*"A STUDY TO IDENTIFY A **FEASIBLE ROUTE** FOR THE PRODUCTION OF THE MONOMER **2-VINYLFURAN** FROM FURAN BY EVALUATING THE **EFFECT OF VARIABLES** ON THE FINAL YIELD AND **TO RECOMMEND** SUITABLE CONDITIONS APPLICABLE TO THE CHEMICAL INDUSTRY"*

by

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Submitted in part fulfilment
of the requirements for the
MASTERS DIPLOMA OF TECHNOLOGY
in the Department of Chemistry
in the Faculty of Science
at the M L Sultan Technikon.

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DATE SUBMITTED	***DECEMBER 1992***

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ACKNOWLEDGEMENTS

I hereby wish to express my sincere gratitude and appreciation to:

Dr R H Reimann and Mr D K Chetty for their guidance and valuable criticisms during the course of this investigation.

Mr A Wills of C G Smith Chemicals for proposing this project and supervising my work in the early stages, and retaining an interest in the work throughout the course of this investigation.

The staff of C G Smith Chemicals for their assistance.

My colleagues and technical staff in the Department of Chemistry for their assistance.

Mr D Govender of Sanachem for assistance with part of the literature search and the use of the GC-MS.

Mrs J Naicker and Miss S Rambharos for willingly typing this thesis.

Mr and Mrs R K Harishun for proof-reading the thesis.

My dear wife and two daughters for their patience and understanding over the years spent on this research.

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ABSTRACT

2-Vinylfuran has been synthesised from furan, obtained from furfural a degradation product of bagasse, and has the potential to be used as a monomer in the Polymer Industry.

Furan was successfully reacted with ethylene under catalytic conditions of palladium (II) acetate and copper (II) acetate to produce 2-vinylfuran, via a direct substitution reaction, at atmospheric pressure and a temperature of 95° C for two hours in dimethylformamide.

2-Vinylfuran was quantitatively analysed by the Gas Chromatographic technique using a Chromosorb 102, porous styrene-divinyl-benzene copolymer, stainless steel column. The yield of 2-vinylfuran was 429% with respect to palladium (II) acetate.

Palladium (II) chloride was also investigated but was not as effective as palladium (II) acetate as catalyst. Iron (III) chloride and silver (I) acetate were also used as re-oxidants of palladium (II) acetate but was found to be less effective than copper (II) acetate.

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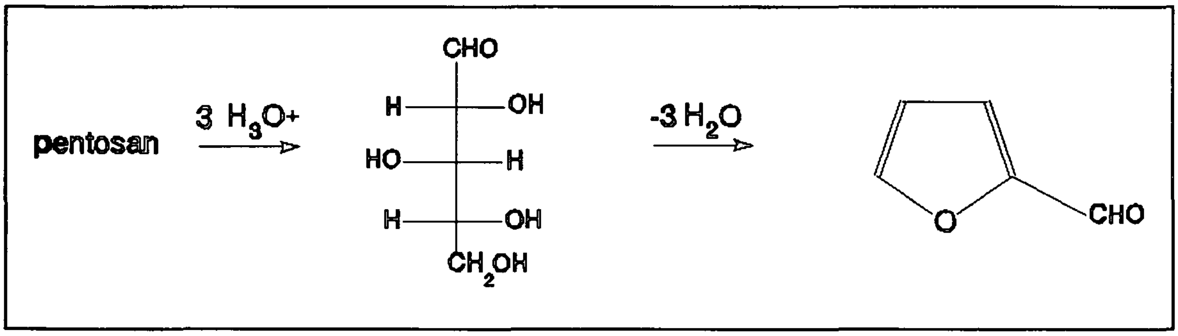
CHAPTER ONE

INTRODUCTION

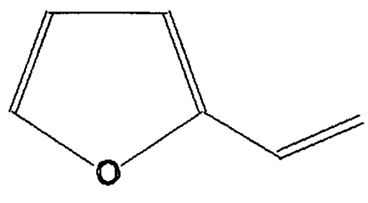
1.1 IMPORTANCE OF 2-VINYLFURAN

At C G Smith Chemicals, furfural is being produced commercially from the hydrolysis of pentosans (bagasse) to pentoses and subsequent cyclodehydration as shown below :



The above reaction is an example of acid hydrolysis of natural polysaccharides. The abundance of polysaccharides in biomass indicates that there is a major potential source of raw materials for the chemical industry[1-2].

Another important compound is 2-vinylfuran.



2-vinylfuran

Its potential as an industrial monomer[3] has not been widely investigated since its synthesis was difficult. (see page 4 - 8). There are nevertheless numerous compounds that can be produced as summarised by figure 1.1 (a) and figure 1.1 (b) and discussed on pages 9-17.

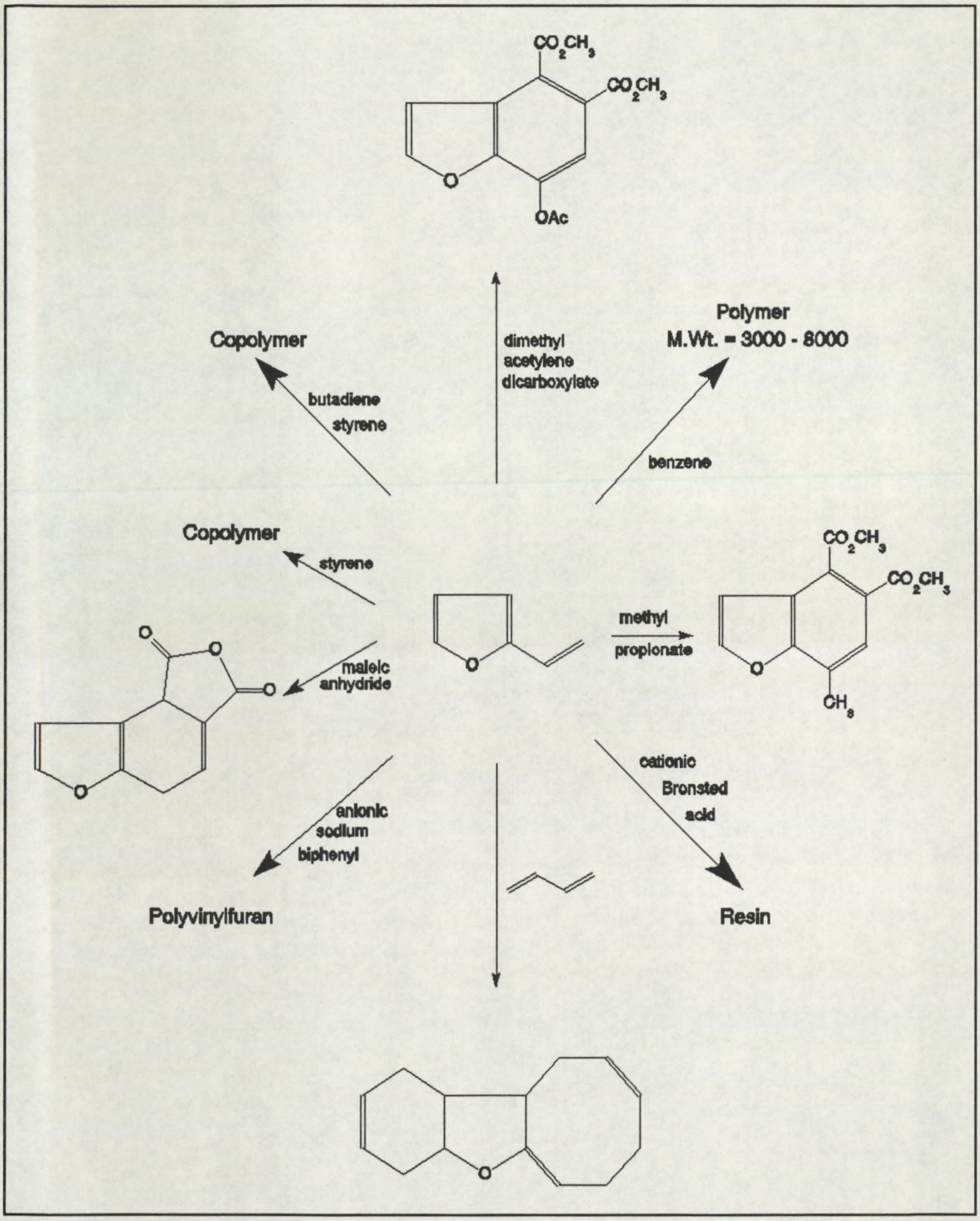


FIGURE 1.1 (a) COMPOUNDS DERIVED FROM 2-VINYLFURAN

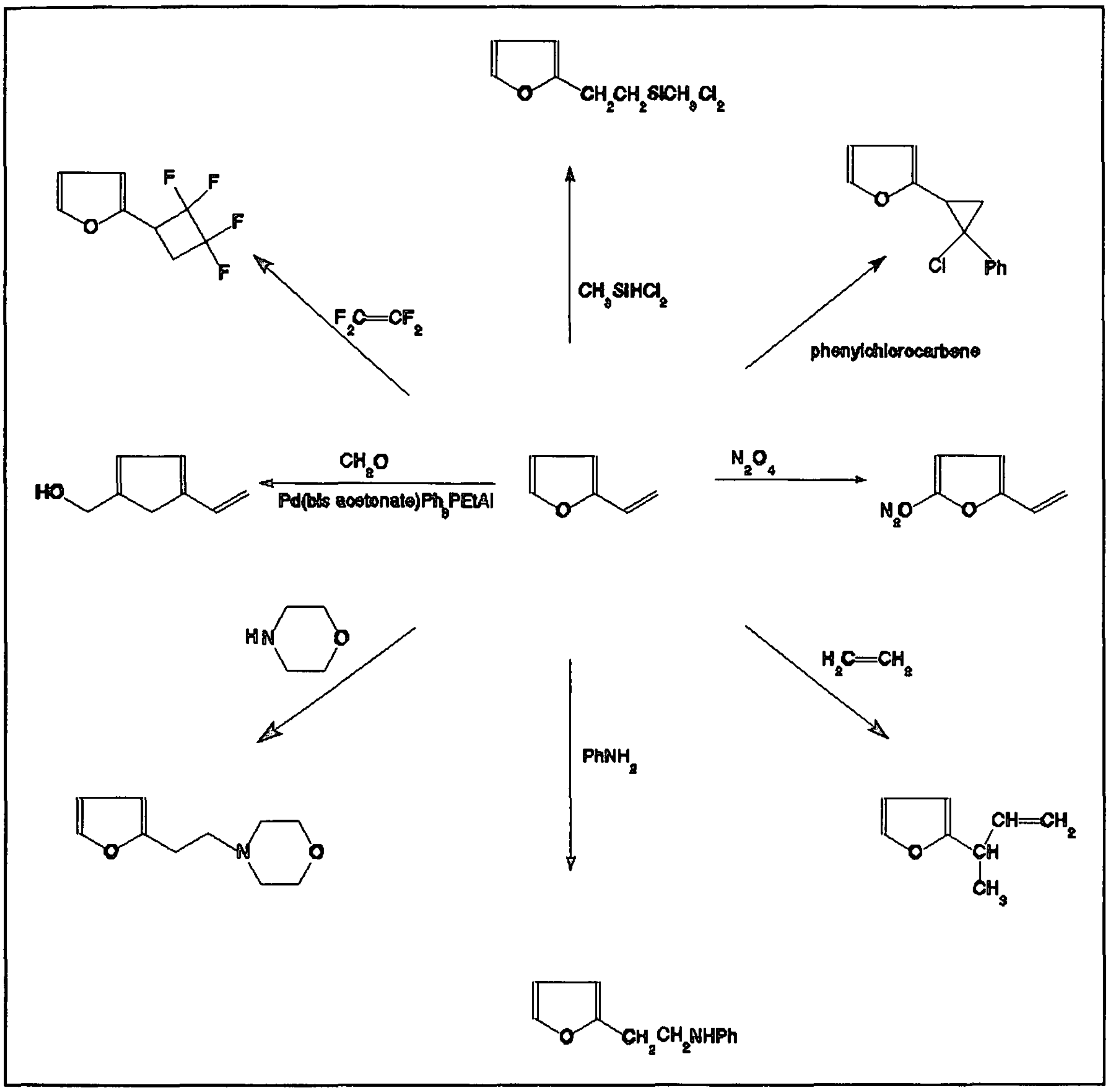
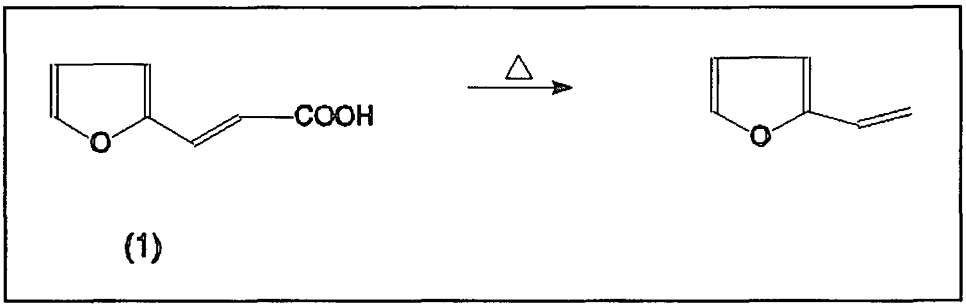


FIGURE 1.1 (b) COMPOUNDS DERIVED FROM 2-VINYLFURAN

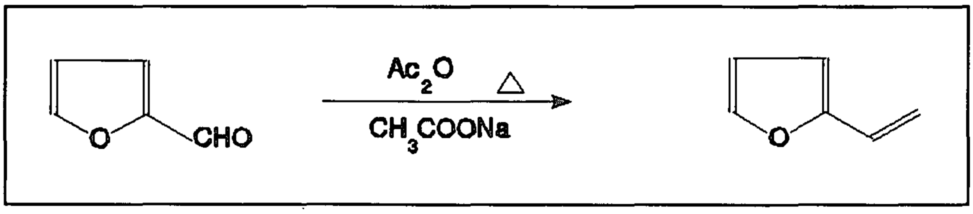
The production of 2-vinylfuran from furan and ethylene, using mild reaction conditions, could have a beneficial effect on the chemical industry as this would provide a new compound for synthesis of complex speciality chemicals.

1.2 HISTORY OF 2-VINYLFURAN

Liebermann[4], in 1894, noted that 2-furylacrylic acid (1) decomposed at a temperature between 255°C - 265°C to yield a colourless liquid identified as 2-vinylfuran. Having produced small amounts of this liquid, he was only able to determine its boiling point as 101° C - 102° C.



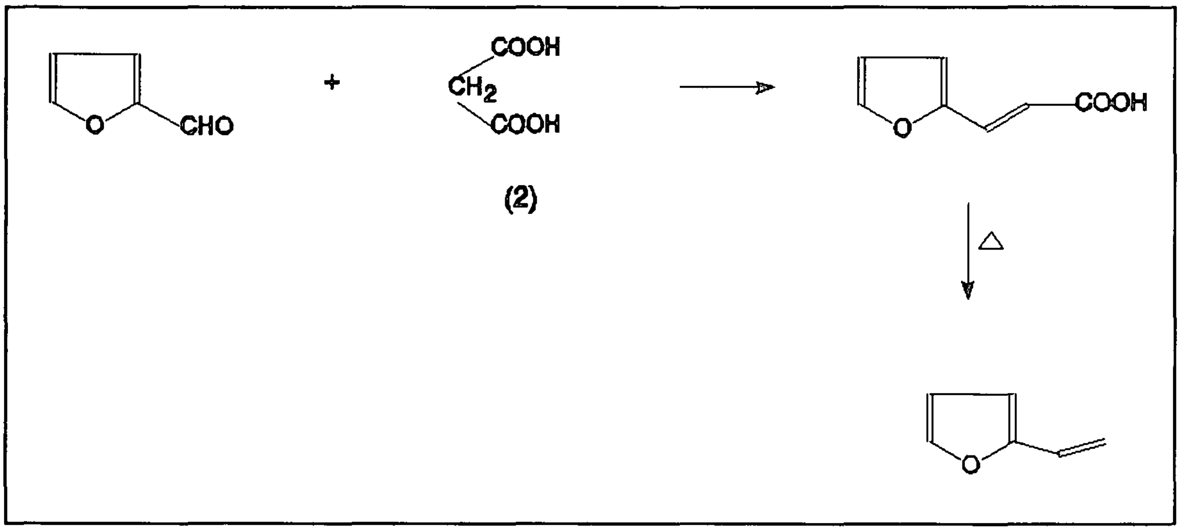
Moureux[4] et al, using the Perkin reaction as shown below, obtained a yield of 10%. They encountered purification difficulties and therefore concentrated on a study of the properties of 2-vinylfuran. It was found that the molecule underwent polymerisation very rapidly, especially in the presence of light and oxygen and could not be stored for long periods unless hydroquinone was used as an inhibitor.



At a later stage, it was found that 2-vinylfuran :

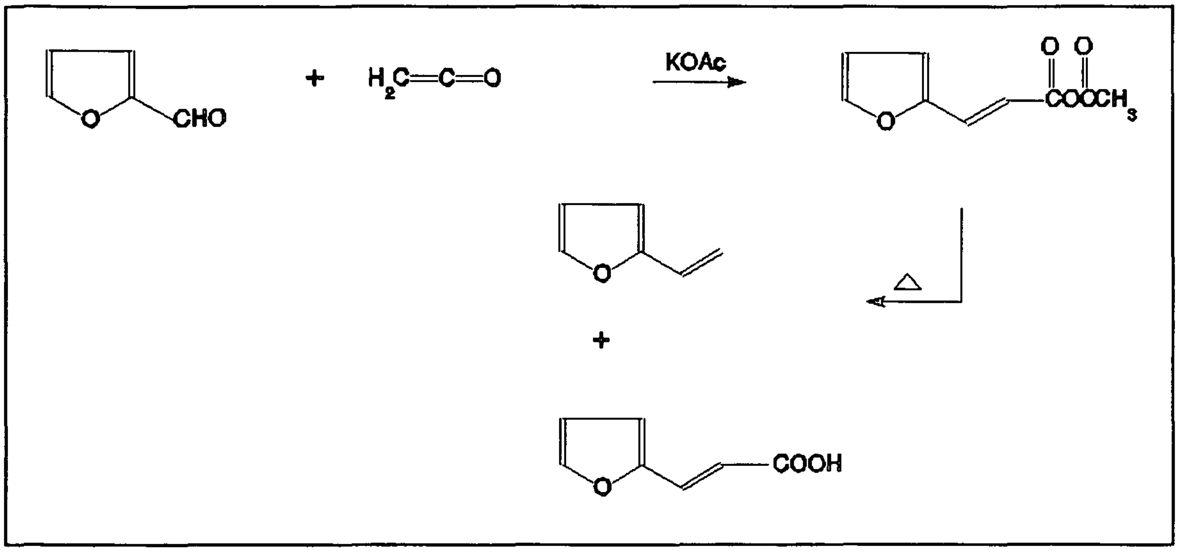
- underwent auto-oxidation more rapidly than styrene[5].
- was oxidized instantly by aqueous $KMnO_4$[6] and
- absorbed bromine in carbon disulphide very rapidly[4].

Tchelitcheff[7] et al, using the method of Pfau who synthesised 2-furylacrylic acid by using furfural and malonic acid (2), was able to synthesise 2-vinylfuran as shown below :



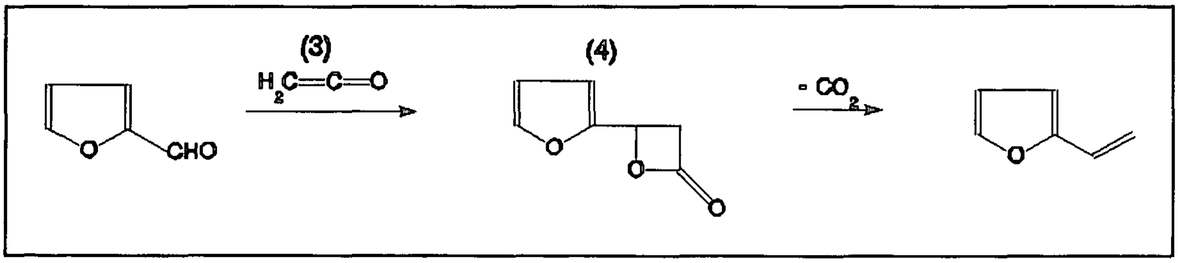
Since 2-furylacrylic acid was not isolated in the reaction, a yield of 71% 2-vinylfuran was obtained of low purity. This method could not be industrialised because of the low purity of 2-vinylfuran due to purification difficulties.

The Perkin reaction on furfural was used by Thomas and Hurd[6] as shown below :



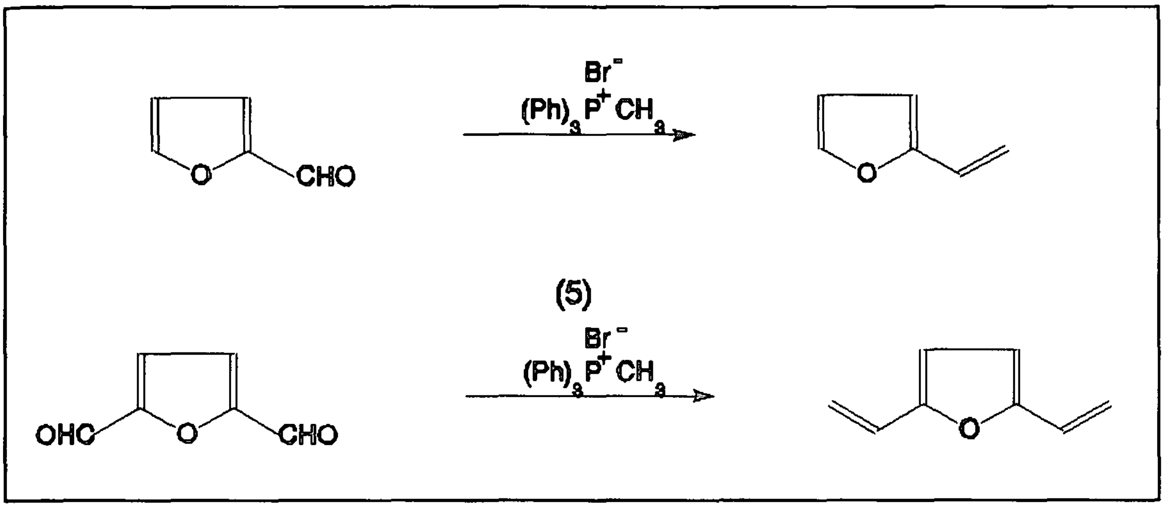
This method could also not be industrialized due to purification difficulties.

Hagemeyer[8-9] was able to synthesise 2-vinylfuran, by reacting furfural with a ketene (3), forming an intermediate lactone (4), according to the following scheme :



The yield of 2-vinylfuran by this method was 59%. The problem they encountered, in addition to the low yield, was the limited availability of the ketene which had to be prepared from acetone by pyrolysis. The ketene had to be removed from acetone vapour by passing the gases through a -80° C condenser.

Van Reijendam[10-11] et al, in 1969 used the Wittig reaction for the synthesis of vinyl and divinylfuran from the corresponding aldehydes as shown below :

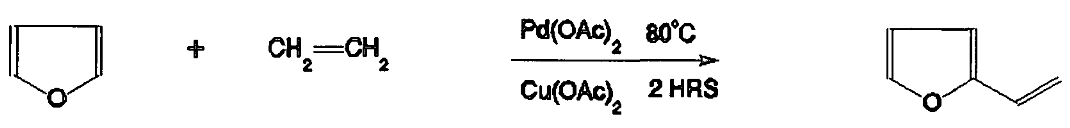


In the experimental method, sodium methoxide was added to methyltriphenylphosphonium bromide (5) in anhydrous ether and anhydrous dimethylformamide. The reaction was carried out under nitrogen atmosphere.

The yield of 2-vinylfuran was so low that they opted for the 2-furylacrylic acid decomposition reaction.

Davidson and Elix[12], using the Wittig reaction, produced 2-vinylfuran with a 60% yield. An anhydrous reaction medium was used under an inert atmosphere (nitrogen). Due to these strict reaction conditions, the method was not feasible for industrial purposes.

Kozhenikov[13], in 1977 reacted furan and ethylene in the presence of palladium (II) acetate and copper (II) acetate in a sealed autoclave to produce 2-vinylfuran as shown below:



The percentage yield of 2-vinylfuran was 510% with respect to palladium (II) acetate.

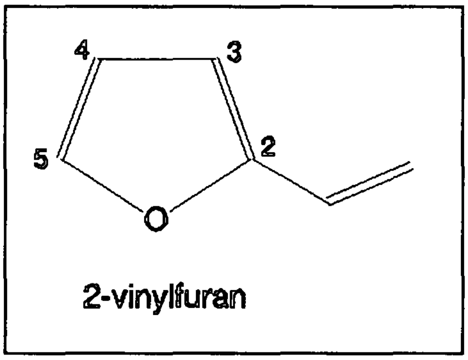
From 1980 Delmas[14-16] et al, used the Wittig reaction in a solid liquid phase transfer process. They found that the separation of 2-vinylfuran from the reaction medium was difficult because of the formation of product - solvent azeotropes. The reaction scheme is given below :

1.3 CHEMICAL REACTIVITY AND APPLICATIONS OF 2-VINYLFURAN

2-Vinylfuran has three reaction sites, namely :

- an aromatic heterocycle
- the conjugated dienic system and
- the exocyclic double bond

It also has a distinctive tendency for polymerisation.



1.3.1 Reactivity of the heterocycle

2-vinylfuran undergoes electrophilic attack preferentially at the 5 position as illustrated in Fig.1.2[17-19].

Although a few nitration compounds were synthesised from 2-vinylfuran, their subsequent synthesis led to interesting products of which the anti-tumoural and anti-microbial properties has been extensively studied[20-21].

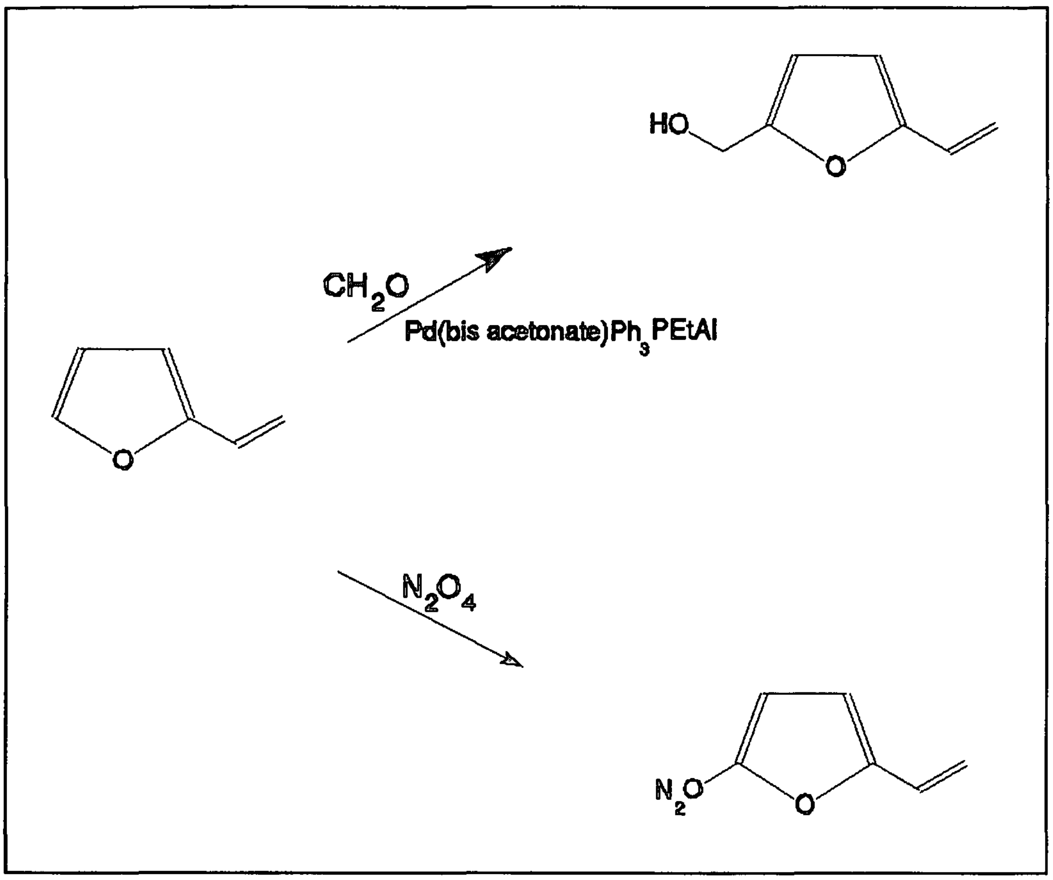


FIGURE 1.2 EXAMPLES SHOWING THE REACTIVITY OF 2-VINYLFURAN

1.3.2 Diels-Alder reaction with 2-vinylfuran

The Diels-Alder reaction was studied from 1939 and the products are illustrated in figure 1.3 (a)[22-25]. The reaction shows that 2-vinylfuran has two dienic systems namely:

- the cis-oriented diene of the ring system and
- the exocyclic double bond and the adjacent furan ring "double bond".

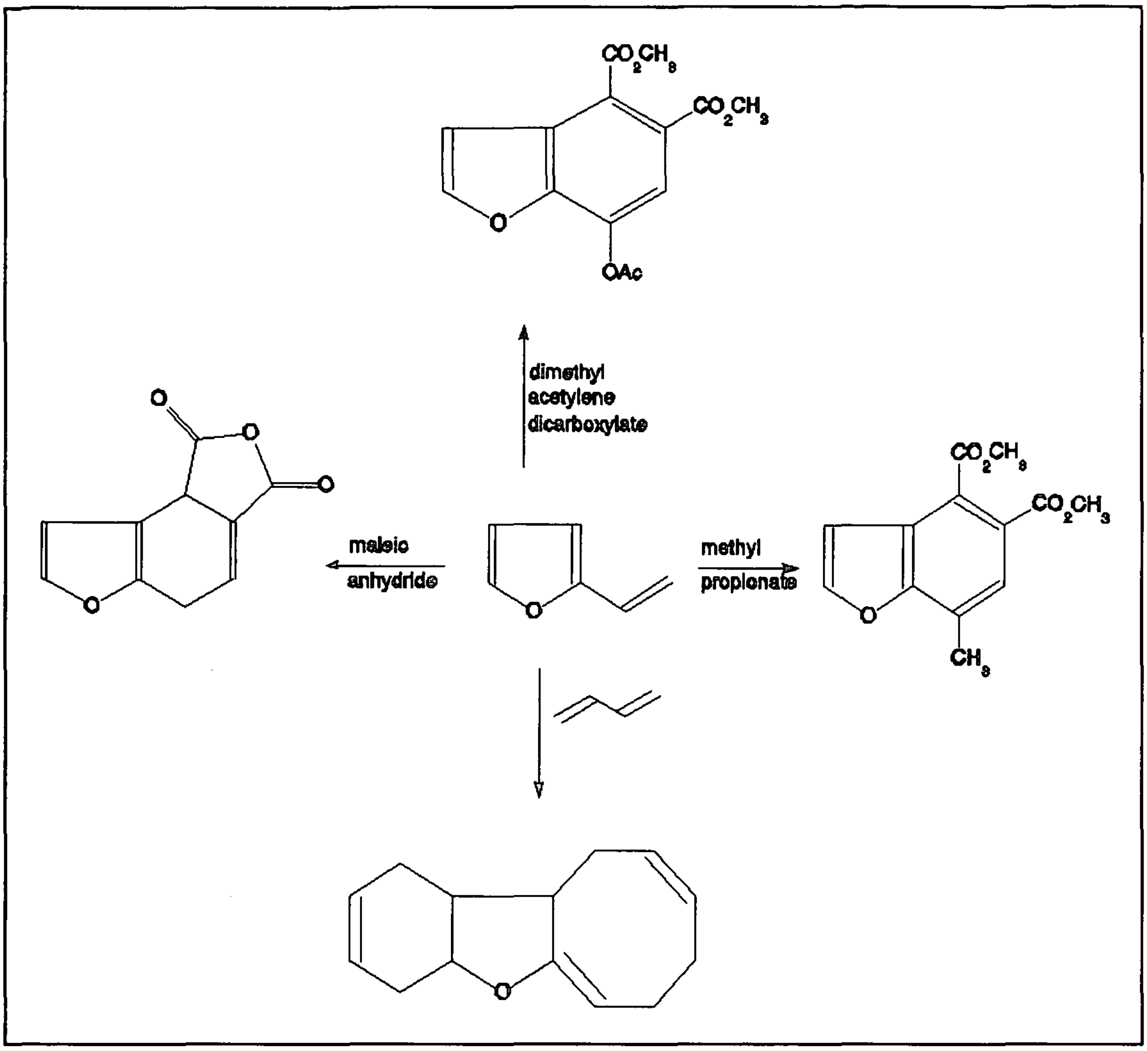


FIGURE 1.3 (a) APPLICATION OF DIELS-ALDER REACTION

TO 2-VINYLFURAN

Davidson and Elix[22] found that the conjugated system made up of the exocyclic double bond and the adjacent furan ring bond was more reactive than the furan ring itself. This is shown in figure 1.3 (b).

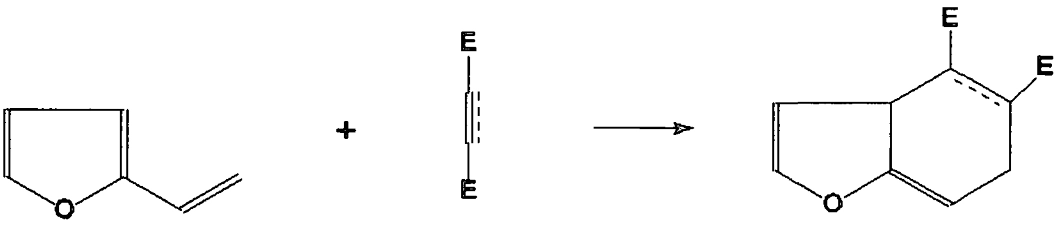


FIGURE 1.3(b) THE DIELS-ALDER REACTION

1.3.3 Reactivity of the exocyclic double bond

The exocyclic double bond of 2-vinylfuran has been used for the synthesis of useful derivatives in the fine chemical industry. This is shown in figure 1.4 (a)[26-31].

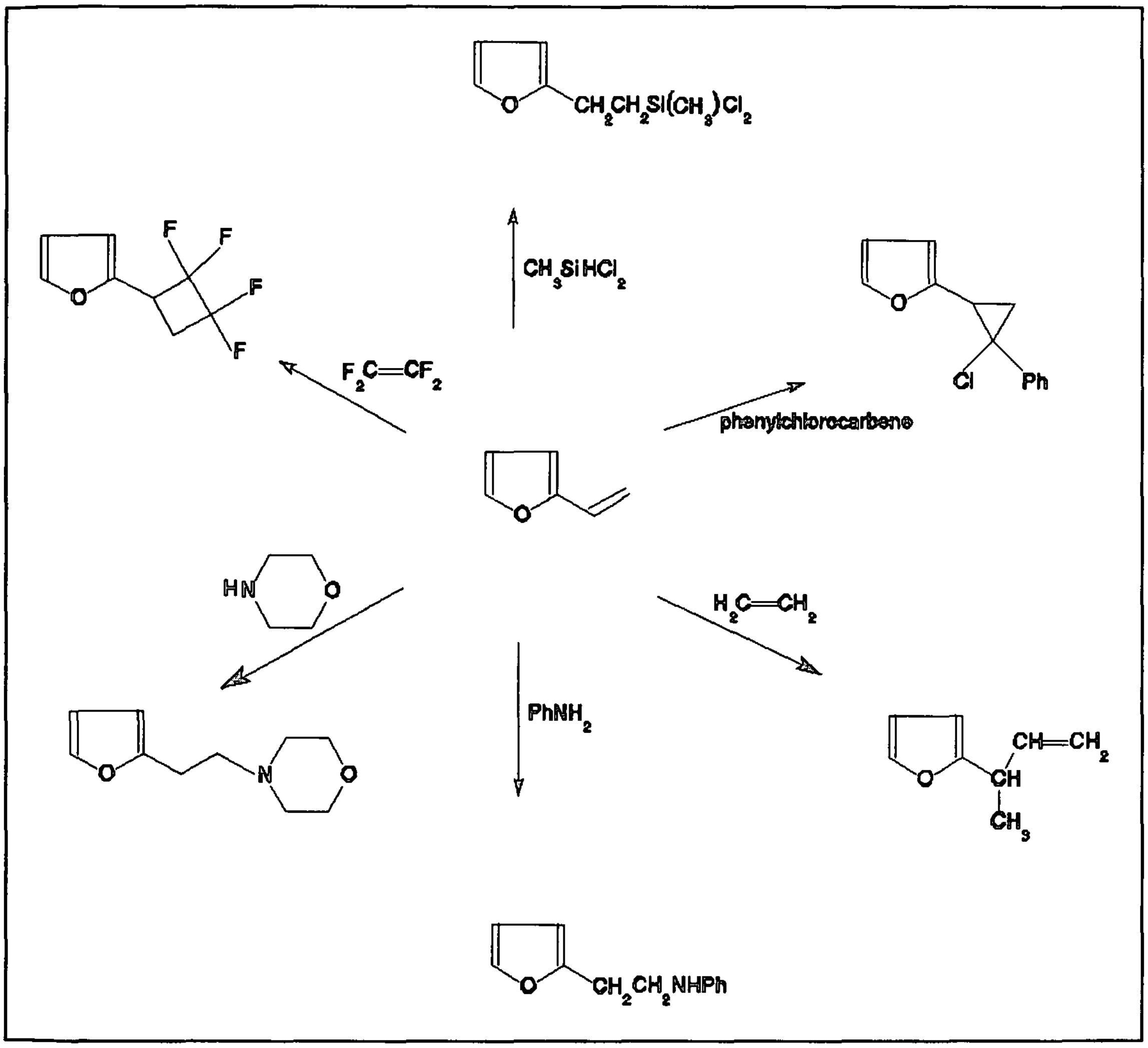


FIGURE 1.4 (a) COMPOUNDS OBTAINED FROM 2-VINYLFURAN AND SHOWING THE REACTIVITY OF THE EXOCYCLIC DOUBLE BOND

In these reactions the furanic ring is preserved.

The resonance structures shown below can explain the preservation of the furan ring system :

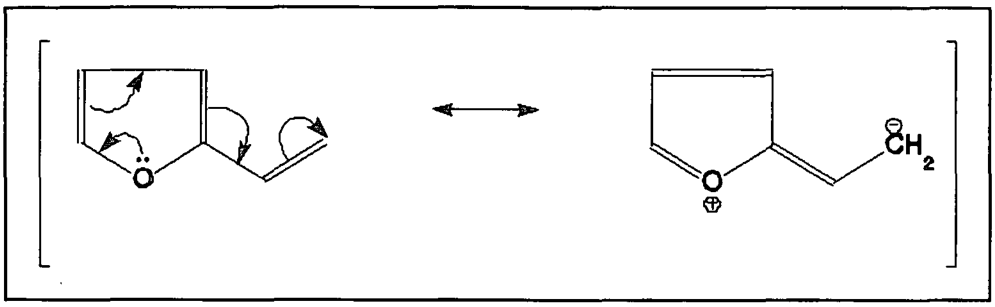


FIGURE 1.4 (b) RESONANCE STRUCTURES OF 2-VINYLFURAN SHOWING THE PRESERVATION OF THE FURAN RING IN REACTIONS

1.3.4 Polymerization

Six different polymer units have been identified[32]. This is shown in figure 1.5 (a).

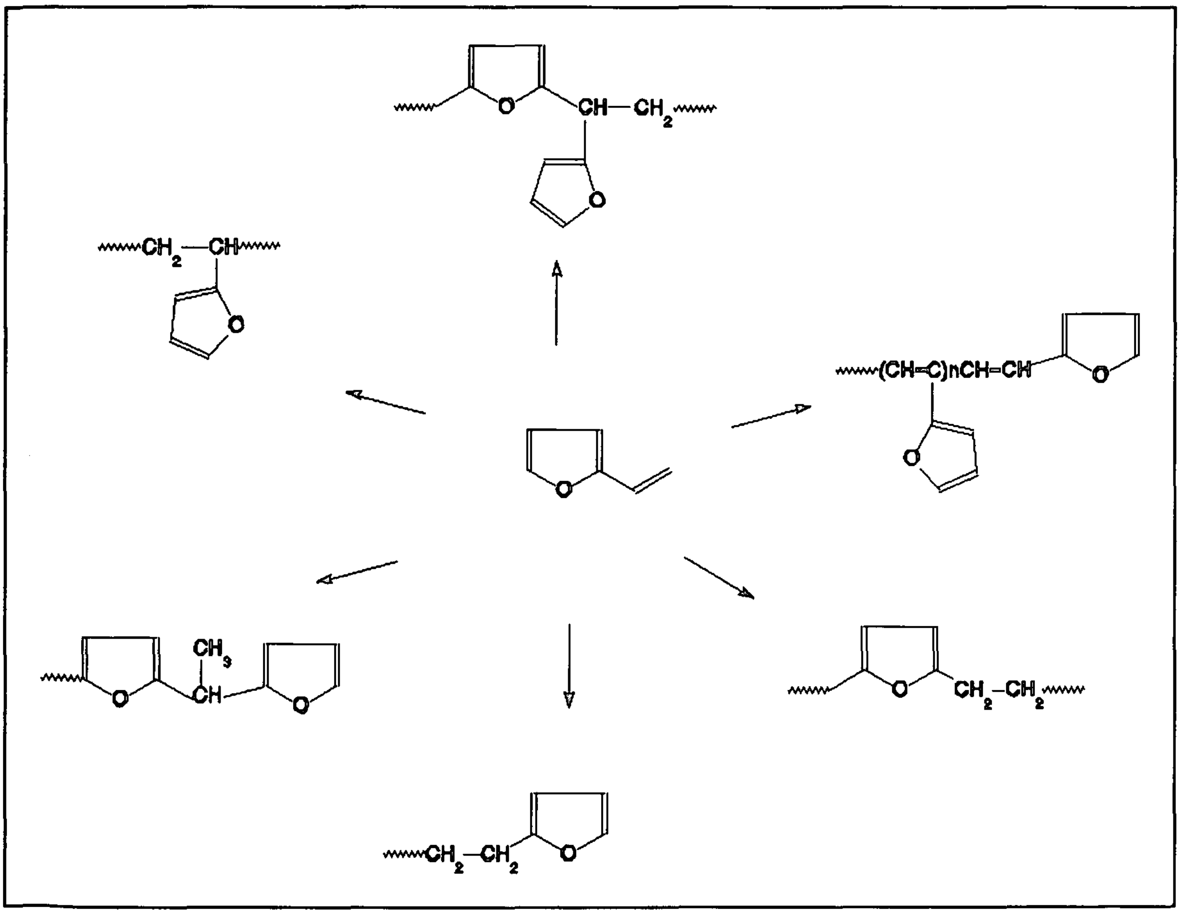


FIGURE 1.5 (a) THE POLYMERIC UNITS OF 2-VINYLFURAN

Three mechanisms for the polymerization of 2-vinylfuran have been proposed, namely:

- radical initiation : in solution and in the absence of oxygen the polymerization has been observed at temperatures of 110° C - 150° C. This conversion occurs at low rates to produce small polymer masses[33].

- anionic polymerization : this does not occur readily[34], but its sodium adduct can initiate the polymerization of acrylonitrile, methyl methacrylate and styrene[35].

- cationic polymerization : this type has been most studied. Gandini[34] etal showed that the complexity of cationic polymerization was linked to the three main reactions, namely :
  - propagation through the vinylic link
  - alkylation at the 5 position and
  - hydrogen transfer

The various polymer products are shown in figure 1.5 (b)[33-37].

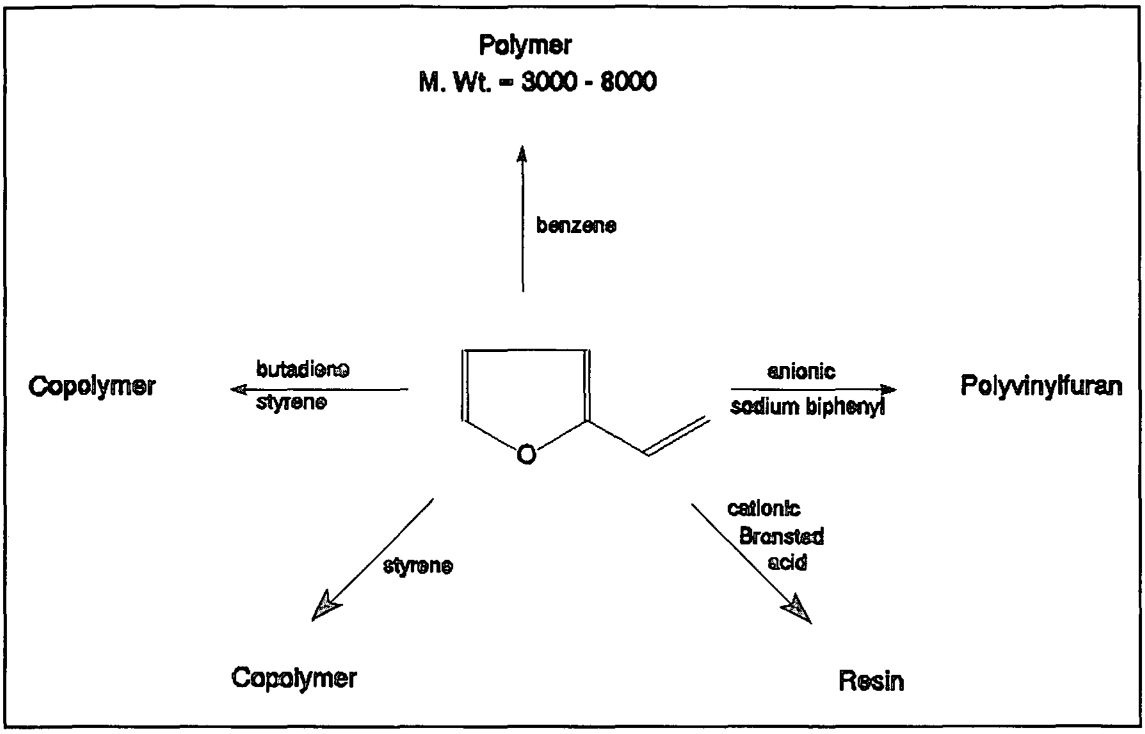
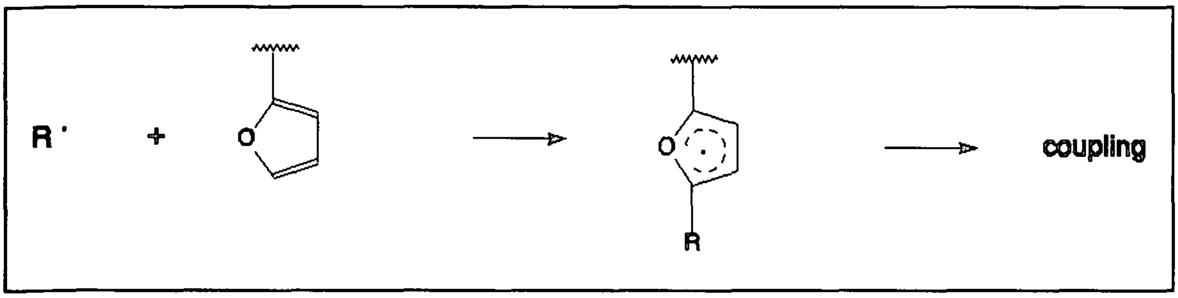


FIGURE 1.5 (b) POLYMERS OF 2-VINYLFURAN

Polymers of 2-vinylfuran can be used :

- to form coating compositions and be combined with the usual film forming ingredients[38].
- as lacquer raw materials and also in the manufacture of moulded materials[39].
- as synthetic drying oil of homogenous composition of a co-polymer of 2-vinylfuran and a fatty oil[40].

The dual dienic-aromatic character of the furan ring has been revealed by the two side reactions encountered in radical and cationic polymerization. In this case, a primary or polymer radical R· can add to the 5 position of a ring belonging to a monomer or a polymer chain to give a less stabilised furyl radical[32].



Just as styrene provides a wide scope of uses in the polymer industry, so too will 2-vinylfuran if it can be mass produced.

1.4 CATALYTIC REACTIONS USING GROUP VIII TRANSITION METALS

1.4.1 Importance of Palladium

1.4.1.1 Introduction

It was discovered by Smidt[41] et al, that ethylene could interact with Noble metal salts to form ethylene-noble metal salt complexes. This led to the Wacker process. In this process, palladium (II) chloride was used to oxidize ethylene to acetaldehyde as shown by the following reaction :

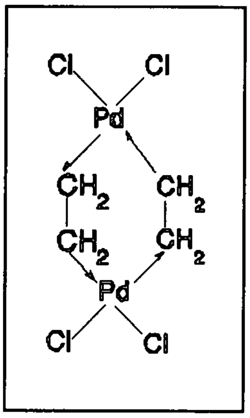
$$CH_2{=}CH_2 + PdC\ell_2 + H_20 \rightarrow CH_3CHO + Pd + 2HC\ell$$

This process only became industrialized after the discovery that cupric or ferric chloride could be used to make palladium catalytic. In such a system, the following reactions occurred :

$Pd + 2\ CuC\ell_2 \rightarrow PdC\ell_2 + 2\ CuC\ell$ (Catalyst Regeneration)

$2\ CuC\ell + 2HC\ell + \frac{1}{2}0_2 \rightarrow CuC\ell_2 + H_20$ (Co-catalyst Regeneration)

It was proposed that palladium (II) chloride formed a dimeric compound with ethylene as shown below :



The purpose of oxygen was to regenerate copper (II) chloride.

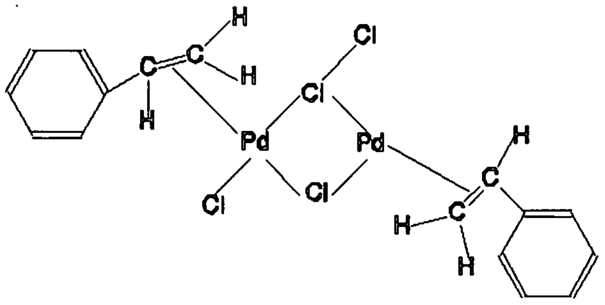
In the presence of water, these dimers decomposed to acetaldehyde and palladium metal.

These findings, subsequently led to the production of vinyl acetate on an industrial scale. The chemical reaction was given as :

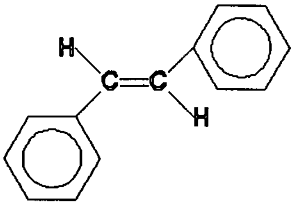
$CH_2{=}CH_2 + CH_3COO^- + PdC\ell_2 \rightarrow CH_2{=}CHOOCCH_3 + Pd$

1.4.1.2 Vinylation of Aromatic Compounds

The use of palladium (II) compounds, in aromatic - olefin coupling reactions (vinylation), was first shown by Fujiwara[42]. In his synthesis he used styrene - palladium (II) chloride (compound I) in the presence of acetic acid, in benzene, to form stilbene (compound II).



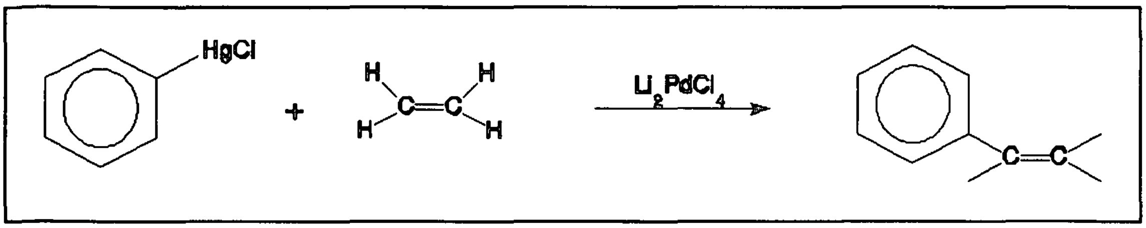
I



II

Further research showed that aromatic - olefin coupling reaction could occur *in situ* without prior formation of an aromatic - palladium (II) compound. He found that, when comparing two systems of palladium (II) salts with respect to yield, the palladium (II) acetate system was better than the palladium (II) chloride - sodium acetate system[43]. This, he suggested, was due to the acetate ion being a weaker ligand.

Homogenous solutions of Group VIII metal salts (lithium palladium salts) were used by Heck[44]. He found that arylmercuric halides could be used, in the presence of Group VIII metal salts, for aromatic - olefin coupling as shown below :



He also found that palladium (II) salts were the most useful, while rhodium and ruthenium were good alternatives. These reactions were found to occur even at room temperature. The reaction was considered a true organometallic reaction and not a radical or ionic reaction. This was based on the fact that ethylene was the most reactive olefin as determined by relative rates shown below :

$CH_2=CH_2 > CH_30COCH=CH_2 > CH_3CH=CH_2 > C_6H_5\ CH=CH_2$

14000 970 220 42

Due to these findings, related aromatic compounds such as monosubstituted benzene, polyaromatic compounds (naphthalene and anthracene) and condensed ring compounds (benzofuran and indene) were used to couple olefins which contained a hydrogen attached to a doubly bonded carbon such as ethylene, ethylene derivatives and cyclo-olefins.

1.4.2 Reaction Conditions for the Vinylation of Aromatic Compounds[45]

1.4.2.1 Solvents

Reactions could be carried out using neat reactants, or either solutions or dispersions of the reactant. Solvents which did not interfere with the reaction, or react with the product or reactant, could be used. Suitable solvents included ethanol, acetic acid, formamide, dimethylformamide, acetone, diethylether and cyclohexane.

Kozhenikov[46] found that of the two solvents, acetic acid and dimethylformamide, the latter was better in the vinylation of furan. He also found that, in the vinylation of thiophene, addition of water or acetic acid to dimethylformamide, decreased the yield of the product.

1.4.2.2 Catalysts

The Group VIII metals formed part of the catalytic system. Preferred metals of this group were ruthenium, rhodium, palladium, osmium, iridium and platinum. Platinum and palladium were the most useful of the Group VIII metals. The metal could be used initially as the free metal, if an oxidizing agent was present, or it could be used as a salt. The most preferred examples of these salts were palladium (II) bromide, palladium (II) chloride, platinum (II) chloride, palladium (II) acetate and platinum (II) acetate.

It was found that stoichiometric equivalent quantities of the Group VIII metals and the aromatic or olefinic compound had to used in order for the reaction to go to completion. The Group VIII metal compounds, after reduction, could be separated from the reaction system and subsequently regenerated to a higher oxidation state.

The regenerated catalyst could be returned to the reaction system thereby making the reaction catalytic. Alternatively the regeneration of the Group VIII metal could occur *in situ* by including an oxidizing agent capable of reoxidizing the Group VIII metal compound to its higher valence state as it was reduced during the reaction.

The Group VIII metal compound could be made to function catalytically as long as there was sufficient oxidizing agent present.

1.4.2.3 Co-Catalysts

In order for the reaction to be made catalytic, the oxidizing agent must have an oxidation potential more positive than the Group VIII metal used under conditions at which the aromatic - olefin coupling reaction was carried out.

It was found that oxygen under certain conditions could act as an oxidizing agent. A large number of other oxidizing agents could also be used for example nitric acid, potassium permanagate, potassium dichromate, sodium thiosulphate, chlorine and bromine gas. The most preferred oxidizing agents were those which could function as a redox agent under the reaction conditions. These were cupric and ferric salts since they could be reoxidized to their original valence state by molecular oxygen.

1.4.2.4 Methods of Operation

Two methods of operation could be used for catalytic reactions.

Method One

The reactants were added to an autoclave, sealed and heated to a specified temperature and the autoclave pressured with the olefin gas and the contents stirred. After a specified time, the autoclave was cooled, vented and opened. The products were analysed. This method was employed by Kozhenikov[46] in the synthesis of 2-vinylfuran from furan and ethylene, and in the synthesis of 2-vinylthiophene from thiophene and ethylene.

Method Two

The reactants were added to a reactor vessel, provided with a condenser, at atmospheric pressure and heated to a specified temperature. The olefin was bubbled in continuously throughout the reaction whilst stirring the contents. After a specified time, the products were analysed. This method was used by Fujiwara[47] in the synthesis of styrene from benzene and ethylene.

1.5 SCOPE OF INVESTIGATION

1.5.1 Heterogenous Catalysis

Since the separation of fluid product mixtures from solid catalyst are easier, it was decided to investigate heterogenous catalysis. Palladium supported on alumina was to be investigated as this catalyst was used for the production of vinyl acetate from ethylene and acetic acid by an electrophilic substitution reaction. Temperatures between 60° C - 240° C could be employed as this was the effective temperature range of the catalyst.

1.5.2 Homogenous Catalysis

Method of Operation

Since sealed autoclaves involved reactions under pressure and could be potentially dangerous and a bomb calorimeter was not available, it was decided to investigate the reaction at atmospheric pressure with continuous bubbling of ethylene as described by Fujiwara[47]. Furthermore, from an industrial point of view, it would be more convenient to carry out reactions at atmospheric pressures.

Solvent

Based on the findings of the Monsanto Company[45] it was decided to investigate which of dimethylformamide, acetic acid, hexane, and cyclohexane would be best for the reaction. It was also necessary to investigate the effect of co-solvents such as water, acetic acid and/or dimethylformamide.

Catalyst

As palladium and platinum were the most preferred for the coupling reaction, it was decided to investigate palladium (II) salts since these are relatively cheaper catalysts. It was also decided to use palladium (II) acetate and palladium (II) chloride since Fujiwara[48] and other researchers found that these were the best for their reaction. It was further decided to determine which of the two catalysts were more effective.

Temperature

Based on the fact that coupling of aromatic compounds with olefins can be carried out at a temperature range of 30° C - 200° C and pressures of 1 - 300 atmospheres, it was decided to investigate the reaction in a temperature range of 30 - 140° C at atmospheric pressure. High temperatures tend to cause the catalyst components to deteriorate thereby making it difficult to regenerate the catalyst components[49].

In addition, solvents which were selected had a boiling point less than 140°C and consequently higher temperatures could not be used.

An investigation of the reaction at atmospheric pressure is essential since an increase of a mere 10° C could lead to a two to four fold increase in reaction rates as opposed to a pressure change of 700 bars required to affect the same rate increase[50].

Co-Catalyst

Since a host of co-catalysts could be used, it was decided to investigate the most preferred redox agents, namely copper (II) acetate and iron (III) chloride in optimum quantities for the maximum yield of 2-vinylfuran. A non redox agent namely silver (I) acetate, as used by Fujiwara[48] was also to be investigated and the optimum quantity determined.

CHAPTER TWO

RESULTS AND DISCUSSION

2.1 Analysis of Standard 2-vinylfuran

In order to confirm that the standard 2-vinylfuran sample (supplied[51]) was authentic, a structural investigation was undertaken.

2.1.1 Gas Chromatography - Mass Spectrometry (GC-MS)

Using the GC-MS, the normalised mass spectrum was obtained (figure 2.1) to show prominent peaks at 94; 68; 39 and 29.

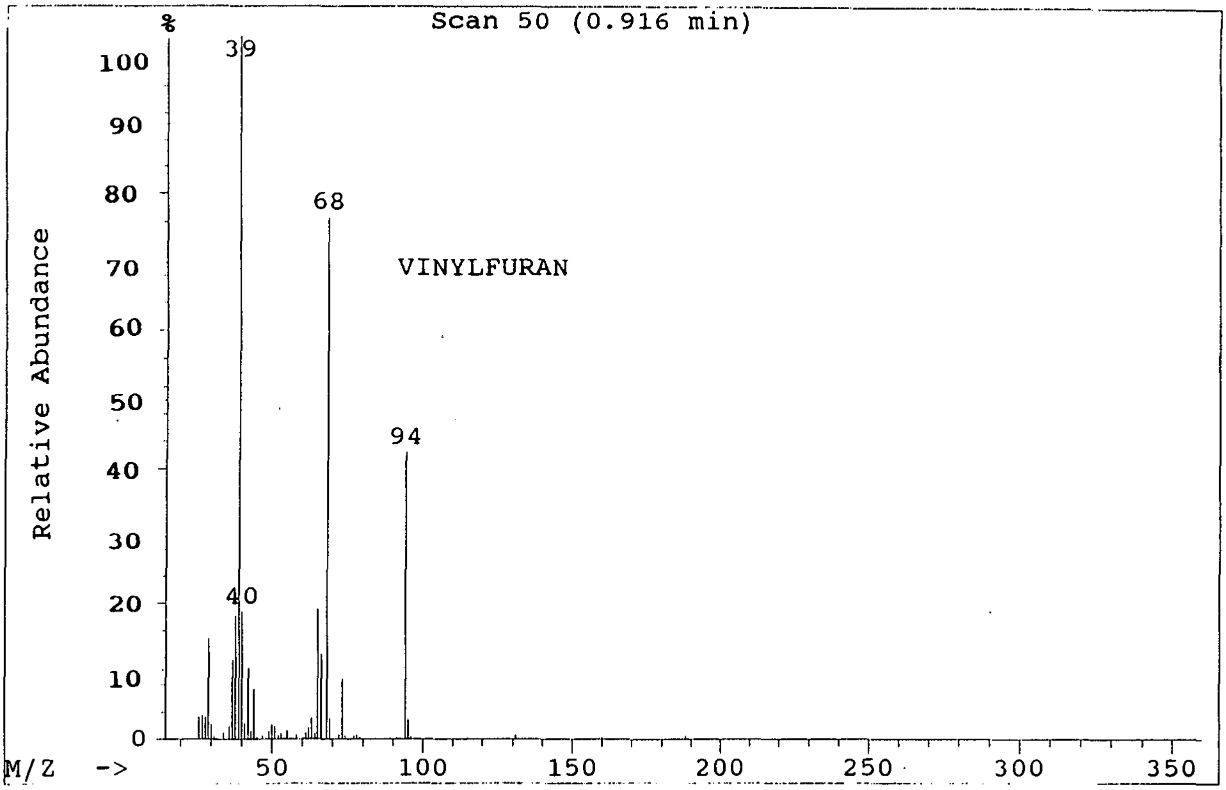


FIGURE 2.1 NORMALISED MASS SPECTRUM OF 2-VINYLFURAN

Since there was no information on the fragmentation pattern of 2-vinylfuran, the following was postulated:

- 2-vinylfuran has an intense molecular ion peak at 94.
- The charge on the molecular ion must be localised on the hetero atom rather than in the π ring system, so that satisfactory rationale can be provided for the cleavage.
- The first step in the cleavage must occur at the carbon-carbon bond of furan and ethylene.
- Subseqently cleavage must involve the carbon-hetero atom bond.

Based on these postulates, 2-vinylfuran would therefore undergo fragmentation as shown by figure 2.2 (a-c).

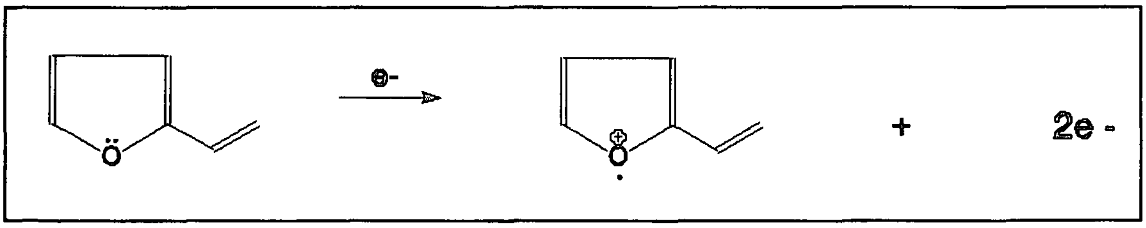


FIGURE 2.2 (a) THE IONISATION OF 2-VINYLFURAN

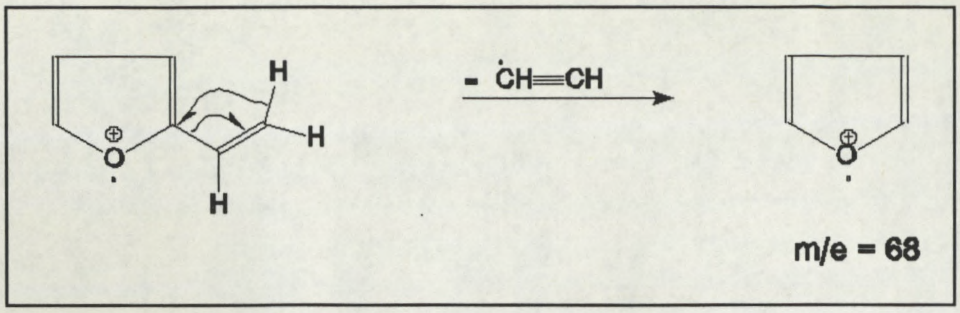


FIGURE 2.2 (b)INITIAL CLEAVAGE OF THE MOLECULAR ION OF 2-VINYLFURAN

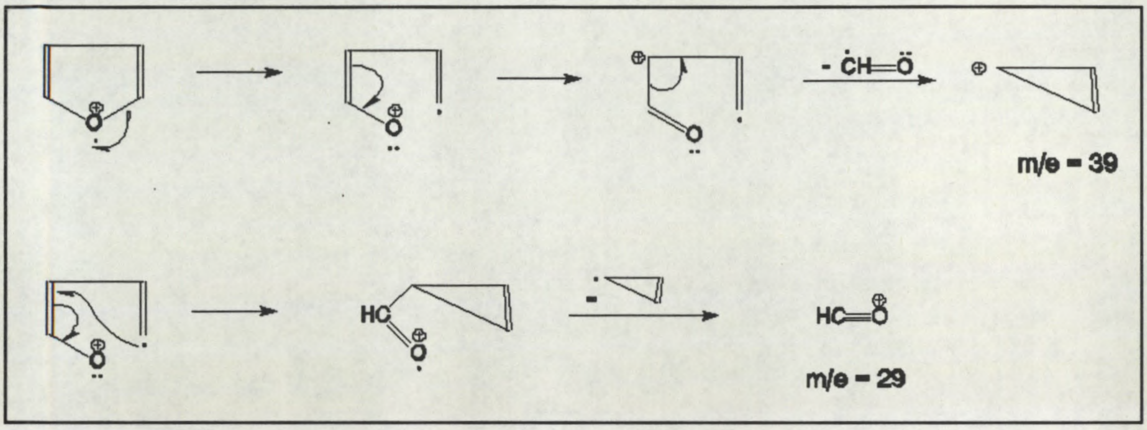


FIGURE 2.2 (c) PART OF THE FRAGMENTATION OF 2-VINYLFURAN

2.1.2 Fourier Transform Infra Red Spectroscopy (FT-IR)

Using the FTIR, the infra-red spectra of 2-vinylfuran and furan were obtained as shown in figure 2.3 and figure 2.4 respectively.

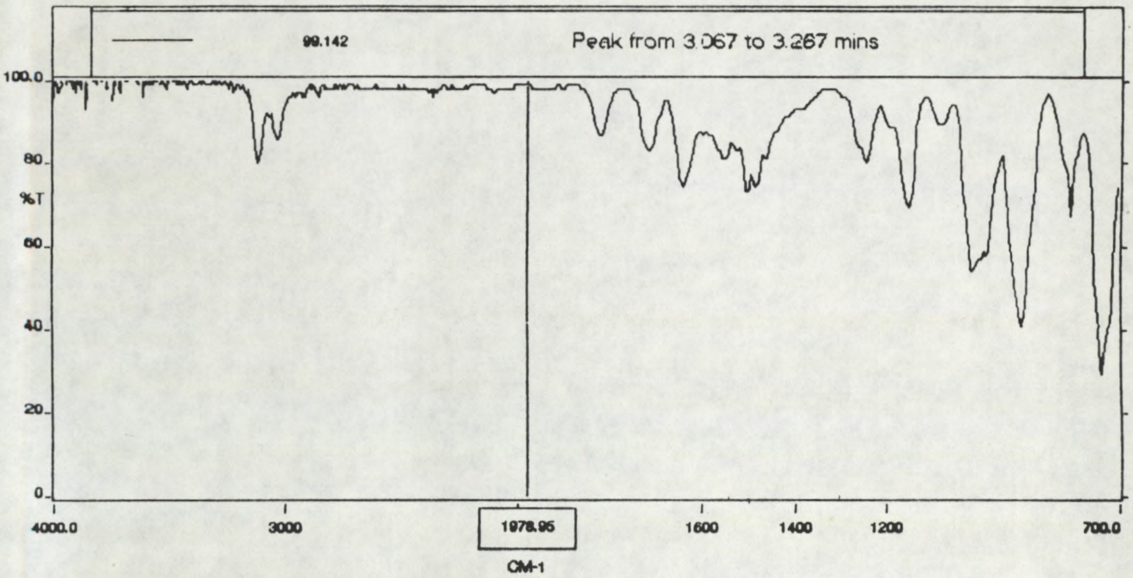


FIGURE 2.3 INFRA-RED SPECTRUM OF 2-VINYLFURAN

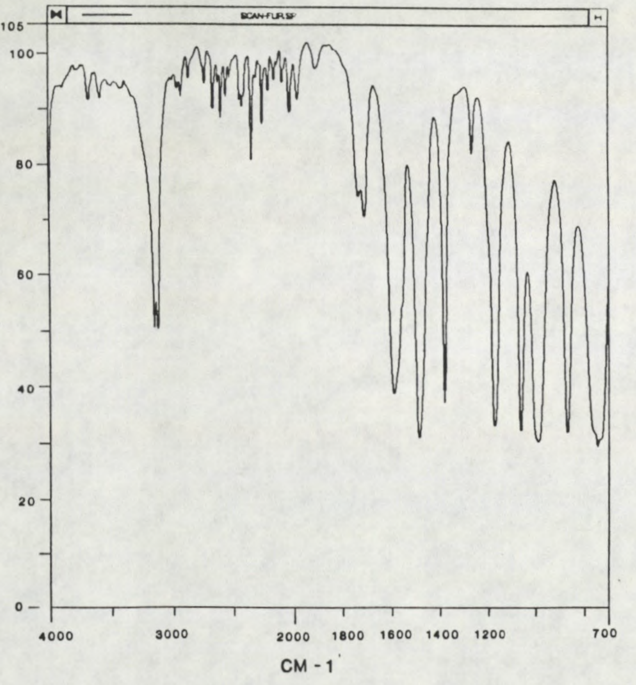


FIGURE 2.4 INFRA-RED SPECTRUM OF FURAN

The infra-red spectrum showed absorption bands characteristic of a vinylic group and an aromatic ether. These are shown below.

TABLE 2.1 (a) TYPICAL ABSORPTION FREQUENCIES OF 2-VINYLFURAN

AROMATIC AND VINYLIC GROUP	
FREQUENCY (cm^{-1})	**GROUP**
3100 3000	Asymmetric vinyl C-H stretch : $RCH=CH_2$ Aromatic C-H stretching
920	Vinyl C-H out of plane deformation : $R\text{-}CH=CH_2$
750	Vinyl C-H out of plane deformation : $R_1CH=CHR_2$

TABLE 2.1 (b) TYPICAL ABSORPTION FREQUENCIES OF 2-VINYLFURAN

AROMATIC AND AROMATIC ETHER	
FREQUENCY (cm^{-1})	**GROUP**
1820 1700	5-Membered ring
1540 1490	Aromatic C=C stretching
1640	Vinyl ether C=C : stretch
1250 1160	C-O stretching of ether : conjugated C=C
1050	Cyclic ether (aromatic)

Comparison of the two infra-red spectra confirmed the presence of the vinylic group. The absorption of this group occured at 3100 cm^{-1}.

2.1.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

It was not possible to run a NMR scan and therefore the spectrum which was supplied by Professor Delmas, L' Institut National Polytechnique De Toulouse, was examined. This is shown in figure 2.5.

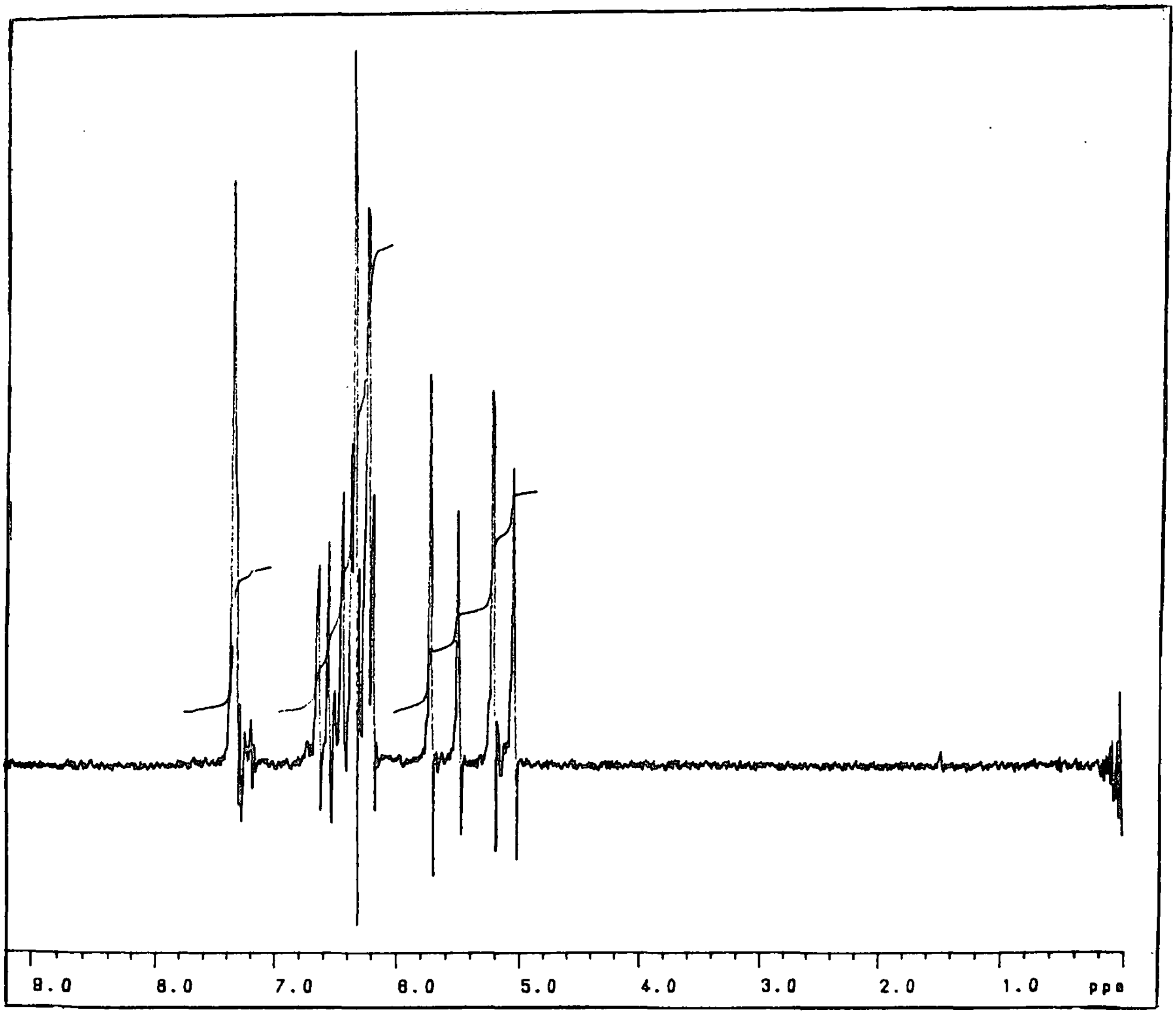


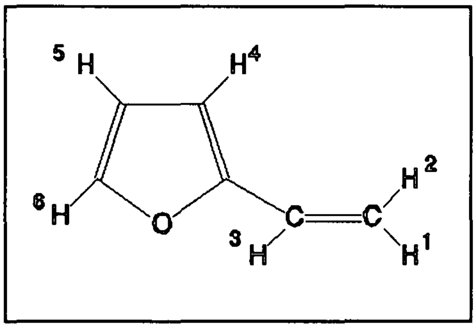
FIGURE 2.5 NMR SPECTRUM OF 2-VINYLFURAN

The NMR spectrum was recorded on a Cameca Spectrometer at 250 MHz ($CDCl_3$: TMS).

The chemical shifts (δ, ppm) and the coupling constants (J,Hz) were obtained and these values are given in table 2.2.

TABLE 2.2 THE CHEMICAL SHIFTS AND COUPLING CONSTANTS OF 2-VINYLFURAN

NMR CHARACTERISTICS OF 2-VINYLFURAN						
	H_1	H_2	H_3	H_4	H_5	H_6
δ(ppm)	5,11	5,65	6,47	6,20	6,31	7,25
J(Hz)	$J_{1.3}$ = 10,00	$J_{1.2}$ = 1,00	$J_{2.3}$ = 17,5	$J_{4.5}$ = 3,50	$J_{5.6}$ = 1,5	$J_{6.4}$ = <0,5



With reference to the above structure, it can be seen that protons 1 and 2 are not chemical shift equivalent. Proton 1 is deshielded as opposed to proton 2 because of its relative proximity to the ring. Proton 3 is strongly deshielded by the ring and is split by proton 1 and proton 2. The proton 1 signal is in turn split by proton 3 and proton 2. Proton 2 is split by proton 3 and proton 1.

The coupling constants for a vinylic system are characteristic; the trans coupling is larger than the cis, and the geminal coupling is very small.

2.1.4 Gas Chromatography (GC)

2.1.4.1 Determination of the Purity of Standard 2-vinylfuran

Since a 100% pure standard 2-vinylfuran sample was required for accurate quantification of the experimental data, the purity of the standard 2-vinylfuran sample (supplied) had to be determined so that a correction factor could be utilised (see Page 35).

The GC method was chosen to determine the purity of the standard 2-vinylfuran sample. The average integrated area percentage, obtained from ten chromatograms, of the neat standard 2-vinylfuran sample was used to express the percentage purity. This was found to be 96,07%. Ten measurements were used to ensure reproducibility.

2.1.4.2 The Method used for Quantification of Experimental Results

2.1.4.2.1 Percentage 2-vinylfuran based on the Quantity of Catalyst

The external standard method was chosen because the progress of the reaction had to be monitored in order to obtain optimum reaction conditions.
An average of three integrated areas of the chromatogram for each 2-vinylfuran standard solution (prepared in dimethylformamide) was used.
A plot of percentage (m/m) of 2-vinylfuran standard solution against intergrated area was obtained as shown in figure 2.6(a).

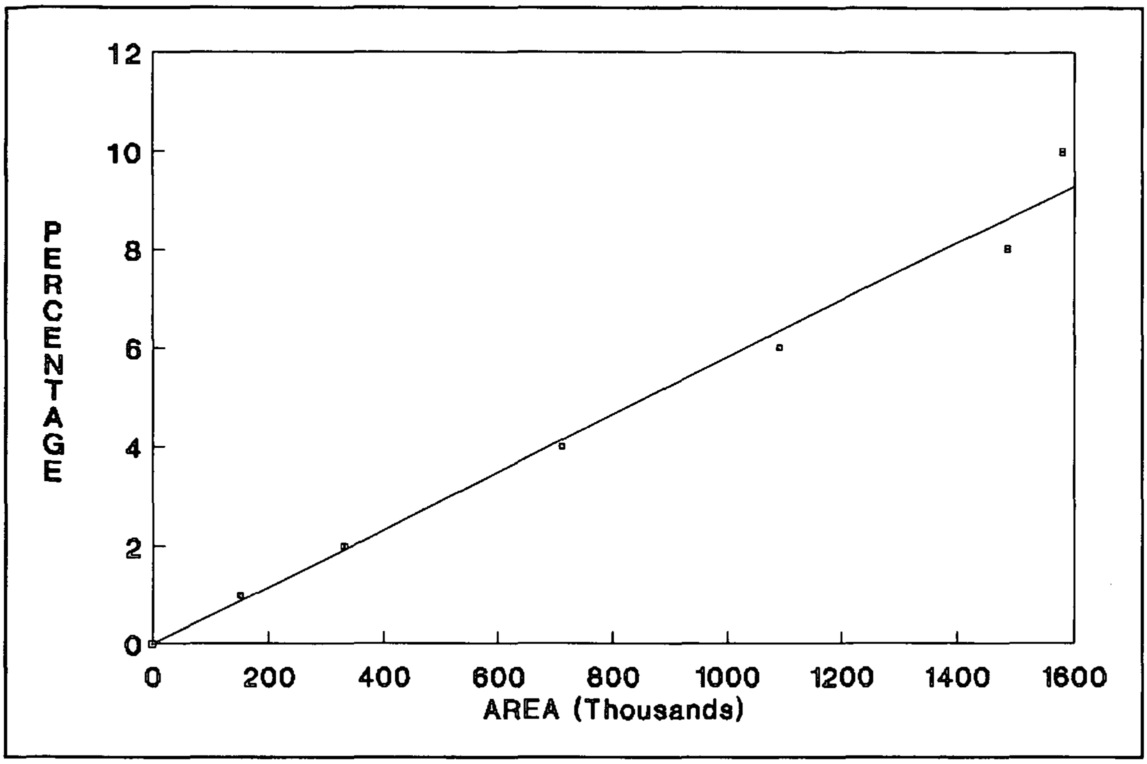


FIGURE 2.6(a). A PLOT OF PERCENTAGE 2-VINYLFURAN STANDARD SOLUTION AGAINST INTEGRATED AREA

Since the results were represented by a straight line, the values of the slope (m) and the y intercept (c) were calculated using statistical formulae (Appendix 1) (109).

The slope was calculated to be 5,8073 x 10^{-6} with a correlation of 0,993. Since the purity of 2-vinylfuran standard sample was found to be 96,07%, a corrected value for the slope had to be determined:

$$m' = (m) \div 0,9607$$

$$= 6,05 \times 10^{-6}$$

The mass of 2-vinylfuran (experimental result) was calculated by using :

- the slope (m′) and
- the integrated area (x)

in the following equation :

$$y = m'x + c$$

Since $c = 0$ ....(c = y intercept)

the equation was reduced to :

$$y = m' x$$

The percentage of 2-vinylfuran was obtained by using the formula :

$$\%\ 2\text{-vinylfuran} = \frac{\text{moles 2-vinylfuran}}{\text{moles catalyst}} \times 100$$

The percentage of 2-vinylfuran was based on the quantity of catalyst used because this was relatively the most expensive reagent.

2.1.4.2.2 Percentage Conversion 2-vinylfuran based on the Quantity of Furan Consumed

The quantity of unreacted furan was determined by using the method described above. A plot of % (m/m) of furan standard solution against integrated areas was obtained as shown in figure 2.6(b).

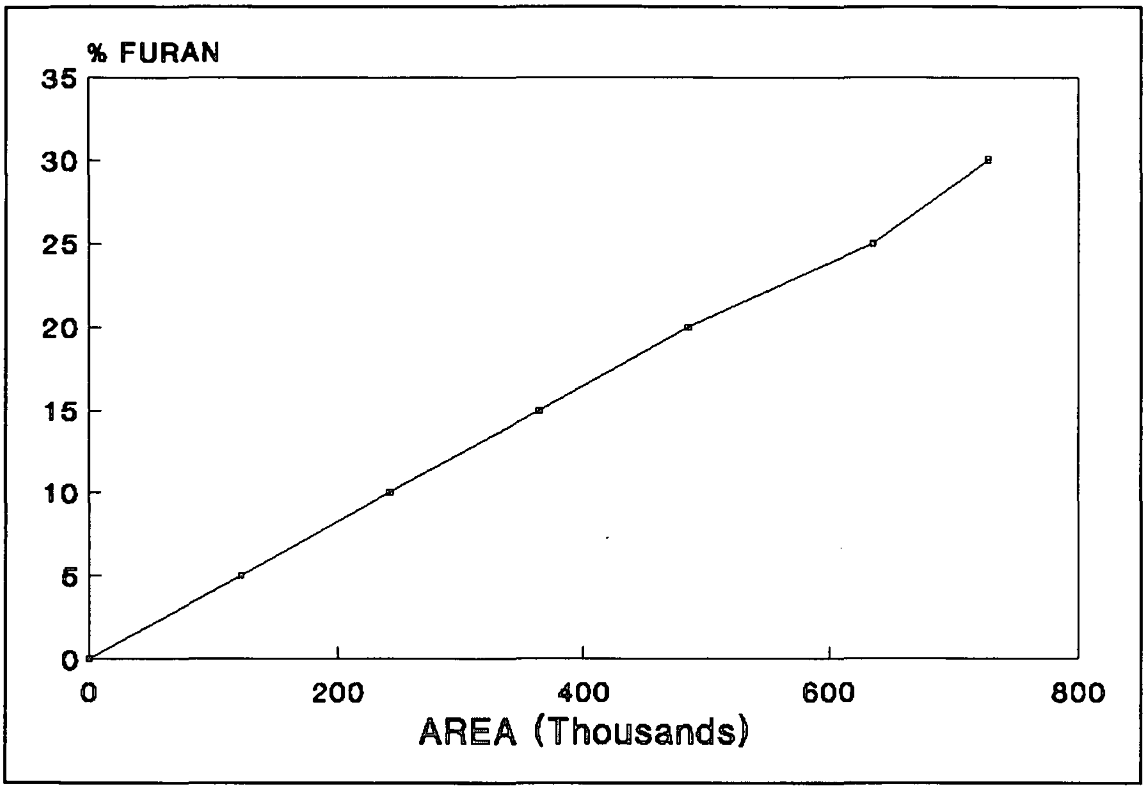


FIGURE 2.6(b). A PLOT OF PERCENTAGE FURAN STANDARD SOLUTION AGAINST INTERGRATED AREA.

The slope was calculated as 4,0447 x 10^{-5} (Appendix 1) (109).

The percentage conversion was obtained by using the formula :

$$\%\ \text{conversion 2-vinylfuran} = \frac{\text{moles 2-vinylfuran}}{\text{(Moles furan consumed)}} \times 100$$

where moles furan consumed = total moles furan added - unreacted moles furan.

2.2 Qualitative Determination of the Relative Solubility of furan and 2-vinylfuran

In order to choose an appropriate solvent for the reaction, the solubility of reactants and product had to be examined.

2.2.1 Solubility of Furan

Tests were done on the solubility of furan in different solvents. The solubility was based on visual observation.

It was found that furan was :

- soluble in ethanol, acetone and dimethylformamide
- partially soluble in hexane, cyclohexane and acetic acid
- insoluble in water and carbon tetrachloride

These results showed that furan had a solubility between a polar and non polar solvent. On account that the reactant furan was soluble in ethanol, acetone and dimethylformamide, any one of these solvents could be used for the reaction.

It was realised that visual observation could not give accurate results.

On account that vinylation reactions were carried out in excess aromatic reactant[45] examples benzene, substituted benzene, naphthalene and anthracene, the quantitative aspect of solubility was not investigated.

2.2.2 Solubility of 2-vinylfuran

The solubility of 2-vinylfuran in various solvents had to be determined so that a simple method could be used in its recovery.

2-Vinylfuran was found to be :

- soluble in acetic acid, furan, dimethylformamide, tetrahydrofuran and 1,4-dioxane.
- insoluble in water, methanol and acetonitrile.

These results indicated the possibility of using water or methanol for separating 2-vinylfuran and furan from the solvents by solvent extraction. The method which can be used would entail the addition of water to the reaction mixture. Since 2-vinylfuran and furan were insoluble in water, they could be separated from the aqueous layer. 2-Vinylfuran could be separated from furan by fractional distillation due to the difference in their boiling points.

2.3 Quantitative Determination of the Relative Solubility of Ethylene

2.3.1 Relative Solubility in Different Solvents

There was no data available for the solubility and therefore a saturated solution of ethylene had to be prepared and the integrated area percentage of the gas chromatogram used.

The results of the relative solubility, expressed in $\frac{\text{grams ethylene}}{\text{grams solvent}}$, are tabulated below :

TABLE 2.3 THE RELATIVE SOLUBILITY OF ETHYLENE IN FOUR SOLVENTS

SOLVENT	RELATIVE SOLUBILITY
Acetic Acid	$1{,}3 \times 10^{-2}$
Hexane	$6{,}8 \times 10^{-3}$
Cyclohexane	$2{,}5 \times 10^{-4}$
Dimethylformamide	$1{,}43 \times 10^{-2}$

The results above indicated that ethylene was more soluble in dimethylformamide (DMF) than the other solvents which were investigated.

Using the results obtained from the solubility of reactants and products, it was decided that dimethylformamide be used as the solvent because:

- Ethylene had a relatively greater solubility in DMF than the three solvents acetic acid, hexane and cyclohexane.
- DMF had a significantly different boiling point (153°C) from 2-vinylfuran (boiling point 100° C - 101° C). Therefore fractional distillation can be used.

- DMF was soluble in water while 2-vinylfuran was insoluble in water. This makes separation by solvent extraction possible.
- DMF can be used as a solvent on an industrial scale.

2.3.2 Relative Solubility of Ethylene in Dimethylformamide at Different Temperatures

The relative solubility of ethylene at different temperatures, expressed in

$\frac{\text{grams ethylene}}{\text{grams dimethylformamide}}$, are tabulated below :

TABLE 2.4 THE RELATIVE SOLUBILITY OF ETHYLENE IN DIMETHYLFORMAMIDE AT VARIOUS TEMPERATURE

TEMPERATURE	RELATIVE SOLUBILITY
25° C	$1{,}43 \times 10^{-2}$
70° C	$1{,}28 \times 10^{-2}$
80° C	$1{,}25 \times 10^{-2}$
90° C	$1{,}23 \times 10^{-2}$
95° C	$1{,}22 \times 10^{-2}$
140° C	$1{,}12 \times 10^{-2}$

From these results, it was observed that temperature had an effect on solubility. An increase in temperature resulted in a decrease in solubility. However, this decrease was relatively small and therefore dimethylformamide was chosen as a suitable solvent for the reaction.

2.4 The Gas Phase Heterogenous Catalysis of Ethylene and Furan

2.4.1 Design of a Reactor

Since no reactors were available for the reaction, a reactor had to be designed as shown in figure 2.7.

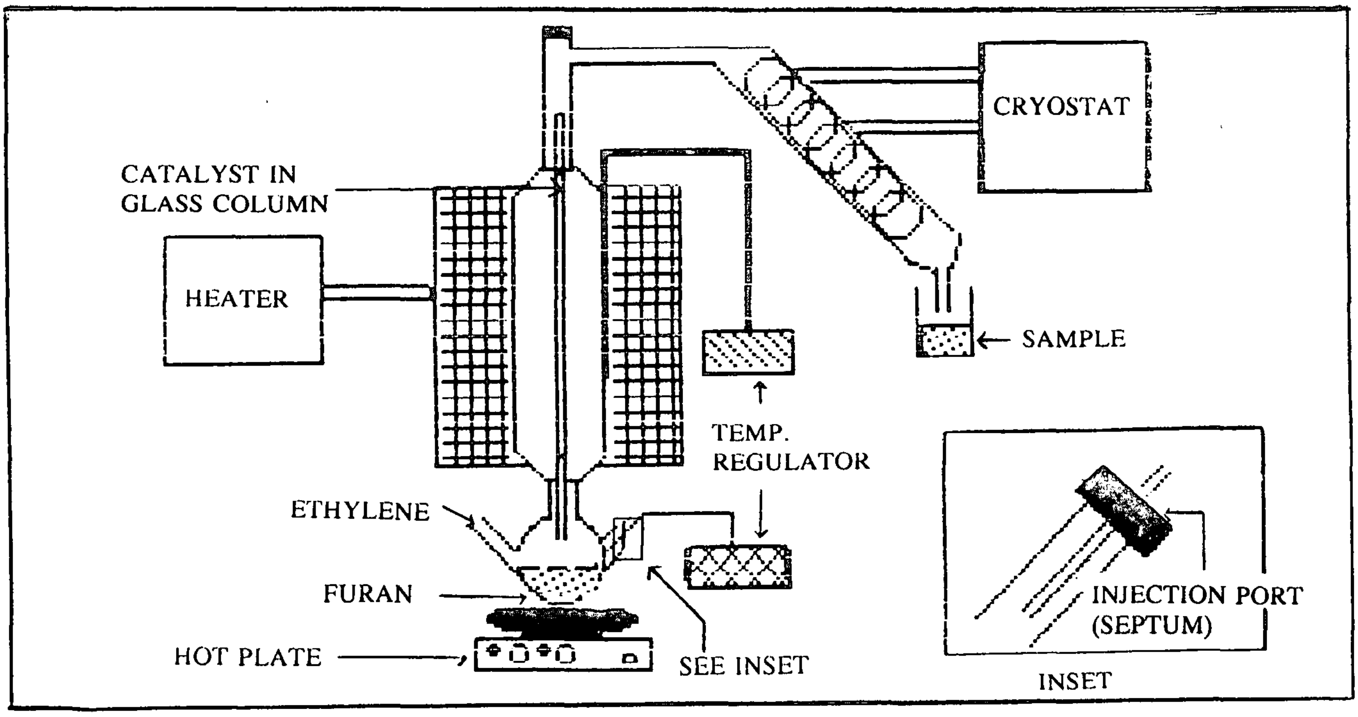


FIGURE 2.7 APPARATUS USED FOR HETEROGENOUS CATALYSIS

A 600 mm long glass column of internal diameter 5 mm had to be used since a small amount of catalyst was available and the residence time of furan and ethylene in the column would be long enough for reaction. Furthermore, furan was heated gently (40° C) so that the vapour could not escape by passing through the column rapidly. The flow rate (1,67 mℓ/min) of ethylene was also kept low.

2.4.2 Catalysis by Palladium Supported on Alumina

It was decided that the gas phase heterogenous catalysis should be investigated since catalysts are quite valuable and their re-use is demanded.

It was found that at temperatures of 60° C ; 100° C ; 150° C ; 200° C and 240° C for the solid state, palladium supported on alumina, catalyst of 0,1% ; 0,2% ; 0,5% and 0,8%, no 2-vinylfuran was produced.

A compound, however, was detected at a retention time of 4,64 minutes. The chromatogram is shown in appendix 2 (111). This product was not further investigated.

Since no 2-vinylfuran was produced, this meant that the palladium supported catalyst was not suitable for the reaction under the conditions employed. Therefore the mechanism for the reaction of furan and ethylene could be expected to be different from that of vinyl acetate and acetaldehyde production[52-53]. However, since the distilled furan was not recycled, this could be further investigated to determine the suitability of palladium supported catalyst on the reaction.

2.4.3 Catalysis by Palladium (II) acetate - Copper (II) acetate

Using palladium (II) acetate : copper (II) acetate ≡ 1:10 at reaction temperatures of 60° C ; 80° C and 100° C, no 2-vinylfuran was produced.

This catalytic system was not further investigated.

2.5 The Liquid Phase Homogenous Catalysis of Ethylene and Furan

2.5.1 Design of a Glass Reactor for Small Scale Reactions

Since the reaction had to be conducted at atmospheric pressure, a suitable reactor had to be used as shown in figure 2.8.

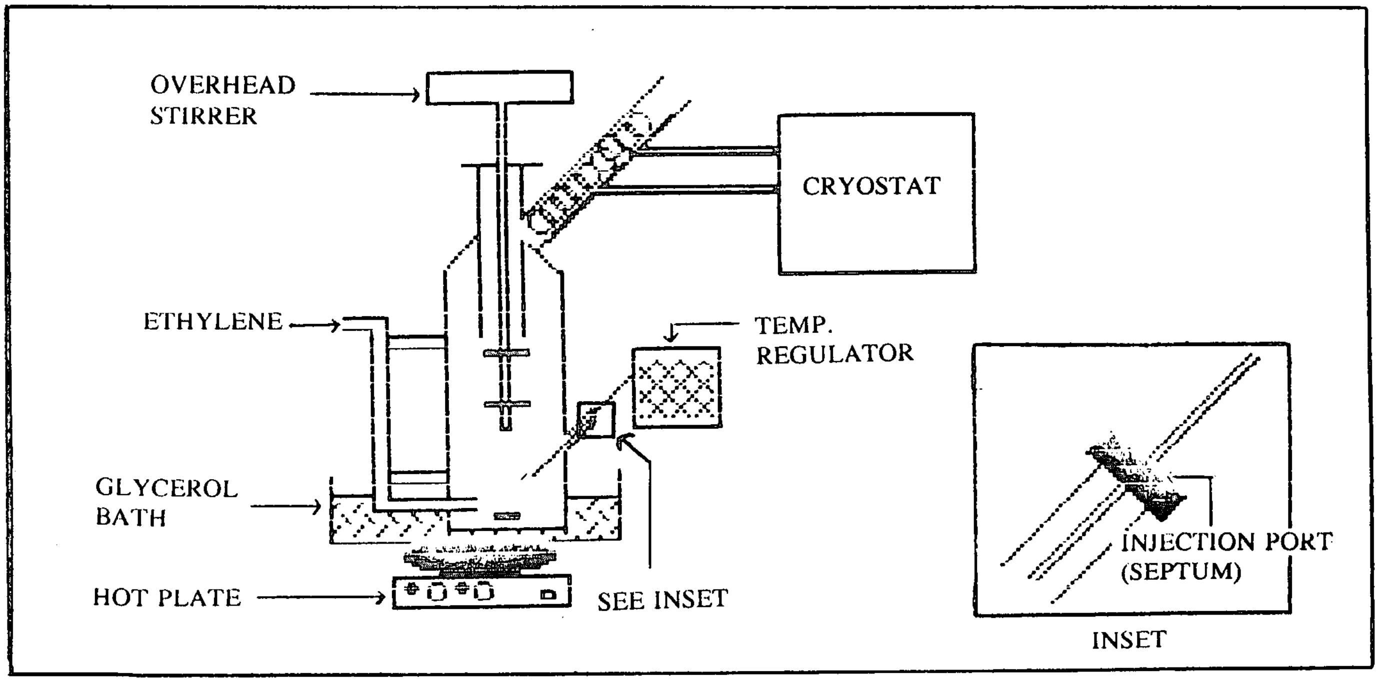


FIGURE 2.8 APPARATUS USED FOR HOMOGENOUS CATALYSIS

A 100 mℓ cylindrical reaction vessel, fitted with a gas inlet system, was used. Since ethylene had to be bubbled continuously, the gas inlet was positioned as close as possible to the bottom of the reaction vessel.

An overhead motor driven stirrer and a magnetic stirrer were used for effective mixing.

A reflux condenser, fitted with a cryostat, was used to prevent volatile components from escaping. The cryostat was used to maintain the condenser temperature at 5° C.

Since the reaction had to be monitored continuously, an injection port, fitted with a GC septum, was positioned such that the liquid could be sampled.

A temperature regulator was inserted through the septum so that the reaction temperature could be monitored.

2.5.2 Reaction of Ethylene and Furan Under Various Catalytic Conditions

2.5.2.1 Stoichiometric Quantities of Catalyst

It was decided to investigate the reaction at atmospheric pressure by using stoichiometric equivalent quantities of palladium (II) acetate and ethylene.

Reactants were used in the mole ratio :

Furan to ethylene to $Pd(OAc)_2 \equiv 10 : 1 : 1$

The reaction was conducted for two hours at a reaction temperature of 80° C with dimethylformamide as the solvent. The percentage yield of 2-vinylfuran is 93,89% with respect to the catalyst and ethylene.

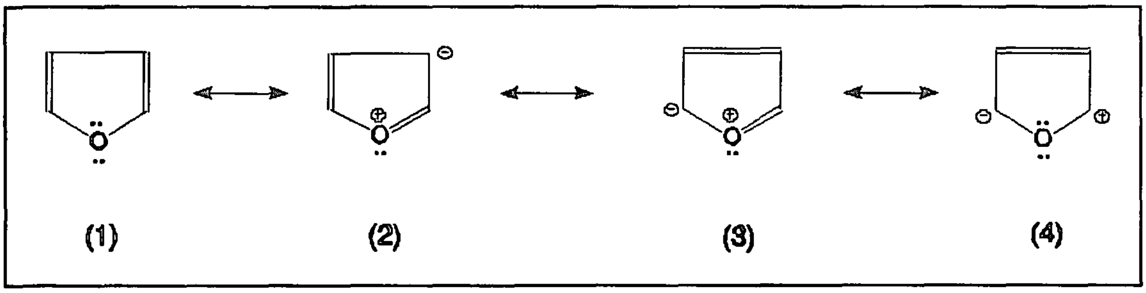
This result showed that the reaction could be conducted at atmospheric pressure. The chromatogram which was obtained for this reaction is shown in appendix 3 (112). Since it was found that this chromatogram was similar to those of subsequent reactions, it was used as a representative for the reaction.

It must be noted that throughout this investigation, emphasis was not placed on the GC flow rate condition as specified in appendix 5. (114) because the integrated area of the chromatogram was of more importance. Also, 2-vinylfuran standard sample was available and was used to compare the retention time of the experimental result.

The identity of the product was confirmed by GC-MS. The retention time of the product was also identical to the authentic sample.

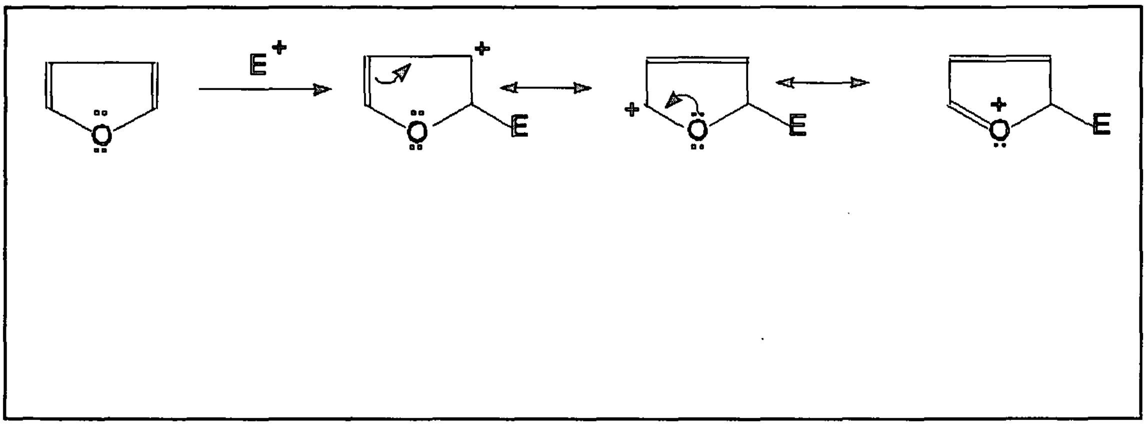
Analysis of the reaction content by GC-MS also confirmed the presence of 2,2′-bifuran. Details of the identity of this compound is given on page 56.

Since vinylation reactions were classified as electrophilic substitution reaction, the electron density of the furan nucleus was examined. It was found that the overall electron distribution could be represented by canonical forms (1) through (4) as shown below.

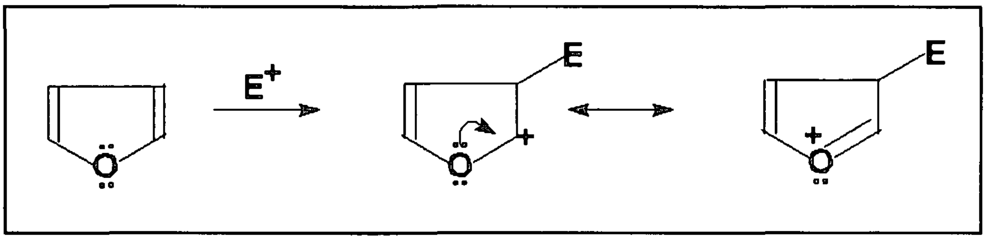


The reactivity of the furan nucleus is directly related to the electron density at particular ring atoms. Since there was more delocalization of the charge on the α position rather than the ß position, electrophilic substitution was found to occur preferentially at the α or 2 position.

This was supported by the fact that electrophilic attack at position two resulted in the formation of three resonance structures as shown below.



In the case of electrophilic attack at position three only two resonance structures could be obtained as shown below.



Furthermore, centres of high electron density at the α position of the ring can be readily supported by the behaviour of furan in electrophilic substitution reactions[54].

Proposed Mechanism

Fujiwara[52-53], using deuterium labelled ethylene and benzene, analysed the D-content of the product. He found that there was no hydride shift in the reaction thereby confirming the existance of a sigma bonded intermediate. He also concluded that the rate determining step was the formation of a sigma bond between palladium and the olefin.

The following mechanism was therefore proposed, based on the work of Fujiwara, for the reaction of furan and ethylene.

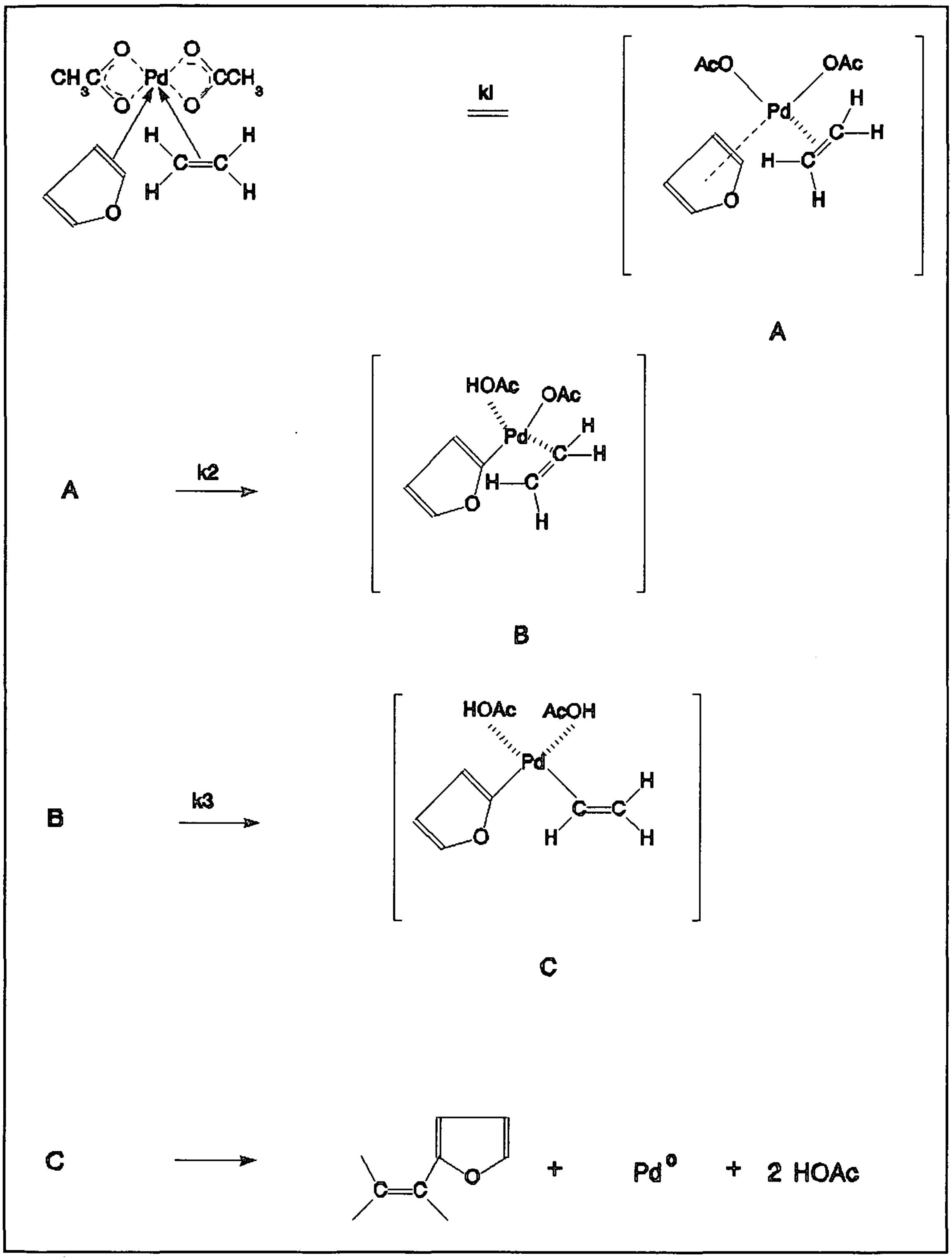


FIGURE 2.9 PROPOSED MECHANISM FOR THE REACTION OF FURAN AND ETHYLENE

According to this mechanism, furan and ethylene will be able to co-ordinate with palladium (II) acetate because of the availability of the empty d orbitals of the transition metal to form intermediate A.

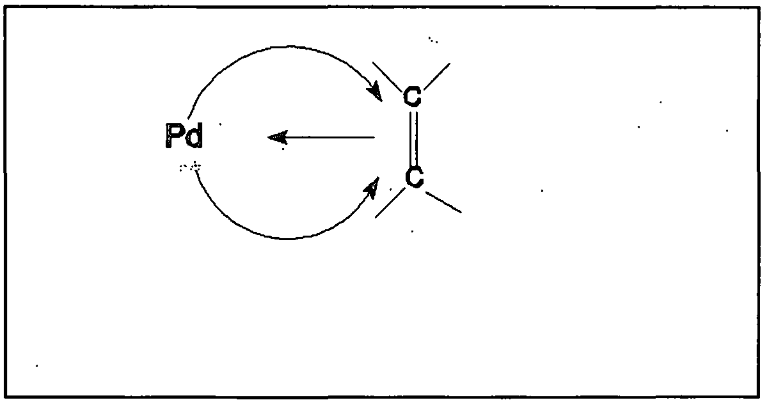
Since furan has a greater tendency towards co-ordination than ethylene, a sigma bond could be formed first between palladium and furan to form intermediate B.
This would result in the weakening of the Pd-OAc bond enabling a proton to be attracted towards the oxygen.

In a similar manner, a Pd-σ bond could be formed with ethylene to form intermediate C.

Finally the intermediate C would decompose immediately to form metallic palladium and 2-vinylfuran.

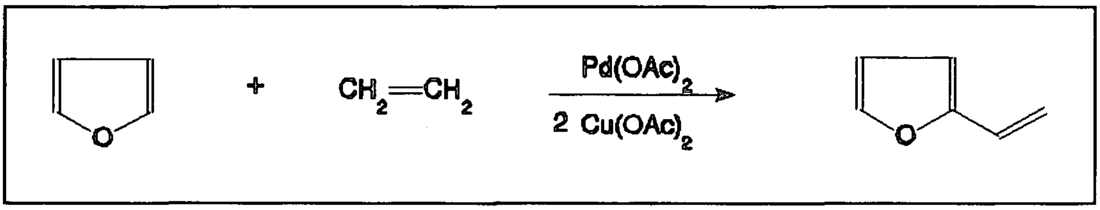
The bonding consisted of :

- a σ type bond formed by the overlap of an empty metal hybrid orbital with the filled π orbital of the olefin and
- a π type bond formed by the overlap of filled d orbitals of the metal with the unfilled π^* orbitals of the olefin as shown below :



Chemical Reaction

It was found that palladium metal coated the inner wall of the reaction vessel showing that palladium (II) underwent a reduction reaction. From this observation it was concluded that the following reaction occured :



2.5.2.2 Use of Co-catalyst (Copper (II) acetate) with Non-stoichiometric Quantities of Catalyst (Palladium (II) acetate)

In order to use catalytic amounts of palladium (II) acetate, a co-catalyst had to be used. It was decided to use copper (II) acetate as a co-catalyst since :

- It was found that when using copper (II) chloride as a co-catalyst (>0,5 M), 1-aryl-2-chloroethane compounds were formed[44]. This implied that for the reaction of ethylene and furan, 1-furyl-2-chloroethane would be a possible product.

- the acetate anion was less reactive towards electrophilic substitution with olefins compared to aromatic compounds.

In view of the fact that ± 7 catalytic cycles[43] could be achieved using palladium (II) salts (this information only became available at a later stage in the work), two experiments were conducted using reactants in the ratio

- Furan to ethylene to $Pd(OAc)_2$ to $Cu(OAc)_2$ ≡ 100 : 10 : 1 : 2

  and

- Furan to ethylene to $Pd(OAc)_2$ to $Cu(OAc)_2$ ≡ 50 : 5 : 1 : 2

The yield of 2-vinylfuran was 17,64% and 33,40% respectively.

The function of copper (II) acetate was to re-oxidize Pd *in situ* :

$$Pd \longrightarrow Pd^{2+} + 2\ e^-$$

Therefore copper (II) acetate in turn was reduced :

$$2\ Cu^{2+} + 2e^- \longrightarrow 2\ Cu^+$$

Combining these two half equations :

$$Pd + 2\ Cu^{2+} \longrightarrow Pd^{2+} + 2\ Cu^+$$

Since Pd^{2+} was not the active catalyst (discussed in page 74) but had to exist as the acetate compound, the final equation was given by :

$$Pd + 2\ Cu(OAc)_2 \longrightarrow Pd(OAc)_2 + 2\ CuOAc$$

2.5.3 Optimization of Temperature and Time for the Reaction of Furan and Ethylene with Palladium (II) acetate and Palladium (II) chloride

Since reaction temperatures have a significant influence on reaction rates, an optimum temperature for the reaction had to be ascertained. For this reason the progress of the reaction was monitored at thirty minute intervals by gas chromatography. The mole ratio of the reactants

Ethylene to $Pd(OAc)_2$ to $Cu(OAc)_2$ $\equiv$ 5 : 1 : 2 were kept constant.

2.5.3.1 Palladium (II) acetate as a Catalyst in the Temperature Range 30° C to 95° C.

2.5.3.1.1 Reaction Temperature of 30° C and 40° C

Using a mole ratio of

Furan to ethylene to $Pd(OAc)_2$ to $Cu(OAc)_2$ $\equiv$ 50 : 5 : 1 : 2

the progress of the reaction was monitored by gas chromatography. Analysis of the chromatogram showed no 2-vinylfuran was produced. A standard 2-vinylfuran sample was injected to ascertain whether the flow rate of the carrier gas (in the GC) had changed. It was found that there was no change in the carrier gas flow rate and therefore the product which was being produced was not 2-vinylfuran.

A 0,2 $\mu\ell$ sample of the reaction content was injected into the GC-MS using the temperature program specified (see page 83) in order to identify the product of the reaction. A normalised mass spectrum was obtained as shown in figure 2.10.

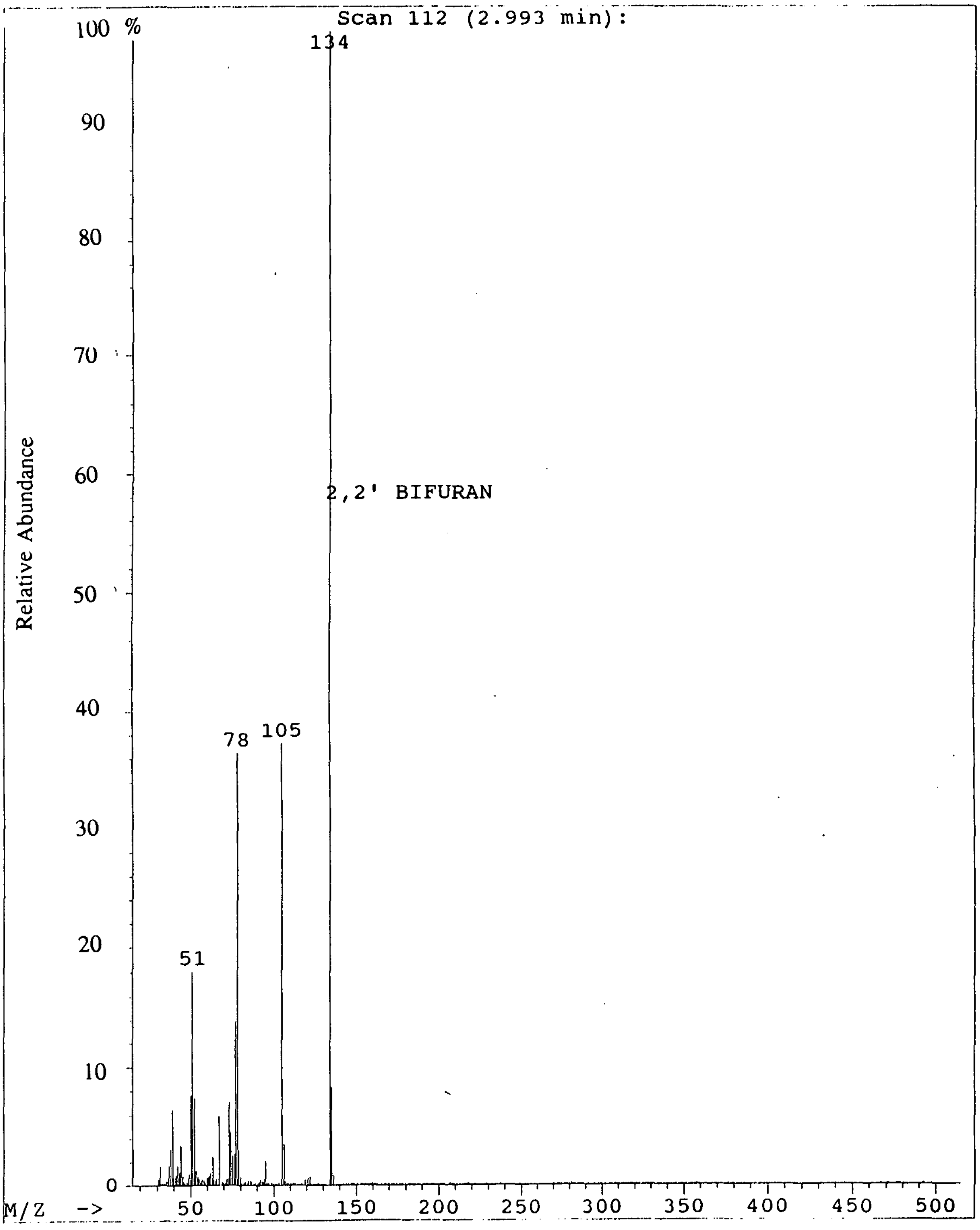


FIGURE 2.10 NORMALISED MASS SPECTRUM OF BIFURAN

The product was identified as 2,2′ bifuran.

In view of the fact that no data of the fragmentation pattern was available, the following was postulated :

- The molecular ion peak at 134 was the base peak.
- Ionisation must occur at the oxygen atom rather than the π ring system (similar to vinylfuran).
- Initial cleavage must occur between the oxygen and the carbon in the same ring system.

Figure 2.11 shows part of the fragmentation pattern of 2,2′-bifuran.

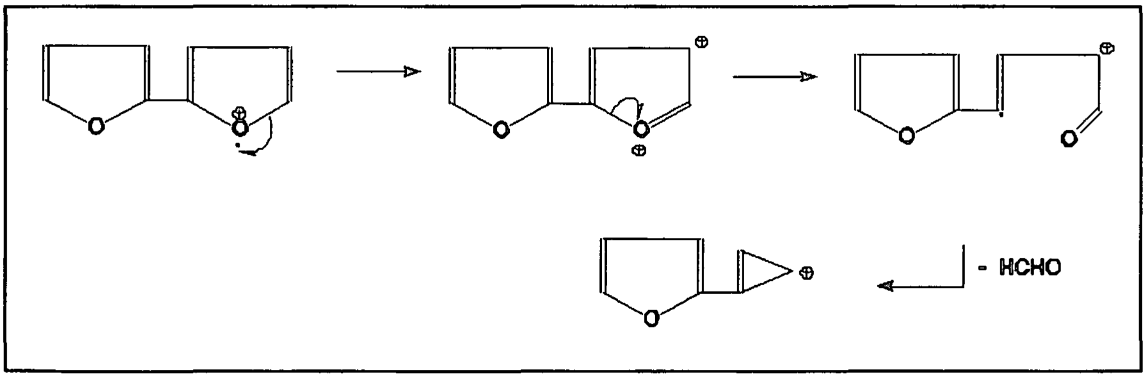


FIGURE 2.11 PART OF THE FRAGMENTATION OF 2,2′-BIFURAN

The chromatogram obtained for 2,2′-bifuran is shown in appendix 4 (113). This product has a retention time of 2,61 minutes.

In addition to the formation of bifuran, another impurity was found and identified by GC-MS. This compound was 2,2′,2″-trifuran. The normalised mass spectrum is shown in figure 2.12.

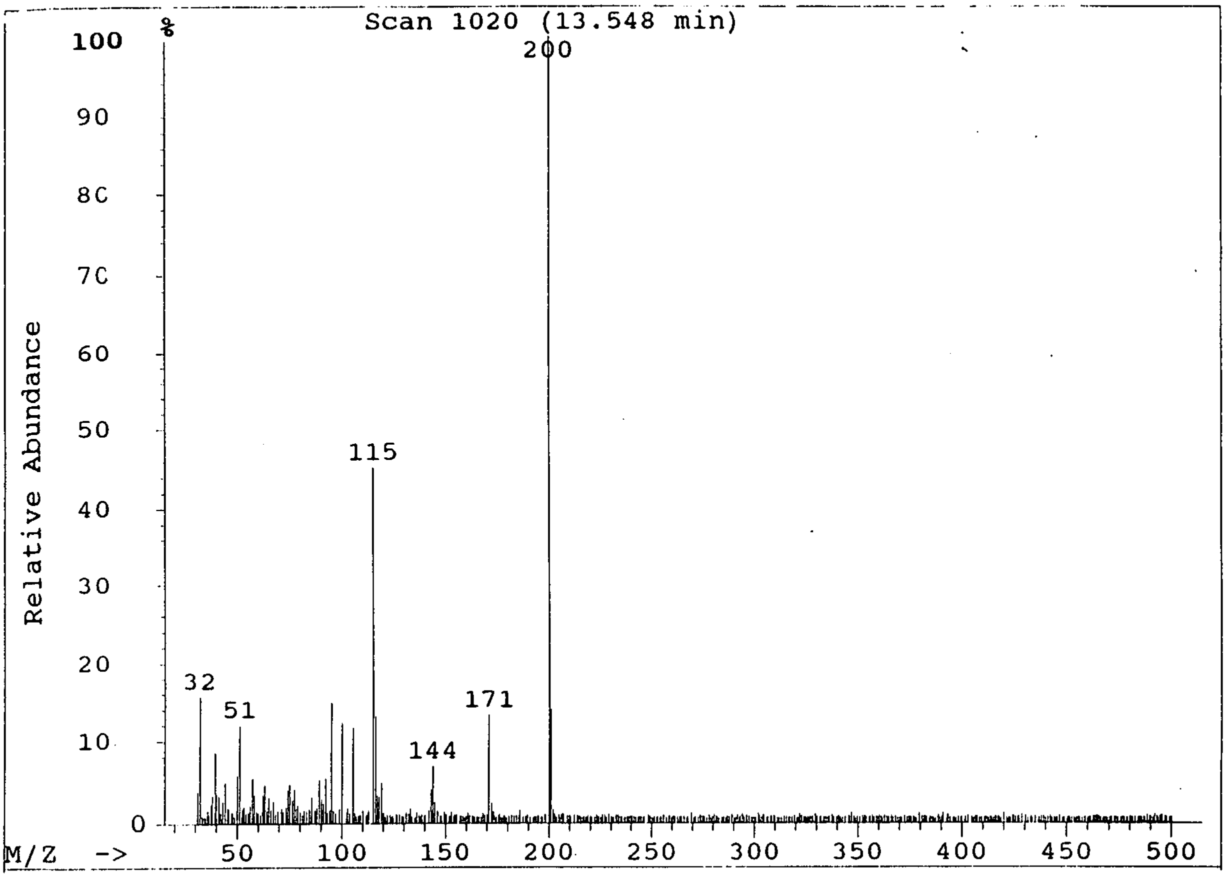


FIGURE 2.12 NORMALISED MASS SPECTRUM OF TRIFURAN

There was no data available for the fragmentation pattern of trifuran. In view of this, it was postulated that:

- The molecular ion at 200 was the base peak.
- Ionisation must occur at the oxygen atom rather than in the π ring system (similar to vinylfuran).
- Initial cleavage must occur between the oxygen and carbon in the same ring system.

Figure 2.13 shows part of the fragmentation pattern.

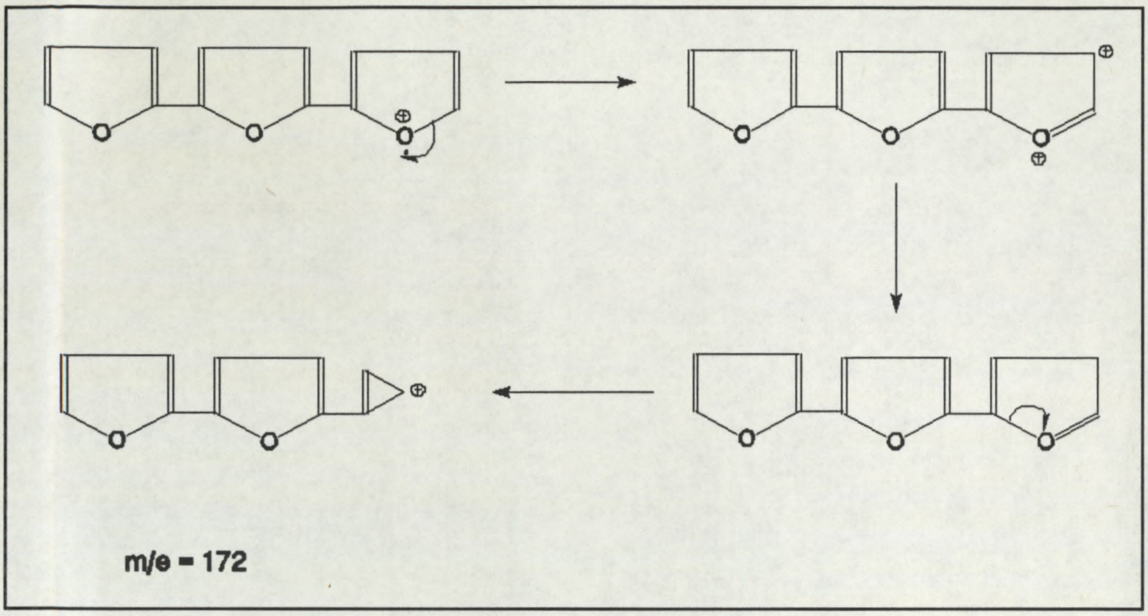


FIGURE 2.13 PART OF THE FRAGMENTATION OF 2,2′, 2″-TRIFURAN

Since no standards were available for quantification of bifuran, the integrated area obtained from the chromatograms were used.

A plot of integrated area bifuran against time was obtained as shown in figure 2.14.

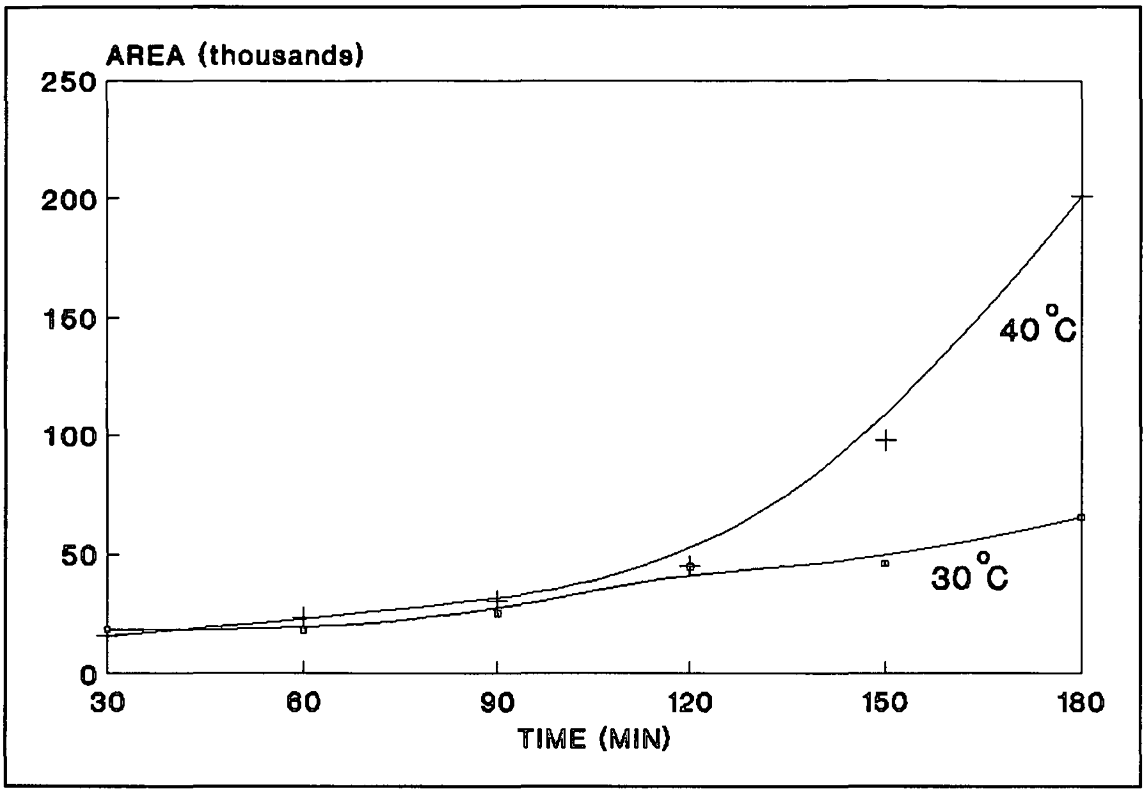


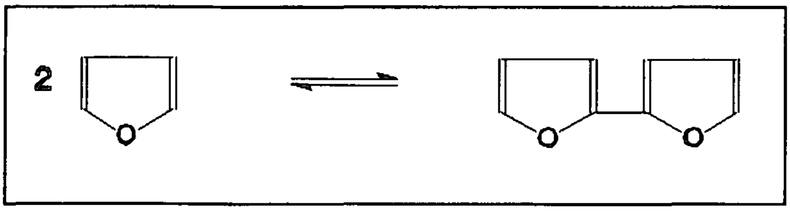
FIGURE 2.14 PLOT OF INTEGRATED AREA OF BIFURAN AGAINST TIME

The enthalpy change in the formation of 2,2′-bifuran, from thermo chemical data[55], was calculated as follows :

$\Delta H^\circ_f(\text{Bifuran}) \quad = \quad \Delta H^\circ_f(\text{Furan}) + \Delta H^\circ_f(\text{Furan})$

$= \quad -29,8$ kcal/mol ..... (uncatalysed)

This reaction was represented by :



Since the reaction was exothermic, low temperatures would favour the forward reaction. Therefore at higher temperatures there would be a decrease in the amount of 2,2′-bifuran. It was noted in subsequent experiments that both 2-vinylfuran and 2,2′-bifuran were formed.

The absence of 2-vinylfuran at temperatures of 30° C and 40° C indicated that the activation energy for the reaction had not been attained under the prevailing conditions. Since no activated complex could be formed at this temperature, products were therefore absent.

Having found that at temperatures of 30° C and 40° C bifuran was formed, a smaller amount of furan was used in the hope of minimizing the amount of bifuran formation at higher temperatures.

2.5.3.1.2 Reaction Temperature of 70° C, 80° C, 90° C and 95° C

Using reactants in the mole ratio

Furan to ethylene to $Pd(OAc)_2$ to $Cu(OAc)_2$ $\equiv$ 25 : 5 : 1 : 2

at the temperatures specified above, the experimental results were tabulated as shown below :

TABLE 2.5 PERCENTAGE YIELD OF 2-VINYLFURAN AT DIFFERENT REACTION TEMPERATURES AND REACTION TIME

TIME (MINUTES)	**PERCENTAGE YIELD 2-VINYLFURAN**			
	REACTION TEMPERATURE			
	70° C	**80°**	**90° C**	**95° C**
0	0	0	0	0
30	13,40	15,92	19,28	52,99
60	33,66	34,12	58,38	89,64
90	42,79	48,35	73,53	123,95
120	54,56	61,76	112,64	131,27
150	59,23	66,93	100,05	103,68
180	57,74	70,64		

A plot of percentage 2-vinylfuran against reaction time was obtained as shown in figure 2.15.

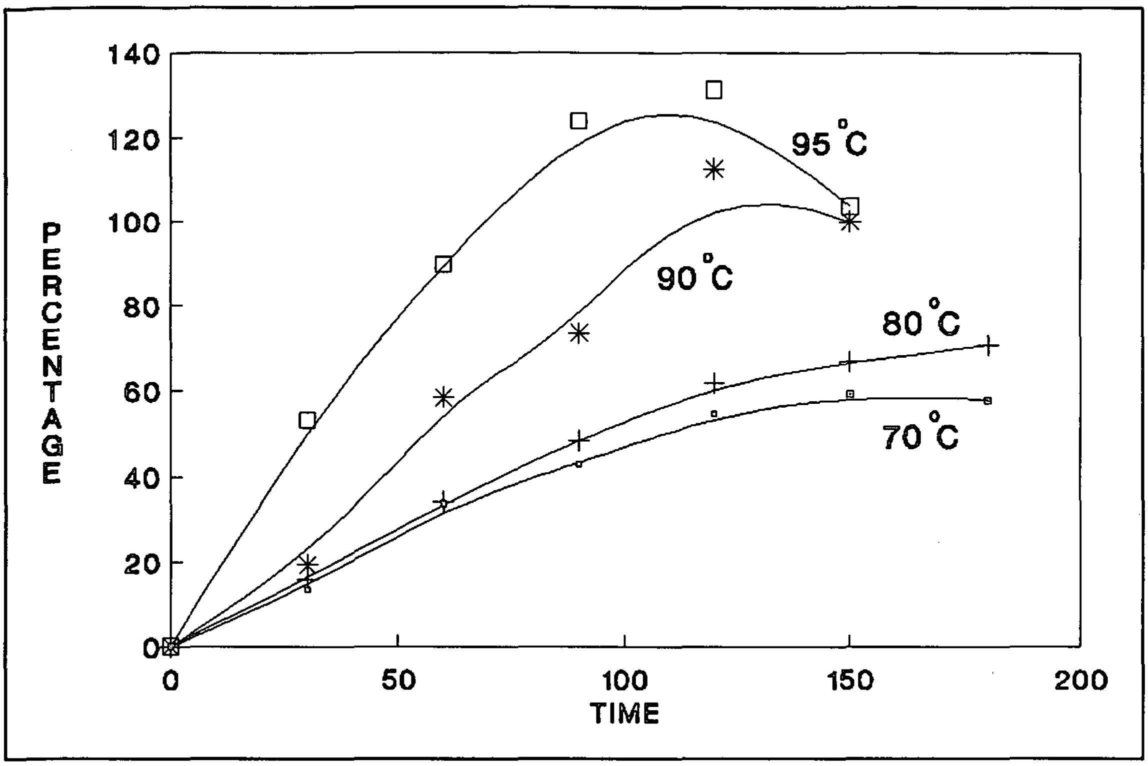


FIGURE 2.15 PLOT OF PERCENTAGE 2-VINYLFURAN AGAINST REACTION TIME AT DIFFERENT TEMPERATURES

The rate of formation (at 120 minutes) was calculated as follows :

$$\text{Rate} = \frac{\text{no. of moles 2-vinylfuran produced}}{\text{time}}$$

Rate (70° C) = $8{,}9 \times 10^{-2}$

Rate (80° C) = $1{,}0 \times 10^{-1}$

Rate (90° C) = $1{,}8 \times 10^{-1}$

Rate (95° C) = $2{,}1 \times 10^{-1}$

A plot of reaction rate against temperature was obtained as shown in figure 2.16.

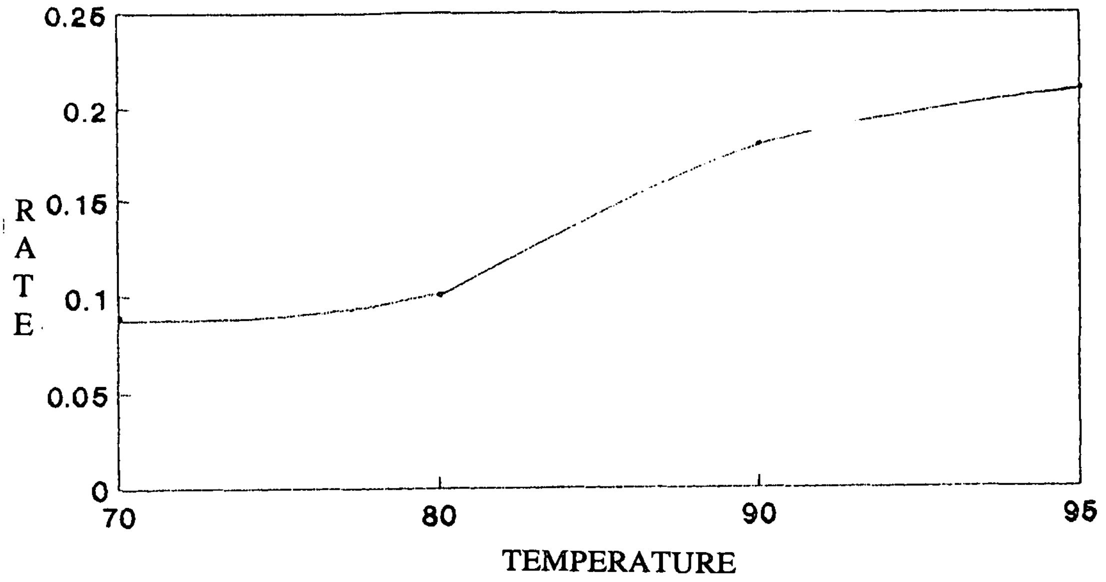


FIGURE 2.16 PLOT OF REACTION RATE AGAINST TEMPERATURE

From the above graph it was concluded that the rate increased rapidly with an increase in temperature. This typical temperature dependance indicated an exponential increase of the rate with temperature, or rate constant. Therefore the empirical relation could be written as :

$k = Ae^{-E/RT}$ .... Arrhenius equation.

An increase in rate with an increase in temperature indicated that the formation of 2-vinylfuran from furan and ethylene was an endothermic reaction. This however, was not observed experimentally because small quantities of reactants were used.

The following figure[56] may be used to explain the increase in vinylfuran formation with an increase in temperature.

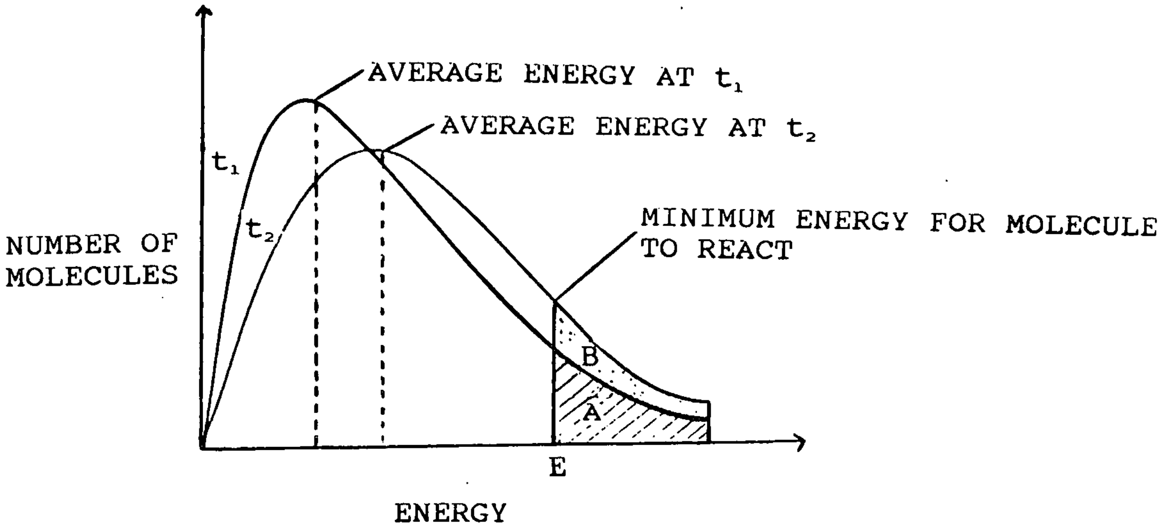


FIGURE 2.17 ENERGY DISTRIBUTION AMONG MOLECULES AT TWO DIFFERENT TEMPERATURES

By increasing the temperature, collision between molecules increased and a greater proportion of the molecules had sufficient energy to react therefore more molecules had the necessary energy to form the activated complex resulting in the increase in the products.

From figure 2.15 it was concluded that :

- a change of 5° C (90° C to 95° C) did not improve the yield of 2-vinylfuran to a large extent.
- that a reaction temperature of 90° C - 95° C for a reaction time of approximately two hours was adequate for the reaction.

2.5.3.2 Palladium (II) chloride as a Catalyst at Temperature of 90° C and 95° C

Using reagents in the mole ratio

Furan to ethylene to $PdC\ell_2$ to $Cu(OAc)_2 \equiv 25 : 5 : 1 : 2$

the effect of the catalyst was investigated at temperatures of 90° C and 95° C. The selection of these two temperatures were based on the observation that a reaction temperature of 90° - 95° C, using palladium (II) acetate, was adequate for the reaction.

Using the data obtained from these experiments, the following table was obtained.

TABLE 2.6 PERCENTAGE YIELD 2-VINYLFURAN AT DIFFERENT REACTION TEMPERATURES AND REACTION TIME

TIME (MINUTES)	PERCENTAGE YIELD 2-VINYLFURAN	
	REACTION TEMPERATURE	
	90° C	95° C
0	0	0
30	10,89	44,68
60	22,35	64,04
90	48,36	69,92
120	54,56	78,02
150	78,36	83,62

A plot of percentage 2-vinylfuran against time was obtained as shown in figure 2.18.

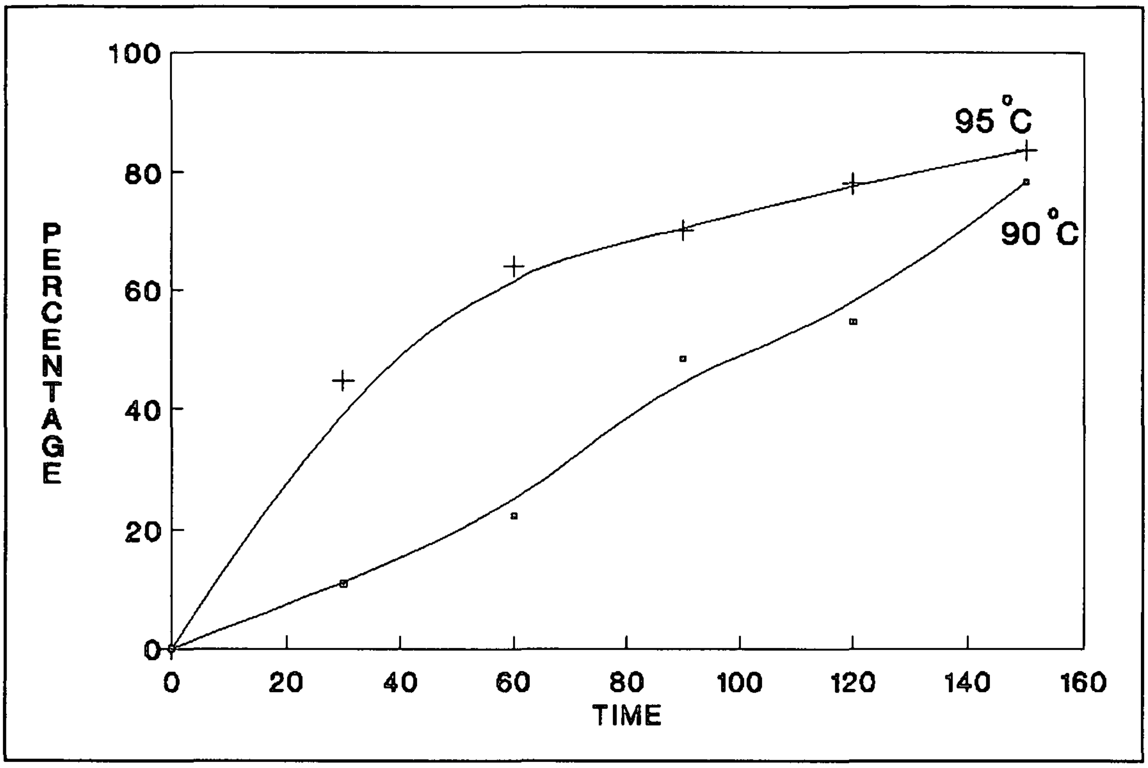


FIGURE 2.18 PLOT OF PERCENTAGE 2-VINYLFURAN AGAINST REACTION TIME

From the figure, it was concluded that the rate of the reaction improved as the temperature increased. It was also found that a reaction time > 150 minutes would be required for maximum yield using palladium (II) chloride as the catalyst. The progress of the reaction was not monitored for a time > 150 minutes since a shorter reaction time (as shown by the use of palladium (II) acetate) was more favourable than a longer reaction time using palladium (II) chloride.

2.5.3.3 Comparison of the Catalyst Palladium (II) acetate and Palladium (II) Chloride

Since the best catalyst for the reaction had to be determined, the data from tables 2.5 and 2.6 was extracted and a plot of percentage 2-vinylfuran against time was made at temperatures of 90° C and 95° C as shown in figure 2.19.

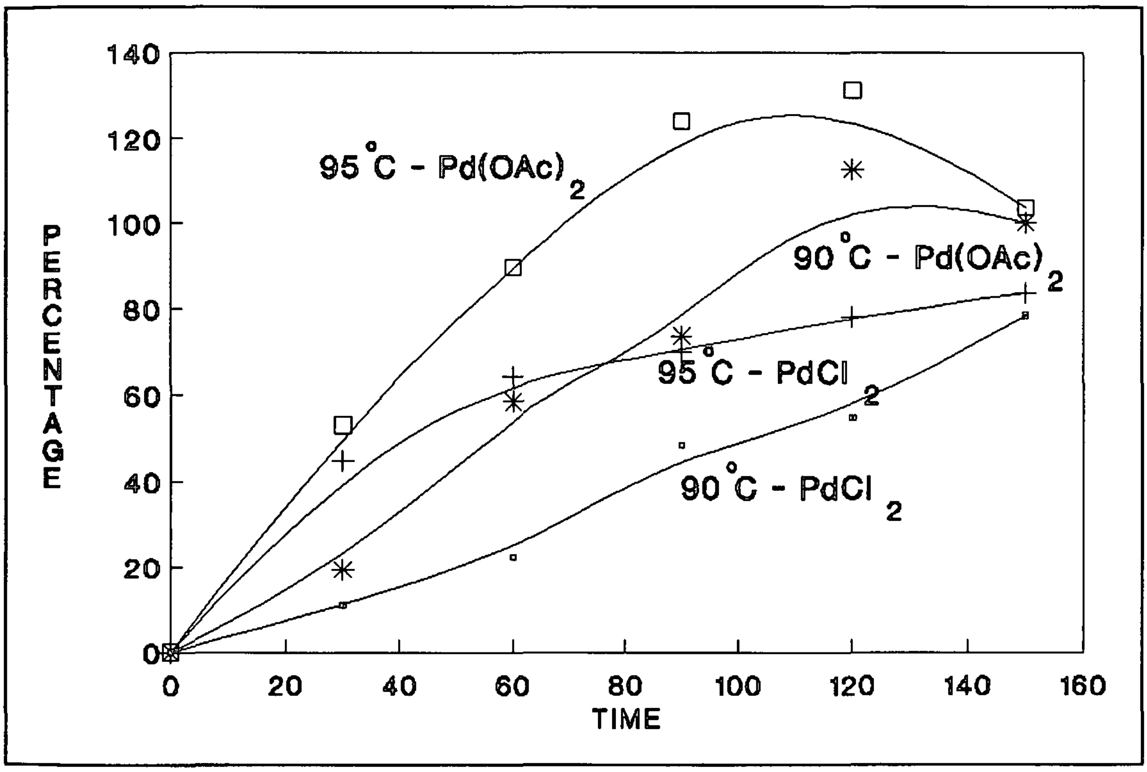


FIGURE 2.19 COMPARISON OF PALLADIUM (II) ACETATE AND PALLADIUM (II) CHLORIDE AT DIFFERENT TEMPERATURES

From the figure it was observed that the yield of 2-vinylfuran and the rate of formation was greater with palladium (II) acetate as the catalyst.

From the figure, it was also observed that there was a decrease in the yield of 2-vinylfuran, for a reaction time greater than two hours, when palladium (II) acetate was used as a catalyst. This decrease in yield could be attributed to the formation of the disubstituted furan viz. 2,5-divinylfuran. This, however, was not further investigated.

Since only the ligand was changed on the Group VIII metal, it was clear that the ligand was responsible for a change in the rate of the reaction.

The acetate ion, being a weaker ligand, and a better leaving group than the chloride ion, allowed the formation of sigma bonds (as seen in the mechanism page 49) to be more rapid[43]. This resulted in an increase in the yield of 2-vinylfuran when using palladium (II) acetate as a catalyst compared to palladium (II) chloride.

From these observations it was concluded that the ligand affected the stability of intermediates and therefore altered the reaction rates.

2.5.4 The Effect of Solvents[57] Using Fixed Quantities of Reactant.

Having established that a reaction time of approximately two hours and a temperature of 90 - 95° C could be used, the role played by the common solvents, used by Fujiwara and Kozhenikov, was investigated.

Using reactants in the mole ratio

Furan to ethylene to $Pd(OAc)_2$ to $Cu(OAc)_2 \equiv 25 : 5 : 1 : 2$

at a reaction temperature of 95° C and a reaction time of two hours, the following results were obtained.

TABLE 2.7 PERCENTAGE YIELD 2-VINYLFURAN USING DIFFERENT SOLVENTS AT A REACTION TEMPERATURE OF 95° C AND REACTION TIME OF TWO HOURS

SOLVENT	**% 2-VINYLFURAN**
DMF	133,98
DMF/H_2O : 4/1	103,07
DMF/H_2O : 1/1	85,92
HOAc	79,86
DMF/HOAc	71,71

The percentage yield of 2-vinylfuran was the highest in the case of neat dimethylformamide since :

- DMF co-ordinates weakly to the metal
- since DMF is an aprotic solvent with non-bonding electrons available for forming hydrogen bond.

In addition DMF has the ability to solvate anions to a smaller extent. This can increase the reactivity of the acetate ion enabling the regenerated Pd^{2+} to form its acetate compound rapidly.

On addition of water as a co-solvent (DMF : H_20 = 4 : 1), the yield of 2-vinylfuran decreased. This decrease can be accounted for by the fact that metals coordinate strongly to water. Therefore the active sites of the catalyst were hindered. This implied that the approach of the reactants to palladium was made, relatively, difficult.

Also since water is a protic hydrogen bond donor solvent, it can solvate anions more strongly than aprotic solvents. This solvation is due to hydrogen bonding tendencies whereas in aprotic non hydrogen bond donors, solvation is due to weak ion - dipole and ion-induced dipole forces. The stronger the solvation process, the weaker the activity of the anion.

The addition of more water (DMF : H_20 ≡ 1 : 1) led to a further decrease in the yield of 2-vinylfuran. There was formation of more hydrogen bonds which is characterised by a co-ordinative divalency of the hydrogen atom. Hydrogen bonds could not be ignored since it is approximately ten times weaker than covalent single bonds. In fact the bond dissociation enthalpy for hydrogen bonds is approximately 13 - 42 kJ/mol whereas for covalent single bonds it is approximately 210 - 420 kJ/mol[57].

In the case of neat acetic acid, the yield of 2-vinylfuran decreased. Acetic acid is a protic hydrogen bond donor solvent and has a good tendency to solvate anions due to hydrogen bonding tendencies. This stronger solvation resulted in a decrease in the activity of the acetate ion. In addition to hydrogen bonding, ion-pairing would stabilise the carboxylate ion.

In the case of acetic acid as a co-solvent in DMF, the yield of 2-vinylfuran was low compared to neat dimethylformamide as solvent. This result was due to acetic acid solvating the acetate ion more effectively thus reducing the activity of the acetate ion.

It was realised that due to solvation processes, the Gibbs free energy of activation would be affected and therefore product formation would also be affected. Also, a change in the solvent system can have a thousand fold increase/decrease in the rate of the reaction[57]. Therefore the lower yield obtained for the solvent - co-solvent systems indicated that the rate of the reaction decreased. Hence the percentage yield of 2-vinylfuran obtained for each solvent system for a reaction time of two hours was not the optimum.

In conclusion, the best solvent for this reaction, as found by Kozhenikov and Fujiwara, was dimethylformamide.

2.5.5 Optimisation of the Quantity of Co-Catalyst Required for the Reaction by Using Fixed Quantities of Reactants

Having found the conditions :

- Reaction temperature = 90 - 95° C
- Reaction time = approximately two hours and

- Dimethylformamide as a solvent

produced the best results, the amount of co-catalyst required for the reaction was investigated.

2.5.5.1 Copper (II) Acetate

Using reactants in the mole ratio :

Furan to ethylene to $Pd(OAc)_2 \equiv 25 : 5 : 1$

at a reaction temperature of 95° C and a reaction time of two hours, with dimethylformamide as a solvent, the following results were obtained.

TABLE 2.8 PERCENTAGE YIELD 2-VINYLFURAN USING DIFFERENT QUANTITIES OF COPPER (II) ACETATE

$\frac{\text{Copper (II) Acetate (mole)}}{\text{Palladium (II) Acetate (mole)}}$	PERCENTAGE YIELD 2-VINYLFURAN
5	274,91
6	325,44
7	360,53
8	429,39 64,41[a]
9	429,03
10	428,39

a represents percentage conversion 2-vinylfuran based on quantity of furan consumed.

Using the data obtained, a plot of percentage 2-vinylfuran against ratio $Cu(OAc)_2/Pd(OAc)_2$ was obtained as shown in figure 2.20.

For the half reaction :

$$Pd^{2+} + 2e^- \rightarrow Pd \qquad E^\circ = 0,951V$$

the Nernst equation was given by :

$$E = 0,951 + 0,063 \log [Pd^{2+}]$$

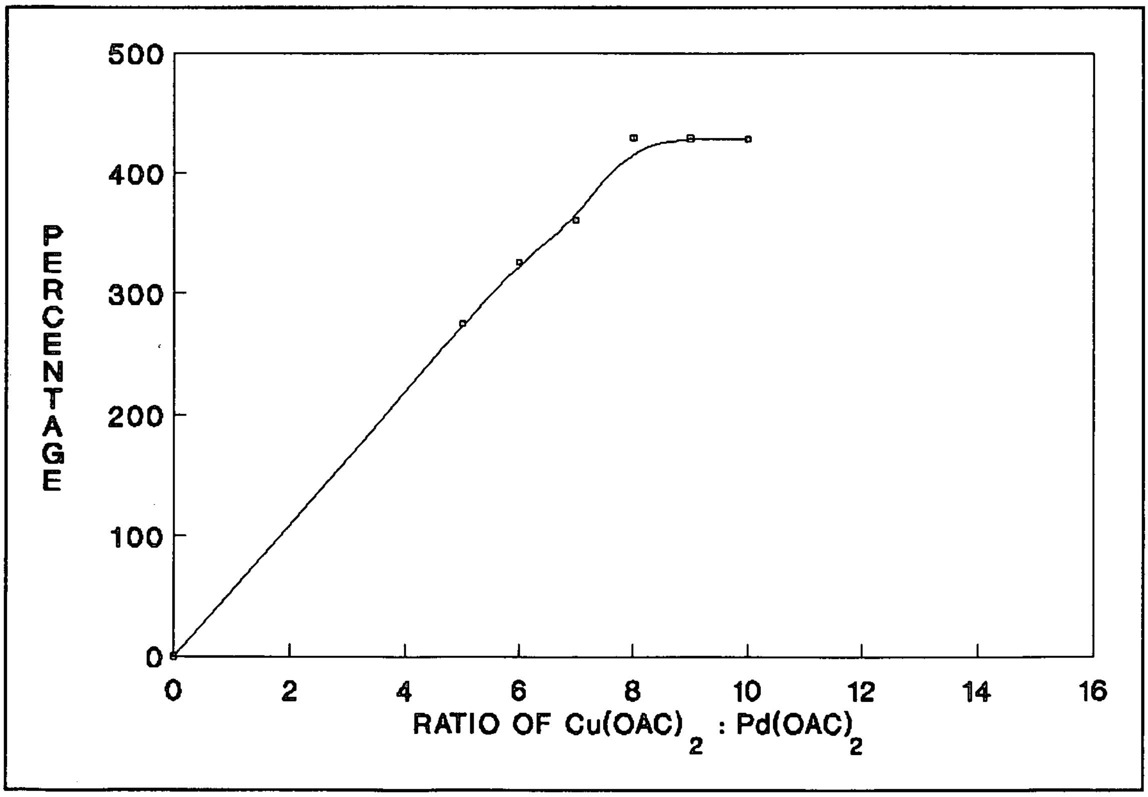


FIGURE 2.20 PLOT OF PERCENTAGE 2-VINYLFURAN AGAINST QUANTITY OF COPPER (II) ACETATE

The reduction of palladium ion to palladium metal, due to the formation of 2-vinylfuran, resulted in a decrease in the concentration of the palladium ion which in turn led to a decrease in the reduction potential of the half equation. This implies that the oxidation potential will increase and therefore the following reaction will be promoted by a suitable oxidizing agent :

$$Pd \longrightarrow Pd^{2+} + 2e^-$$

The cupric ion will undergo reduction to form cuprous ion as shown by the following half equation :

$$2Cu^{2+} + 2e^- \longrightarrow 2Cu^+$$

The addition of copper (II) acetate was found to be effective in oxidizing palladium to its active state, namely Pd^{2+} ion.

It was found that a quantity of 8-9 times more copper (II) acetate than palladium (II) acetate was required for the best yield. Further addition of co-catalyst had no effect on the yield of 2-vinylfuran. This was attributed to the deactivation of the catalyst in which case the reactive sites became inactive.

It was observed that due to the large quantities of copper (II) salts being used, a thick slurry was formed. In addition, there was an observable colour change of the solution from blue to greenish-blue.

2.5.5.2 Iron (III) Chloride

Using reactants in the mole ratio :

Furan to ethylene to $Pd(OAc)_2 \equiv 25 : 5 : 1$

at a reaction temperature of 95° C and a reaction time of two hours, with dimethylformamide as a solvent, the following results were obtained.

TABLE 2.9 PERCENTAGE YIELD 2-VINYLFURAN USING DIFFERENT QUANTITIES OF IRON (III) CHLORIDE

Iron (III) Cloride (mole) / Palladium (II) Acetate (mole)	**PERCENTAGE YIELD 2-VINYLFURAN**
5	144,74
10	238,85
11	280,59
12	315,78
13	314,57

Using the data obtained, a plot of percentage 2-vinylfuran against ratio $FeC\ell_3/Pd(OAc)_2$ was obtained as shown in figure 2.21.

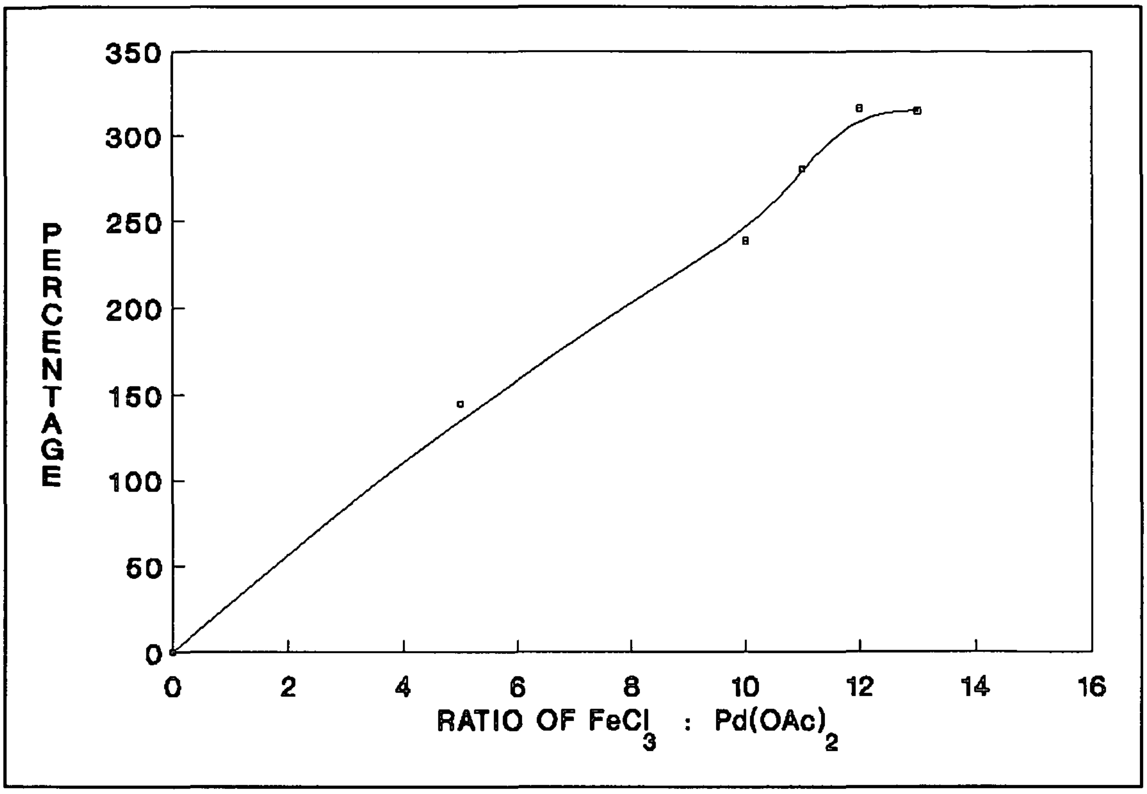


FIGURE 2.21 PLOT OF PERCENTAGE 2-VINYLFURAN AGAINST QUANTITY OF IRON (III) CHLORIDE

The addition of iron (III) chloride was also found to be effective in oxidizing palladium to the active state as discussed for copper (II) acetate. The ferric salts were reduced to ferrous salts as shown by the following half equation:

$$2\ Fe^{3+} + 2e^{-} \longrightarrow 2\ Fe^{2+}$$

It was observed that due to the large quantities of iron (III) salts being used, a thick slurry was formed.

From the graph it was concluded that a quantity of 12-13 times more iron (III) chloride than palladium (II) acetate was required for the optimum yield of 2-vinylfuran.

2.5.5.3 Silver (I) acetate

Using reactants in the mole ratio

Furan to ethylene to $Pd(OAc)_2 \equiv 25 : 5 : 1$

at a reaction temperature of 95° C and a reaction time of two hours, with dimethylformamide as a solvent, the following results were obtained as shown in table 2.10.

TABLE 2.10 PERCENTAGE YIELD 2-VINYLFURAN USING DIFFERENT QUANTITIES OF SILVER (I) ACETATE

$\frac{\text{Silver (I) Acetate (moles)}}{\text{Palladium) (II) Acetate (moles)}}$	PERCENTAGE 2-VINYLFURAN
5	86,22
6	106,55
7	137,11
8	180,79
9	191,08
10	222,43

Using the data obtained, a plot of percentage 2-vinylfuran against the ratio $AgOAc/Pd(OAc)_2$ was obtained as shown in figure 2.22.

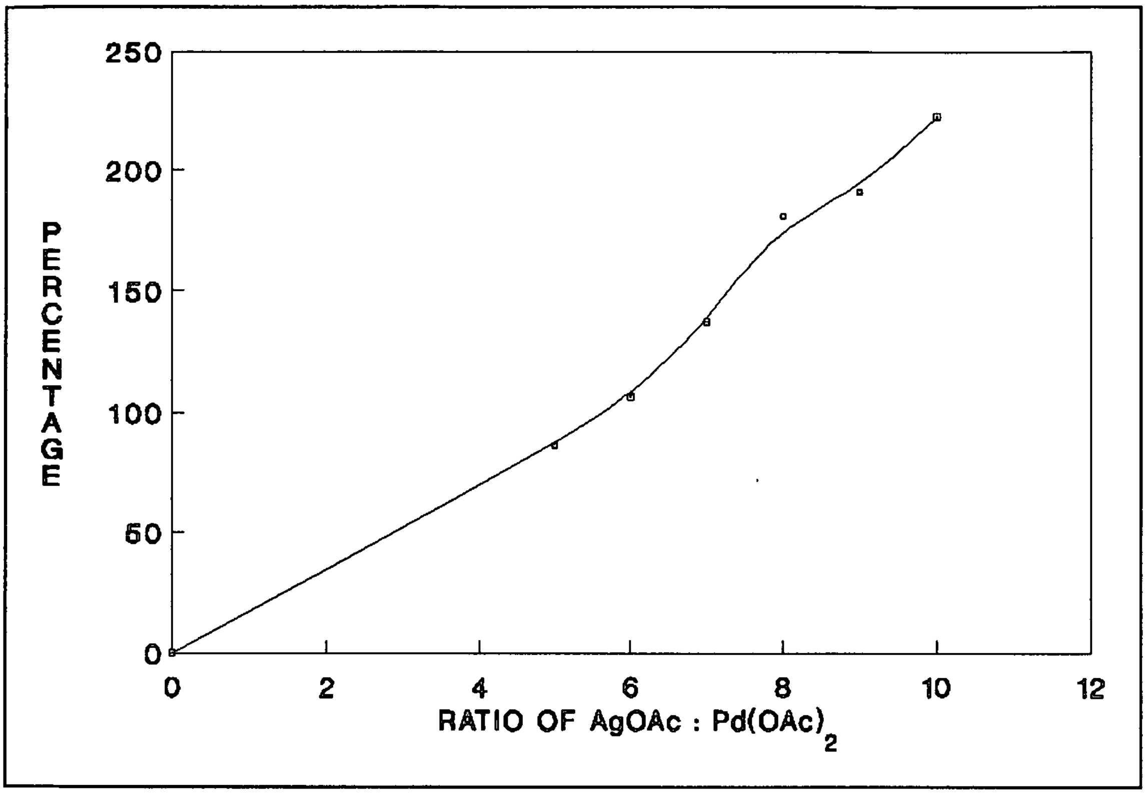


FIGURE 2.22 PLOT OF PERCENTAGE 2-VINYLFURAN AGAINST QUANTITY OF SILVER (I) ACETATE

It was found that extremely large quantities of silver (I) acetate were being used to produce a small yield of 2-vinylfuran. This meant that large quantities of silver (I) acetate, relative to copper (II) acetate and iron (III) chloride, would be required for a relatively lower yield of 2-vinylfuran. Furthermore it was observed that metallic silver coated the walls of the reaction vessel which posed a serious problem for industrial application. Hence silver (I) acetate was found to be relatively ineffective and could not be recommended as a co-catalyst.

2.5.5.4 Comparison of the Co-Catalysts

Having found the optimum quantity of the co-catalyst copper (II) acetate and iron (III) chloride and using the largest quantity of silver (I) acetate which was investigated, the data from tables 2.8 ; 2.9 and 2.10 was used for comparison purposes. The optimum quantity of each co-catalyst was plotted against the percentage yield 2-vinylfuran to give a bar graph as shown in figure 2.23.

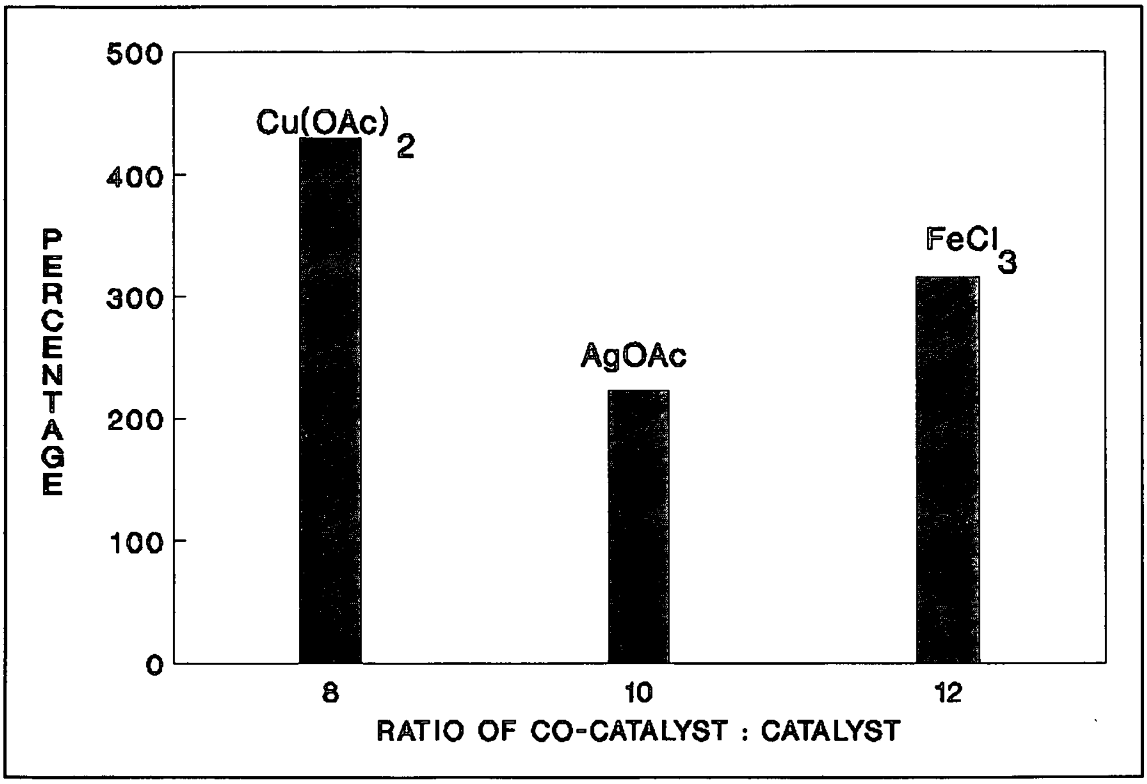


FIGURE 2.23 PLOT OF PERCENTAGE 2-VINYLFURAN AGAINST OPTIMUM QUANTITY OF CO-CATALYST

For redox reactions to be spontaneous, the difference in the potential between the two half equations must be at least 0,25V. In the case of the palladium (II) acetate and copper (II) acetate couple, this difference exceeded 0,25V. Therefore a smaller quantity of copper (II) acetate was required for optimum yield of 2-vinylfuran. In the case of palladium (II) acetate and iron (III) chloride couple this difference was less than 0,25V. Therefore a larger quantity of iron (III) chloride was required for a relatively lower optimum yield of 2-vinylfuran. For silver (I) acetate and palladium (II) acetate couple, the difference was even smaller thus accounting for the larger quantity of silver (I) acetate required for the reaction.

It was found that copper (II) acetate :

- produced the highest yield of 2-vinylfuran and
- was required in smaller quantities than iron (III) chloride and silver (I) acetate

thus providing sufficient evidence for its recommendation as a co-catalyst.

2.6 Conclusion and Recommendation

This study has established that the reaction of furan and ethylene with palladium (II) acetate as catalyst and copper (II) acetate as co-catalyst can be conducted at atmospheric pressure. The optimum yield of 2-vinylfuran was obtained under the following conditions :

- Furan to ethylene to $Pd(OAc)_2$ to $Cu(OAc)_2$ $\equiv$ 25 : 5 : 1 : 8
- Reaction time of two hours
- Reaction temperature of 95° C
- Dimethylformamide as a solvent

The chromatogram obtained for these reaction conditions is shown in appendix 12 (121).

The percentage conversion of 2-vinylfuran was 64,41 % based on the quantity of furan consumed.

The yield of 2-vinylfuran was 429% with respect to palladium (II) acetate. This result is comparable to that obtained by Kozhenikov (510%) who used a bomb calorimeter.

It is recommended that :

- a bomb calorimeter be used using the conditions above to determine the effect on the yield of 2-vinylfuran.
- a method be used to separate 2-vinylfuran from the reaction content. Since furan was supplied in excess, attention should be given to the recovery of the unused furan. The furan having a lower boiling point (40°C) than 2-vinylfuran (100°C) can be recovered via fractional distillation and recycled.
- deuterium labelled ethylene be used to investigate the rate determining step of the reaction and hence confirm the proposed mechanism. (see page 49).
- a method be investigated to extract the spent catalyst for subsequent regeneration since large quantities of co-catalysts resulted in the formation of a thick slurry.

It would be appropriate that points 1, 2 and 4, as mentioned above, be investigated before Pilot Plant scale could be investigated to determine the feasibility of industrial production.

CHAPTER THREE

EXPERIMENTAL

3.1 Instrumentation

The mass spectra were recorded on a Hewlett Packard 3200 X GC, fitted with a fused silica cross linked methyl silicone capillary column, interfaced to a Hewlett Packard 5971 A mass selective detector equipped with a hyperbolic quadrupole mass filter. All recordings were obtained from a Hewlett Packard Vectra 486 computer linked to a Laser Jet III printer.

For all analysis, a temperature programme was used with the following parameters : initial temperature = 70° C ; ramp rate = 5° C/min ; final temperature = 220° C.

A 0,2 $\mu\ell$ sample (standard 2-vinylfuran or reaction content) was injected into the GC under the conditions specified and the normalised mass spectrum was obtained.

The infra-red spectrum was recorded on a Perkin Elmer 9000 GC, fitted with a megabore fused silica glass capillary column, interfaced with a 1700 X GC-IR, to a PE 1725 X FT-IR spectrophotometer. Recording was obtained from a Epson EL 2 computer linked to a Epson LX 400 printer.

A temperature programme was used of the following parameters : initial temperature = 70° C ; ramp rate = 5° C/min ; final temperature = 220° C.

A 0,2 $\mu\ell$ of the neat standard 2-vinylfuran sample was injected manually into the GC under the conditions specified and the IR spectrum was obtained from the printer. All gas chromatograms were recorded on a Varian 6000 GC, fitted with a chromosorb 102 stainless steel column, with a flame ionization detector. All recordings were obtained from a SP 4290 Integrator. Details of the GC conditions are given in appendix 5 (114).

All experimental results were obtained by injecting a 0,2 $\mu\ell$ sample of the reaction content manually into the GC. The chromatograms were obtained from the integrator.

3.2 Chemicals

Standard 2-vinylfuran was supplied by Professor Delmas, L′ Institut National Polytechnique De Toulouse. It was prepared from furfural by the Witting reaction.

All chemicals were reagent grade.

Ethylene was obtained from Fedgas.
Anhydrous palladium (II) acetate and palladium (II) chloride were obtained from Osmium Corporation.
Furan and dimethylformamide were obtained from PGM Chemicals (Pty) Ltd.
Copper (II) acetate monohydrate was obtained from Holpro Analytics (Pty) Ltd.

3.3 Determination of the Purity of Standard of 2-vinylfuran

A standard 2-vinylfuran neat sample (0,2$\mu\ell$) was injected manually into the GC under the conditions specified. Ten injections were performed to ensure reproducibility. Chromatograms were obtained from an integrator and a sample chromatogram is given in appendix 6 (115). The integrated area percent obtained from ten injections are tabulated below.

TABLE 2.1 INTEGRATED AREA PERCENT OF 2-VINYLFURAN FOR 10 INJECTIONS

INJECTION	INTEGRATED AREA PERCENT OF 2-VINYLFURAN
1	95,01
2	95,04
3	95,19
4	95,22
5	95,37
6	95,79
7	96,11
8	96,18
9	98,02
10	98,29
	AVERAGE : 96,07

3.4 The Method Used for Quantification of Experimental Results

3.4.1 Percentage 2-vinylfuran based on the Quantity of Catalyst

Six standard solutions of 2-vinylfuran were prepared, in dimethylformamide, in the concentration range of 1-10% (m/m) as follows:

General Procedure:

To an accurate mass of dimethylformamide (at 25° C), in a 10,00 mℓ volumetric flask, was added an accurate mass of neat standard 2-vinylfuran sample. The flask was gently swirled and a 0,2 $\mu\ell$ sample was injected manually into the GC under the conditions specified. Three injections, for each standard solution, were performed to ensure reproducibility. The chromatograms were obtained from an integrator and a sample chromatogram is given in appendix 7 (116). The average integrated area for each standard solution are tabulated below :

TABLE 3.2(a) AVERAGE INTEGRATED AREA OF 2-VINYLFURAN FOR STANDARD SOLUTIONS PREPARED IN DIMETHYLFORMAMIDE

PERCENTAGE 2-VINYLFURAN	AVERAGE INTEGRATED AREA OF THREE INJECTIONS
1	151650
2	330702
4	710869
6	1090645
8	1486692
10	1581265

3.4.2 Percentage Conversion 2-vinylfuran based on the Quantity Furan Consumed

Six standard solutions of furan were prepared, in dimethylformamide, in the concentration range of 5-30% (m/m) as follows:

General Procedure:

To an accurate mass of dimethylformamide (at 25° C), in a 50,00 mℓ volumetric flask, was added an accurate mass of neat furan sample. The flask was gently swirled and a 0,2 μℓ sample was injected manually into the GC under the conditions specified. Three injections, for each standard solution, were performed to ensure reproducibility. The chromatograms were obtained from an integrator and a sample chromatogram is given in appendix 8 (117). The average integrated area for each standard solution are tabulated below :

TABLE 3.2(b) AVERAGE INTEGRATED AREA OF FURAN FOR STANDARD SOLUTIONS PREPARED IN DIMETHYLFORMAMIDE

PERCENTAGE FURAN	AVERAGE INTEGRATED AREA OF THREE INJECTIONS
5	121365
10	242730
15	364095
20	485460
25	634978
30	728191

3.5 Qualitiative Determination of the Relative Solubility of Furan and 2-vinylfuran

3.5.1 Solubility of Furan

General Procedure:

To 5 mℓ of the solvent in a clean dry test tube was added 0,5 mℓ of furan. The test tube was gently shaken and observed for miscibility/immiscibility. The observations are tabulated below :

TABLE 3.3 RELATIVE SOLUBILITY OF FURAN

SOLVENT	OBSERVATION
Ethanol	Soluble
Acetone	Soluble
Dimethylformamide	Soluble
Hexane	Partially soluble
Cyclohexane	Partially soluble
Acetic Acid	Partially soluble
Water	Insoluble
Carbon tetrachloride	Insoluble

3.5.2 Solubility of 2-vinylfuran

General Procedure:

To 5 mℓ of the solvent in a clean dry test tube was added 0,5 mℓ of 2-vinylfuran. The test tube was gently shaken and observed for miscibility/immiscibility. The observations are tabulated below :

TABLE 3.4 RELATIVE SOLUBILITY OF 2-VINYLFURAN

SOLVENT	OBSERVATION
Acetic Acid	Soluble
Furan	Soluble
Dimethylformamide	Soluble
Tetrahydrofuran	Soluble
1,4-Dioxane	Soluble
Water	Insoluble
Methanol	Insoluble
Acetonitrile	Insoluble

3.6 Quantitative Determination of the Relative Solubility of Ethylene

3.6.1 Relative Solubility in Different Solvents

General Procedure:

Ethylene was bubbled into the reaction vessel containing 100,00 g of solvent. A 0,2 $\mu\ell$ sample was injected manually into the GC. The chromatogram was obtained from the integrator. This procedure was repeated until a chromatogram was obtained showing maximum integrated area of ethylene. This indicated a saturated solution of ethylene. The integrated area percentage of ethylene obtained from the chromatogram are tabulated below :

TABLE 3.5 INTEGRATED AREA PERCENT OF ETHYLENE IN DIFFERENT SOLVENTS AT ROOM TEMPERATURE

SOLVENT (25^{o} C)	AREA % OF ETHYLENE
Acetic Acid	1,30
Hexane	0,68
Cyclohexane	0,25
Dimethylformamide	1,43

A sample chromatogram showing the solubility of ethylene in cyclohexane is given in appendix 8 (118).

3.6.2 Relative Solubility of Ethylene in Dimethylformamide at Different Temperatures

General Procedure:

Ethylene was bubbled into the reaction vessel containing 100,00 g of solvent. A 0,2 $\mu\ell$ sample was injected manually into the GC. The chromatogram was obtained from the integrator. This procedure was repeated until a chromatogram was obtained showing maximum integrated area of ethylene. This indicated a saturated solution of ethylene. The integrated area percentage of ethylene obtained from the chromatogram are tabulated below :

TABLE 3.6 INTEGRATED AREA PERCENT OF ETHYLENE IN DIMETHYLFORMAMIDE AT DIFFERENT TEMPERATURES

DIMETHYLFORMAMIDE (SOLVENT)	
TEMPERATURE (^{o} C)	AREA %
25	1,43
70	1,28
80	1,25
90	1,23
95	1,22
140	1,12

A sample chromatogram showing the solubility of ethylene in dimethylformamide at the temperature of 25° C is given in appendix 10 (119).

3.7 The Gas Phase Heterogenous Catalysis of Ethylene and Furan

3.7.1 Design of a Reactor

The reactor which was designed, as shown in page 41, had the following dimensions:

- length of outer glass tube = 720 mm
- internal diameter of outer glass tube = 30 mm
- length of inner glass tube = 600 mm
- internal diameter of inner glass tube = 5 mm

3.7.2 Catalysis by Palladium Supported on Alumina

Furan (50 mℓ) was placed into the 100 mℓ reactor (figure 2.7, page 42). The solid catalyst (3 g) was packed into the glass column. The reactor was heated to the specified temperature and furan was gently heated (40° C) using a heating mantle. Ethylene was continuously bubbled at a flow rate of 1,67 mℓ/min. The distillate was collected at 10 minute intervals. The reaction was stopped (after 1 hour) when approximately 5 mℓ of furan remained in the round bottom flask.

The reaction was conducted at temperatures of 60° C, 100° C, 150° C, 200° C and 240° C for each of the following catalysts :

- 0,1% Palladium on alumina
- 0,2% Palladium on alumina
- 0,5% Palladium on alumina
- 0,8% Palladium on alumina

A 0,2 $\mu\ell$ sample of each fraction was injected manually in the GC and the chromatogram obtained from the integrator. A typical chromatogram is given in appendix 2 (111).

3.7.3 Catalysis by Palladium (II) acetate - Copper (II) acetate

Furan (50 mℓ) was placed into the 100 mℓ reactor (figure 2.7, page 42) and 8 g (mole ratio $Pd(OAc)_2 : Cu(OAc)_2 \equiv 1 : 10$) of the solid catalyst mixture was packed into the glass column. The reactor was heated to the specified temperature and furan was gently heated (40° C) using a heating mantle. Ethylene was continuously bubbled at a flow rate of 1,67 mℓ/min. The distillate was collected at 10 minute intervals. The reaction was stopped when approximately 5 mℓ of furan remained in the round bottom flask.

The reaction was conducted at temperatures of 60° C ; 80° C and 100° C. acetate.

A 0,2 $\mu\ell$ sample of each fraction was injected manually in the GC and the chromatogram obtained from the integrator.

3.8 The Liquid Phase Homogenous Catalysis of Ethylene and Furan

3.8.1 Design of a Glass Reactor for Small Scale Reactions

The glass reactor which was designed, as shown in figure 2.8 (44), had the following dimensions :

- length of reactor = 140 mm
- internal diameter of reactor = 30 mm
- height of gas bubbler from base of the reactor = 30 mm
- length of injection port from the base of the reactor = 60 mm

3.8.2 Reaction of Ethylene and Furan Under Various Catalytic Conditions

3.8.2.1 Stoichiometric Quantities of Catalyst

To 100 g of dimethylformamide, in the reaction vessel, was added 5,004 grams (22,30 mmoles) of palladium (II) acetate and 15,17 grams (223 mmoles) of furan. The apparatus was set up as described in figure 2.8 (44).

The reaction vessel was placed in a hot glycerol bath (pre-heated to 80° C), and ethylene was bubbled in immediately at a flow rate of 5,38 mℓ/min (pre-set). [The flow rate was calculated as shown in appendix 11]. The solution was stirred continuously for two hours.

A 0,2 $\mu\ell$ sample of the reaction content was manually injected into the GC and the chromatogram obtained from the integrator. The integrated area of

2-vinylfuran was 325303. A sample chromatogram is given in appendix 3 (112).

3.8.2.2 Use of Co-catalyst (Copper (II) acetate with non-stoichiometric Quantities of Catalyst (Palladium (II) acetate)

General Procedure:

To 100 g of dimethylformamide in the reaction vessel was added palladium (II) acetate, copper (II) acetate and 15,17 g of furan. The reaction vessel was placed in a hot glycerol bath (pre-heated to 80° C), and ethylene was bubbled in immediately at a flow rate of 5,38 mℓ/min (pre-set). The solution was stirred continuously for two hours.

The quantity of palladium (II) acetate and copper (II) acetate used and the integrated area of 2-vinylfuran for the two experiments are given below :

TABLE 3.7 QUANTITIES OF PALLADIUM (II) ACETATE AND COPPER (II) USED AND THE INTEGRATED AREA OF 2-VINYLFURAN

MASS OF COPPER (II) ACETATE	**MASS OF PALLADIUM (II) ACETATE**	**AREA OF 2-VINYLFURAN**
0,8116 (4,09 mmoles)	0,5004 g (2,23 mmoles)	6115
1,7345 (8,72 mmoles)	1,001 g (4,46 mmoles)	23564

3.8.3 Optimization of Temperature and Time for the Reaction of Ethylene and Furan with Palladium (II) acetate and Palladium (II) chloride

3.8.3.1 Palladium (II) acetate as a Catalyst in the Temperature Range 30° C - 95°C

3.8.3.1.1 Reaction Temperature of 30° C and 40° C

To 100 g of dimethylformamide in the reaction vessel was added 1,1458 g (5,10 mmoles) of palladium (II) acetate, 2,0419 g (11,51 mmoles) of copper (II) acetate and 17,36 g (255,30 mmoles) of furan. The reaction vessel was placed on a hot glycerol bath (pre-heated to temperatures 30° and 40° C), and ethylene was bubbled in immediately at a flow rate of 3,25 mℓ/min (pre-set). The solution was stirred continuously. The sample was analysed at 30 minutes intervals.

The results are given below:

TABLE 3.8 INTEGRATED AREA OF 2,2′-BIFURAN AT DIFFERENT REACTION TEMPERATURE AND REACTION TIME

INTEGRATED AREA OF 2,2′-BIFURAN		
TIME (MINS)	30^{0} C	40^{0} C
30	8506	15565
60	17847	23177
90	25129	30333
120	44681	44857
150	46086	97863
180	65189	201059

3.8.3.1.2 Reaction Temperature of 70° C, 80° C, 90° C and 95° C

General Procedure:

To 100 g of dimethylformamide in the reaction vessel was added 1,0256 g (4,57 mmoles) of palladium (II) acetate, 1,8275 g (9,15 mmoles) of copper (II) acetate and 7,70 g (113,24 mmoles) of furan. The reaction vessel was placed in a hot glycerol bath (pre-heated to temperatures 70° C ; 80° C ; 90° C and 95° C), and ethylene was bubbled in immediately at a flow rate of 3,58 ; 3,68 ; 4,55 and 4,61 mℓ/min respectively (pre-set). The solution was stirred continuously. The sample was analysed at 30 minutes intervals. The results are given below :

TABLE 3.9 INTEGRATED AREA OF 2-VINYLFURAN AT DIFFERENT REACTION TEMPERATURE AND TIME

TIME (MINUTES)	INTEGRATED AREA OF 2-VINYLFURAN			
	REACTION TEMPERATURE			
	70° C	80° C	90° C	95° C
30	9517	11307	13688	37628
60	23899	24229	41457	63654
90	30386	34337	52212	88015
120	38745	43856	79988	93218
150	42063	47528	71048	73621
180	41000	50159		

3.8.3.2 Palladium (II) chloride as a Catalyst at Temperatures of 90° C and 95° C

General Procedure:

To 100 g of dimethylformamide in the reaction vessel was added 0,8104 g (4,52 mmoles) of palladium (II) chloride, 1,8275 g (9,15 mmoles) of copper (II) acetate and 7,70 g (113,24 mmoles) of furan. The reaction vessel was placed in a hot glycerol bath (pre-heated to temperatures 90° C and 95° C), and ethylene was bubbled in immediately at a flow rate of 4,55 and 4,61 mℓ/min respectively (pre-set). The solution was stirred continuously. The sample was analysed at 30 minutes intervals. The results are given below:

TABLE 3.10 INTEGRATED AREA OF 2-VINYLFURAN AT DIFFERENT REACTION TEMPERATURE AND TIME

TIME (MINUTES)	INTEGRATED AREA OF 2-VINYLFURAN	
	REACTION TEMPERATURE	
	90° C	95° C
30	7730	31728
60	15870	45472
90	34337	49648
120	38745	55401
150	55645	59376

3.8.4 The Effect of Solvents Using Fixed Quantities of Reactants

General Procedure:

To 100 g of the solvent in the reaction vessel was added 1,0256 g (4,57 mmoles) of palladium (II) acetate, 1,8275 g (9,15 mmoles) of copper (II) acetate and 7,70 g (113,24) of furan. The reaction vessel was placed in a hot glycerol bath (pre-heated to 95° C), and ethylene was bubbled in immediately at a flow rate of 5,75 mℓ/min (pre-set). The solution was stirred continuously. The sample was analysed after two hours. The results are given below :

TABLE 3.11 INTEGRATED AREA OF 2-VINYLFURAN IN DIFFERENT SOLVENTS

SOLVENT	INTEGRATED AREA OF 2-VINYLFURAN
DMF	95141
DMF/H_20 : 4/1	73191
DMF/H_20 : 1/1	61016
HOAc	56710
DMF/HOAc : 4/1	50923

PROCESSING DEPARTMENT

(Please tick tasks completed)

PASTED ACCESSION LABEL	
PASTED ISSUE LABEL	
POCKET STUCK	
BOOK STAMPED	
BOOK SPINED	
CARD TYPED	
BOOK HAS BARCODE	
BOOK TATTLED	
PROCESSING COMPLETE CHECK BOOK	

3.8.5 Optimization of the Quantity of Co-Catalyst Required for the Reaction by Using Fixed Quantities of Reactants

3.8.5.1 Copper (II) Acetate

General Procedure:

To 100 g of dimethylformamide in the reaction vessel was added 1,0256 g (4,57 mmoles) of palladium (II) acetate, copper (II) acetate and 7,70 g (113,24 mmoles) of furan. The reaction vessel was placed in a hot glycerol bath (pre-heated to 95° C), and ethylene was bubbled in immediately at a flow rate of 5,75 mℓ/min (pre-set). The solution was stirred continuously. The sample was analysed after two hours.

The results are given below :

TABLE 3.12 INTEGRATED AREA OF 2-VINYLFURAN USING DIFFERENT QUANTITIES OF COPPER (II) ACETATE

QUANTITY OF $Cu(OAc)_2$	$\frac{\text{Copper (II) Acetate (mole)}}{\text{Palladium (II) Acetate (mole)}}$	INTEGRATED AREA OF VINYLFURAN
4,569 g (22,89 mmoles)	5	195220
5,4828 g (27,46 mmoles)	6	231096
6,3970 g (32,04 mmoles)	7	256018
7,3108 g (36,62 mmoles)	8	304916 141140[a]
8,2250 g (41,20 mmoles)	9	304662
9,1385 g (45,77 mmoles)	10	304205

a represents area of furan.

3.8.5.2 Iron (III) Chloride

General Procedure:

To 100 g of dimethylformamide in the reaction vessel was added 1,0256 g (4,57 mmoles) of palladium (II) acetate, iron (III) chloride and 7,70 g (113,24 mmoles) of furan. The reaction vessel was placed in a hot glycerol bath (pre-heated to 95° C), and ethylene was bubbled in immediately at a flow rate of 5,75 mℓ/min (pre-set). The solution was stirred continuously. The sample was analysed after two hours.

The results are given below :

TABLE 3-13 INTEGRATED AREA OF 2-VINYLFURAN USING DIFFERENT QUANTITITES OF IRON (III) CHLORIDE

QUANTITY OF $FeC\ell_3$	$\frac{\text{Iron (III) Chloride (mole)}}{\text{Palladium (II) Acetate (mole)}}$	INTEGRATED AREA OF VINYLFURAN
3,7135 g (22,87 mmoles)	5	102779
7,4178 g (45,69 mmoles)	10	169610
8,1560 g (50,24 mmoles)	11	199252
8,900 g (54,82 mmoles)	12	224240
9,643 g (59,40 mmoles)	13	223378

3.8.5.3 Silver (I) Acetate

General Procedure:

To 100 g of dimethylformamide in the reaction vessel was added 1,0256 g (4,57 mmoles) of palladium (II) acetate, Silver (I) acetate and 7,70 g (113,24 mmoles) of furan. The reaction vessel was placed in a hot glycerol bath (pre-heated to 95° C), and ethylene was bubbled in immediately at a flow rate of 5,75 mℓ/min (pre-set). The solution was stirred continuously. The sample was analysed after two hours.

The results are given below :

TABLE 3.14 INTEGRATED AREA OF 2-VINYLFURAN USING DIFFERENT QUANTITIES OF SILVER (I) ACETATE

QUANTITY OF AgOAc	Silver (I) Acetate (mole) / Palladium (II) Acetate (mole)	INTEGRATED AREA OF VINYLFURAN
3,8133 g (22,85 mmoles)	5	61227
4,5760 g (27,42 mmoles)	6	75661
5,3390 g (31,99 mmoles)	7	97364
6,0694 g (36,37 mmoles)	8	128383
6,8290 g (40,92 mmoles)	9	135688
7,5865 g (45,36 mmoles)	10	157956

REFERENCES

1. Paalz, W., Chartier, P., Hall, D. V., Energy from biomass, (1981), Applied Science Publishers, London.

2. Lewis, C. W., Biomass, (1981), 1, 5-15.

3. Gandini, A., Advanced Polymer Science, (1977), 25, 47-96.

4. Moureux, C., Dufraisse, C., Johnson, J. R., Annales de Chime, (1927), 7, 14-42.

5. Moureux, C., Dufraisse, C., Johnson, J. R., Bull. Soc. Chim., (1928), 43, 586.

6. Hurd, C. D., Thomas, C. R., Journal of American Chemical Society, (1933), 55, 275-276

7. Paul, R., Tchelitcheff, S., Bull. Soc. Chim. France, (1947), 453-4.

8. Hagemeyer, H. J., United States Patent, (1949), 2466420.

9. Hagemeyer, H. J., United States Patent, (1949), 2469110.

10. Van Reijendam, C., Janssen, W., Matthijs, D., Tetrahedron, (1970), 26, 1303-10.

11. Van Reijendam, C., Heres, M., Janssen, W., Matthijs, D., Tetrahedron, (1970), 26, 1291-301.

12. Davidson, Elix., Australian Journal of Chemistry, (1973), 26, 1059-67.

13. Kozhevnikov, I. V., Yemel, T. I., Matveyev, K. I., Rudakov, E. S., Russian Patent, (1977), 2183177/04.

14. Delmas, M., Le Bigot, Y., Gaset, A., Tetrahedron Letter, (1980), 21, 4831-5.

15. Delmas, M., Le Bigot, Y., Gaset, A., United States Patent, (1982), 285-488.

16. Arekion, J., Delmas, M., Gaset, A., Biomass, (1983), 3, 59-65.

17. Rodriguez, V., Aguiar, D., Monterro, C., Spanish Patent, (1977), 91/174636.

18. Ozhemilev, W., Cribaidullin, K., Yu Tolstikov, P., Russian Patent, (1976), 84/179947.

19. Klimenko, D., Sitkin, S., Fridman, K., Nikolaeva, D., Russian Patent, (1974), 87/39207.

20. Drobnica, S., Folia Microbiology, (1980), 25, 467-75.

21. Drobnica, S., Kavac, V., Neoplasma, (1981), 28, 281-9.

22. Davidson, V., Elix. C., Australian Journal of Chemistry, (1973), 26, 1059-69.

23. Gubardullin, L. Yu., Russian Patent, (1975), 85/77968).

24. Nolana, L., Journal of Organic Chemistry, (1983), 48, 2488-91.

25. Paul, R., Bull Soc. Chim., (1943), 10, 163-8.

26. Lukevics, V., Russian Patent, (1965), 64/3584.

27. Nefedov, S., Russian Patent, (1980), 93/7141.

28. Ozhemilev, W., Gubaidullin, K., Tolstikov, P., Ser Khim, (1976), 2124.

29. Yu Yur'eu, K., Russian Patent, (1965), 67/32532.

30. Yu Yur'eu, K., Russian Patent, (1965), 63/11471.

31. Paul, L., United States Patent, (1949), 2462345.

32. Carraher, C. E., Sperling, L. H., Polymer Science and Technology, (1983), 7, 462.

33. Aso, K., Japanese Patent, (1967), 68/22275.

34. Gandini, A., Hernandez, C., Polymer Bulletin, (1978) 1, 221.

35. Kuwati, K., Kawazura, H., Hirota, K., Nippon Kajaku Zasshi, (1960), 81, 1770.

36. Bock, W., United States Patent, (1939), 2, 442-283.

37. Farbenind, B., French Patent, (1938), 830122.

38. Imperial Chemical Limited, United Kingdom Patent, (1929), 349, 442.

39. Farbenindustrie Aktiengesellschaft, German Patent, (1937), 487, 604.

40. Du Pont, E. I., de Nemours and Company, English Patent, 2, 401, 769.

41. Smidt, J., Hafner, W., Jira, R., Sedlmeier, J., Sieber, R., Ruttinger, R., Roger, H., Agnew Chemistry, (1959), 71, 5, 176.

42. Fujiwara, Y., Tetrahedron Letter, (1967), 24, 4819.

43. Fujiwara, Y., Tetrahedron Letter, (1968), 5, 633-635.

44. Heck, R. F., Journal of American Chemical Society, (1968), 90, 5518-5535.

45. Monsanto Company, United States Patent, (1974), 3, 848, 010.

46. Kozhevnikov, I. V., Reaction Kinetics Catalyst Letter, (1976), 5, 439-443.

47. Fujiwara, Y., Journal of American Chemical Society, (1969), 91, 7166-7167.

48. Fujiwara, Y., Tetrahedron Letter, (1968), 35, 3863-3865.

49. Takaki, U., European Patent, (1987), 0242072.

50. Streitwieser, A., Heathcock, C H., Introduction to Organic Chemistry, (1981), 2nd edition, 54, McMillan Publishers.

51. Fujiwara, Y., Tetrahedron Letter, (1969), 25, 4819 - 4823.

52. Fujiwara Y., Moritam I., Bulletin of the Chemical Society of Japan (1970), 43, 863.

53. Professor M Delmas L' Institut National Polytechnique de Toulouse.

54. Kirk-Othmer Encyclopedia of Chemical Technology, (1984), 11, 499. John Wiley.

55. Fujiwara, Y., Tetrahedron Letter, (1969), 25, 4817.

56. Cox, J. D., Pilcher, G., Thermochemistry of Organic and Organometallic

Compounds, (1970), Academic Press.

57. Quagliano, J. V., Vallarino, L. M., Chemistry, (1969), 3rd edition, 581, Prentice Hall.

58. Reichardt, C., Solvents and Solvent Effects in Organic Chemistry, (1988), 2nd Ed. (R), 5-276.

APPENDIX 1

METHOD USED TO CALCULATE SLOPE OF A STRAIGHT LINE

The data was used from table 3.2 (a) (83) and 3.2 (b) (84)

The 6 pairs of values $(x_1 ; y_1)$, $(x_2 ; y_2)$ ... $(x_6 ; y_6)$ was represented by $y = mx + c$,

and the relationship between them was represented by the following equations:

$$m = \frac{n\sum xy - \sum x\sum y}{n\sum x^2 - (\sum x)^2} \qquad \text{...(1)}$$

$$c = \frac{\sum x^2\sum y = \sum x\sum xy}{n\sum x^2 - (\sum x)^2} \qquad \text{...(2)}$$

n = number of ordered pairs.

The correlation, or the degree of relationship between variables $(x_1 ; y_1)$ ... $(x_6 ; y_6)$ was used to determine how well the linear equation described the relationship between the variables. The measure of the correlation was given by the correlation coefficient

$$r = \frac{n\sum xy - \sum x\sum y}{\sqrt{[n\sum x^2 - (\sum x)^2]\,[n\sum y^2 - (\sum y)^2]}} \qquad \text{.................} (3)$$

substitution of the x and y variables into equations (1) and (3), gave the following values :

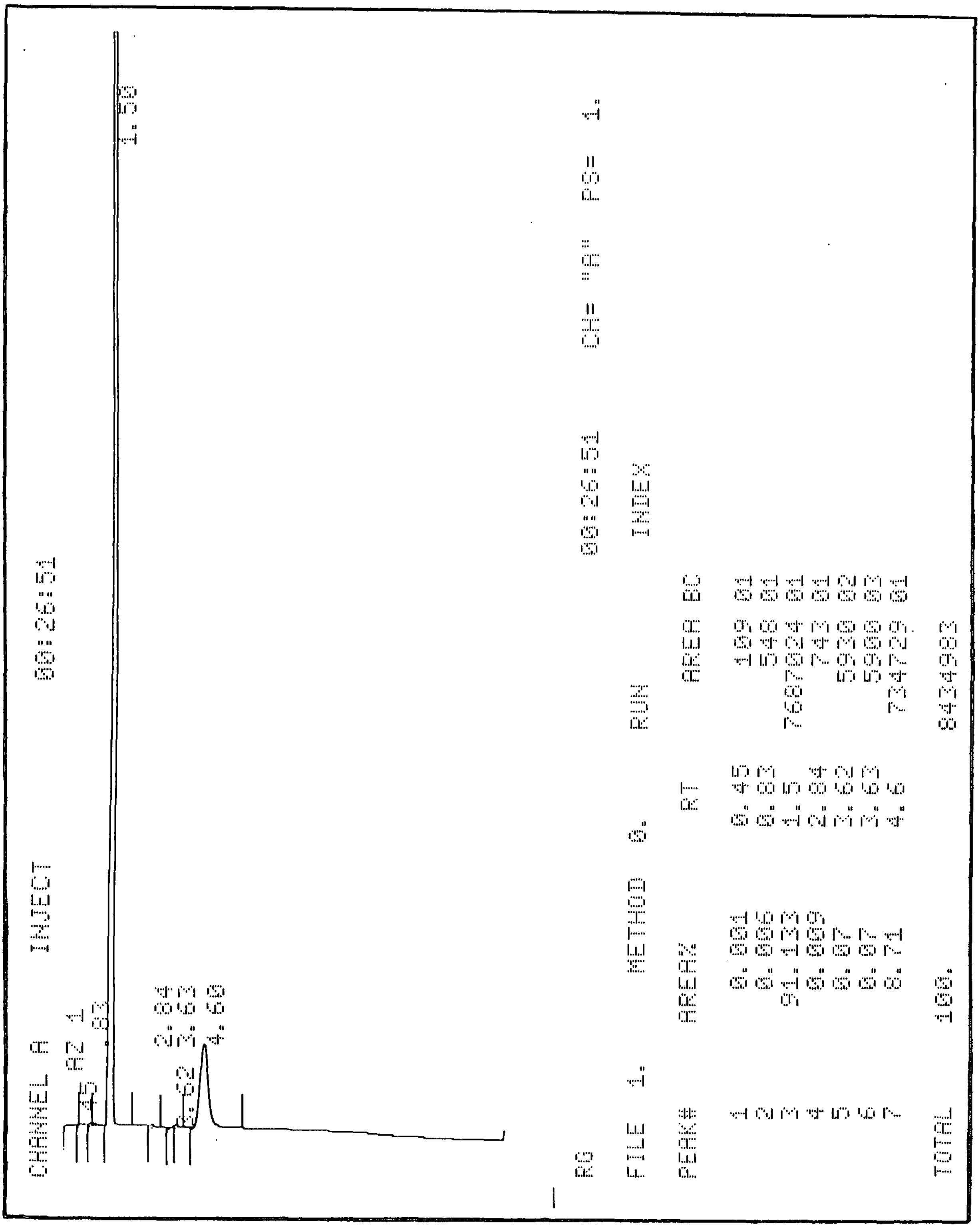
- $m = 5{,}8073 \times 10^{-6}$

and $r = 0{,}993$

The correlation coefficient of 0,993 represented a good linear correlation between the X(area) and Y(% 2-vinylfuran) variables.

- $m = 4{,}0447 \times 10^{-4}$

APPENDIX 2



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FILE  1.      METHOD  0.      RUN          INDEX

PEAK#      AREA%         RT       AREA BC

    1        0.001      0.45       109 01
    2        0.006      0.83       548 01
    3       91.133      1.5    7687024 01
    4        0.009      2.84       743 01
    5        0.07       3.62      5930 02
    6        0.07       3.63      5900 03
    7        8.71       4.6     734729 01

TOTAL      100.                8434983
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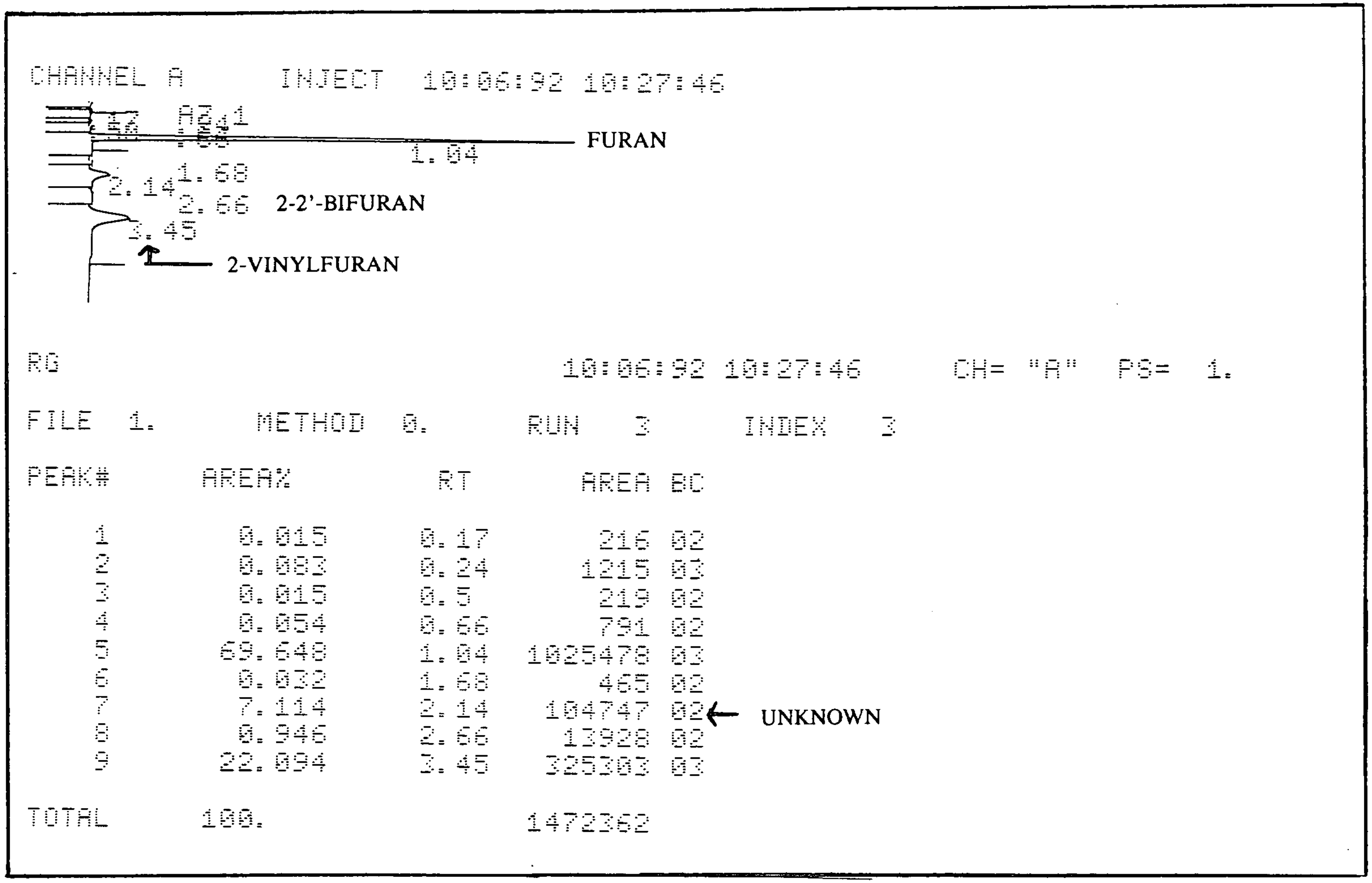
TYPICAL CHROMATOGRAM OF PRODUCTS OBTAINED FROM HETEROGENEOUS CATALYSIS.



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RG                              10:06:92 10:27:46     CH= "A"   PS=  1.

FILE  1.       METHOD  0.       RUN   3      INDEX   3

PEAK#       AREA%         RT        AREA BC

    1        0.015       0.17        216 02
    2        0.083       0.24       1215 03
    3        0.015       0.5         219 02
    4        0.054       0.66        791 02
    5       69.648       1.04    1025478 03
    6        0.032       1.68        465 02
    7        7.114       2.14     104747 02
    8        0.946       2.66      13928 02
    9       22.094       3.45     325303 03

TOTAL      100.                  1472362
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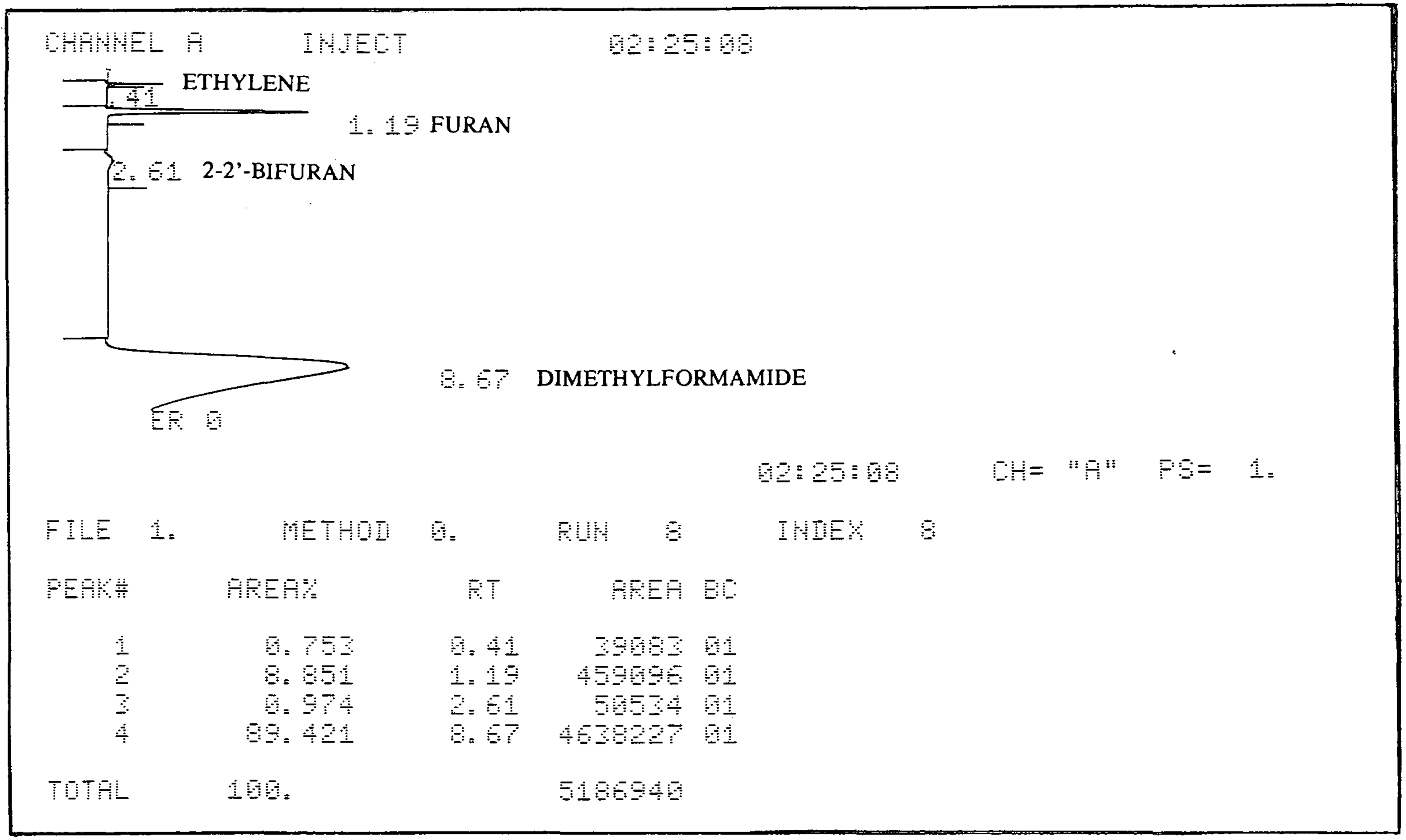
TYPICAL CHROMATOGRAM OF VINYLFURAN

APPENDIX 4



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                                   02:25:08     CH= "A"   PS=  1.

FILE  1.      METHOD  0.      RUN   8      INDEX   8

PEAK#      AREA%          RT       AREA BC

    1        0.753      0.41     39083 01
    2        8.851      1.19    459096 01
    3        0.974      2.61     50534 01
    4       89.421      8.67   4638227 01

TOTAL      100.                5186940
```

TYPICAL CHROMATOGRAM OF BIFURAN

APPENDIX 5

GAS CHROMATOGRAPHY INSTRUMENT PARAMETERS

1. Injector Temperature = 220° C

2. Column Temperature = 220° C

3. Detector FID

3.1 Temperatures 250° C

3.2 Attenuation 10

3.3 Range 10

4. Column :

Chomosorb 102 - Mesh = 80/100

Length = 2m S/S OD = 2 mm ID = 2 mm

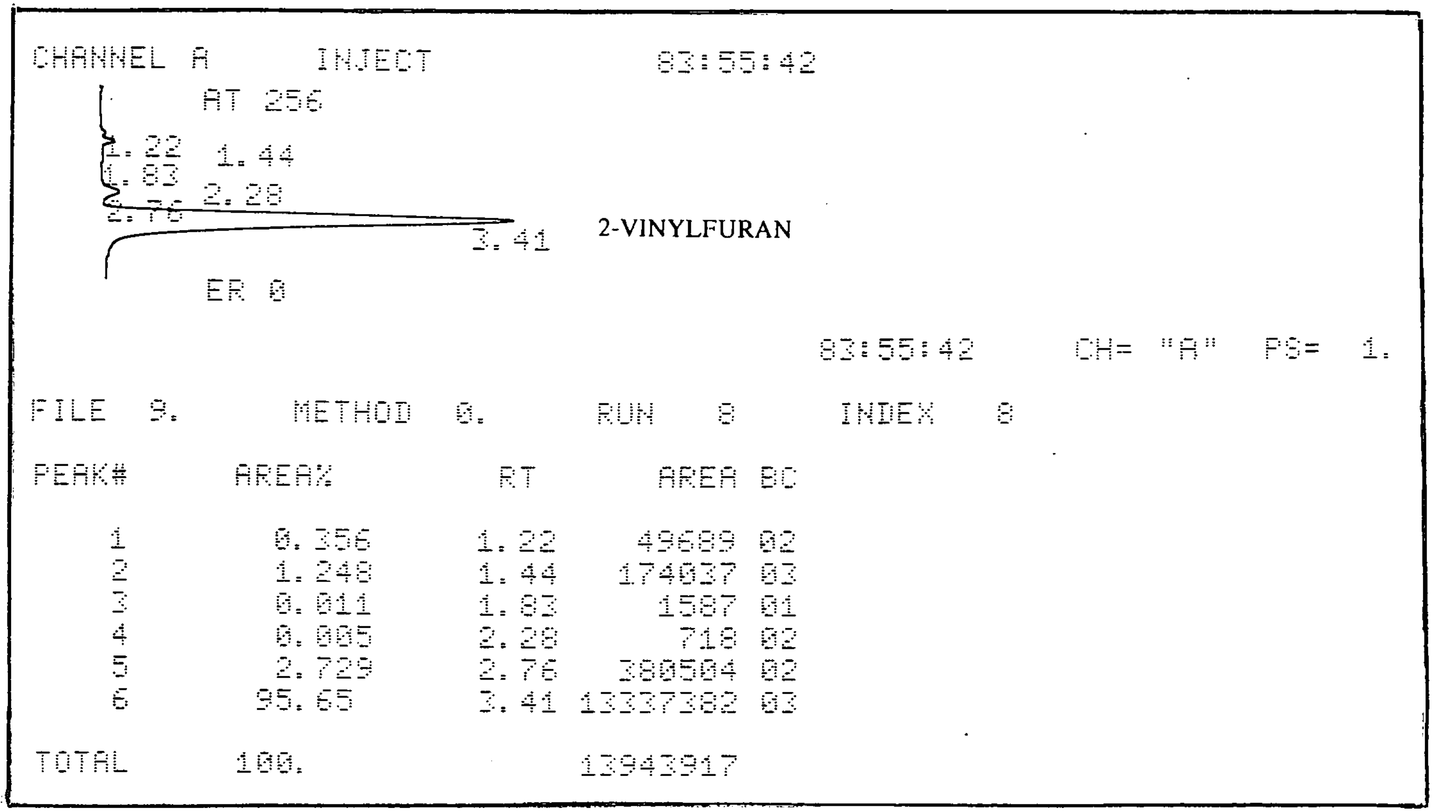
Max. Temp = 250° C

5. Gas Flow :

5.1 Nitrogen 20 mℓ/min

5.2 Hydrogen 30 mℓ/min

5.3 Air 300 mℓ/min



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  1.22  1.44
  1.83  2.28
  2.76
                      3.41  2-VINYLFURAN
           ER 0

                                         83:55:42     CH= "A"   PS=  1.

FILE  9.      METHOD  0.      RUN   8      INDEX   8

PEAK#      AREA%         RT       AREA BC

    1        0.356      1.22     49689 02
    2        1.248      1.44    174037 03
    3        0.011      1.83      1587 01
    4        0.005      2.28       718 02
    5        2.729      2.76    380504 02
    6       95.65       3.41  13337382 03

TOTAL      100.                13943917
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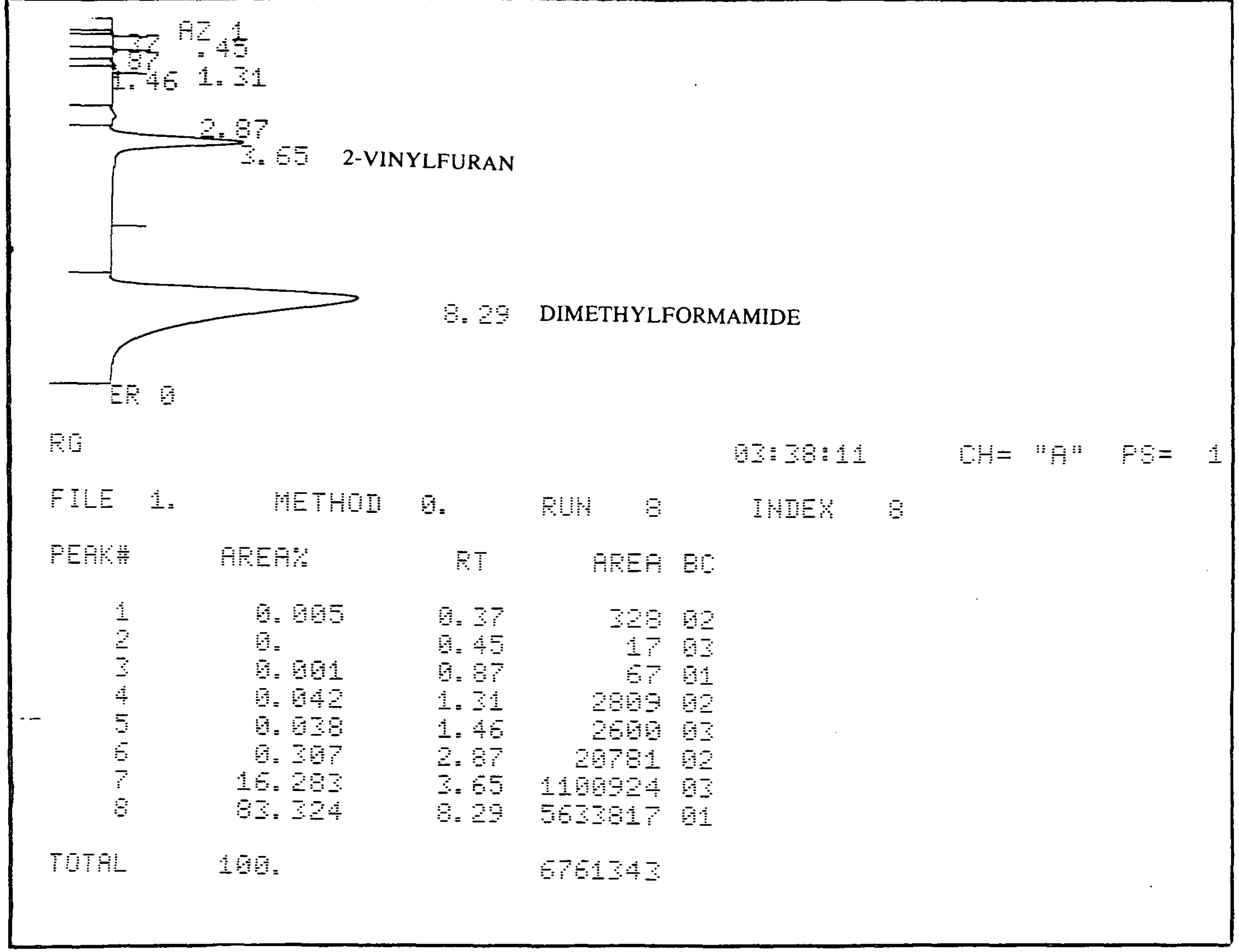
TYPICAL CHROMATOGRAM OF STANDARD 2-VINYLFURAN SAMPLE(NEAT)

APPENDIX 7



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RG                                          03:38:11     CH= "A"   PS=  1

FILE  1.       METHOD  0.      RUN   8     INDEX   8

PEAK#      AREA%         RT       AREA  BC

   1        0.005        0.37       328  02
   2        0.           0.45        17  03
   3        0.001        0.87        67  01
   4        0.042        1.31      2809  02
   5        0.038        1.46      2600  03
   6        0.307        2.87     20781  02
   7       16.283        3.65   1100924  03
   8       83.324        8.29   5633817  01

TOTAL     100.                  6761343
```
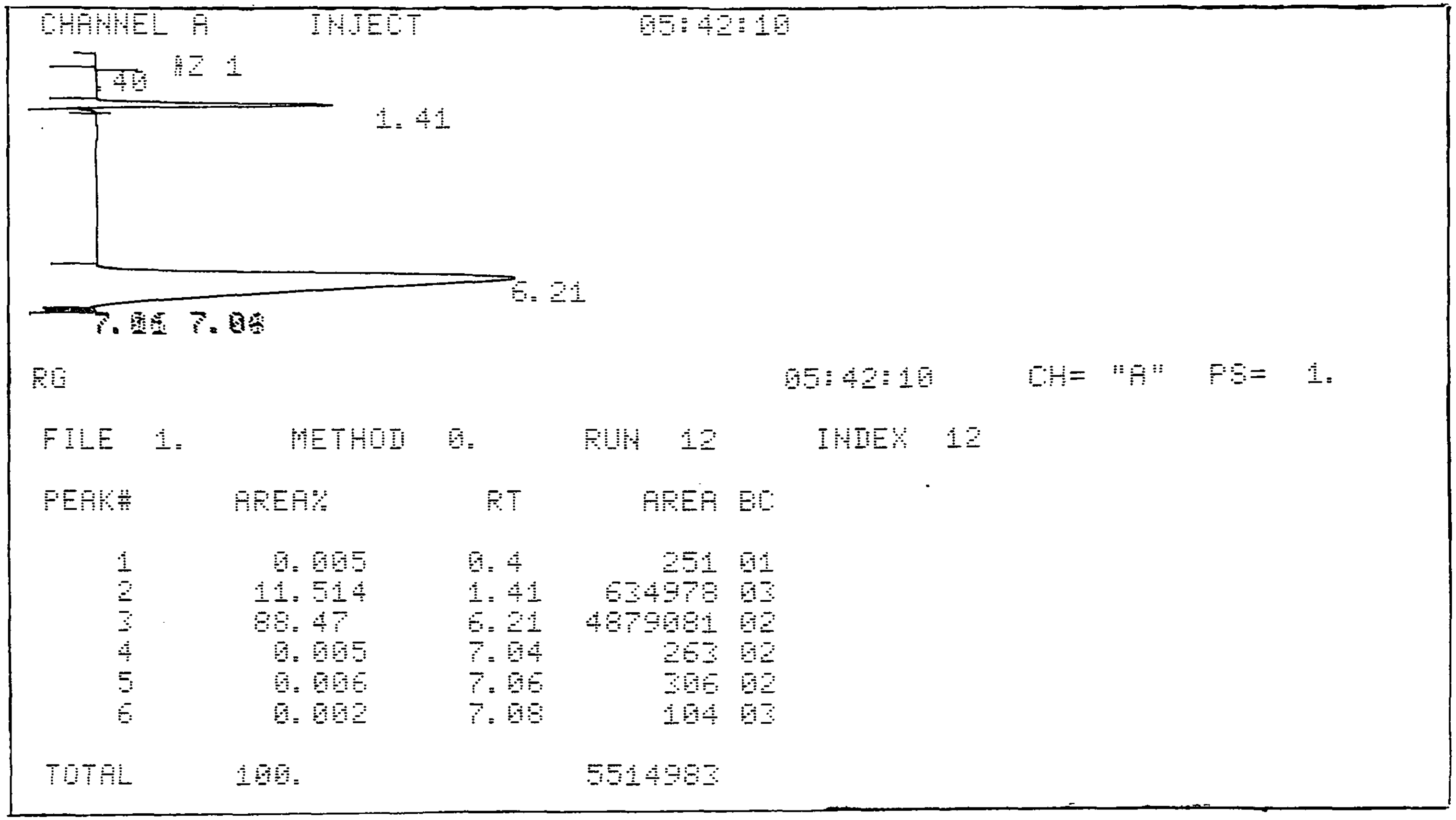
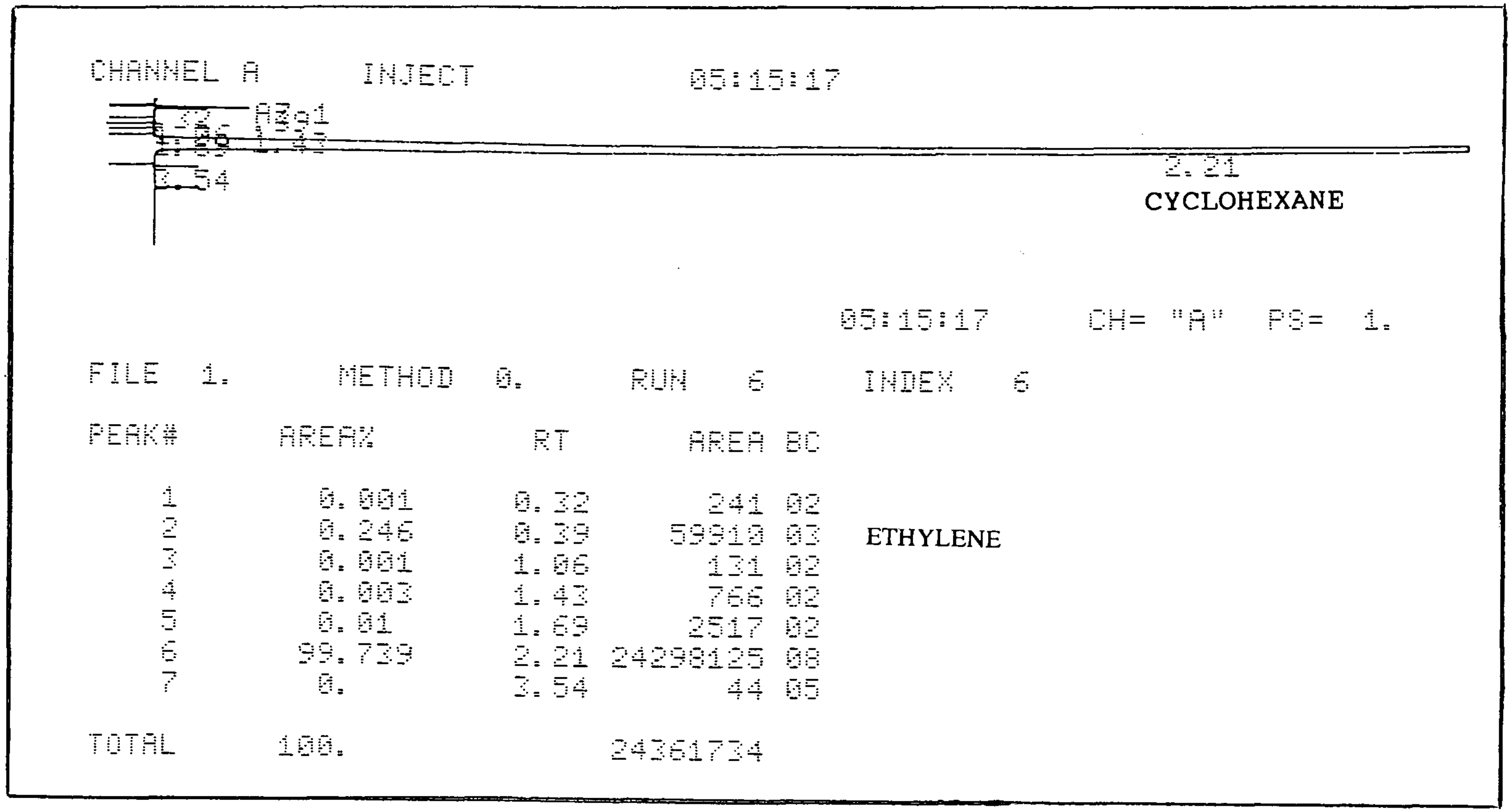

TYPICAL CHROMATOGRAM OF A STANDARD SOLUTION OF 2-VINYLFURAN IN DIMETHYLFORMAMIDE.

APPENDIX 8



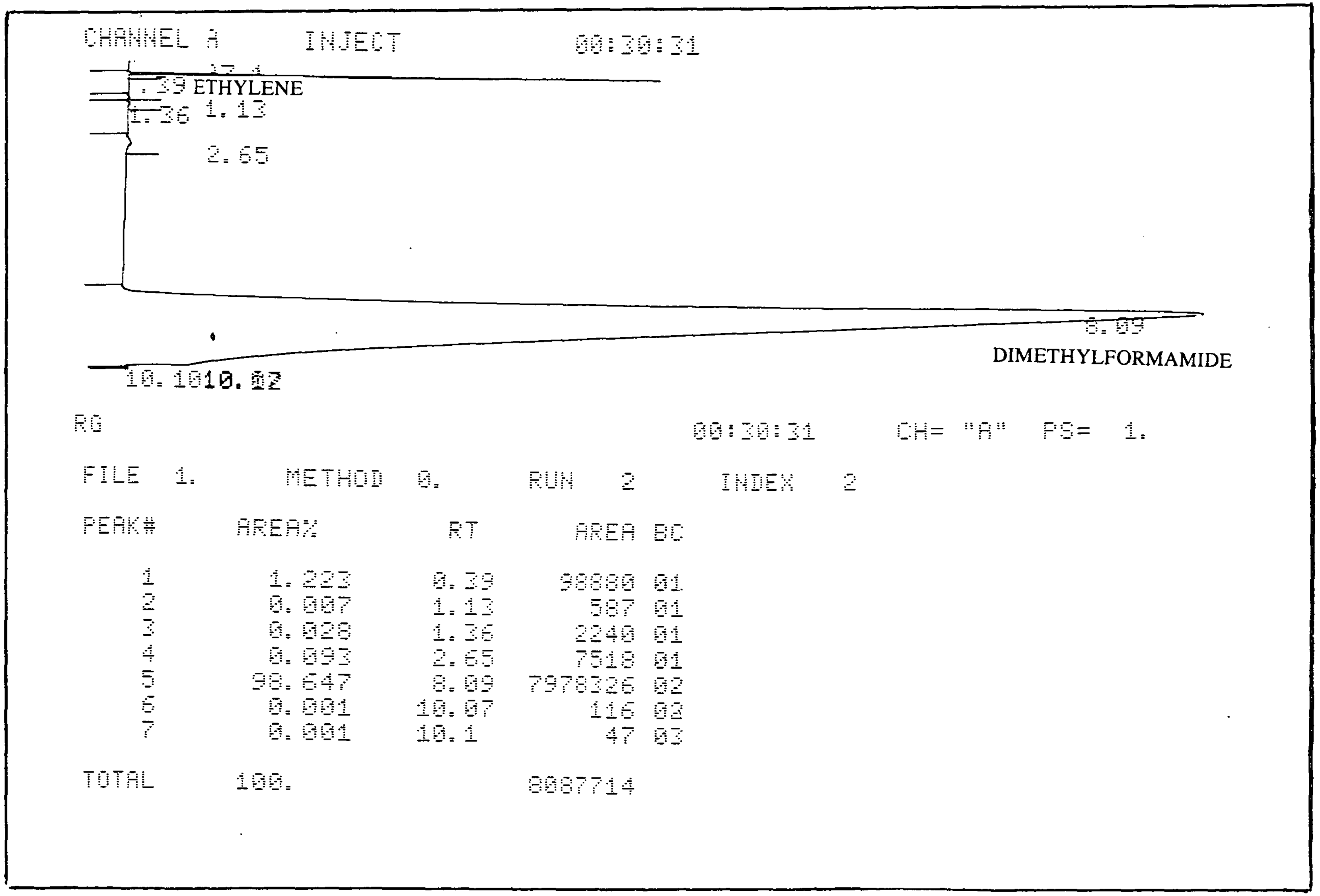
```
CHANNEL A     INJECT               05:42:10

RG                                               05:42:10     CH= "A"   PS=  1.

FILE  1.      METHOD  0.      RUN  12      INDEX  12

PEAK#      AREA%         RT        AREA BC

    1        0.005      0.4         251 01
    2       11.514      1.41     634978 03
    3       88.47       6.21    4879081 02
    4        0.005      7.04        263 02
    5        0.006      7.06        306 02
    6        0.002      7.08        104 03

TOTAL      100.                 5514983
```

TYPICAL CHROMATOGRAM OF A STANDARD SOLUTION OF FURAN IN DIMETHYLFORMAMIDE



```
                                     05:15:17     CH= "A"  PS=  1.
FILE  1.     METHOD  0.     RUN   6     INDEX   6

PEAK#     AREA%        RT       AREA BC

   1       0.001      0.32       241 02
   2       0.246      0.39     59910 03    ETHYLENE
   3       0.001      1.06       131 02
   4       0.003      1.43       766 02
   5       0.01       1.69      2517 02
   6      99.739      2.21  24298125 08
   7       0.         3.54        44 05

TOTAL     100.              24361734
```

TYPICAL CHROMATOGRAM SHOWING SOLUBILITY OF ETHYLENE IN CYCLOHEXANE AT ROOM TEMPERATURE (25°C)



```
CHANNEL A        INJECT          00:30:31

RG                                     00:30:31      CH= "A"   PS=  1.

FILE  1.        METHOD  0.        RUN   2       INDEX   2

PEAK#       AREA%          RT         AREA BC

    1        1.223       0.39       98880 01
    2        0.007       1.13         587 01
    3        0.028       1.36        2240 01
    4        0.093       2.65        7518 01
    5       98.647       8.09     7978326 02
    6        0.001      10.07         116 02
    7        0.001      10.1           47 03

TOTAL       100.                  8087714
```

TYPICAL CHROMATOGRAM SHOWING SOLUBILITY OF ETHYLENE IN DIMETHYLFORMAMIDE

APPENDIX 11

CALCULATING FLOW RATES

TYPICAL EXAMPLE

$$\text{moles } Pd(OAc)_2 = \frac{5{,}004}{224{,}4} = 2{,}23 \times 10^{-2}$$

$$= \text{moles ethylene}$$

$$pV = nRT \quad \text{.........(ideal gas equation)}$$

$$v = \frac{2{,}23\times10^{-2} \times 8{,}314 \times 353}{101300}$$

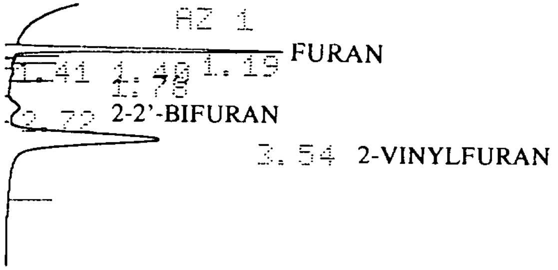
$$= 6{,}46 \times 10^{-4}\ m^3$$

$$= 646\ cm^3$$

$$= 646\ m\ell \text{ in 120 minutes}$$

$$= 5{,}38\ m\ell/min$$

```
CHANNEL A     INJECT          00:04:09
```



```
                                      00:04:09     CH= "A"  PS=  1.

FILE  1.      METHOD  0.      RUN   2      INDEX   2

PEAK#      AREA%        RT      AREA BC

    1      30.219      1.19   141140 01
    2       0.029      1.4       137 02
    3       0.074      1.41      345 03
    4       0.332      1.78     1550 01
    5       4.061      2.72    18968 02
    6      65.285      3.54   304916 03

TOTAL     100.                467056
```

CHROMATOGRAM OF VINYLFURAN SHOWING OPTIMUM YIELD