^{-1}. At these conditions it gave an ethanol conversion of 41%, at a selectivity to ethyl ethanoate of 95%. The polishing reactor was started at 60°C, 4500kPa and a LHSV of 0.5hr^{-1}. At these conditions there were no detectable aldehydes and ketones in the reactor product.

After 20 hours online, the distillation section had been filled with product, and the first on-specification product obtained. After 48 hours of operation the plant was producing ethyl ethanoate at a rate of 4-4.5 tonnes per hour (32,000 to 36,000 TPA) at a purity of 99.93-99.95 wt%. Given that only half the dehydrogenation catalyst had been charged, the rate of production was remarkable – the projected rate of ethyl ethanoate production was 3.15 tonnes per hour. Compared to the actual rate of 4-4.5 tonnes per hour, this equates to the plant making 64-72,000 TPA when a full charge of catalyst is loaded – 130% of the guaranteed rate.

6.3 Conclusions and future work

The successful start-up of the Sasol ethyl ethanoate unit was a very satisfying time and a huge relief. In any programme of development, there is always the possibility that, at the final hurdle, something that did not cause problems at the small scale would become a serious problem at the larger scale. The unit operations - feed purification, dehydrogenation, polishing, distillation - all operated as expected. This is a testament to the work of the chemical engineers who designed the full scale unit from the experimental data generated at DPTs laboratories. Some technical difficulties, outside the scope of this thesis, had forced the unit to be temporarily shut-down three months after start-up, but the difficulties had been resolved. At the time of writing, the unit was operating and producing ethyl ethanoate at the same high purity as at the start-up. The unit at Secunda remains the world's only commercial ethanol to ethyl ethanoate unit.

The world does not stand still, and to make sure that the DPT process remains competitive more work needs to be done. The development of the ethyl ethanoate process has entered a further stage of catalyst and process optimisation. The catalyst that had been developed for the dehydrogenation step has many attractive features, but it is costly. A charge of catalyst costs in the region of £2,000,000 and is expected to last 1 year. A cheaper and longer lasting catalyst would improve process economics, and make the process more attractive to bio-ethanol producers. Catalyst developments on-going include the addition of a precious metal to a PG 85/1 type catalyst that improves selectivity to ethyl ethanoate from 85% to 96% at normal operating conditions. The metal works by blocking the Bronsted acid sites discovered by Waugh (see chapter 5) and so gives the benefit of increased activity and selectivity without the need of a high temperature heat treatment, which is difficult to perform at the scale of a commercial unit. The catalyst is still under development, and a patent application is underway, so the experimental work has not been included in this thesis.

Activation of the catalyst is a weak area in the process, as not every producer has 15 tonnes of nitrogen per hour available. The use of an inert hydrocarbon as a hydrogen carrier has been developed. This method will be included in all future ethyl ethanoate units.

The polishing catalyst has also been the subject of development work , again unreported. The metal loading on the catalyst has been reduced to 2% from 5%, the life extended to two years, the pressure of operation reduced to as low as 1360 kPa (from 4500 kPa) and the temperature envelope where the catalyst can operate widened from 60-110°C to 40-110°C.

The reaction mechanism is still not completely understood, and in particular the distribution of by-products is under investigation with a view to improving catalyst performance. Once these investigations are complete, catalysts may then be developed that can reduce specific side reactions and so improve the yield of ethyl ethanoate.

Appendix 1

Standard Davy Reduction Procedure For Catalysts Used In Dehydrogenation Of Ethanol To Ethyl Ethanoate

1. At room temperature, set the nitrogen to a flow of 300SLPH and establish a reactor pressure of 50psig.

2. Establish a H_2 concentration of 1.0% and bring the inlet temperature up to 120^{0}C over 3 hours. Monitor H_2 in/out above 100^{0}C keeping the H_2 inlet at 1.0%. For steps 3 to 5 ensure that the exotherm does not exceed 10^{0}C by reducing the H_2 inlet composition if necessary, and hold at the current conditions until the exotherm reduces.

3. Increase the temperature by 10^{0}C an hour until it reaches 160^{0}C.

4. Hold at 160°C until the H_2 in the exit gas = H_2 in the inlet gas.

5. Increase temperatures to 170°C over 1 hour and hold until H_2 inlet = H_2 exit.

6. Increase H_2 inlet slowly to 10% and maintain until H_2 inlet = H_2 exit. Monitor exotherm keeping it below 10°C.

7. Increase H_2 inlet to 100% making sure exotherm does not exceed 10^{0}C.

8. Increase to operating pressure and leave under H_2 for 4 hours before turning the liquid feed on. The catalyst is now fully activated.

Appendix 2

Analytical Methods

Introduction

Analysis of all organic streams reported in this thesis are analysed by the two methods listed in this appendix. Two analytical methods are described:

Analysis of ethyl acetate streams by capillary GC – HY 374

Ethyl Acetate – water content by Karl Fischer Titration – HY 355/1

Both methods were employed at the Sasol ethyl ethanoate production unit in Secunda, South Africa. The analytical method HY 374 was developed by the author.

Kvaerner Process Technology	SPECIFICATION NUMBER / REVISION:	HY374/0
	ANALYTICAL PROCEDURE	SHEET 1 of 8
	TITLE: ETHYL ACETATE DISTILLATION SECTION – COMPOSITION - CAPILLARY GC	

1 SCOPE

1.1 This method covers the determination of ethyl acetate, ethanol and by-products in liquids from the distillation section of the ethyl acetate process.

2 OUTLINE OF METHOD

2.1 A suitable volume of sample, 0.2 microlitre, is injected into a capillary column installed into a gas chromatograph fitted with a flame ionisation detector.

2.2 The concentrations of each component are determined by measurement of peak areas corrected by response factors determined from previously prepared standard mixtures.

3 PRECAUTIONS

3.1 THE SAMPLER MUST BE AWARE OF ANY KNOWN HAZARDS ASSOCIATED WITH THE COMPOUNDS FOUND IN SAMPLES FROM THE PROCESS.

3.2 GLOVES AND GOGGLES MUST BE WORN WHEN TAKING SAMPLES, AND ANY SPLASHED ONTO THE SKIN SHOULD BE WASHED OFF IMMEDIATELY.

4 APPARATUS AND REAGENTS

4.1 Air, compressed gas

Balance, analytical

Chromatograph, capillary, equipped with flame ionisation detector, injection splitter, temperature programmer and heated injection system, e.g.) Hewlett Packard 6890 Series, Unicam ProGC, or equivalent
- Column, Chrompack CP SIL 19, 50 m x 0.32 mm, 1.2 μm film thickness
- Chromatography data system or computing integrator

Helium, compressed gas

Hydrogen, compressed gas

Syringe, 1.0 μl

Volumetric flask, 100 ml

iso-Propanol, pure

2-Pentanone, pure

iso-Propyl Acetate, pure

5 PREPARATION OF APPARATUS

5.1 Install the CP SIL 19 column into the chromatograph according to the manufacturers instructions. Normally capillary columns do not require conditioning as this has already been completed by the column manufacturer. Adjust the operating conditions to those specified.

6 OPERATING CONDITIONS

6.1	Column Oven	-	Hold at 50°C for 20 minutes, programme from 50°C to 200°C at 5°C/min. Hold at 200°C for 10 minutes
	Injection Port	-	250°C
	Detector	-	280°C
	Carrier Gas	-	Helium
	Carrier Gas Pressure at column Inlet	-	5 psig
	FID Hydrogen	-	Set to manufacturers recommended flow
	FID Air	-	Set to manufacturers recommended flow
	Sample Inlet Splitter Ratio	-	100:1
	Sample Injection Size	-	0.2 μl

7 CALIBRATION

7.1 Prepare a known mixture containing the components at concentrations covering the ranges expected in samples to be analysed.

7.2 Inject 0.2 μl into the chromatograph capillary column.

7.3 Record chromatograms of each calibration mixture used.

Kvaerner Process Technology	SPECIFICATION NUMBER / REVISION:	HY374/0
	ANALYTICAL PROCEDURE	SHEET 5 of 8
	TITLE: ETHYL ACETATE DISTILLATION SECTION – COMPOSITION - CAPILLARY GC	

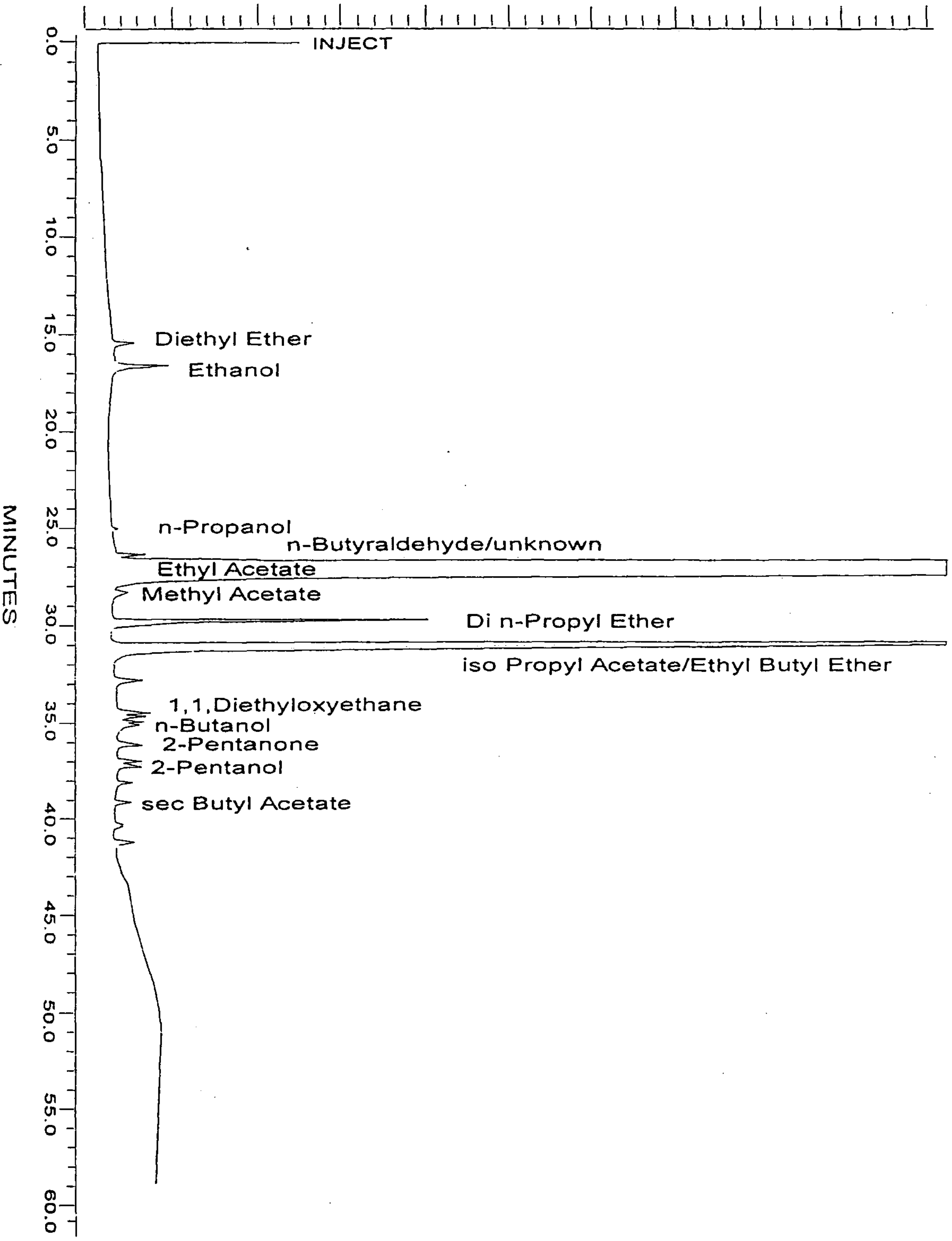
10 COMPONENT CONSTANTS

10.1 (Note: retention times are given as a guide only and may vary because of differences between instruments and capillary columns).

Component	Retention Time (mins)
Acetaldehyde	12.60
Methanol	13.30
Methyl Formate	13.70
Diethyl Ether	15.10
Ethyl Vinyl Ether	15.70
Ethanol	16.64
Acetone	18.50
Iso-Propanol	19.10
Methyl Acetate	19.90
di-iso-Propyl Ether	21.65
n-Propanol	25.60
n-Butyraldehyde/Unknowns	16.50
Ethyl Acetate	27.05
Methyl Ethyl Ketone	27.90
Sec-Butanol	28.75
di-n-Propyl Ether	29.95
iso-Propyl Acetate\Ethyl Butyl Ether	31.00
Crotonaldehyde	34.40
1,1-Diethoxy Ethane	35.10
n-Butanol	35.20
Ethyl Propionate	35.55
2-Pentanone	35.95
2-Ethoxy Pentane	36.10
2-Pentanol	37.10
sec-Pentanol	37.14
1-Propoxy Butane	38.35
sec-Butyl Acetate	39.20
1-Ethoxy Pentane	39.35
Ethyl Cyclohexane	41.80
Ethyl Butyrate	42.15
n-Butyl Acetate	43.40
di-n-Butyl Ether	45.00

Prepared by:	D Blackburn	DBlackburn	Rev: 0
Approved by:	T F Shevels	TF Shevels	Date: 28.01.99

Kvaerner Process Technology	SPECIFICATION NUMBER / REVISION:	HY374/0
	ANALYTICAL PROCEDURE	SHEET 7 of 8
	TITLE:	ETHYL ACETATE DISTILLATION SECTION – COMPOSITION - CAPILLARY GC



TYPICAL CHROMATOGRAM – HP COLUMN BOTTOMS

FIGURE 2

Kvaerner Process Technology	SPECIFICATION NUMBER / REVISION:	HY375/0
	ANALYTICAL PROCEDURE	SHEET 1 of 6
	TITLE:	ETHYL ACETATE DEHYDROGENATION PRODUCT - COMPOSITION – CAPILLARY GC

1 SCOPE

1.1 This method covers the determination of ethyl acetate, ethanol and by-products in samples from the dehydrogenation and polishing sections of the ethyl acetate process.

2 OUTLINE OF METHOD

2.1 A suitable volume of sample, 0.2 microlitre, is injected into a capillary column installed into a gas chromatograph fitted with a flame ionisation detector.

2.2 The concentrations of each component are determined by measurement of peak areas corrected by response factors determined from previously prepared standard mixtures.

3 PRECAUTIONS

3.1 THE SAMPLER MUST BE AWARE OF ANY KNOWN HAZARDS ASSOCIATED WITH THE COMPOUNDS FOUND IN SAMPLES FROM THE PROCESS.

3.2 GLOVES AND GOGGLES MUST BE WORN WHEN TAKING SAMPLES, AND ANY SPLASHED ON TO THE SKIN SHOULD BE WASHED OFF IMMEDIATELY.

4 APPARATUS AND REAGENTS

4.1 Air, compressed gas

Balance, analytical

Chromatograph, capillary, equipped with flame ionisation detector, injection splitter, temperature programmer, heated injection system e.g.) Hewlett Packard 6890 series, Unicam Pro GC, or equivalent.
- Column, Chrompack CP SIL 19, 50 m x 0.32 mm, 1.2 μm film thickness
- Chromatography data system or computing integrator.

Helium, compressed gas

Hydrogen, compressed gas

Syringe, 1.0 μl

Volumetric flask, 100 ml

4.2 Acetaldehyde, pure

5 PREPARATION OF APPARATUS

5.1 Install the CP SIL 19 column into the chromatograph according to the manufacturers instructions. Normally capillary columns do not require conditioning as this has already been completed by the column manufacturer. Adjust the operating conditions to those specified.

6 OPERATING CONDITIONS

6.1 Column Oven - Hold at 50°C for 20 minutes, programme from 50°C to 200°C at 5°/min. Hold at 200°C for 10 minutes

Injection Port - 250°C

Detector - 280°C

Carrier Gas - Helium

Carrier Gas Pressure at Column Inlet - 5 psig

FID Hydrogen - Set to manufacturers recommended flow

FID Air - Set to manufacturers recommended flow

Sample Inlet Splitter Ratio - 100:1

Sample Injection Size - 0.2 µl

7 CALIBRATION

7.1 Prepare a known mixture containing the components at concentrations covering the ranges expected in samples to be analysed.

7.2 Inject 0.2 µl into the chromatograph capillary column.

7.3 Record chromatograms of each calibration mixture used.

Kvaerner Process Technology	SPECIFICATION NUMBER / REVISION:	**HY355/1**
	ANALYTICAL PROCEDURE	SHEET 1 of 3
	TITLE: ETHYL ACETATE - WATER CONTENT - KARL FISCHER	

1 SCOPE

1.1 This method covers the determination of water in ethyl acetate process streams.

1.2 The method is written for the operation of volumetric Karl Fischer titrators which have potentiometric end-point detection.

2 OUTLINE OF METHOD

2.1 This method is based on ASTM E.203.

2.2 The original method proposed by Karl Fischer titrated dissolved water with a solution of iodine and sulphur dioxide in pyridene according to the reaction:

$$3\ C_5H_5N + SO_2 + I_2 + H_2O \rightarrow 2\ C_5H_5NH^+I + C_5H_5NSO_3$$

2.3 Because of the possibility of interference's in the titration by aldehydes and ketones which may be present in the ethyl acetate process streams this method uses a titrant which contains iodine, sulphur dioxide and imidazole in di-ethylene glycol mono-ethyl ether as solvent.

3 PRECAUTIONS

3.1 THE SAMPLER MUST BE AWARE OF THE KNOWN HAZARDS ASSOCIATED WITH THE ETHYL ACETATE PROCESS STREAM BEING SAMPLED.

3.2 HYDRANAL (KARL FISCHER) REAGENTS ARE TOXIC AND SHOULD BE HANDLED WITH CARE TO AVOID UNNECESSARY INHALATION OR DIRECT SKIN CONTACT.

3.3 IT SHOULD BE EMPHASIZED THAT THE EQUIVALENT VALUE OF THE KARL FISCHER REAGENT WILL DECREASE WITH TIME, AND THE REAGENT MUST, THEREFORE, BE RECALIBRATED FREQUENTLY.

4 APPARATUS AND REAGENTS

4.1 Balance, Analytical

Karl Fischer Titration Apparatus, volumetric type, e.g.) Orion AF8, Metrohm Karl Fischer titrator or equivalent.

7 CALCULATION

8.1 Water, %, by weight = $\frac{A \times F}{10 \times W}$

where A = volume of reagent required to titrate the sample, in ml.

F = water equivalent value of Karl Fischer reagent, in mg of water/ml.

W = weight of sample, in g

Prepared by:	D Blackburn		Rev: 1
Approved by:	T F Shevels		Date: 01.02.99

Appendix 3

Calculation of Selectivity to Ethyl Ethanoate and Conversion of Ethanol

1) Selectivity to Ethyl Ethanoate

Selectivity is estimated by a calculation based on the composition of the dehydrogenation reactor product. In this scheme, the reactor product is analysed by the analytical methods noted in Appendix 2 (HY 374 and HY 355) and a mass% (M_C) composition obtained.

Each individual component in the reaction mixture is assigned a relative molecular mass (R_C). Those components that have not been identified are assigned the mass of the closest known component. The mass% ($M_{C[n]}$) is divided by the relative molecular mass ($R_{C[n]}$) to obtain the number of mols ($Mol_{C[n]}$)of the component in 100g of product. Ethanol and ethanal are not included in the calculation as(a) ethanol is unconverted feed and (b) ethanal is reconverted to ethanol in the polishing reactor.

$Mol_{C[n]} = M_{C[n]} / R_{C[n]}$

Mol_C values for all components (except ethanol and ethanal) are summed to give $\Sigma[Mol_{C[a...n]}]$

Selectivity for an individual component is therefore: $Sel_{C[n]}= 100 \times (Mol_{C[n]} / \Sigma[Mol_{C[a...x]}])$

For Ethyl Ethanoate in particular

$Mol_{C[n]} = M_{C[EtOAc]} / 88$

$\mathbf{Sel_{C[EtOAc]}= 100 \times (Mol_{C[n]} / \Sigma[Mol_{C[a...x]}])}$

2) Conversion of Ethanol

Ethanol conversion is calculated as the difference in ethanol content of the product, compared to the feed. The sample that is subject to calculation is analysed as for (1) and the number of moles of ethanol in 100g calculated as:

$Mol_{C[EtOH]} = M_{C[EtOH]} /46$

The feed ethanol is analysed in the same manner and a similar calculation performed

$Mol_{F[EtOH]} = M_{F[EtOH]} / 46$

Conversion of Ethanol = $\mathbf{100 \times ((Mol_{F[EtOH]} - Mol_{C[EtOH]}) / Mol_{F[EtOH]})}$

Appendix 4

Publications

Relating to Work in This Thesis

EP 99947694.8 EtAc: Dehydrogenation followed By Polishing (attached)

EP 0992484 A1 EtAc: Complete Flowsheet (attached)

EP 99947692.2 EtAc: Pressure Swing Distillation

UK 0106309.8: Ethyl Acetate: Overall Process

Other Publications by the same author

EP 97914476.3 BD: Acetal removal

EP 00985546.1 BDO Mixed Hydrogenation Bed

US 155441 Process for the Purification of butane-1,4-diol

RSC Innovation Awards 2001: Runner up

Team Effort, Chemistry in Britain, August 2001

PROCESS

This invention relates to a process for the production of ethyl acetate from ethanol.

Ethyl acetate is a relatively expensive bulk chemical which is conventionally produced by esterification of acetic acid with ethanol according to equation (1):

$$CH_3.CO.OH + CH_3CH_2OH = CH_3.CO.O.CH_2.CH_3 + H_2O \qquad (1).$$

Ethyl acetate can also be produced from acetaldehyde according to the Tischenko condensation reaction given in equation (2):

$$2CH_3.CHO = CH_3.CO.O.CH_2.CH_3 \qquad (2).$$

Ethanol may be available in large quantity, either as a product of hydration of ethylene, Fischer Tropsch, or, in certain countries, as a fermentation product. In certain circumstances ethanol may be available in excess capacity, whilst acetic acid is not readily available in the necessary quantity. Accordingly, there are many reasons why, particularly in countries having a relative abundance of ethanol with respect to acetic acid, it would be desirable to provide a commercial process for the manufacture of ethyl acetate from ethanol according to equation (3):

$$2CH_3.CH_2.OH = CH_3.CO.O.CH_2.CH_3 + 2H_2 \qquad (3).$$

The production of esters directly from primary alcohols has been described on various occasions in the literature. For example, dehydrogenation of methanol over Cu-Zr-Zn catalysts at temperatures of between 100°C and 400°C to yield methyl formate have been described in Belgian Patent Specification No. 879915 (see also *Chemical Abstracts, Vol. 93 (1980), No. 204080f at page 635)*.

French Patent Specification No. 1000505 (see *Chemical Abstracts, Vol. 51 (1957), 3061b)* describes described by dehydrogenation of ethyl acetate at 180°C to 300°C in the presence of a copper catalyst containing zinc as an activator with an ethanol feed rate of 250 to 700 litres per litre of catalyst per hour.

None of these prior disclosures has resulted in adoption of the dehydrogenation of ethanol as a commercial method of producing ethyl acetate.

EP-A-0151886 describes a process for the preparation of C_{2+} esters of alkyl carboxylic acids from C_{2+} primary alcohols which comprises contacting a vaporous mixture containing a primary C_{2+} alkanol and hydrogen in an alkanol:hydrogen molar ratio of from 1:10 to about 1000:1 at a combined partial pressure of alkanol and hydrogen of from about 0.1 bar (10^3 Pa) up to about 40 bar (4×10^6 Pa) and at a temperature in the range of from about 180°C to about 300°C in a catalytic reaction zone with a catalyst consisting essentially of a reduced mixture of copper oxide and zinc oxide, and recovering a reaction product mixture containing a primary C_{2+} alkyl ester of an alkyl carboxylic acid which ester contains twice as many carbon atoms as the primary C_{2+} alkanol.

It would be desirable to provide an improved commercial method of upgrading ethanol to ethyl acetate, a more valuable product, particularly where there is an over-capacity for ethanol. It would also be desirable to provide a novel route to high purity ethyl acetate which obviates the need for expensive capital plant, such as a separate acetic acid plant.

One particular problem in production of ethyl acetate by dehydrogenation of ethanol is that the reaction product mixture tends to be a complex mixture including esters, alcohols, aldehydes and ketones. The reaction product mixtures contain components with boiling points

(b) recovering from the dehydrogenation zone an intermediate reaction product mixture comprising hydrogen and liquefiable products comprising ethyl acetate, ethanol, hydrogen and by-products containing reactive carbonyl groups;

(c) contacting at least a portion of the liquefiable products of the intermediate reaction product mixture with a selective hydrogenation catalyst in the presence of hydrogen in a selective hydrogenation zone maintained under selective hydrogenation conditions effective for selective hydrogenation of by-products containing reactive carbonyl groups thereby to hydrogenate said by-products selectively to hydrogenated by-products comprising corresponding alcohols;

(d) recovering a selectively hydrogenated reaction product mixture comprising ethyl acetate, ethanol, hydrogen and hydrogenated by-products;

(e) supplying material of the selectively hydrogenated reaction product mixture to a first distillation zone maintained under distillation conditions effective for distillation therefrom of an azeotropic mixture comprising ethanol and ethyl acetate;

(f) recovering an azeotropic mixture comprising ethanol and ethyl acetate from the first distillation zone;

(g) supplying material of the azeotropic mixture to a second distillation zone maintained under distillation conditions effective for distillation therefrom of a substantially pure ethyl acetate product; and

(h) recovering from the second distillation zone a substantially pure ethyl acetate product.

Usually, the azeotropic mixture produced in step (f) will also comprise water, which is produced as a by-product in the dehydrogenation zone.

The liquefiable products present in the intermediate reaction product mixture of step (b) are reacted in step (c) with hydrogen over a suitable selective hydrogenation catalyst. The catalyst type and reaction conditions are chosen so that aldehydes and ketones are hydrogenated to their respective alcohols, while hydrogenation of ethyl acetate is negligible. Among aldehyde and ketone by-products which may be present, butan-2-one or methyl ethyl ketone and *n*-butyraldehyde, in particular, would otherwise cause problems in any subsequent distillation. These compounds are hydrogenated in the selective hydrogenation zone in step (c) to the corresponding alcohols, i.e. 2-butanol and *n*-butanol respectively, which do not cause problems in distillation.

The selectively hydrogenated reaction product mixture of step (d) is passed through at least two distillation zones designed to remove unreacted ethanol and by-products, yielding high purity ethyl acetate and an ethanol stream suitable for recycling to the dehydrogenation zone. Ethyl acetate purification can be accomplished by a novel two column pressure-swing unit.

Removal of "heavies" (i.e. products, including unknown products, with high boiling points compared to those of ethanol and ethyl acetate) and purification of the unreacted ethanol is accomplished in a first distillation column (to remove "heavies"), preferably followed by treatment of the resulting bottoms stream in an absorption unit (to remove water).

The vaporous mixture supplied to the dehydrogenation zone in step (c) contains, in addition to ethanol, hydrogen either alone or in admixture with other gases (desirably gases that are inert to the reactants and catalysts used in the dehydrogenation step (a) and in the

The dehydrogenation catalyst used in step (a) is desirably a copper containing catalyst containing copper, optionally in combination with chromium, manganese, aluminium, zinc, nickel or a combination of two or more of these metals, such as a copper, manganese and aluminium containing catalyst. Preferred catalysts comprise, before reduction, non-promoted copper oxide on alumina, an example of which is the catalyst sold by Mallinckrodt Specialty Chemicals, Inc., under the designation E408Tu, a catalyst which contains 8% by weight of alumina. Other preferred catalysts include chromium promoted copper catalysts available under the designations PG85/1 (Kvaerner Process Technology Limited), CU0203T (Engelhardt), manganese promoted copper catalysts sold under the designation T4489 (Sud Chemie) and supported copper catalysts sold under the designation D-32-J by Sud Chemie. E408Tu is a particularly preferred dehydrogenation catalyst.

The liquid hourly space velocity (LHSV) in the dehydrogenation zone of step (a) is preferably from about 0.5 hr^{-1} to about 1.0 hr^{-1}.

The process of the present invention includes a selective hydrogenation step (c) which is typically conducted in the selective hydrogenation zone at a temperature of between about 20°C to about 160°C, preferably at a temperature in the range of from about 60°C to 140°C, even more preferably at a temperature of about 90°C.

The combined partial pressure of liquefiable products and hydrogen in the selective hydrogenation zone typically lies in the range of from about 6.9 bar (6.9×10^5 Pa) up to about 69 bar (6.9×10^6 Pa), even more typically about 41.4 bar (4.14×10^6 Pa).

ethanol and water stream may then be passed through a water absorption unit, yielding a relatively dry ethanol stream (typically containing less than about 5 mole%, and preferably less than about 3 mole% of water) which can be recycled to the dehydrogenation zone.

(b) An overhead stream that contains the "light" components from the crude polished dehydrogenation product, i.e. the selectively hydrogenated product from the selective hydrogenation zone. This stream consists mainly of diethyl ether, ethanol, unreacted acetaldehyde and acetone. This stream may be burnt as fuel.

(c) A liquid draw from a point high in the first distillation column. This stream consists of an ethyl acetate/ethanol/water azeotrope containing some other components at low levels. The stream typically contains 68% ethyl acetate, 30% ethanol, 1% water and 1% other components.

The third stream is passed to the second column in the pressure swing set-up. This column is typically run at from about 9 bar (9×10^5 bar) to about 12 bar (1.2×10^6 Pa) and uses the difference in the composition of the ethyl acetate/ethanol azeotrope (or, if water is present, of the ethyl acetate/ethanol/water azeotrope) from that of the corresponding azeotrope of the liquid draw from the first distillation column. In this second column of the pressure swing set-up the azeotrope is removed as an overhead stream with a typical composition of 30% ethyl acetate/68% ethanol/1% water/1% others. The excess ethyl acetate is removed as a bottoms product at a purity of 99.8 - 99.95%, depending on the feed ethanol and operating conditions selected.

that point and is still around 30% at a pressure of 24 bar 2.4 x 10^6 Pa), where ethyl acetate selectivity is at its highest, at around 96%. EP-A-0151886 claims a very broad pressure range of from about 0.1 bar (10^4 Pa) up to about 40 bar (4 x 10^6 Pa) in a process for the production of a primary C_{2+} alkyl ester of an alkyl carboxylic acid by hydrogenation of a primary C_{2+} alkanol. However, in the process described in EP-A-0151886 there are a number of by-products of the ethanol dehydrogenation reaction which tend to form azeotropic mixtures with ethyl acetate. The formation of azeotropic mixtures, particularly azeotropic mixtures comprising methyl ethyl ketone and ethyl acetate, makes it very difficult, if not impossible, to separate substantially pure ethyl acetate from the crude dehydrogenation product mixture by a convenient method, such as distillation. Thus, although EP-A-0151886 refers to azeotropes formed between unreacted primary C_{2+} alkanol and the product ester, it is silent with regard to other azeotropes formed between by-products and the product ester.

Selective hydrogenation of azeotrope-forming by-products such as methyl ethyl ketone, as practised in the process of the present invention, effectively converts these by-products into materials, including corresponding alcohols such as 2-butanol, which can readily be separated from ethyl acetate by distillation. Other problematic by-products include acetaldehyde, which is reactive, and acetone which can also form azeotropic mixtures with ethyl acetate. Selective hydrogenation according to the process of the invention converts acetaldehyde to ethanol and acetone to <u>iso</u>-propanol, both of which compounds may be separated from ethyl acetate by distillation. The selective hydrogenation reactions are strongly responsive to temperature in the selective hydrogenation zone.

one stream by heat exchange with another stream of the plant.

In the plant of Figure 3 a stream of crude ethanol is pumped to the plant from a suitable holding tank (not shown) in line 1 at a pressure of 16.2 bar absolute (16.2 x 10^5 Pa) and at a temperature of approximately 30°C and is admixed with recycled material from line 2. The resulting mixture in line 3 is heated by means of heat exchanger 4 to a temperature of 166°C thereby forming a vaporous stream which passes on in line 5 to be mixed with a stream of hydrogen at 22°C from line 6. The resulting mixture passes on in line 7, is superheated in steam superheater 8, and exits it in line 9 at a pressure of 14.8 bar absolute (14.8 x 10^5 Pa) and at a temperature of 235°C. Line 9 leads to a first dehydrogenation reactor 10 which contains a charge of a reduced copper oxide catalyst. A suitable catalyst is that sold under the designation E408Tu by Mallinckrodt Specialty Chemicals, Inc. In passage through first dehydrogenation reactor 10 the mixture of ethanol and hydrogen is partly converted by dehydrogenation according to equation (3) above to form ethyl acetate.

The first intermediate dehydrogenation mixture exits reactor 10 in line 11 and is reheated in heater 12 under the influence of high pressure steam. The reheated mixture flows on in line 13 to a second dehydrogenation reactor 14 which also contains a charge of the same dehydrogenation catalyst as that in reactor 10. Further dehydrogenation of ethanol to ethyl acetate occurs in passage through second dehydrogenation reactor 14.

A second intermediate dehydrogenation mixture containing ethyl acetate, unreacted ethanol and hydrogen exits reactor 14 in line 15 and is reheated in reheater 16 which is heated by means of high pressure steam. The at a temperature of -10°C, are recovered in line 27. A part of these gases is recycled in line 28 and compressed by means of gas recycle compressor 29 to a pressure of 15.5 bar (1.55×10^6 Pa) absolute to form the gas stream in line 6 for supply to the first dehydrogenation reactor 10. Another part is taken in line 30 for a purpose which will be described hereunder. A purge stream is taken in line 31.

The condensate is removed from knockout pot 26 in line 32 and is pumped by a pump (not shown) to heat exchanger 33. The resulting re-heated liquid, now at a temperature of 90°C, is fed via line 34 and mixed with a hydrogen-containing gas which is at a temperature of 119°C and has been compressed by a second gas compressor 35 to a pressure of 43.1 bar (4.31×10^6 Pa) absolute so as to pass along line 36. The resulting mixture flows on in line 37 into a polishing reactor 38 which contains a charge of a selective hydrogenation catalyst which is chosen so as selectively to hydrogenate reactive carbonyl-containing compounds, such as n-butyraldehyde, butan-2-one and the like, to the respective corresponding alcohols but not to effect any significant hydrogenation of ethyl acetate to ethanol. A preferred catalyst is 5% ruthenium on carbon.

The resulting polished (or selectively hydrogenated) reaction product is now essentially free from reactive carbonyl compounds, such as aldehydes and ketones, and exits reactor 38, in admixture with unreacted hydrogen, in line 39 at a temperature of 90°C. This line leads to a lower part of a first distillation column 40 which is maintained at a pressure of 5.0 bar (5×10^5 Pa) absolute. A bottoms product is withdrawn from distillation column 40 in line 41. Part of this is recycled to distillation column through line 42, column reboiler 43 and line 44. The remainder is passed by way of line 45 to a purification section (or water removal

An overhead product consisting mainly of ethanol and water, ethers and esters besides smaller amounts of ethyl acetate, 1-ethoxybutane, methanol, diethyl ether and dipropyl ether and traces of alkanes, is taken in line 58 and condensed by means of condenser 59. The resulting mixture of gases and condensate passes on in line 60, the uncondensed material being recycled to the first distillation column by way of line 61 while the condensate is recycled as a reflux stream to the second distillation column 52 in line 62.

The compositions in mol% of some of the more important streams in the plant of Figure 3 are set out in Table 1 below.

The invention is further described in the following Examples.

Examples 1 to 5

These Examples investigated the dehydrogenation of ethanol to ethyl acetate in the presence of hydrogen. The apparatus used included a dehydrogenation reactor made of stainless steel tubing which contained a charge of reduced copper oxide catalyst and which was immersed in a hot oil bath for heating purposes.

In operation a mixture of hydrogen and nitrogen was introduced to the dehydrogenation reactor by way of a pressure regulator and flow controller through a line which was immersed in the bottom of the oil bath. Ethanol was fed as a liquid to a vaporiser and mixed with the hydrogen/nitrogen mixture. The resulting vaporous mixture of ethanol, hydrogen and nitrogen was supplied to the dehydrogenation reactor.

At start-up a charge of 200 ml of a granulated copper oxide catalyst available under the designation E408Tu from Mallinckrodt Specialty Chemicals was placed in the reactor which was then purged with nitrogen at 14.5 bar (14.5 x 10^5 Pa). A dilute H_2 in N_2 gaseous mixture at 3 bar (3 x 10^5 Pa) was passed over the catalyst for 24 hours in order to effect catalyst reduction. The oil bath was raised to the temperature indicated in Table 2 below.

TABLE 2

	62	88	89	90	95
Feed Type					
Feed rate to reactor (ml/h)	225	224	224	223	224
LHSV (h^{-1})	1	1	1	1	1
Pressure (psig)	51	25	100	400	667
H_2 Flow In	0.75	0.77	0.76	0.76	3
H_2 Flow Out	12.40	12.40	12.7	2	11.4
Feed Wt (g)	237.6	355.5	316	313.6	238.5
Product Wt (g)	232.7	353.4	308.8	301.7	229.1
Gas Analysis					
CO	0.063	0.069		0	0
CO_2	0.239	0.251		0.055	0
CH_4	0.025	0.024		0.04	0
Ethane	0.160	0.160		0.122	0.073
Acetaldehyde	0.336	1.004		0.003	0.289
Ethanol	0.209	0.357		0.042	0.021
DEE	0.021	0.288		0.003	0.003
Ethyl acetate	0.224	0.044		0.001	0.001
Acetaldehyde	2.578	5.317	1.388	0.114	0.027
Methanol	0.063	0.087	0.034	0.013	0.011
Diethyl ether	0.133	0.120	0.139	0.167	0.186
Ethanol	63.184	66.778	64.050	67.236	73.012
Acetone	2.264	2.883	1.679	0.630	0.328
iso-propanol	1.582	1.081	2.114	3.210	3.527
Di-iso-propyl ether	0.139	0.134	0.138	0.136	0.139
n-butyraldehyde	0.012	0.010	0.006	0.004	0.005
Ethyl acetate	25.605	18.935	27.087	26.377	21.205
MEK	1.230	1.655	0.661	0.074	0.015
sec-butanol	0.768	0.543	0.761	0.360	0.175
iso-propyl acetate	0.184	0.144	0.040	0.316	0.319
2-pentanone	0.316	0.309	0.233	0.055	0.010
n-butanol	0.329	0.410	0.274	0.203	0.433
sec-pentanol	0.138	0.075	0.180	0.148	0.087
sec-butyl acetate	0.058	0.037	0.057	0.052	0.044
Ethyl butyrate	0.132	0.115	0.093	0.030	0.075
n-butyl acetate	0.123	0.096	0.086	0.022	0.079

Examples 6 to 14

In these Examples the selective hydrogenation of reactive carbonyl compounds in the presence of ethyl acetate was investigated using a hydrogenation reactor constructed out of stainless steel which was immersed in a hot oil bath for heating purposes.

In operation hydrogen was introduced by way of a pressure regulator and flow controller to the reactor which contained a charge of an Englehard 5% ruthenium on carbon granular catalyst.

At start up a charge of 200 ml of the granulated catalyst was placed in the reactor which was then supplied with hydrogen at a pressure of 100 psig, and warmed to 180-200°C from room temperature at a rate of 20°C per hour. The reactor was held at 180-200°C for one hour and then cooled. At the end of this procedure the catalyst was fully reduced.

Dehydrogenation reaction product mixture was introduced to a heater at a rate of 130 ml/hr and admixed with the hydrogen-containing gas prior to admission to the selective hydrogenation reactor. The exit gas from the reactor was sampled and analysed by gas chromatography. The results are summarised in Table 3.

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(54) Process

(57) A process is described for the recovery of substantially pure alkyl alkanoate, such as ethyl acetate from an impure feedstock. The impure feedstock is contacted with a selective hydrogenation catalyst in the presence of hydrogen in a selective hydrogenation zone maintained under selective hydrogenation conditions effective for selective hydrogenation of impurities containing reactive carbonyl groups thereby to hydrogenate said impurities to the corresponding alcohols. After recovery from the selective hydrogenation zone of a selectively hydrogenated reaction product mixture comprising said alkyl alkanoate and said corresponding alcohols, this is distilled in one or more distillation zones so as to produce substantially pure alkyl alkanoate therefrom which is recovered.

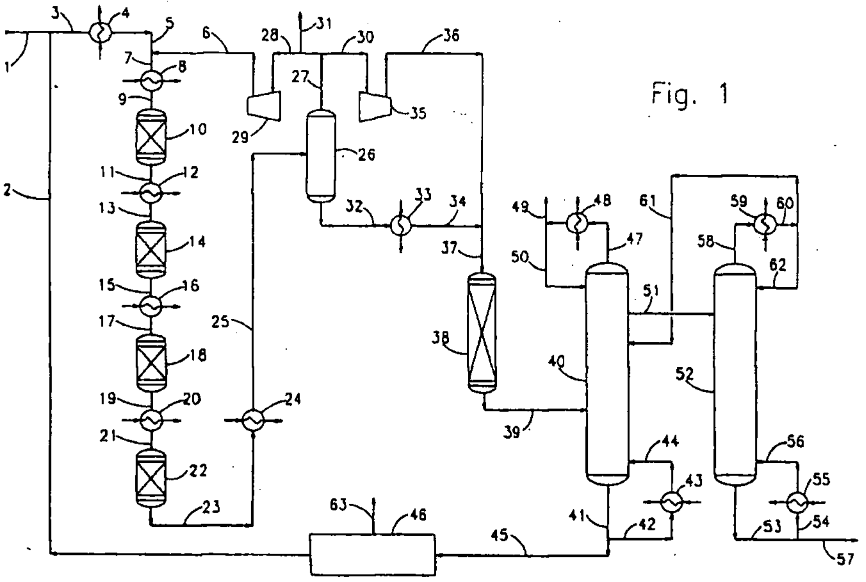

Fig. 1

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tion zone of a copper chromite containing catalyst.

[0015] Separation of ethyl acetate from a composition comprising ethyl acetate, ethanol and water is disclosed in JP-A-05/186392 by feeding the composition to a distillation column to obtain a quasi-azeotropic mixture comprising ethyl acetate, ethanol and water, condensing it, separating the condensate into an organic layer and an aqueous layer, returning the organic layer to the column, and recovering ethyl acetate as a bottom product from the column.

[0016] One particular problem in production of alkyl alkanoates by dehydrogenation of an alkanol is that the reaction product mixture tends to be a complex mixture including esters, alcohols, aldehydes and ketones. The reaction product mixtures contain components with boiling points close to that of the desired alkyl alkanoate or alkanoates. In some cases such components can form azeotropes, including azeotropes with the desired alkyl alkanoate or alkanoates whose boiling points are close to that of the alkyl alkanoate or alkanoates. This is a particular problem when a high purity alkyl alkanoate, such as ethyl acetate, is desired.

[0017] The present invention accordingly seeks to provide a novel process for recovery of a substantially pure alkyl alkanoate from an impure feedstock, for example a crude product produced by dehydrogenation of an alkanol which contains by-products whose boiling point is close to that of the desired alkyl alkanoate or alkanoates and which, in some cases at least, form azeotropes with the alkyl alkanoate or alkanoates whose boiling points are close to that of the desired alkyl alkanoate or alkanoates. It further seeks to provide a process for purification of an impure feedstock containing an alkyl alkanoate containing up to 12 carbon atoms which further contains as an impurity at least one aldehyde and/or ketone which contains the same number of carbon atoms as the alkyl alkanoate so as to result in production of a substantially pure alkyl alkanoate product. In addition the invention seeks to provide an improved process for the production of an alkyl alkanoate by dehydrogenation or oxidation of an alkanol, by reaction of an alkanol with an alkanal, or by oxidation of an alkanol to an alkanal followed by the Tischenko reaction which enables production of a substantially pure alkyl alkanoate product, despite the presence in the crude reaction product of aldehydes and ketones which would otherwise contaminate the alkyl alkanoate product.

[0018] According to the present invention there is provided a process for the purification of an impure feedstock comprising an alkyl alkanoate which contains up to 12 carbon atoms which comprises:

(a) providing an impure feedstock containing an alkyl alkanoate which contains up to 12 carbon atoms, said feedstock further containing at least one impurity which is selected from an aldehyde and a ketone and which contains the same number of carbon atoms as said alkyl alkanoate;
(b) contacting said impure feedstock with a selective hydrogenation catalyst in the presence of hydrogen in a selective hydrogenation zone maintained under selective hydrogenation conditions effective for selective hydrogenation of impurities containing reactive carbonyl groups thereby to hydrogenate said impurities to the corresponding alcohols;
(c) recovering from the selective hydrogenation zone a selectively hydrogenated reaction product mixture comprising said alkyl alkanoate, hydrogen, and said corresponding alcohols;
(d) distilling material of the selectively hydrogenated reaction product mixture in one or more distillation zones so as to produce substantially pure alkyl alkanoate therefrom; and
(e) recovering said substantially pure alkyl alkanoate.

[0019] The invention further provides a process for the production of an alkyl akanoate containing up to 12 carbon atoms by dehydrogenation of an alkanol which comprises:

(i) contacting a vaporous mixture containing an alkanol and hydrogen with a dehydrogenation catalyst in a dehydrogenation zone maintained under dehydrogenation conditions effective for dehydrogenation of an alkanol to yield an alkyl alkanoate containing up to 12 carbon atoms;
(ii) recovering from the dehydrogenation zone an intermediate reaction mixture comprising hydrogen and liquefiable products comprising said alkyl alkanoate, said alkanol, hydrogen and by-products containing reactive carbonyl groups; and
(iii) subjecting at least a portion of the liquefiable products of the intermediate reaction product mixture as impure feedstock to a process as outlined in the preceding paragraph.

[0020] The impure feedstock may be effectively any feedstock which contains an alkyl alkanoate, such as ethyl acetate, or a mixture of alkyl alkanoates, possibly water, an alkanol, such as ethanol, or a mixture of alkanols, and minor amounts of impurities including aldehydes and/or ketones. In the case of ethyl acetate such aldehydes and ketones include n-butyraldehyde, acetone and butan-2-one. Example of such an impure feedstock are the intermediate reaction product mixtures obtained by dehydrogenation of an alkanol, such as ethanol, or of a mixture of alkanols, such as ethanol and iso-butanol.

[0021] A range of undesirable impurities may be present in the feedstock, some of which would cause separation hydrogenation of the alkyl alkanoate, e.g. ethyl acetate, is minimal. Among aldehyde and ketone impurities which may be present in an impure ethyl acetate feedstock, butan-2-one and n-butyraldehyde, in particular, would otherwise cause problems in any subsequent distillation. These compounds are hydrogenated in the selective hydrogenation zone in step (b) to the corresponding alcohols, i.e. 2-butanol and n-butanol respectively, which can be readily separated from ethyl acetate by distillation.

[0026] The mixture supplied to the selective hydrogenation zone in step (b) contains, in addition to ethanol, hydrogen either alone or in admixture with one or more inert gases that are inert to the reactants and catalysts in the selective hydrogenation step (b) of the process of the invention. Examples of such inert gases are nitrogen, methane, and argon. The source of the hydrogen used in the selective hydrogenation step (b) may be hydrogen formed in the dehydrogenation step and accordingly may include gas recycled from the downstream end of the selective hydrogenation zone as described further below.

[0027] The selective hydrogenation step (b) is typically conducted at a temperature of from about 40°C to about 120°C, preferably at a temperature in the range of from about 60°C to about 80°C.

[0028] Typical selective hydrogenation conditions include use of a feedstock:hydrogen molar ratio of from about 1000:1 to about 5:1, for example about 20:1.

[0029] The combined partial pressure of feedstock and hydrogen in the selective hydrogenation zone typically lies in the range of from about 5 bar (5×10^5 Pa) up to about 80 bar (8×10^6 Pa), and is even more typically about 25 bar (2.5×10^6 Pa) to about 50 bar (5×10^6 Pa).

[0030] The selective hydrogenation catalyst used in step (b) of the process of the invention is selected to have good activity for hydrogenation of reactive carbonyl containing compounds, but relatively poor ester hydrogenation activity. Suitable catalysts comprise metals selected from nickel, palladium and platinum. Ruthenium, supported on carbon, alumina or silica is also effective, as are other metal catalysts such as rhodium and rhenium. Preferred catalysts include nickel on alumina or silica and ruthenium on carbon. Particularly preferred catalysts include 5% ruthenium on carbon available from Engelhard.

[0031] The rate of supply of impure feedstock to the selective hydrogenation zone typically corresponds to a liquid hourly space velocity (LHSV) of from about 0.1 hr^{-1} to about 2.0 hr^{-1}, preferably from about 0.2 hr^{-1} to about 1.5 hr^{-1}. When using a nickel containing catalyst the LHSV may be, for example, from about 0.3 hr^{-1} to about 0.5 hr^{-1}.

[0032] Step (c) of the process of the present invention comprises recovering from the selective hydrogenation zone a selectively hydrogenated reaction product mixture comprising alkyl alkanoate (e.g. ethyl acetate), alkanol (e.g. ethanol), hydrogen and hydrogenated impurities. Typically this includes a condensation step in order to separate liquefiable materials from a gaseous stream containing unreacted hydrogen which can be recycled for dehydrogenation or for selective hydrogenation.

[0033] The impure feedstock typically contains water and alkanol (e.g. ethanol) in addition to alkyl alkanoate (e.g. ethyl acetate). In this case step (d) of the process of the invention comprises distilling material of the selectively hydrogenated reaction product mixture in one or more distillation zones. When the alkyl alkanoate is ethyl acetate, distillation is effected so as to produce a first composition comprising substantially pure ethyl acetate and a second composition comprising ethanol and water. In this step the selectively hydrogenated reaction product mixture subjected to distillation typically has a water content of less than about 20 mol %, more usually not more than about 15 mol %.

[0034] Ethanol, water and ethyl acetate form a minimum boiling ternary azeotrope upon distillation thereof.

[0035] One method of separating ethyl acetate from ethanol and water involves extractive distillation with an extractive agent comprising polyethylene glycol and dipropylene glycol, diethylene glycol, or triethylene glycol as described in US-A-4569726 or with an extractive agent containing dimethyl sulphoxide as described in US-A-4379028. Hence step (d) may comprise an extractive distillation procedure.

[0036] Preferably, however, distillation is carried out in step (d) by a procedure which takes advantage of the fact that the composition of the minimum boiling ternary azeotrope formed by ethanol, water and ethyl acetate depends upon the pressure at which distillation is effected. Hence a preferred distillation procedure comprises supplying material of the selectively hydrogenated reaction product mixture to a first distillation zone maintained under distillation conditions effective for distillation therefrom of a first distillate comprising ethyl acetate, ethanol, and water, recovering a first distillate comprising ethyl acetate, ethanol, and water from the first distillation zone and a bottom product comprising ethanol and water, supplying material of the first distillate to a second distillation zone maintained under distillation conditions effective for distillation therefrom of a second distillate comprising ethanol, water, and ethyl acetate (preferably a minor amount of ethyl acetate) and so as to yield a substantially pure ethyl acetate bottom product, and recovering a substantially pure ethyl acetate bottom product from the second distillation zone. The first distillation zone is preferably operated at a pressure less than about 4 bar (4×10^5 Pa), preferably from about 1 bar (10^5 Pa) up to about 2 bar (2×10^5 Pa), while the second distillation zone is operated at a higher pressure than that of the first distillation zone, for example at a pressure of from about 4 bar (4×10^5 Pa) to about 25 bar (2.5×10^6 Pa), preferably from about 9 bar (9×10^5 Pa) to about 15 bar (15×10^5 Pa)

[0037] It can be shown that in this preferred distillation procedure the rate of flow of the first distillate from the first from ethyl acetate, even when they are present in quantities as low a about 0.1 mol % or less, by traditional distillation procedures because they have boiling points which are close to that of ethyl acetate and/or form distillates therewith.

[0045] In the dehydrogenation step ethanol can be converted to ethyl acetate by a dehydrogenation procedure which comprises contacting a vaporous mixture containing ethanol and hydrogen with a dehydrogenation catalyst in a dehydrogenation zone maintained under dehydrogenation conditions effective for dehydrogenation of ethanol to yield ethyl acetate.

[0046] Typical dehydrogenation conditions include use of an ethanol:hydrogen molar ratio of from about 1:10 to about 1000:1, a combined partial pressure of ethanol and hydrogen of up to about 50 bar (5×10^6 Pa), and a temperature in the range of from about 100°C to about 260°C.

[0047] Preferably the combined partial pressure of ethanol and hydrogen ranges from about 3 bar (3×10^5 Pa) up to about 50 bar (5×10^6 Pa), and is more preferably at least 6 bar (6×10^5 Pa) up to about 30 bar (3×10^6 Pa), and even more preferably in the range of from about 10 bar (10^6 Pa) up to about 20 bar (2×10^6 Pa), for example about 12 bar (1.2×10^6 Pa).

[0048] Dehydrogenation is preferably conducted in the dehydrogenation zone at a temperature of from about 200°C to about 250°C, preferably at a temperature in the range of from about 210°C to about 240°C, even more preferably at a temperature of about 220°C.

[0049] The ethanol:hydrogen molar ratio in the vaporous mixture fed into contact with the dehydrogenation catalyst usually will not exceed about 400:1 or about 500:1 and may be no more than about 50:1.

[0050] The dehydrogenation catalyst is desirably a catalyst containing copper, optionally in combination with chromium, manganese, aluminium, zinc, nickel or a combination of two or more of these metals, such as a copper, manganese and aluminium containing catalyst. Preferred catalysts comprise, before reduction, copper oxide on alumina, an example of which is the catalyst sold by Mallinckrodt Specialty Chemicals, Inc., under the designation E408Tu, a catalyst which contains 8% by weight of alumina. Other preferred catalysts include chromium promoted copper catalysts available under the designations PG85/1 (Kvaerner Process Technology Limited) and CU0203T (Engelhard), manganese promoted copper catalysts sold under the designation T4489 (Süd Chemie AG), and supported copper catalysts sold under the designation D-32-J (Süd Chemie AG). E408Tu is a particularly preferred dehydrogenation catalyst.

[0051] In the dehydrogenation step the rate of supply of the ethanol feedstock to the dehydrogenation zone typically corresponds to an ethanol liquid hourly space velocity (LHSV) of from about 0.5 hr^{-1} to about 1.0 hr^{-1}.

[0052] Hydrogen is produced as a result of the dehydrogenation reaction and can be recycled to the dehydrogenation zone from downstream in the process. The hydrogen can be substantially pure hydrogen or can be in the form of a mixture with other gases that are inert to the ethanol feedstock and to the dehydrogenation catalyst. Examples of such other gases include inert gases such as nitrogen, methane and argon.

[0053] In the dehydrogenation zone, side reactions may also occur, including formation of water. It is postulated that such side reactions, in the case of production of ethyl acetate, include formation of acetaldehyde which in turn can undergo aldol formation, followed by dehydration to form an unsaturated alcohol and water. These reactions can be summarised thus:

$$CH_3CH_2OH = CH_3CHO + H_2 \qquad (5)$$

$$2CH_3CHO = CH_3CH(OH)CH_2CHO \qquad (6)$$

and

$$CH_3CH(OH)CH_2CHO = CH_3CH{=}CHCHO + H_2O \qquad (7).$$

[0054] The crotonaldehyde produced by equation (7) can then undergo hydrogenation to form n-butanol thus:

$$CH_3CH{=}CHCHO + H_2 = CH_3CH_2CH_2CH_2OH. \qquad (8).$$

Other side reactions which release water as a by-product include formation of ketones, such as acetone and butan-2-one, and formation of ethers, such as diethyl ether.

[0055] In such a dehydrogenation process there is recovered from the ethyl acetate production zone an intermediate reaction product mixture comprising hydrogen and liquefiable products comprising ethyl acetate, ethanol, hydrogen and by-products containing reactive carbonyl groups; this intermediate reaction product mixture can be used as impure feed to the recovery process of the invention. The step of recovering this intermediate reaction product mixture can be effected in any convenient manner and may include a condensation step in order to condense liquefiable products present in the intermediate reaction product mixture. Alternatively the intermediate reaction product can be passed directly to step (b) without any intermediate condensation step.

of 15.5 bar (1.55 x 10^6 Pa) absolute to form the gas stream in line 6 for supply to the first dehydrogenation reactor 10. Another part is taken in line 30 for a purpose which will be described hereunder. A purge stream is taken in line 31.

[0066] The condensate is removed from knockout pot 26 in line 32 and is pumped by a pump (not shown) to heat exchanger 33. The resulting re-heated liquid, now at a temperature of 60°C to 80°C, is fed via line 34 and mixed with a hydrogen-containing gas which is at a temperature of 119°C and has been compressed by a second gas compressor 35 to a pressure of 43.1 bar (4.31 x 10^6 Pa) absolute so as to pass along line 36. The resulting mixture flows on in line 37 into a reactor 38 which contains a charge of a selective hydrogenation catalyst which is chosen so as selectively to hydrogenate reactive carbonyl-containing compounds, such as n-butyraldehyde, butan-2-one and the like, to the respective corresponding alcohols but not to effect any significant hydrogenation of ethyl acetate to ethanol. The inlet temperature to reactor 37 is adjusted as necessary to a temperature in the range of from 60°C to 80°C in dependance upon the degree of deactivation of the catalyst but is chosen to be as low as possible consistent with obtaining an acceptable reaction rate because the equilibrium is favourable at lower temperatures than at high temperatures. A preferred catalyst is 5% ruthenium on carbon available from Engelhard.

[0067] The resulting selectively hydrogenated reaction product is now essentially free from reactive carbonyl compounds, such as aldehydes and ketones, and exits reactor 38, in admixture with unreacted hydrogen, in line 39 at a temperature of 70°C to 90°C. This line leads to a lower part of a first distillation column 40 which is maintained at a pressure of 1.5 bar (1 x 10^5 Pa) absolute. A bottoms product is withdrawn from distillation column 40 in line 41. Part of this is recycled to distillation column through line 42, column reboiler 43 and line 44. The remainder is passed by way of line 45 to a purification section (or water removal package) 46 in which it is treated in any convenient manner for the removal of water (and possibly other impurities) therefrom so as to yield a stream of moderately dry ethanol for recycle to the first dehydrogenation reactor 10 by way of line 2. The precise design of water removal package 46 will depend upon the composition of the ethanol feed stream in line 1. The bottoms product in line 41 typically comprises mainly ethanol with minor amounts of, for example, iso-propanol, water, C_{4+} alkanols, and traces of ketones, other esters and ethers.

[0068] An overhead stream, which typically comprises a major proportion of diethyl ether and lesser amounts of other ethers, methanol, ethanol, n-butyraldehyde, and alkanes, as well as traces of acetaldehyde, ethyl acetate, and water, is recovered in line 47 and condensed by means of condenser 48. Uncondensed gases are purged in line 49, while the resulting condensate is recycled to the top of distillation column 38 as a reflux stream in line 50. A side draw stream is taken from distillation column 40 in line 51 and pumped by a pump (not shown) to a second distillation column 52 which is maintained at an overhead pressure of 12 bar (1.2 x 10^6 Pa) absolute.

[0069] From the bottom of distillation column 52 a stream comprising substantially pure ethyl acetate is recovered in line 53, part of which is recycled to a lower part of distillation column 52 by way of line 54, column reboiler 55, and line 56. The remainder forms the product stream in line 57 from the plant; this can be taken to storage or further distilled in one or more further distillation columns, if desired, in order to remove minor amounts of iso-propyl acetate, di-propyl ether, and 1-ethoxybutane.

[0070] An overhead product consisting mainly of ethanol, ethyl acetate and water, besides smaller amounts of 1-ethoxybutane, methanol, diethyl ether and di-propyl ether and traces of alkanes, is taken in line 58 and condensed by means of condenser 59. The resulting condensate passes on in line 60, some being recycled to the first distillation column by way of line 61 while the remainder is recycled as a reflux stream to the second distillation column 52 in line 62. Reference numeral 63 indicates a line for recovery of water and other materials from water removal package 46.

[0071] The compositions in mol % of some of the more important streams in the plant of Figure 1 are set out in Table 2 below.

Hg (12.41 x 10^6 Pa). It will be noted that there are significant differences between the distillation lines observed at different operating pressures. In Figure 2 the composition of a typical feed as might be supplied in line 39 of the plant of Figure 1 is indicated by point A. Point B indicates the composition of the side draw stream in line 51 for this feed. Point C indicates the composition of the resulting bottom stream in line 41 and point D indicates the composition of the stream in line 61. The effective feed composition to column 40 lies on the intersection of the straight line joining A and D with the straight line joining points B and C. In Figure 3 the points B and D represents the same compositions as the corresponding points in the triangular diagram of Figure 2. Point E represents the composition of the substantially pure ethyl acetate recovered in line 45.

[0073] The invention is further described in the following Examples.

Examples 1 to 5

[0074] These Examples investigated the dehydrogenation of ethanol to ethyl acetate in the presence of hydrogen. The apparatus used included a dehydrogenation reactor made of stainless steel tubing which contained a charge of reduced copper oxide catalyst and which was immersed in a hot oil bath for heating purposes.

[0075] At start-up a charge of 200 ml of a tabulated copper oxide catalyst available under the designation E408Tu from Mallinckrodt Specialty Chemicals was placed in the reactor which was then purged with nitrogen at 14.5 bar (14.5 x 10^5 Pa). A dilute H_2 in N_2 gaseous mixture at 3 bar (3 x 10^5 Pa) was passed over the catalyst for 60 hours in order to effect catalyst reduction. The oil bath was raised to the temperature indicated in Table 2 below. The gas feed was then changed to pure hydrogen.

[0076] In operation hydrogen was introduced to the dehydrogenation reactor at rate of 2 standard litres per hour by way of a pressure regulator and flow controller through a line which was immersed in the bottom of the oil bath. An ethanol stream whose composition is set out in Table 3 was fed as a liquid at a rate of 200 ml/hr to a vaporiser and mixed with the hydrogen. The resulting vaporous mixture of ethanol and hydrogen was supplied to the dehydrogenation reactor.

[0077] The reaction products were cooled and the liquid condensate was analysed by gas chromatography. The results obtained are summarised in Table 3.

TABLE 4

Example No	Feed	6	7	8	9
Reactor Temperature(°C)	-	91	80	72	110
Pressure (bar)[10^5 Pa]	-	14.2	14.2	14.4	14.1
Product Analysis (Wt%)					
Acetaldehyde	0.904	0.034	0.040	0.038	0.039
Diethyl ether	0.579	0.428	0.418	0.417	0.419
Ethanol	68.223	70.040	70.121	70.163	70.301
Acetone	2.282	trace	trace	trace	trace
iso-propanol	1.004	3.232	3.233	3.213	3.231
Di-iso-propyl ether	0.003	0.098	0.097	0.097	0.097
n-butyraldehyde	0.010	trace	trace	trace	trace
Ethyl acetate	23.263	22.572	22.464	22.437	22.396
Butan-2-one	0.170	0.002	0.004	0.007	0.003
sec-butanol	0.371	0.567	0.566	0.560	0.567
iso-propyl acetate	0.186	0.185	0.184	0.184	0.184
n-butanol	0.507	0.730	0.770	0.776	0.570
Water	1.410	1.170	1.170	1.200	1.270
Others	1.088	0.942	0.933	0.908	0.923
Total	100.00	100.00	100.00	100.00	100.00

Notes: The increased amount of n-butanol noted in Examples 6 to 9 compared with the amount in the feed can be ascribed not only to n-butanol formed by hydrogenation of n-butyraldehyde present in the feed (the amount of which is, in any case, difficult to measure) but also from hydrogenation of other products which contain C_4 groups and which are included in the figure given for "others" in the feed.

Examples 10 to 12

[0082] The general procedure of Examples 6 to 9 was repeated using a different feed and different reaction conditions. The results are set out in Table 5 below.

TABLE 6 (continued)

Line No.	39	51	41	61	53
n-butanol	0.192	0.021	0.519		0.010
Ethyl butyrate	0.117		0.307		
Butyl acetate	0.136		0.358		
Water	0.550	0.590	0.330	2.920	0.010
"Light" unknowns	0.020	0.029		0.003	
"Heavy" unknowns	0.098	0.001	0.290	0.013	0.026
Total	100.00	100.00	100.00	100.00	100.00

Claims

1. A process for the purification of an impure feedstock comprising an alkyl alkanoate which contains up to 12 carbon atoms which comprises:

    (a) providing an impure feedstock containing an alkyl alkanoate which contains up to 12 carbon atoms, said feedstock further containing at least one impurity which is selected from an aldehyde and a ketone and which contains the same number of carbon atoms as said alkyl alkanoate;
    (b) contacting said impure feedstock with a selective hydrogenation catalyst in the presence of hydrogen in a selective hydrogenation zone maintained under selective hydrogenation conditions effective for selective hydrogenation of impurities containing reactive carbonyl groups thereby to hydrogenate said impurities to the corresponding alcohols;
    (c) recovering from the selective hydrogenation zone a selectively hydrogenated reaction product mixture comprising said alkyl alkanoate, hydrogen, and said corresponding alcohols;
    (d) distilling material of the selectively hydrogenated reaction product mixture in one or more distillation zones so as to produce substantially pure alkyl alkanoate therefrom; and
    (e) recovering said substantially pure alkyl alkanoate.

2. A process according to claim 1, in which the impure feedstock comprises a reaction product obtained by converting an alkanol to said alkyl alkanoate by a procedure selected from:

    (i) dehydrogenation,
    (ii) oxidation,
    (iii) reaction with an aldehyde, and
    (iv) oxidation to the corresponding aldehyde followed by the Tischenko reaction.

3. A process according to claim 1 or claim 2, in which said alkyl alkanoate is a C_{2+} alkyl C_{2+} alkanoate.

4. A process according to any one of claims 1 to 3, in which said alkyl alkanoate is selected from ethyl acetate, n-propyl propionate, and n-butyl butyrate.

5. A process according to any one of claims 1 to 4, in which said alkyl alkanoate is ethyl acetate.

6. A process according to any one of claims 1 to 5, in which the selective hydrogenation conditions of step (b) include use of a feedstock:hydrogen molar ratio of from about 1000:1 to about 1:1, a combined partial pressure of feedstock and hydrogen of from about 5 bar (5×10^5 Pa) to about 80 bar (8×10^6 Pa), and a temperature in the range of from about 40°C to about 120°C.

7. A process according to claim 6, in which the combined partial pressure of feedstock and hydrogen in step (b) is from about 25 bar (2.5×10^6 Pa) to about 50 bar (5×10^6 Pa).

8. A process according to any one of claims 1 to 7, in which the selective hydrogenation catalyst comprises a metal selected from nickel, palladium, platinum, ruthenium, rhodium and rhenium.

24. A process for the production of an alkyl alkanoate containing up to 12 carbon atoms by dehydrogenation of an alkanol which comprises:

    (i) contacting a vaporous mixture containing an alkanol and hydrogen with a dehydrogenation catalyst in a dehydrogenation zone maintained under dehydrogenation conditions effective for dehydrogenation of an alkanol to yield an alkyl alkanoate containing up to 12 carbon atoms;
    (ii) recovering from the dehydrogenation zone an intermediate reaction mixture comprising hydrogen and liquefiable products comprising said alkyl alkanoate, said alkanol, hydrogen and impurities containing reactive carbonyl groups;
    (iii) subjecting at least a portion of the liquefiable products of the intermediate reaction product mixture as impure feedstock to a process according to any one of claims 1 to 23.

25. A process according to claim 24, wherein the dehydrogenation conditions include use of an alkanol:hydrogen molar ratio of from about 1:10 to about 1000:1, a combined partial pressure of alkanol and hydrogen of from about 3 bar (3×10^5 Pa) up to about 50 bar (5×10^6 Pa), and a temperature in the range of from about 100°C to about 260°C.

26. A process according to claim 25, wherein the dehydrogenation conditions include use of a combined partial pressure of alkanol and hydrogen of at least about 6 bar (6×10^5 Pa) up to about 30 bar (3×10^6 Pa).

27. A process according to any one of claims 24 to 26 in which the dehydrogenation conditions include use of a temperature of between about 200°C and about 250°C.

28. A process according to any one of claims 24 to 28, in which the dehydrogenation catalyst is a copper containing catalyst which comprises, before reduction, copper oxide on alumina.

29. A process according to any one of claims 24 to 27, in which the rate of supply of the feedstock to the dehydrogenation zone corresponds to an alkanol liquid hourly space velocity (LHSV) of from about 0.5 hr^{-1} to about 1.0 hr^{-1}.

30. A process according to any one of claims 24 to 29, in which the impure feedstock contains water and ethanol and in which in step (d) there is recovered an ethanol stream for recycle to the dehydrogenation zone.

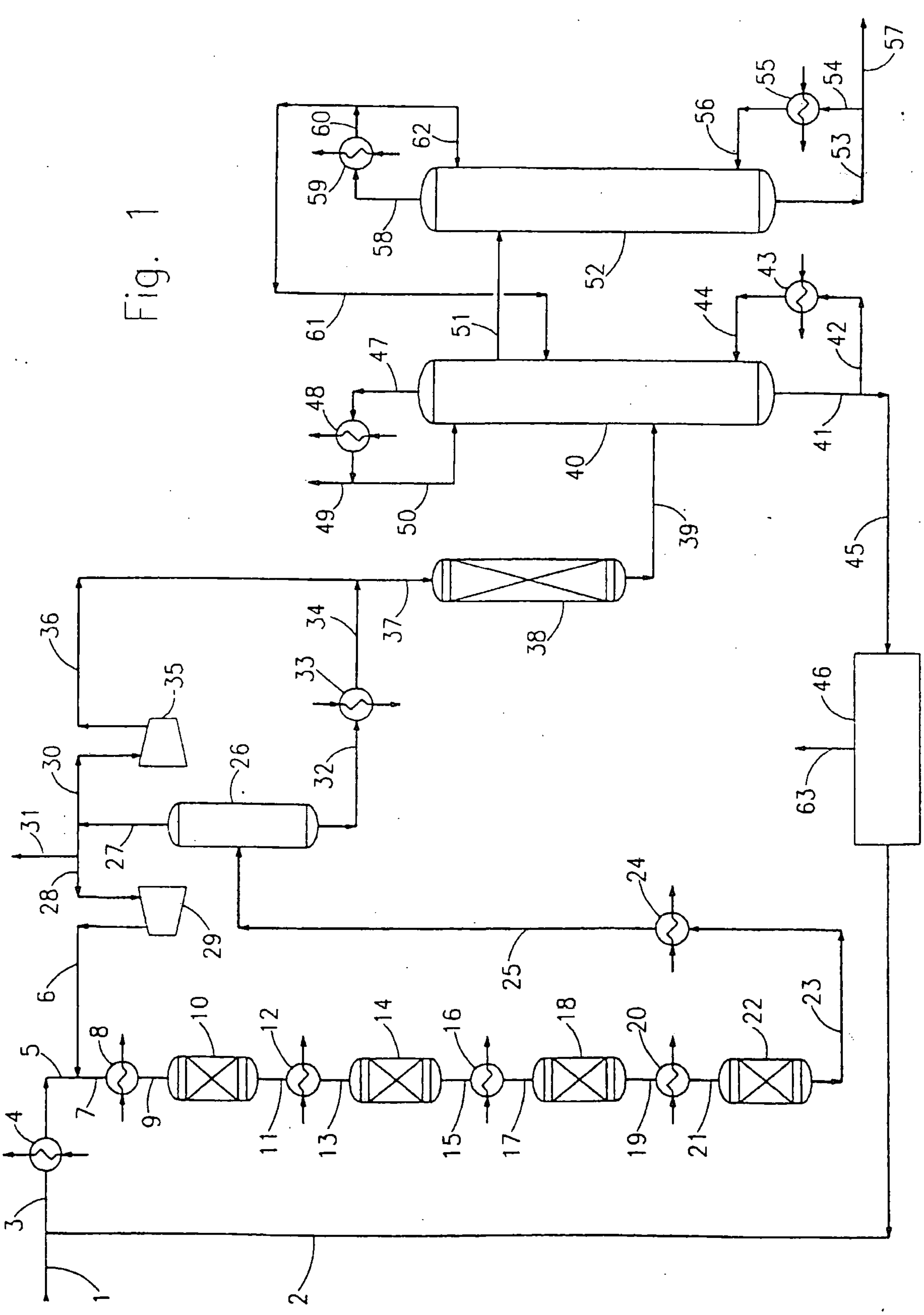
Fig. 1
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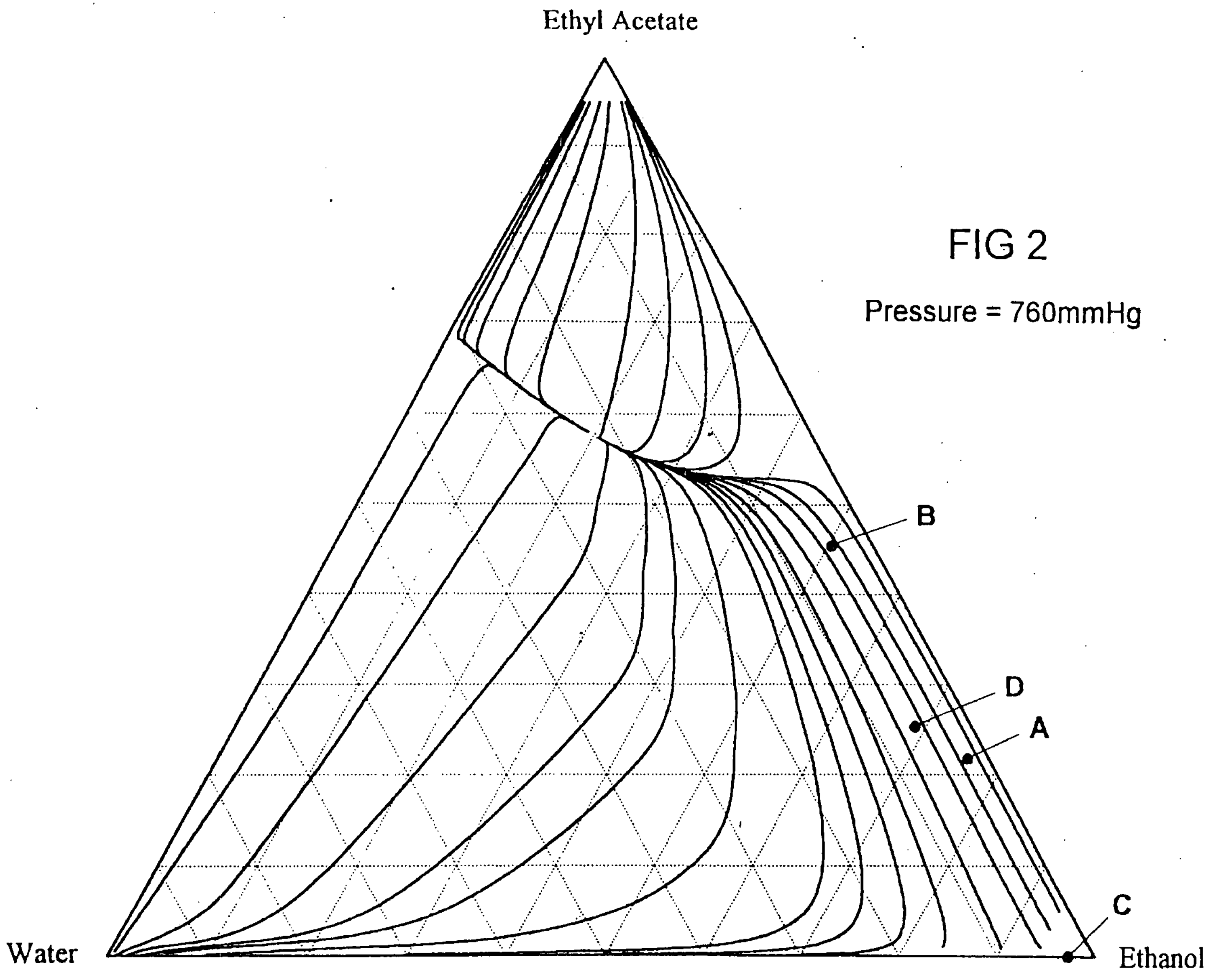
FIG 2



Pressure = 760mmHg

FIG 3

Pressure = 9308mmHg