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# HYDRO-AMINATION OF LOW ALCOHOLS

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# Dedication

To the memory of my father, to my mother,

To my wife and my sons.

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I would like to thank the University Eduardo Mondlane for providing me with the opportunity and financial support to proceed with my postgraduate studies and specially to Dr. Gabriel Amós, Dean of the Faculty of Engineering for the important role he played when in his capacity of Chief of Reactor, Energy and Environment Section, encouraged me to get involved in this field and for making possible to get this project financed.

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# Synopsis

The conversion of basic and renewable organic materials into valuable chemical products via simple processes is essential for generation of economic wealth. Value can be added to low value basic chemical materials produced in large quantities by converting them into speciality chemicals.

The present study is an example. By-products of sugar industry, namely molasses and bagasses, can be used as a feedstock to produce valuable chemicals. By fermentation, molasses can be converted into a variety of organic compounds including ethanol, and other alcohols, lactic, glutamic and citric acids, glycerol and some antibiotics. Hydro-amination of low alcohols ($C_2$-$C_4$) over $Co/SiO_2$ catalysts yielding amines, has been selected as an option to add value to these materials. This process involves reaction of alcohol with ammonia at temperatures ranging from 150 to 210°C and pressures of 18 to 200 bar in presence of hydrogen. Amines are of considerable industrial importance and find a huge application in almost every field of modern technology, agriculture and medicine, as intermediates and end products. Their commercial value is higher than that of sugar.

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A number of general mechanisms for the amination of alcohols over metal catalysts have been proposed, but the mechanism is still under discussion with some steps and/or intermediates not being conclusively proven. Most proposed mechanisms in literature assume the consecutive formation of the higher substituted amines.

Recently, Freese observed the primary formation of di- and tri-ethylamine in the ethanol amination. In the light of these observations a new mechanism was propsed. The mechanism predicts a crucial role of hydrogen on the amines distribution. Hydrogen shifts the equilibrium on the ammonia activation step. Hence, according to this mechanism it was expected that with increasing partial pressure of hydrogen, the mono-ethylamine (MEA) content in the fraction of ethylamines would increase.

In this study hydro-amination of ethanol was performed at hydrogen partial pressures of 0; 1; 5; 10; 30; and 60 bar at loading temperature (20°C), to investigate the role of hydrogen on the activity and selectivity of this reaction. All reactions were carried out in a batch reactor in liquid phase at 200°C over $Co/SiO_2$ catalyst prepared by incipient wetness impregnation. Loadings of 10 g of catalyst were used. Due to experimental impracticability of collecting reaction data at very low reaction times, 1 g of catalyst loads were also applied and the reaction time was normalised to 10 g catalyst.

Thermodynamic calculations indicated that under the conditions applied, the hydro-amination of the considered alcohols is not equilibrium limited. Overall equilibrium conversions of around 99% should be obtained, whereas the observed maximum conversions did not exceed 60% due to loss of material in sampling and catalyst deactivaction.

The experimental results showed that hydrogen does influence ethanol hydro-amination. At high ethanol and ammonia concentrations, the experiment carried out with hydrogen pressure of 10 bar showed the highest ethanol and ammonia conversion as well as highest yield of MEA and di-ethylamine (DEA). The results were in accordance with observation by Sewell (1996), showing the sequence formation of amines. The reactions yielded the same products when performed with or in absolute absence of hydrogen, contradicting predictions by Baiker (1983).

The influence of carbon number in alcohol chain as well as OH group position is also investigated. This has been done by comparing results of amination of ethanol, *n*-propanol and *n*-butanol amination as well as *n*-propanol with *i*-propanol amination. Some changes in conversion, selectivity and yield – time profiles in amination of these alcohols were observed. Despite them the results suggest that hydro-amination of ethanol, *n*-propanol, *i*-propanol and *n*-butanol might be explained by the same or similar reaction mechanism.

University of Cape Town

# Table of Contents

**Acknowledgements** ..... i

**Synopsis** ..... ii

**Table of contents** ..... iv

**List of figures** ..... vii

**List of tables** ..... xii

**List of symbols** ..... xiv

**Glossary** ..... xvi

**1. INTRODUCTION** ..... 1

**2. LITERATURE REVIEW** ..... 4

**2.1. The synthesis of alkylamines: general overview** ..... 4

2.1.1. Alcohol amination over metal catalyst ..... 6

**2.2. Thermodynamic equilibrium in amination of alcohols** ..... 8

2.2.1. Ethanol amination ..... 8

2.2.2. n-Propanol, iso-propanol and n-butanol amination ..... 11

**2.3. Catalyst** ..... 13

2.3.1. Effect of support ..... 15

**2.4. Reaction mechanism** ..... 16

**2.5. Influence of reaction parameters** ..... 22

2.5.1. Influence of reaction temperature ..... 22

2.5.2. Ifluence of hydrogen partial pressure ..... 23

University of Cape Town

2.5.3. Influence of reactant molar ratio ..... 25

**2.6. Objective of study ..... 25**

**3. EXPERIMENTAL ..... 26**

**3.1. Catalyst preparation ..... 26**

**3.2. Experimental apparatus and procedures ..... 26**

3.2.1. Catalyst reduction ..... 26

3.2.2. Amination reaction ..... 27

3.2.3. Ssample analysis and products identification ..... 30

**3.3. Experiments performed and conditions ..... 32**

**3.4. Data evaluation ..... 33**

**4. RESULTS ..... 36**

**4.1. External mass transfer limitations ..... 36**

**4.2. Ethanol amination ..... 37**

4.2.1. Influence of hydrogen on ethanol and ammonia conversion ..... 38

4.2.2. Influence of hydrogen on amine selectivity ..... 44

4.2.3. Influence of hydrogen on amines yield ..... 46

**4.3. *normal*-Propanol amination ..... 50**

**4.4. *iso*-Propanol amination ..... 52**

**4.5. *normal*-Butanol amination ..... 53**

**5. DISCUSSION ..... 56**

**5.1. Catalyst activity ..... 56**

**5.2. Sequence of ethylamines products formation ..... 59**

University of Cape Town

**5.3. Influence of hydrogen partial pressure on reaction kinetics and selectivity** ..... **61**

**5.4. Influence of alcohol length on alcohol and ammonia conversion and amines distribution** ..... **64**

**5.5. Influence of OH position on ammonia conversion and amines distribution** ..... **68**

**5.6. Reaction mechanism** ..... **69**

**6. CONCLUSIONS** ..... **70**

**7. REFERENCES** ..... **72**

**APPENDICES**

**Appendix A.I** **Thermodynamic equilibrium in amination of alcohols** ..... **77**

**A.I-1** Steps of calculation ..... 77

**A.I-2** Polymath program for calculation of equilibrium conversion and composition ..... 80

**Appendix A.II** **Catalyst preparation and characterisation** ..... **83**

**A.II–1** Catalyst preparation ..... 83

**A.II–2** Catalyst characterisation ..... 85

**Appendix A.III** **Reaction data for low alcohols hydro-amination** ..... **87**

**A.III-1** Gas-chromatograms ..... 87

**A.III-2** Reaction data and selectivity, yield and conversion calculations ..... 91

**Appendix A.IV** **Standard procedures for reactor operation** ..... **111**

University of Cape Town

# List of Figures


| | | Page |
|---|---|---|
| **Figure 2.1** | Typical amination reactor and separation train (Turcotte and Johnson, 1992) ..... | 6 |
| **Figure 2.2** | Flow sheet for calculation of equilibrium composition in a batch reactor ..... | 9 |
| **Figure 2.3** | Proposed reaction pathway for amination of an aliphatic alcohol by a primary amine (Baiker *et al.*, 1983) ..... | 19 |
| **Figure 2.4** | Amines distribution in a PFR. Conditions: $T_{reaction}$ = 210°C, $P_{reaction}$ = 1.2 bar, Ratio EtOH: $NH_3$: $H_2$: $N_2$ ratio = 1: 3: 6: 34, Gas flow rate = 100 ml (NTP)/min (Adapted from Freese 2002)..... | 20 |
| **Figure 2.5** | New Ethanol Amination Pathway (Freese,, 2001) ..... | 21 |
| **Figure 2.6** | Effect of the reaction temperature on the activity and selectivity of $Cu/SiO_2$ for the amination of dodecanol with dimethylamine (redrawn from Baiker and Richarz, 1977) ..... | 23 |
| **Figure 2.7** | Influence of hydrogen partial pressure on activity and selectivity of $Cu/Al_2O_3$ in the amination of 1-dodecanol with dimethylamine (DMA). Conditions: Fixed-bed reactor. Molar feed ratios (mol/s): 1-dodecanol, 1.9 x $10^{-5}$; DMA, 1.0 x $10^{-4}$; $H_2$ or $N_2$, 1.2 x $10^{-4}$. Catalyst load, 10 g. $T_{reaction}$, 510 K. Total pressure, 100 kPa. (Baiker and Kijenski, 1985)..... | 24 |
| **Figure 3.1** | Schematic illustration of the catalyst reduction rig ..... | 27 |


University of Cape Town

**Figure 3.2** Experimental Apparatus for Amination Reaction – Schematic representation of the Mini Batch Reactor with all peripherals ..... 28

**Figure 3.3** Temperature profile during reactor heating up and cooling down. Conditions: Molar ratio, $H_2$ : EtOH : $NH_3$ = 0 : 1 : 0.5; $T_{reaction}$ = 200°C ..... 29

**Figure 3.4** Sampling System ..... 30

**Figure 4.1** Ethanol conversion as a function of reaction time at four different stirrer speed rate. Reaction Conditions: $T_{reaction}$,: 200°C; $P_{H2}$: 30 bar; molar ratio: $H_2$ : EtOH : $NH_3$ = 0.29 : 1 : 0.5 ..... 36

**Figure 4.2** Ethanol and ammonia conversions as a function of normalised reaction time (normalised with respect to the reaction time for 10 g catalyst). Conditions: $T_{reaction}$: 200°C; $P_{H2}$: 30 bar; $H_2$: EtOH: $NH_3$ = 0.29: 1: 0.5 ..... 37

**Figure 4.3** Amines selectivity as a function of normalised reaction time (normalised with respect to the reaction time for 10 g catalyst). Conditions: $T_{reaction}$: 200°C; $P_{H2}$: 30 bar; $H_2$ : EtOH : $NH_3$ = 0.29: 1: 0.5 ..... 38

**Figure 4.4** Ethanol conversion profile at different hydrogen partial pressures ... 39

**Figure 4.5** Ammonia conversion profile at different hydrogen partial pressures . 40

**Figure 4.6** Ethanol and ammonia conversion profile on ethanol amination carried out with no hydrogen ..... 41

**Figure 4.7** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 1 bar ..... 41

University of Cape Town

**Figure 4.8** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 5 bar ..... 42

**Figure 4.9** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 10 bar ..... 42

**Figure 4.10** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 30 bar ..... 43

**Figure 4.11** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 60 bar ..... 43

**Figure 4.12** Amine selectivity from ethanol hydro-amination in the absence of hydrogen ..... 44

**Figure 4.13** Amine selectivity from ethanol hydro-amination with 1 bar of hydrogen partial pressure ..... 45

**Figure 4.14** Amine selectivity from ethanol hydro-amination carried out with 10 bar of hydrogen partial pressure ..... 45

**Figure 4.15** Amine selectivity from ethanol hydro-amination performed with 60 bar of hydrogen partial pressure ..... 46

**Figure 4.16** Yield of Amines in a Ethanol Amination Reaction performed in absence of hydrogen..... 47

**Figure 4.17** Yield of amines in reaction performed with 1 bar hydrogen ..... 47

**Figure 4.18** Yield of Amines in a Ethanol Amination performed with 5 bar $H_2$ .. 48

**Figure 4.19** Yield of Amines in a Ethanol Amination carried out at 10 bar $H_2$ .... 48

University of Cape Town

**Figure 4.20** Yield of Amines in a Ethanol Amination performed at 30 bar $H_2$ ..... 49

**Figure 4.21** Yield of Amines in a Ethanol Amination performed at 60 bar $H_2$ .... 49

**Figure 4.22** *n*-Propanol and ammonia conversion as a function of reaction time.. $P_{H2}$ = 25 bar ..... 51

**Figure 4.23** Amine Selectivity in *n*-propanol amination. $P_{H2}$ = 25 bar..... 51

**Figure 4.24** *Iso*-Propanol and ammonia conversion in iso-propanol amination. $P_{H2}$ = 25 bar. ..... 52

**Figure 4.25** Amine selectivity in *iso*-propanol amination. $P_{H2}$ = 25 bar ..... 53

**Figure 4.26** *n*-Butanol and ammonia conversion in *n*-butanol amination. $P_{H2}$ = 20 bar. ..... 54

**Figure 4.27** Amine selectivity in *n*-butanol amination. $P_{H2}$ = 20 bar. ..... 55

**Figure 5.1** Ethanol and ammonia conversion as a function of hydrogen partial pressure at 0.1 hr (first data points). Mass of catalyst: 1 g ..... 57

**Figure 5.2** Ethanol and ammonia conversion as a function of hydrogen partial pressure at 1.0 hr (first data points). Mass of catalyst: 10 g ..... 58

**Figure 5.3** Sequence of product formation in ethanol hydro-amination. Ratio MEA/(MEA+DEA+TEA) selectivity as function of reaction time .... 60

**Figure 5.4** Sequence of product formation in ethanol hydro-amination. Ratio DEA/(DEA+TEA) selectivity as function of reaction time ..... 60

**Figure 5.5** Yield of amines as a function of hydrogen partial pressure at 0.1 hr. Mass of catalyst: 1 g..... 62

University of Cape Town

**Figure 5.6** Yield of amines as a function of hydrogen partial pressure at 1.0 hrs. Mass of catalyst: 10 g ..... 63

**Figure 5.7** Alcohol conversion as a function of reaction time. Conditions: Molar ratio, *n*-ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{reaction}$, 200°C; $P_{H2,EtOH}$ = 30 bar, $P_{H2,n\text{-}PrOH}$ = 25 bar and $P_{H2,n\text{-}BuOH}$ = 20 bar ..... 65

**Figure 5.8** Ammonia conversion in n-alcohols amination as a function of reaction time. Conditions: Molar ratio, *n*-ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{reaction}$, 200°C; $P_{H2,EtOH}$ = 30 bar, $P_{H2,n\text{-}PrOH}$ = 25 bar and $P_{H2,n\text{-}BuOH}$ = 20 bar..... 65

**Figure 5.9** Mono-amine selectivity-time profile in *n*-alcohols amination ..... 66

**Figure 5.10** Di-amine selectivity-time profile in *n*-alcohol amination ..... 66

**Figure 5.11** Tri-amine selectivity-time profile in *n*-alcohol amination ..... 67

**Figure 5.12** *n*-Propanol and *iso*-propanol conversion as a function of reaction time. Conditions: Molar ratio ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{recation}$, 200°C; $P_{H2,n\text{-}PrOH}$ = $P_{H2,i\text{-}PrOH}$ = 25 bar ..... 68

**Figure 5.13** Ammonia conversion in *n*-Propanol and *iso*-propanol amination as a function of reaction time. Conditions: Molar ratio ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{recation}$, 200°C; $P_{H2,n\text{-}PrOH}$ = $P_{H2,i\text{-}PrOH}$ = 25 bar ..... 69

University of Cape Town

# List of Tables


| | | Page |
|---|---|---|
| **Table 1.1** | Average sucrose losses as a percentage of sucrose entering the factory (http://www.sugartech.co.za/sucroselosses/index.php3, 2002) ..... | 2 |
| **Table 1.2** | Prices of some common amines (Turcotte and Johnson, 1992) ..... | 3 |
| **Table 2.1** | Processes for manufacturing lower alkylamines (Hayes, 2001)..... | 6 |
| **Table 2.2** | Equilibrium constant of ethanol hydro-amination at three different temperatures ..... | 8 |
| **Table 2.3** | Equilibrium conversion and composition for ethanol amination ..... | 10 |
| **Table 2.4** | Reaction conditions and equilibrium constants for *n*-Propanl, *iso*-propanol and *n*-butanol amination ..... | 11 |
| **Table 2.5** | Equilibrium conversion and composition for *n*-Propanl, *iso*-propanol and *n*-butanol amination at 473 K ..... | 12 |
| **Table 3.1** | Gas Chromatographic conditions for separation of amines ..... | 31 |
| **Table 3.2** | GC-MS characteristics and conditions ..... | 31 |
| **Table 3.3** | Synoptical Table of Performed Experiments and Conditions ..... | 33 |
| **Table 3.4** | Stoichiometric Table ..... | 35 |
| **Table 4.1** | Maximums of ammonia conversion as a function of hydrogen pressure | 51 |


University of Cape Town

**Table 5.1** Estimated fugacities based on the Peng-Robinson equation of the state ($k_{ij}$ = 0) and the pressure in the reactor at 200°C at the start of the reaction ..... 59

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# List of Symbols

| Symbol | Description | Units |
|---|---|---|
| $a_i$ | Activity of component i | - |
| $\gamma_i^L$ | Activity coefficient of component i | bar |
| CN | Carbon number | - |
| $f_i$, $\Phi_i^V$ | Fugacity coefficient of component i | bar |
| $\bar{f}_i^L$ , $\bar{f}_i^V$ | Fugacity of component i in liquid and vapor phase | |
| $\Delta G_i$ | Gibbs free energy for reaction i | J/mol |
| $K_{ai}$ | Equilibrium constant of reaction i | - |
| $N_i$ | Number of moles of component i | moles |
| $N^L_i$ | Number of moles of component i in liquid phase | moles |
| $N^L$ | Total number of moles in liquid phase | moles |
| $N^V_i$ | Number of moles of component i in vapor phase | moles |
| $N^V$ | Total number of moles in vapor phase | moles |
| P | Total pressure | bar or kPa |
| $P_i$ | Partial pressure for component i | bar or kPa |

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| | | |
|---|---|---|
| $P_i^{VAP}$ | Vapor pressure of component i | bar or kPa |
| **R** | Gas constant | 8.314 J/mol.K |
| **RF** | Response factor | - |
| **RT** | Retention time | min. |
| **T** | Temperature | K |
| $\mathbf{V^L}$ | Volume of Liquid | ml |
| $\mathbf{x_i}$ | Molar fraction of component i in liquid phase | - |
| **Xi** | Conversion of component i | mol-% or C-% |
| $\mathbf{y_i}$ | Molar fraction of component i in vapor phase | - |
| $\mathbf{Y_i}$ | Yield of component i | C-% |
| $\xi$ | Initial number of moles of $NH_3$ per mole of EtOH | - |

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# Glossary

| | |
|---|---|
| AAS | Atomic Absorption Spectroscopy |
| n-BuOH | Normal-butanol |
| DBA | Di-butylamine |
| DEA | Di-ethylamine |
| DMA | Di-methylamine |
| DIPA | Di-iso-propyalmine |
| DPA | Di-propylamine |
| EtOH | Ethanol |
| GC | Gas-Chromatograph |
| GC-MS | Gas-Chromatograph – Mass Spectroscopy |
| MBA | Mono-butyalmine |
| MEA | Mono-ethylamine |
| MPA | Mono-propylamine |
| MIPA | Mono-iso-propylamine |
| NTP | Normal Temperature and Pressure |
| i-PrOH | Iso-propanol |
| n-PrOH | Normal-propanol |
| TBA | Tri-butylamine |
| TEA | Tri-ethylamine |
| TPA | Tri-propylamine |
| TIPA | Tri-iso-propylamine |
| $RNH_2$ | Mono-alkylamine |
| $R_2NH$ | Di-alkylamine |
| $R_3N$ | Tri-alkylamine |

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| | |
|---|---|
| ROH | Alcohol |
| WHSV | Weight Hourly Space Velocity |

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# 1. INTRODUCTION

The goal of the present study is the amination of alcohols yielding amines. This represents a conversion of basic renewable materials into valuable chemical products using a simple, competitive method. The envisaged raw material is a by-product of the sugar production, namely molasses.

More than 100 countries produce sugar, approximately 72% of which is produced from sugar cane growing primarily in the tropical and sub-tropical zones of the southern hemisphere (http://www.illovosugar.com, 2002). The balance is produced from sugar beet. Sugar production for the 2000/1 season is estimated to be 128 million tons.

Sugar cane has been grown and milled in the South African region. Excellent growing conditions, high yielding cane varieties and relatively low milling costs combined make the Southern African Development Community one of the world's largest sugar producing with an average annual production of 3.8 million tons (http://www.illovosugar.com, 2002).

The sugar manufacture from cane, which contains above 99% sucrose (white sugar) involves several steps (Clarke, 1992): cane preparation (weighing, cutting into small pieces), juice extraction, clarification, evaporation, crystallisation, crystal sugar formation and packing. The extraction and crystallisation processes are not efficient enough to remove all sucrose from the cane juice. An average of about 14.5% of sucrose is lost mainly in molasses and bagasse (see Table 1.1). These loss data correspond to the industry average figure from South African factories (http://www.sugartech.co.za/sucroselosses/index.php3, 2002).

Molasses is the mother liquor separated from massecuite (the mixture of crystals and mother liquor) by centrifugation. Bagasse is the residue obtained after crushing cane.

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**Table 1.1** Average sucrose losses as a percentage of sucrose entering the factory (http://www.sugartech.co.za/sucroselosses/index.php3, 2002)

| By-product | Molasses | Bagasse | Filter cake | Undetermined | Total |
|---|---|---|---|---|---|
| Sucrose losses, wt-% | 10.05 | 2.26 | 0.25 | 2.00 | 14.56 |

Due to its potential economic value, many techniques to recover the remaining sucrose from molasses are actually employed. Typically, molasses contains ca. 27.0 % sucrose (Chen and Chou, 1993). Molasses is world-wide used as a fermentation feedstock for production of a variety of other organic compounds including ethanol, and other alcohols, lactic, glutamic and citric acids, glycerol and some antibiotics. Lesser amounts of itaconic aconitic and kojic acids, as well as acetone are also produced (Colonna and Samaraweera, 1992). Different products in this range can be obtained by changing the conditions of the fermentation process (selection of the suitable organism, preparation of the raw material and the inoculum, conduct of microbial action). For instance, Illovo Sugar (in KwaZulu Natal) manufactures a diverse range of downstream valued products from molasses, like furfural, furfuryl alcohol, diacetyl, acetoin and 2,3-pentanedione (http://www.illovosugar.com, 2002).

The present study is considering another alternative of getting high value from sugar by-products. Products obtained from specific molasses fermentation, e.g. alcohols can be used for conversion with ammonia yielding amines. Among various alternative methods of producing amines the hydro-amination of alcohols over metal catalysts has been chosen, since it has been referred as the most important (Turcotte and Johnson, 1992). This process involves reaction of alcohol with ammonia over a supported metal catalyst, typically nickel or cobalt on silica or alumina at temperatures ranging from 150 to 210°C and pressures of 18 to 200 bar (Hayes, 2001). The reaction is conducted in presence of hydrogen to maintain catalyst activity (Baiker and Kijensky, 1984).

Amines are of considerable industrial importance and find application in almost every field of modern technology, agriculture and medicine (Turcotte and Johnson, 1992). Aliphatic amines are important intermediates for the chemical (intermediates and end

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products) and pharmaceutical industries. A large number of drugs, herbicides, pesticides, dyes adjuvants, corrosion inhibitors, fungicides, softening agents for fabrics, rubber, plastic and other chemicals contain amino groups which originate from reactions with such intermediates. More than 90 different products are made on alkylamines basis (primary, secondary and tertiary). Amines are toxic, colourless gases and liquids, highly flammable and have strong odour. Prices of some commonly commercialised and widely applied amines are given in the Table 1.2.

**Table 1.2** Prices of some common amines (Turcotte and Johnson, 1992)

| Compound | Assay, wt % | 1991 Price, US$/Kg |
|---|---|---|
| Methylamine | 99.5 | 1.04 |
| Dimethylamine | 99.5 | 1.04 |
| Trimethylamine | 99.5 | 1.04 |
| Ethylamine | 99.5 | 2.58 |
| Diethylamine | 99.0 | 2.67 |
| Triethylamine | 99.5 | 2.76 |
| *n*-Propylamine | 99.0 | 2.45 |
| Di-*n*-propylamine | 99.0 | 2.69 |
| Tri-*n*-propylamine | 98.0 | 3.59 |
| Isopropylamine | 99.0 | 2.16 |
| Di-*iso*propylamine | 99.5 | 2.95 |
| *n*-Butylamine | 99.5 | 2.76 |
| Di-*n*-butylamine | 99.0 | 2.89 |
| Tri-*n*-butylamine | 98.0 | 3.48 |
| Di-*iso*butylamine | 98.0 | 2.78 |

World raw sugar prices from 1990 to 1995 ranged from 20.2 to 32.1 cents of US$ per kg (Turcotte and Johnson, 1992). The current world sugar price (October 2001) is US$183 per ton (http://www.illovosugar.com, 2002). Comparing amines prices with sugar price per kilogram it becomes evident that by using sugar by-products to generate amines more value can be added to the sugar industry.

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# 2. LITERATURE REVIEW

## 2.1. THE SYNTHESIS OF ALKYLAMINES: GENERAL OVERVIEW

The formation of amines from ammonia and alcohols has been studied since the early work of Sabatier and Mailhe (1909).

A variety of methods exists to prepare lower aliphatic amines, using different types of raw material (Turcotte and Johnson, 1992):

1. **Alcohol Amination – acid catalysed:** high temperature reaction of ammonia/amine with alcohol, in particular methanol over a solid acid catalyst;

2. **Alcohol Amination – hydro-amination**: reaction of alcohol and ammonia/amine over a metal catalyst under reducing conditions;

3. **Reductive Amination:** reaction of an ammonia/amine and hydrogen with an aldehyde or ketone over a hydrogenation catalyst;

4. **Olefin amination:** reaction of a olefin with ammonia/amine;

5. **Alkyl halide amination:** reaction of ammonia/amine with an alkyl halide;

6. **Ritter Reaction:** reaction of hydrogen cyanide with an olefin in an acidic medium to produce a primary amine;

7 **Nitrile Reduction:** reaction of a nitrile with hydrogen over hydrogenation catalyst.

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Most processes result in the synthesis of an equilibrium distribution of primary, secondary, and tertiary amines, which is different for every family of alkylamines. The challenge for amines manufacturers is to match production volumes of the respective amines with their market demands. The largest commercial applications involve the reaction of alcohol with ammonia to form the corresponding amine (Turcotte and Johnson, 1992) depending on the desired amine. This is the most economical and simplest process (Abe *et al.*, 1989). Although many of the lower alkylamines may be produced via acid-catalysed alcohol amination, this technology finds limited application. A major drawback to this approach is the production of alkene as a by-product (Hayes, 2001).

The alcohol amination over supported metal catalysts (hydro-amination) will be the focus of this study. This reaction is in literature often referred to as reductive amination (see e.g. Turcotte and Johnson, 1992; Baiker and Mallat, *et al.* 1997; Sewell *et al.*, 1996). This term is not correct, since no reduction takes place in the metal catalysed alcohol amination. Hydrogen needs to be present to avoid catalyst deactivation (Baiker *et al.*, 1984). It is therefore better to refer to the metal catalysed amination of alcohols as **hydro-amination.**

Table 2.1 lists the main processes used to produce the lower alkylamines on a commercial scale (Hayes, 2001). It also shows that the majority of these products can be made by hydro-amination.

The world wide production of methylamines exceeds 800,000 mt per year whereas the capacity for producing other lower alkylamines ($C_2$ to $C_4$) is greater than 400,000 mt per year (Hayes, 2001).

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**Table 2.1** Processes for manufacturing lower alkylamines (Hayes, 2001).

| Product | Feedstock | Process |
|---|---|---|
| Ethylamines | Ethanol | Hydro-amination |
| | Acetaldehyde | Reductive-amination |
| *n*-Propylamines | *n*-Propanol | Hydro-amination |
| Di-*n*-propylamines | Propionitrile | Hydrogenation |
| Isopropylamines | Isopropanol | Hydro-amination |
| | Acetone | Reductive amination |
| *n*-Butylamines | *n*-Butanol | Hydro-amination |
| Isobutylamines | Isobutanol | Hydro-amination |
| *t*-Butylamines | Isobutylene | Alkene amination |
| | Isobutylene | Ritter reaction |

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### 2.1.1. ALCOHOL AMINATION OVER METAL CATALYST

The Figure 2.1 presents a scheme of typical industrial process for alcohol amination. Flows of product mixture and their separation are also depicted.

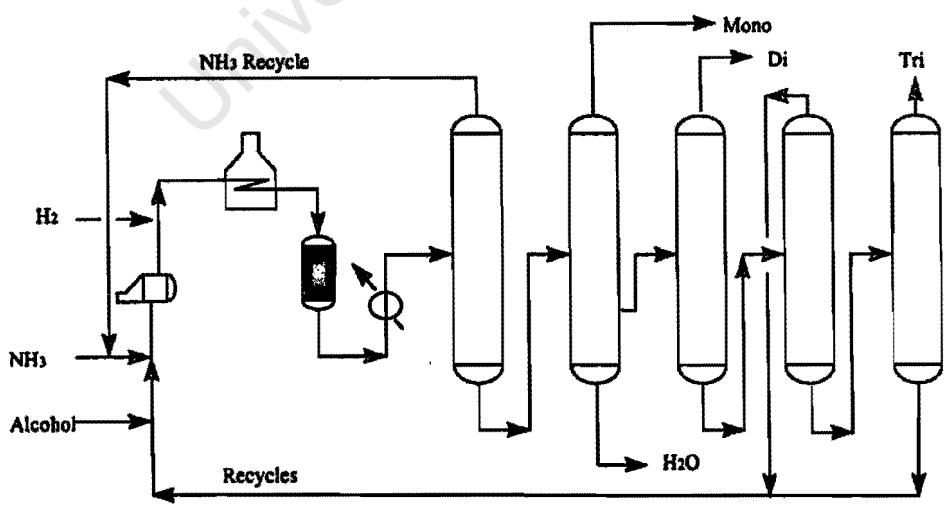


**Figure 2.1** Typical amination reactor and separation train (Hayes, 2001)

The product stream undergoes successive separation processes for recovering and recycling the non-processed reactants and getting amines (primary, secondary, and tertiary). Limitations in separation capability may restrict some manufacturers from recovering all three products. In these situations, the product having lowest demand is recycled to the reactor (Hayes, 2001).

In this process, the following reactions take place:

$$ROH + NH_3 \rightarrow RNH_2 + H_2O \quad [1]$$

$$2\,ROH + NH_3 \rightarrow R_2NH + 2\,H_2O \quad [2]$$

$$3\,ROH + NH_3 \rightarrow R_3N + 3\,H_2O \quad [3]$$

Disproportionation reactions also occur (Baiker and Kijenski, 1985). Braun *et al.*, (1923) as cited by Baiker and Kijenski (1985) proposed the following mechanism for the disproportionation of simple amines over hydrogenation/dehydrogenation catalyst:

$$RNH_2 \rightarrow R{=}NH + H_2 \quad [4]$$

$$HN{=}R + H_2NR \rightarrow H_2N\text{-}R\text{-}NH\text{-}R \quad [5]$$

and $$HN{=}R + H_2NR \rightarrow NH3 + R{=}N\text{-}R \quad [6]$$

$$R_3N + NH_3 \rightarrow R_2NH + RHN_2 \quad [7]$$

$$H_2N\text{-}R\text{-}NH\text{-}R + H_2 \rightarrow HNR_2 + NH_3 \quad [8]$$

$$R{=}N\text{-}R + H_2 \rightarrow HNR_2 \quad [9]$$

According to Baiker and Kijenski (1985), these are the major side reactions and they can strongly decrease the selectivity to the desired product amine.

Most active catalysts for the amination also tend to catalyse the disproportionation of amines (Mallat and Baiker, 1997). However, by changing the nature of the catalysts it is sometimes possible to control the selectivity of a given reaction towards a specific desired product.

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## 2.2. THERMODYNAMIC EQUILIBRIUM IN AMINATION OF ALCOHOLS

The equilibrium conversion and yields for amination of alcohols was calculated taking the co-existence of both liquid and gas phase in equilibrium and the non-ideality of the system into considerations. Using iterations, the equilibrium composition for both phases and fugacity and activities coefficients for all components were calculated. The methodology used for calculations of equilibrium conversion and composition for ethanol amination at the reaction temperature is outlined in Appendix A.I. The approach is the same for n-propanol, iso-propanol, and n-butanol amination.

### 2.2.1. ETHANOL AMINATION

For equilibrium constants ($K_{ai}$) estimation, Gibbs free energies of reaction at reaction temperature were calculated using data from Daubert and Danner, (1991).

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**Table 2.2** Equilibrium constants of ethanol hydro-amination at three different temperatures

| Reaction | Equilibrium Constant | Temperature, K | | |
|---|---|---|---|---|
| | | 423.15 | 473.15 | 523.15 |
| $EtOH + NH_3 = MEA + H_2O$ | $K_{a1}$ | 7.14 | 5.83 | 4.99 |
| $EtOH + MEA = DEA + H_2O$ | $K_{a2}$ | 665.99 | 225.76 | 120.04 |
| $EtOH + DEA = TEA + H_2O$ | $K_{a3}$ | 152.07 | 56.29 | 25.45 |

The calculation of equilibrium conversion for different reaction conditions were done by using SANDLER PROGRAM for fugacity and activity coefficients and POLYMATH 5.1 (program in Appendix A.I-2) for conversion and equilibrium composition both in liquid and gas phases. The fugacity and activity coefficients were calculated assuming that the binary interaction between the species in reaction mixture are equal to zero. The methodology of calculation is summarised by the flow diagram in Figure 2.2. Table 2.3 shows results for ethanol amination.

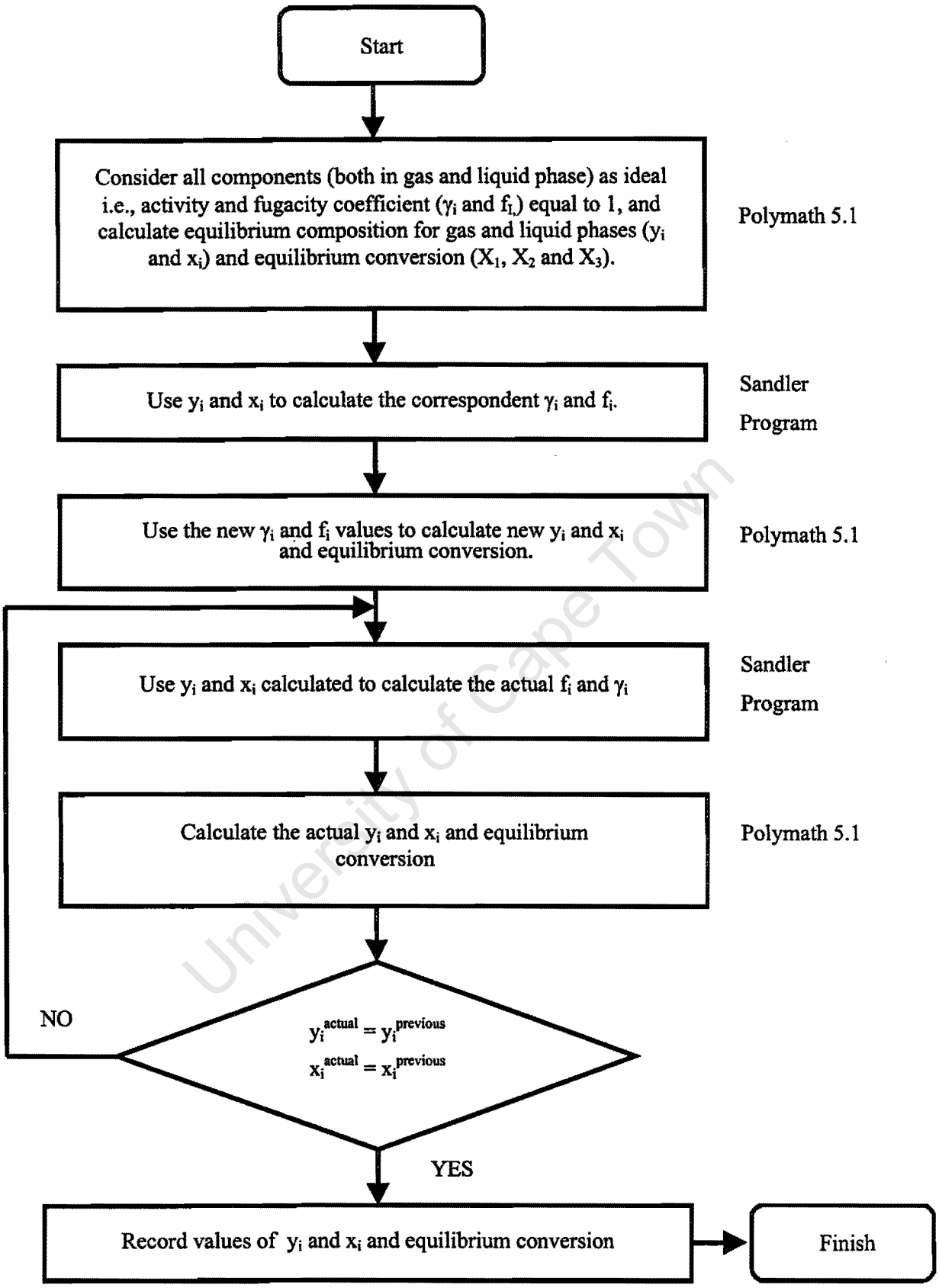


**Figure 2.2** Flow sheet for calculation of equilibrium composition in a batch reactor

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**Table 2.3** Equilibrium conversion and composition for ethanol amination

| $P_{H2}$, bar | | 0 | 1 | 5 | 10 | | | 30 | 60 |
|---|---|---|---|---|---|---|---|---|---|
| T, K | | 473.15 | 473.15 | 473.15 | 423.15 | 473.15 | 523.15 | 473.15 | 473.15 |
| P, bar [a] | | 39 | 40 | 45 | 43 [b] | 48 | 53 [c] | 72 | 110 |
| $N_{H2,0}$, moles | | 0 | 0.02 | 0.09 | 0.18 | 0.18 | 0.18 | 0.55 | 1.09 |
| Equilibrium conversion | $X_1$ | 0.392 | 0.391 | 0.391 | 0.391 | 0.390 | 0.392 | 0.391 | 0.394 |
| | $X_2$ | 0.373 | 0.372 | 0.372 | 0.375 | 0.372 | 0.368 | 0.373 | 0.374 |
| | $X_3$ | 0.230 | 0.231 | 0.231 | 0.233 | 0.231 | 0.216 | 0.231 | 0.227 |
| | **Overall X** | **0.995** | **0.994** | **0.994** | **0.999** | **0.993** | **0.976** | **0.995** | **0.995** |
| Equilibrium composition $y_i$ : Gas phase | $y_{EtOH}$ | 0002 | 0.002 | 0.002 | 7.7E-5 | 0.002 | 0.173 | 6.9E-4 | 2.9E-4 |
| | $y_{NH3}$ | 0.605 | 0.552 | 0.439 | 0.319 | 0.324 | 0.137 | 0.186 | 0.101 |
| | $y_{MEA}$ | 0.033 | 0.030 | 0.024 | 0.007 | 0.017 | 0.023 | 0.010 | 0.005 |
| | $y_{DEA}$ | 0.068 | 0.064 | 0.050 | 0.014 | 0.037 | 0.090 | 0.020 | 0.010 |
| | $y_{TEA}$ | 0.357 | 0.034 | 0.026 | 0.007 | 0.019 | 0.075 | 0.010 | 0.005 |
| | $y_{H2O}$ | 0.256 | 0.243 | 0.193 | 0.025 | 0.200 | 0.522 | 0.076 | 0.034 |
| | $y_{H2}$ | 0 | 0.075 | 0.266 | 0.628 | 0.402 | 0.136 | 0.697 | 0.845 |
| | **$N^V$, mol** | **0.235** | **0.266** | **0.339** | **0.287** | **0.448** | **1.322** | **0.789** | **1.290** |
| Equilibrium composition $x_i$ : Liquid phase | $x_{EtOH}$ | 0.004 | 0.004 | 0.004 | 0.001 | 0.004 | 0.014 | 0.004 | 0.003 |
| | $x_{NH3}$ | 0.022 | 0.020 | 0.020 | 0.040 | 0.022 | 0.011 | 0.021 | 0.025 |
| | $x_{MEA}$ | 0.011 | 0.011 | 0.011 | 0.010 | 0.010 | 0.009 | 0.011 | 0.012 |
| | $x_{DEA}$ | 0.098 | 0.097 | 0.097 | 0.097 | 0.097 | 0.100 | 0.097 | 0.101 |
| | $x_{TEA}$ | 0.164 | 0.166 | 0.166 | 0.161 | 0.167 | 0.183 | 0.165 | 0.161 |
| | $x_{H2O}$ | 0.701 | 0.702 | 0.703 | 0.690 | 0.698 | 0.684 | 0.702 | 0.699 |
| | **$N^L$, mol** | **2.595** | **2.584** | **2.581** | **2.723** | **2.562** | **1.688** | **2.591** | **2.630** |
| | **$V_L$, ml** | 61.76 | 61.53 | 61.43 | 59.05 | 61.00 | 39.87 | 61.52 | 62.28 |

(a) Experimental total pressure at 473.15 K

(b) Estimated total pressure at 423.15 K

(c) Estimated total pressure at 523.15K

The results presented in the Table 2.3 show that the equilibrium conversion and the equilibrium composition, in liquid phase, is practically not affected by hydrogen partial pressure and temperature, in the ranges considered. In general, the small fluctuations verified might be due to calculation errors. In the gas phase, the higher the hydrogen partial pressure, leads to lower the equilibrium composition of ethanol and ammonia.

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The volume of liquid at equilibrium was calculated considering that the system is composed by DEA, TEA and water.

### 2.2.2. N-PROPANOL, ISO-PROPANOL AND N-BUTANOL AMINATION

The considered reactions are similar to those of ethanol amination:

$$ROH + NH_3 = RNH_2 + H_2O \quad , K_{a1} \qquad [10]$$

$$ROH + RNH_2 = R_2NH + H_2O \quad , K_{a2} \qquad [11]$$

$$ROH + R_2NH = R_3N + H_2O \quad , K_{a3} \qquad [12]$$

thus, the stoichiometric table and all calculation approach will also be similar.

Alike for ethanol amination, Gibbs free energies of reaction at reaction temperature were calculated using data from Daubert and Danner, (1991), except for tri-iso-propylamine which were estimated using the methods of Benson and Joback (Reid *et al.*, 1989) due to the lack of data thermodynamic and physical properties of this compound in literature. The critical properties (Temperature, $T_C$ and Pressure, $P_C$) as well as the acentric factor ($w_c$), the normal boiling point and the vapor pressure at 473.15 K for TIPA were also estimated by using Joback method (Reid *et al.*, 1989). The accuracy of these values is not guaranteed. Reaction conditions and equilibrium constants are listed in Table 2.4.

**Table 2.4** Reaction conditions and equilibrium constants for *n*-Propanl, *iso*-propanol and *n*-butanol amination

| Alcohol | $N_{ROH,0}$ moles | $N_{NH3,0}$ moles | $N_{H2}$ Moles | $P_{H2}$ [(d)] bar | P [(e)] bar | $K_{a1}$ | $K_{a2}$ | $K_{a3}$ |
|---|---|---|---|---|---|---|---|---|
| *n*-Propanol | 1.47 | 0.74 | 0.45 | 25 | 50 | 12.67 | 41.29 | 38.20 |
| *i*-Propanol | 1.45 | 0.72 | 0.45 | 25 | 55 | 5.40 | 703.65 | 419.19 |
| *n*-Butanol | 1.20 | 0.60 | 0.36 | 20 | 52 | 21.46 | 102.56 | 3249.68 |

(d) At 20°C

(e) Experimental pressure at 200°C

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Using same approach as for the calculation of equilibrium conversion for ethanol amination, the results obtained are given in Table 2.5.

**Table 2.5** Equilibrium conversion and composition for *n*-Propanl, *iso*-propanol and *n*-butanol amination at 473 K

| | | **Ethanol** (*) | ***n*-Propanol** | ***iso*-Propanol** | ***n*-Butanol** |
|---|---|---|---|---|---|
| **Equilibrium conversion** | $X_1$ | 0.391 | 0.416 | 0.352 | 0.366 |
| | $X_2$ | 0.373 | 0.359 | 0.346 | 0.327 |
| | $X_3$ | 0.231 | 0.211 | 0.300 | 0.303 |
| | **Overall X** | **0.995** | **0.986** | **0.998** | **0.996** |
| **Equilibrium composition** $y_i$ **: Gas phase** | $y_{ROH}$ | 6.9E-4 | 0.001 | 2.8E-4 | 6.9E-5 |
| | $y_{NH3}$ | 0.186 | 0.160 | 0.233 | 0.228 |
| | $y_{RNH2}$ | 0.010 | 0.016 | 0.002 | 0.002 |
| | $y_{R2NH}$ | 0.020 | 0.005 | 0.003 | 8.7E-5 |
| | $y_{R3N}$ | 0.010 | 0.002 | 0.002 | 1.2E-4 |
| | $y_{H2O}$ | 0.076 | 0.156 | 0.159 | 0.166 |
| | $y_{H2}$ | 0.697 | 0.660 | 0.601 | 0.604 |
| | **$N^V$, mol** | **0.789** | **0.682** | **0.749** | **0.596** |
| **$x_i$ : Liquid phase** | $x_{ROH}$ | 0.004 | 0.010 | 0.001 | 0.003 |
| | $x_{NH3}$ | 0.021 | 0.010 | 0.019 | 0.016 |
| | $x_{RNH2}$ | 0.011 | 0.037 | 0.004 | 0.029 |
| | $x_{R2NH}$ | 0.097 | 0.108 | 0.035 | 0.018 |
| | $x_{R3N}$ | 0.165 | 0156 | 0.231 | 0.233 |
| | $x_{H2O}$ | 0.702 | 0.679 | 0.710 | 0.701 |
| | **$N^L$, mol** | **2.591** | **1.978** | **1.871** | **1.564** |
| | **$V_L$, ml** | 61.52 | 45.07 | 39.40 | 34.82 |

(*) Hydrogen partial pressure: 30 bar

For the thermodynamic point of view, more mono-amine and less tri-amine are expected for *n*-propanol amination, compared with other alcohols. Overall conversion is also relatively lower for *n*-propanol. For all alcohols the composition of liquid phase is higher than that of gas phase at equilibrium.

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## 2.3 CATALYST

The catalysts used for amination of aliphatic alcohols can be divided into two main classes: supported metals and metal oxides. Metals are suitable due to their hydrogenation-dehydrogenation activity, whereas the performance of oxides resides on their acidity catalysing dehydration (Mallat and Baiker, 1997).

The commonly suggested heterogeneous catalysts for alcohol amination include metals supported onto silica, alumina or aluminosilicates. The metals are cobalt, nickel, copper and copper chromite, ruthenium, antimony, manganese, palladium, rhenium, and iridium (Roundhill, 1991). These catalysts have been used to prepare amines in the $C_2$ – $C_{25}$ range and have led to conversions up to 100% and selectivities of up to 97%. Although all of these materials have been applied in research, copper, nickel and cobalt appear to be the preferred catalysts for industrial application (Baiker *et al.*, 1985).

Baiker and co-workers (Vultier *et al*, 1986; Baiker and Kijenski, 1985; and Mallat and Baiker, 1997) performed comparative tests of a series of catalysts under identical conditions, using amination of dodecanol with dimethylamine to N,N-dimethyldodecylamine. The results suggested that copper and copper chromite catalysts were the best in activity and selectivity. Supported cobalt exhibited fairly good selectivity but comparatively low activity. Nickel showed high activity but markedly lower selectivity to N,N-dimethyldodecylamine. Other metals like rhodium, ruthenium, palladium, and platinum supported on active carbon or γ-alumina did not yield satisfactory results.

A characteristic difference of copper compared to other metals is that it does not exhibit significant activity for carbon-carbon bond cleavage under amination conditions (Mallat and Baiker, 1997). This activity is maintained over extended periods of time (Vultier *et al.*, 1986). The high selectivity is partly due to the fact that under reaction conditions, C-N bond cleavage is suppressed and thus only insignificant isomerization of reactants and product amines occurs (Vultier *et al.*, 1986). Corresponding nickel and cobalt systems showed irreversible deactivation due to the nitrogen and /or carbon incorporation (Baiker and Maciejewski, 1984b). The addition of hydrogen to the feed

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was found to be essential for maintaining catalyst activity and selectivity (Vultier *et al.*, 1986; Mallat and Baiker, 1997), despite the fact that from a purely stoichiometric viewpoint it does not participate in the reaction. Additionally, hydrogen was found to inhibit the disproportionation reactions. Even at low partial pressures, it plays important role preventing catalyst deactivation by incorporation of nitrogen and/or carbon into the metal lattice (Mallat and Baiker, 1997). The catalyst deactivation is characterised by the formation of metal nitride (Me = metal, R = alkyl):

$$NH_3 + 3\ Me = Me_3N + 1.5\ H_2 \qquad [13]$$

The metal nitride can also be formed by the interaction of the metal with the product amines (Baiker and Maciejewski, 1984 b):

$$3\ R_2NH + 3\ Me = Me_3N + 2\ R_3N + 1.5\ H_2 \qquad [14]$$

$$2\ RNH_2 + 3\ Me = Me_3N + R_2NH + 1.5\ H_2 \qquad [15]$$

$$1.5\ RNH_2 + 3\ Me = Me_3N + 0.5\ R_3N + 1.5\ H_2 \qquad [16]$$

These reactions are thermodynamically feasible under typical conditions selected for reductive amination.

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However, studying the catalytic process for preparing ethyl amines, Gardner and Clark (1980) discovered that catalyst consisting essentially of reduced cobalt, uniformly dispersed on a high surface area is superior in performance to the best commercial nickel catalyst. This observation followed a comparison of performance of 4 different catalysts prepared from nickel and cobalt, namely 40% Nickel/Alumina (Calsicat Ni235T), 59% Nickel/Kieselghur (Harshaw Ni-0104), 24% Cobalt/Kieselghur and 36.3% Cobalt/Alumina on amination of ethanol by ammonia. The results showed that using same space velocities of about 3650 $hr^{-1}$, high conversion of 64% was obtained with cobalt at a temperature of only 170°C, whereas using nickel the same conversions are achieved at bed temperature of 194.3°C. Thus, reduced cobalt has a much higher productivity than nickel catalyst at the same temperature. Both metals showed high carbon efficiency to ethylamines (> 98%) with the balance being methane. They have also stated that the total amount of cobalt on the support is not critical and can vary

from 10 to 65 wt-% based on support. The preferable cobalt loading was between 20 to 40 wt-%.

Sewell *et al.* (1995) has also compared the catalyst performance of cobalt, nickel and copper. At a reaction temperature of 180°C, a WHSV of 2 $g_{EtOH}/g_{cat}$.hr and EtOH : $NH_3$ : $H_2$ : $N_2$ molar feed ratio of 1 : 2 : 4.1 : 13.6 the turnover frequency decreased from 0.11 to 0.09 to 0.05 $molec_{EtOH}$/active site/sec. as the metal was changed from cobalt to nickel to copper. On this basis, it was concluded that principally cobalt is the best catalyst for the reductive amination.

### 2.3.1. EFFECT OF SUPPORT

The selection of the carrier is of significant importance in designing supported metal catalysts and is governed by such parameters as surface area, characteristic porosity, mechanical strength and thermal and chemical stability (Foger, 1984).

The method of catalyst pre-treatment and the type of carrier used affect considerably both the extent of reduction and the metal dispersion (Sewell *et al.*, 1997). This is important since it was observed that ethanol conversion is proportional to the number of zero-valent cobalt atoms at the surface.

Sewell *et al.* (1997) compared the performance of a number of supported cobalt catalysts in order to determine the influence of the carrier on the activity and selectivity during the amiation reaction. Basically, the neutral $SiO_2$, acidic $\gamma$-$Al_2O_3$ and $SiO_2$-$Al_2O_3$ and basic MgO support were used. The results showed a decrease in ethanol conversion from 66 to 47 to 2% as the cobalt support was changed from $SiO_2$ to $\gamma$-$Al_2O_3$ to MgO. The selectivity was also affected. The increase in the aluminium content in the $SiO_2$-$Al_2O_3$ supported cobalt catalyst results in an increase in the monoethylamine selectivity and the decrease in the selectivity to diethylamine and triethylamine. Therefore, the composition of the support appears to influence the product selectivity. The differences are most likely to be ascribed to the secondary conversion of the product amine on acidic sites on the support via disproportionation. The use of silica as a carrier was

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found to result in the most efficient amination catalyst, principally due to increased extent of metal reduction (Sewell *et al.*, 1997).

To avoid the excessively high pressure drops encountered with powders, the support materials are usually formed into spheres, granules, extrudates or cylinders before industrial application. The mechanical strength of the catalyst may be increased by fusion and by the addition of binders in order to prevent degradation during catalytic processing (Sewell, 1996).

## 2.4. REACTION MECHANISM

Only a few studies have been performed with the aim of investigating the reaction mechanism of amination of alcohols over hydrogenation/dehydrogenation catalysts. A number of general mechanisms have been proposed (Jones *et al.*, 1994) but they are still under discussion with some steps and/or intermediates to be fully proven.

In presence of hydrogenation/dehydrogenation catalysts, alcohols react with ammonia or amines (primary or secondary) to form corresponding amines. Since tertiary alcohols do not show this type of reaction, Schwoegler and Adkins (1939) considered plausible to assume that the primary function of the catalyst was to dehydrogenate the alcohol to an aldehyde or ketone.

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$$RCH_2OH = RCHO + H_2 \quad [17]$$

$$RCH(OH)CH_3 = RCOCH_3 + H_2 \quad [18]$$

The latter would then condense with ammonia (or an amine) to yield an imine (reaction 19) which may be hydrogenated to the primary amine (reaction 20):

$$RCHO + NH_3 = RCH{=}NH + H_2O \quad [19]$$

$$RCH{=}NH + H_2 = RCH_2NH_2 \quad [20]$$

According to this mechanism, further reactions of product amines with the carbonyl compound formed in (reaction 17) give rise to secondary and tertiary amines (reactions from 21 to 23):

$$RCH_2NH_2 + RCHO = RCH_2N{=}CHR + H_2O \quad [21]$$

$$RCH_2N{=}CHR + H_2 = (RCH_2)_2NH \quad [22]$$

$$RCH_2N{=}CHR + RCHO + 2H_2 = (RCH_2)_3N + H_2O \quad [23]$$

Although Mallat and Baiker (1997) suggested that the adduct formation and the condensation steps do not require a metal catalyst, the proposed pathway by Kliger *et al.* (1975) postulated this to be catalysed by the metal as well.

$$RCH_2OH + * = RCH_2OH* \quad [24]$$

$$H_2 + * = H_2* \quad [25]$$

$$NH_3 + * = NH_3* \quad [26]$$

$$RCH_2OH* + * = RCHO* + H_2* \quad [27]$$

$$RCH{=}NH* + H_2* = RCH_2NH_2* + * \quad [28]$$

$$RCHO* + RCH_2NH_2* = RCH{=}NCH_2R* + H_2O* \quad [29]$$

$$RCH{=}NCH_2R* + H_2* = (RCH_2)_2NH* + * \quad [30]$$

$$RCH_2NH_2* = RCH_2NH_2 + * \quad [31]$$

$$(RCH_2)NH* = (RCH_2)_2NH + * \quad [32]$$

$$H_2O* = H_2O + * \quad [33]$$

*: Active site

This pathway was supported on basis of identified products, on the response of activity and selectivity to changes in the reaction parameters, and on experiments with isotope-labelled alcohols. Mallat and Baiker (1997) identified the corresponding aldehyde, imine and enamine intermediates in various product mixture.

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Popov (1952) assumed that the first stage of the reaction is a process involving the dehydration of alcohol to an alkene. The alkene then reacts with ammonia or a primary or secondary amine to give the corresponding amine product. The, amination of olefins is however strongly equilibrium limited. This proposed reaction pathway does not seem to be feasible certainly in light of ethanol dehydrogenation being the rate limiting step.

Jones *et al.* (1994) cited that other workers have shown that the mechanism involves the direct substitution of the hydroxyl group with ammonia. Baiker *et al.*, (1983) compared the amination of octanol and α,α-dideuterated octanol ($C_7H_{15}CD_2OH$) in the gas phase on Cu/alumina at 443 K and octanol : DMA : $H_2$ partial pressures of 5 : 32 : 10 kPa. They observed that at octanol conversions around 20%, the ratio of conversions of octanol and α,α-dideuterated octanol was 1.9 ± 0.3. This is consistent with kinetic isotope effects for the dehydrogenation of alcohols, reported earlier, and supported the belief that the rate limiting step involves abstraction of an α-hydrogen leading to a carbonyl formation (Baiker *et al.*, 1983). This is not in agreement with direct substitution.

Originally, the reaction was thought to proceed via the aldehyde as proposed by Schwoegler and Adkins. Jones *et al.* (1994) investigated this using isotopic labelling. They stated that if ethanal was the reaction intermediate, an extensive hydrogen isotope exchange on methylene group of the unconverted alcohol was to be expected when [1-$^3$H]-ethanol was aminated. Similarly, when ethanol was aminated in a [$^3$H]-hydrogen atmosphere, incorporation of the label into the methylene group of the residual ethanol would be expected. This was not observed. This was an indication that the reaction intermediate could not be ethanal. However, it was shown that abstraction of methylene hydrogen is involved in the rate determining step. This was a crucial moment on alcohol amination mechanism determination as new elements leading to clarification of some uncertainties have been discovered.

At this point, and following the above evidences, Baiker *et al.* (1983) proposed another reaction pathway which predicts the formation of an aldehyde from the intermediate species from the α-hydrogen abstraction (see Figure 2.3).

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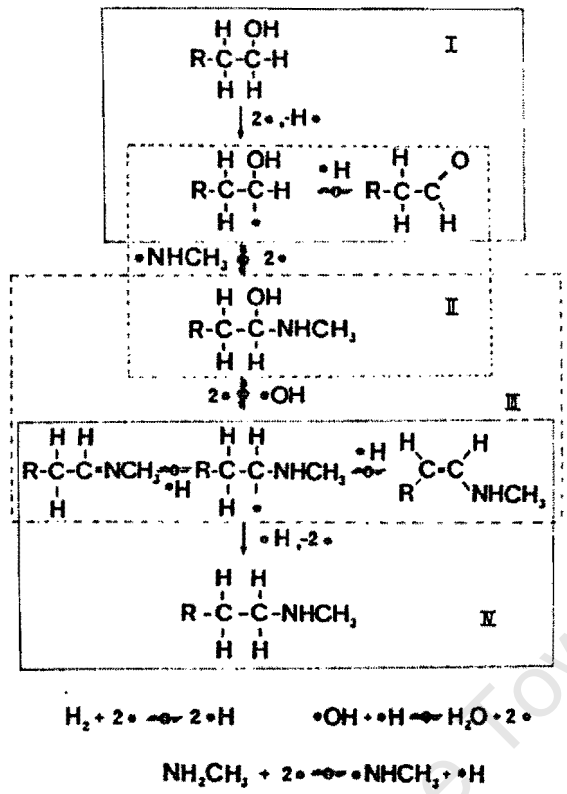

* active site

**Figure 2.3** Proposed reaction pathway for amination of an aliphatic alcohol by a primary amine (Baiker *et al.*, 1983)

Although this mechanism presents some improvements, it still does not explain completely the observation of other research workers:

1. The mechanism predicts a sequential formation of mono-, di-, and tri-substituted amine. However, Freese (2001) has shown that even at low ethanol conversion (i.e. high space velocity) high selectivity for di- and tri-ethylamine is observed in the ethanol amination (see Figure 2.4). The TEA distribution stars at around 30 C-%, goes quickly to a maximum and then falls down smoothly. The DEA content starts high (approximately 70%) and shows a initially fast decrease, followed by a slow one. This is contrasting the continuously increasing MEA distribution. This may suggest that MEA is formed from both DEA and TEA.

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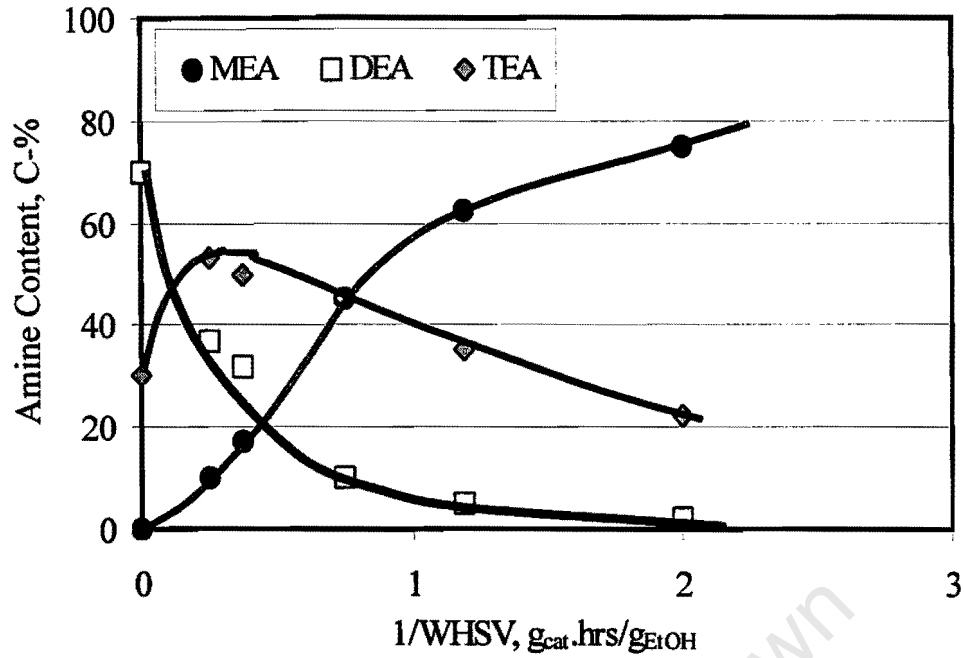


**Figure 2.4** Amines distribution in Ethanol Amination in a PFR. **Conditions:** Catalyst: Co-Pt/$SiO_2$, $T_{reaction}$ = 210°C, P = 1.2 bar, Ratio EtOH: $NH_3$: $H_2$: $N_2$ ratio = 1 :3: 6: 34, Gas flow rate = 100 ml (NTP)/min (Adapted from Freese, 2001).

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2. The intermediate $RCH_2CHOHNHCH_3$ (formed in the step II) was never observed (Baiker *et al.*, 1983).

3. By this mechanism, an aldehyde is proposed to be formed as a side product from an intermediate, however, Jones *et al.* (1994) has observed that in reducing atmosphere, ethanol was converted into a hydrocarbon by dehydration. The proposed surface reaction intermediate is $CH_3CH=$. According to Jones's observations, the formation of ethanal is another possibility, considered only in an inert atmosphere. In this case, ethanol is adsorbed by dehydrogenation. This depends on the reaction conditions.

Considering all these new observations and proofs, a new reaction pathway has been proposed by Freese (2001). Basically, this mechanism (presented below) illustrates the observed distribution of amines by proposing a sequential equilibrium adsorption of

different forms of ammonia. Each species leads to different substituted amine. In the ammonia activation step, the formation of different ammonia adsorbed species suggests the influence of hydrogen partial pressure on the primary amine distribution. This influence still has to be tested to prove this prediction.

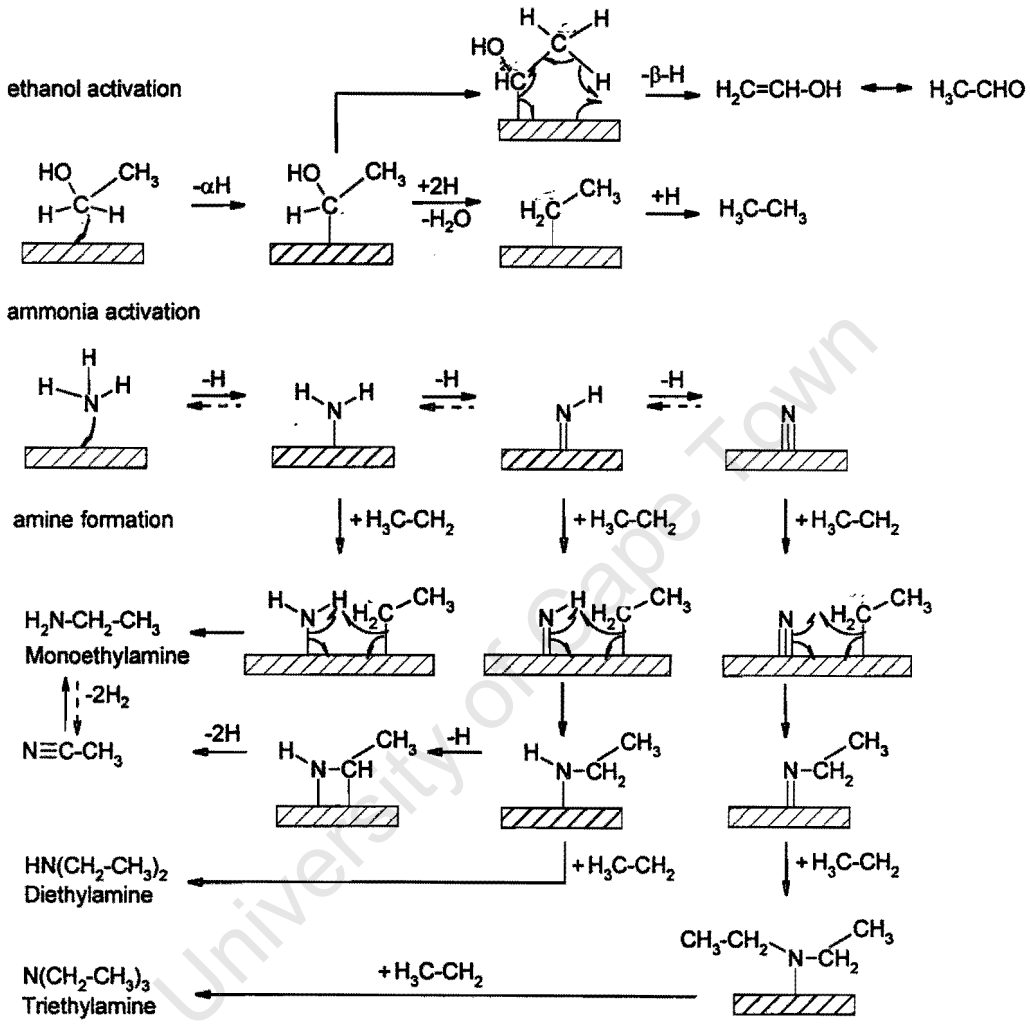


**Figure 2.5** New Ethanol Amination Pathway (Freese, 2001)

Apart from ammonia activation, the main difference between the proposed mechanism by Baiker *et al.* (1983) and that proposed by Freese (2001) can be found in the reaction sequence and formed main intermediates. The first one predicts the interaction between the adsorbed alcohol (after the α-hydrogen abstraction) with adsorbed aminating agent species and then the abstraction of the OH group. The resulting intermediate interacts

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ultimately with an adsorbed hydrogen to yield the final product (amine). The former mechanism proposes the elimination of oxygen (yielding $H_2O$) and subsequent interaction with the activated ammonia followed by sequential arrangements yielding the corresponding substituted amine (depending on the activated aminating agent involved).

## 2.5. INFLUENCE OF REACTION PARAMETERS

The alcohol amination process is governed by a set of parameters. In order to achieve good results in terms of selectivity, activity and conversion, such parameters must be optimised. There are: reaction temperature, hydrogen partial pressure and reactant molar ratio. The optimum conditions depend on the type of catalyst/support and on reactor type (batch, semi-batch or continuous).

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### 2.5.1. INFLUENCE OF REACTION TEMPERATURE

Observations made on alcohol amination over supported cobalt, nickel and copper have shown that the reaction temperature is critical and should be maintained between 140 and 225°C (Gardner and Clark, 1981). Below 140°C the reaction rate is too slow to be practical whereas above 225°C losses occur as a consequence of undesired side reactions (dehydrogenation of alcohol, dehydrogenation of amine products, formation of tars and the like). In the amination of long-chain aliphatic alcohols, the optimal reaction temperature was found to increase with increasing chain length of the reactant alcohol (Mallat and Baiker, 1997).

Increasing reaction temperature results in an increase of the alcohol conversion at the expense of selectivity. The increase on disproportionation rate between reactant and product amines are responsible for the decrease in selectivity when reaction temperature is increased (Baiker and Richarz, 1977). Figure 2.6 illustrates the influence of the reaction temperature on the conversion and selectivity of a silica supported copper catalyst for the amination of dodecanol with dimethylamine. The decrease in the alcohol

conversion at temperatures above 340°C was attributed to excessive catalyst deactivation (Baiker and Richarz, 1977).

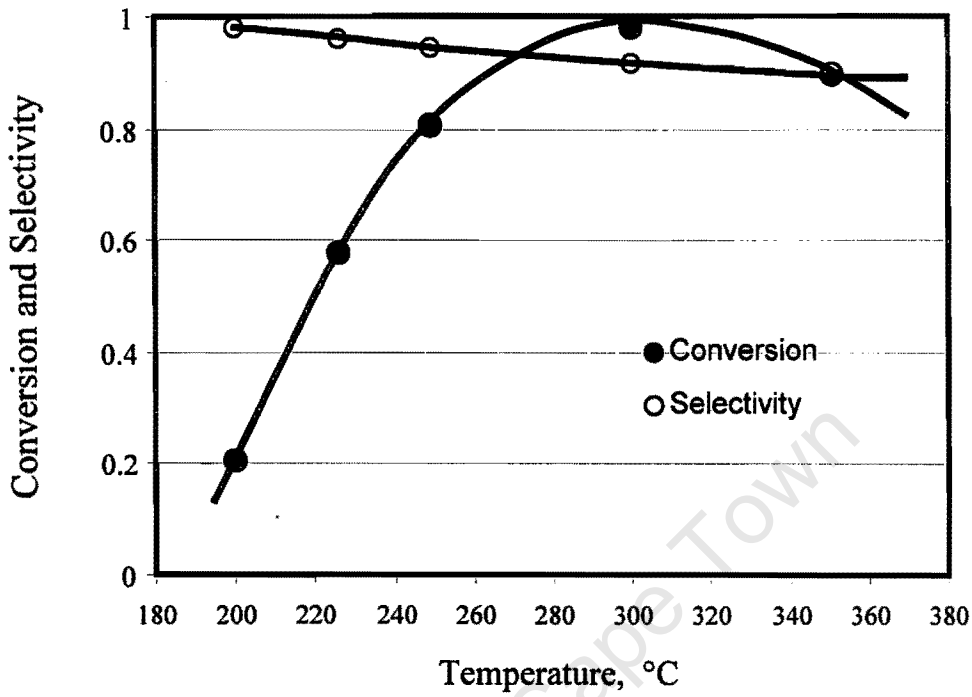


**Figure 2.6** Effect of the reaction temperature on the activity and selectivity of $Cu/SiO_2$ for the amination of dodecanol with dimethylamine (redrawn from Baiker and Richarz, 1977)

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## 2.5.2. INFLUENCE OF HYDROGEN PARTIAL PRESSURE

According to the stoichiometric equation hydrogen should have no direct influence on the ethanol amination. It may enhance catalyst stability by supression of disproportionation by reactants and products and thus inhibition of catalyst deactivation caused by the metal nitride and/or metal carbide formation (Baiker and Kijenski, 1985). The influence of hydrogen partial pressure on the activity and selectivity of Cu/alumina in the amination of dodecanol with dimethylamine to N,N-dimethyldodecylamine have been investigated by Mallat and Baiker, (1997) (see Figure 2.7).

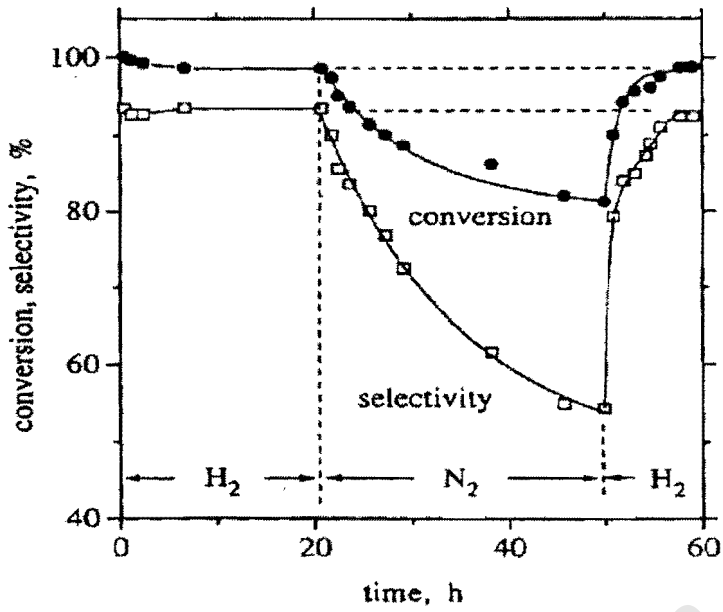


**Figure 2.7** Influence of hydrogen partial pressure on activity and selectivity of $Cu/Al_2O_3$ in the amination of 1-dodecanol with dimethylamine (DMA). **Conditions:** Fixed-bed reactor. Molar feed ratios (mol/s): 1-dodecanol, $1.9 \times 10^{-5}$; DMA, $1.0 \times 10^{-4}$; $H_2$ or $N_2$, $1.2 \times 10^{-4}$. Catalyst load, 10 g. $T_{reaction}$, 510 K; Total pressure, 100 kPa. (Baiker and Kijenski, 1985).

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When hydrogen was replaced by nitrogen both the activity and selectivity of the reaction decreased. and when hydrogen was restored conversion and selectivity returned to they initial values. The decreased activity in the absence of hydrogen was ascribed to the formation of copper nitride which is inactive for the reaction. For supported cobalt catalysts, hydrogen must be present to the extent of at least 10 mole percent at all times in order to ensure efficient catalyst utilisation, (Gardner and Clark, 1981).

The overall rate of alcohol conversion has been found to be affected differently by the hydrogen partial pressure as the metal catalyst was changed (Sewell, 1996). The rate of ethanol conversion increased considerably with increasing hydrogen partial pressure when using the $Co/SiO_2$ catalyst and the measured reaction order with respect to hydrogen was 1.91. Hydrogen does not influence the rate of ethanol conversion of nickel and copper supported on silica significantly and the measured reaction orders with respect to the hydrogen pressure are -0.07 and 0.07, respectively.

### 2.5.3. INFLUENCE OF REACTANT MOLAR RATIO

The molar ratio of reactants (alcohol and aminating agent) is a crucial parameter for selectivity of amination (Buehler and Pearson, 1970). An excess of ammonia is conducive to the formation of the primary amine whereas an excess of reactant alcohol favours secondary and tertiary amine synthesis (Sewell, 1996 and reference therein). The optimal reactant ratio depends also on other conditions such as temperature, total pressure, hydrogen partial pressure and on reactor type (Mallat and Baiker, 1997).

## 2.6. OBJECTIVE OF STUDY

The objective of the present research is focused on the influence of the hydrogen partial pressure on alcohol amination. For this purpose, alcohol amination reactions in the liquid phase will be carried out in a batch reactor. All operating conditions except hydrogen partial pressure are kept unchanged. $Co/SiO_2$ catalyst has been selected to be used. The resulting amines distribution will be measured.

The problem is approached also by investigating the influence of alcohol carbon number and OH group position on the amination process, in order to determine how can they fit the mechanism in consideration. This will be done by aminating alcohols with different carbon number and different OH position, namely ethanol, *n*-propanol, *i*-propanol, and *n*-butanol.

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# 3. EXPERIMENTAL

## 3.1. CATALYST PREPARATION

A supported cobalt on silica catalyst has been used in this study. It was prepared by incipient wetness impregnation of silica (silica gel, Davisil, grade 646, 30 - 60 mesh, 150 Å, 99+%, pore volume: 2.25 ml/g) purchased from Aldrich Chemical Company Inc.

49.42 g of $Co(NO_3)_2.6H_2O$ supplied by the Gruppo Montedison Carlo Erba (with 24.98 wt-% of Co as determined by AAS) were put into a volumetric flask and exactly filled up to 250 ml with de-ionised water. Subsequently, the solution was poured over 111.11 g of dried $SiO_2$ in a cupboard at 100°C (calculations in Appendix A.II-1). The impregnated $SiO_2$ was placed in a drying cupboard at 100°C for 16 hours in a shallow bed and then, stored over silica gel until being reduced.

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## 3.2. EXPERIMENTAL APPARATUS AND PROCEDURES

### 3.2.1. CATALYST REDUCTION

The catalyst reduction was performed in a 40 ml tubular fixed bed down flow reactor.

Glass wool was placed above and below of the bed containing 13 g of the catalyst precursor (to yield 10 g of catalyst with the load of 10 wt-% Co) in order to fix it. After sealing the reactor, hydrogen was passed through the reactor with a flow of 60 ml/min (NTP). The temperature was raised from room temperature up to 400°C with a rate of 1.7°C/min and kept at this temperature 16 hours. Thereafter the reactor was allowed to cool down to room temperature under flowing nitrogen ca. 50 ml/min (NTP).

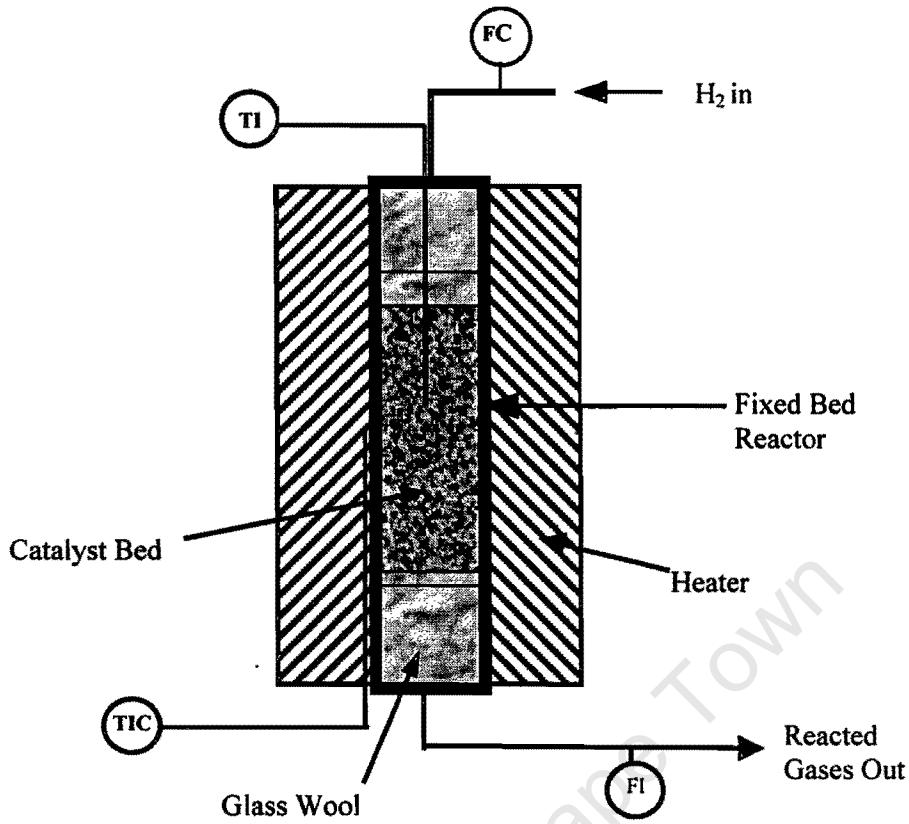


**Figure 3.1** Schematic illustration of the catalyst reduction rig

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Immediately after reducing, the catalyst was transferred into the autoclave in an inert atmosphere (nitrogen), in order to prevent re-oxidation of the metal. The autoclave then was closed immediately.

### 3.2.2. AMINATION REACTION

The amination of alcohols was carried out in a 600 ml batch reactor. The reactor is made of T316 Stainless Steel. Its pressure and temperature limits are respectively 3000 psig (20,68 MPa) and 350°C. The system is comprised of the bomb and peripherals (magnetic stirrer, pressure gage, heating mantel and its respective regulator).

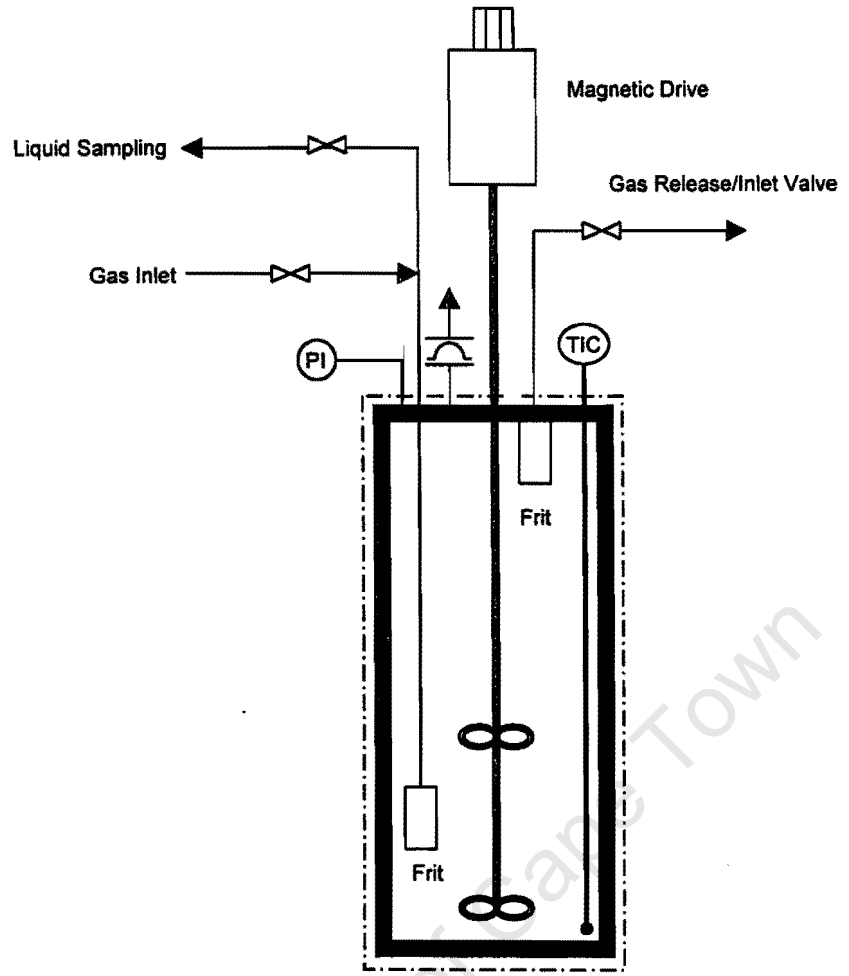


**Figure 3.2** Experimental apparatus for amination aeaction – Schematic representation of the Mini Batch Reactor with all peripherals

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The reactor is initially cleaned with water and soap, flushed with alcohol, dried and flushed continuously with $N_2$ to remove $O_2$. The appropriate amount of alcohol to be aminated is loaded into the reactor. The reduced catalyst is transferred into the reactor under a $N_2$ atmosphere. The reactor is subsequently sealed. All peripherals of the reactor are then added.

Next the reactor is loaded with ammonia. An intermediate 150 ml U shape container is used to condense and measure the amount of ammonia. It is connected to the $NH_3$ supply line while placed in a bucket filled in with dry ice and methanol. Alternatively ice and water can be used even though the condensation is slow. The bucket is placed on a balance. Then ammonia is allowed to condense into the reactor by connecting the

container to the reactor and placing the reactor into a bucket with ice and water and the $NH_3$ container into a bucket filled in with warm water.

The reactor is afterwards loaded with hydrogen at 20°C by attaching it to the $H_2$ supply line and open the valve until the desired $H_2$ partial pressure is reached (full experimental standard procedure in Appendix A.IV).

The reaction is allowed to run by heating the reactor up to the reaction temperature, 200°C. In general heating up from 20 to 190°C, when the reaction time is set to start (in order to compensate the conversion occurred above 140°C, minimum temperature in which the reaction occurs) takes between 10 to 13 minutes. Temperature setting has to be increased stepwise to avoid temperature overshooting. From time to time, the reactor is quickly cooled down in order to take samples of the liquid phase. For this purpose the reactor is inserted in a bucket with ice and water. The cooling down process (to below 140°C) takes around 3 min. Figure 3.3 illustrates temperature profile during reactor heating up and cooling down.

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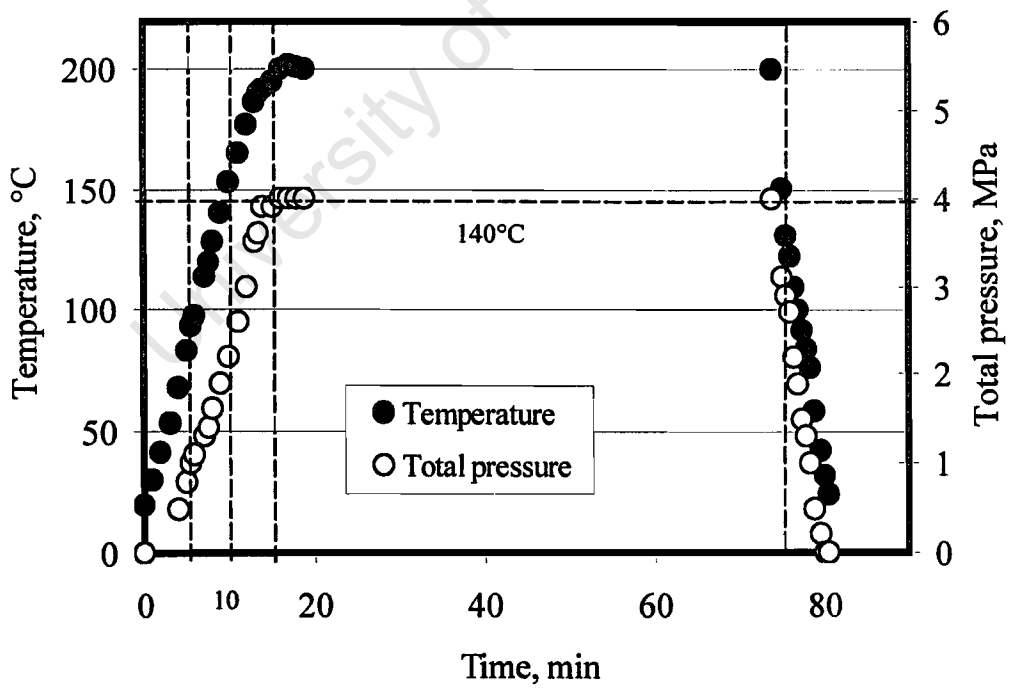


**Figure 3.3** Temperature profile during reactor heating up and cooling down. **Conditions**: Molar ratio, $H_2$ : EtOH : $NH_3$ = 0 : 1 : 0.5; $T_{reaction}$ = 200°C

The sampling valve is followed by a sampling system consisting on a 15 ml U shape tube containing glass beads and filled with de-ionised water to dissolve all components of the reaction mixture sampled. During the sampling, the U tube is placed in a bucket with ice and water to cool down the system and thus increase the solubility of all gas components of the sample. Samples were kept in fridge or ice to avoid losses due to possible evaporation.

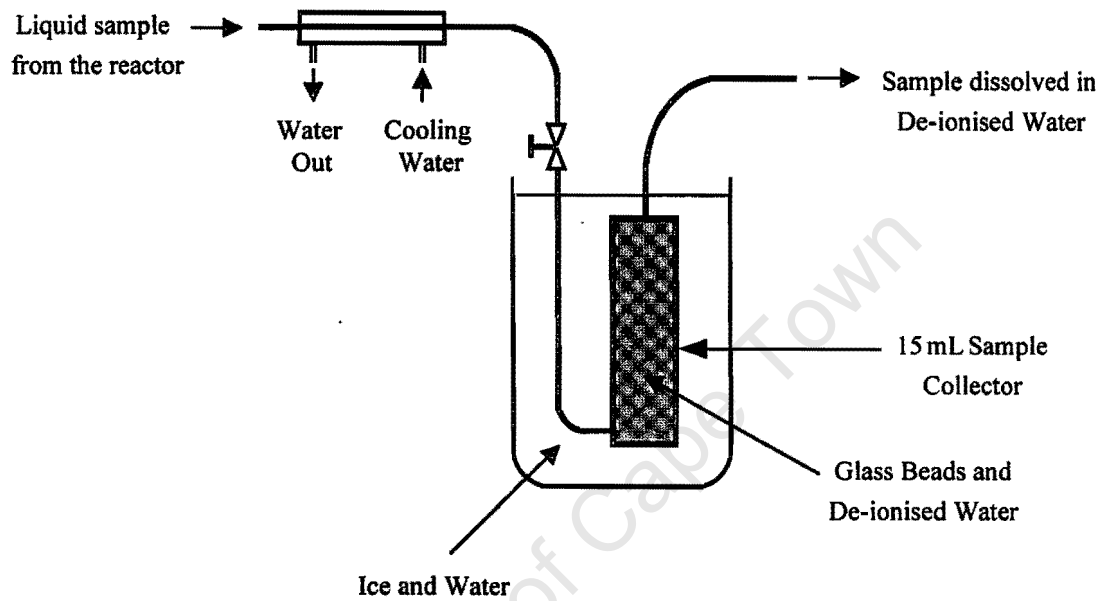


**Figure 3.4** Sampling system

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### 3.2.3. SAMPLE ANALYSIS AND PRODUCTS IDENTIFICATION

The sample compositions were determined using a VARIAN 3400 Gas Chromatograph (GC) equipped with a Flame Ionisation Detector (FID) and an electronic integrator. The gas chromatographic analysis were carried out in isothermal mode under the following conditions.

**Table 3.1** Gas Chromatographic conditions for separation of amines

| | |
|---|---|
| Column | OV-101 |
| Stationery phase | Phenyl-dimethyl Siloxane |
| Column length | 100 m |
| Inner Diameter | 0.32 mm |
| Film thickness | 0.5 μm |
| Injection volume | 0.2 μl |
| Carrier gas | Hydrogen |
| Injector port temperature | 150°C (*) |
| Column temperature | 40°C |
| Detector temperature | 250°C |
| Head pressure | 35 psi (*) |
| Split ratio | 1 : 100 |
| Gas flows: | $H_2$: 30 ml (NTP)/min |
| | Air: 300 ml (NTP)/min |
| | $N_2$: 20 ml (NTP)/min |

(*) For $C_3$ and $C_4$ alcohols the injector temperature was increased to 175°C and head pressure was reduced to 15 psi.

Individual products identification was done by GC-MS analysis. A HP 5890 Series II Gas Chromatograph combined with a HP 5971A Selective Mass Detector was used for this purpose. Table 3.3 presents GC-MS characteristics and conditions.

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**Table 3.2** GC-MS characteristics and conditions

| | |
|---|---|
| Column | Crossbond 5% diphenyl – 95% dimethyl polysiloxane |
| Column length | 60 m |
| Inner diameter | 0.25 mm |
| Film thickness | 0.10 μm |
| Injection volume | 0.2 μl |
| Carrier gas | Helium |
| Head Pressure | 100 kPa |

These analyses were performed in various conditions in isothermally and non-isothermal mode in order to improve peaks quality. Two samples were analysed at the Department of Chemistry of the University of Oldenburg.

## 3.3. EXPERIMENTS PERFORMED AND CONDITIONS

All reactions took place at 200°C. A mass of 10 g of catalyst was loaded. Additional runs were done with loads of 1 g of catalyst in order to collect data for normalised residence times below 1 hr. This procedure was taken to reduce the error originated by sampling at very low reaction time due to the length of heating and cooling time. The ratio ROH : $NH_3$ was invariably 2 : 1, whereas the ratio $H_2$ : ROH were changed in ethanol amination. The reaction mixture was stirred with a magnetic impeller at 400 rpm except when mass transfer effects were investigated. In that study, the stirrer speed rate was varied.

In the Table 3.3 performed experiments and the respective charge conditions are listed. The amount of $NH_3$ loaded in each run may not be precise due to difficulties on the procedure of its transference from the gas cylinder into the reactor. Average inaccuracies of 3.5% are estimated. Also the loading of alcohol and hydrogen may be affected both by random and/or systematic errors. They are estimated to be respectively less than 2% and 5%.

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**Table 3.3** Synoptical table of performed experiments and conditions

| ROH Compound | Run Code | Molar Ratio $H_2$ : ROH : $NH_3$ | $V_{ROH}$ (ml) | $P_{H2}$ (bar) at 20°C | $m_{NH3}$ (g) |
|---|---|---|---|---|---|
| Ethanol | A | 0.10 : 1 : 0.5 | 110 | 10 | 16.04 |
| | B | 0.29 : 1 : 0.5 | 110 | 30 | 16.04 |
| | C | 0.58 : 1 : 0.5 | 110 | 60 | 16.04 |
| | D* | 0.29 : 1 : 0.5 | 110 | 30 | 16.04 |
| | E | 0.05 : 1 : 0.5 | 110 | 5 | 16.04 |
| | G | 0.0 : 1 : 0.5 | 110 | 0 | 16.04 |
| | H | 0.01 : 1 : 0.5 | 110 | 1 | 16.04 |
| *n*-Propanol | NP | 0.30 : 1 : 0.5 | 110 | 25 | 12.53 |
| *i*-Propanol | IP | 0.31 : 1 : 0.5 | 110 | 25 | 12.30 |
| *n*-Butanol | NB | 0.30 : 1 : 0.5 | 110 | 20 | 10.23 |

In all runs the stirrer speed rate was 401 rpm, except the experiment D* which was performed with 203; 401; 571 and 755 rpm with the aim of investigating mass transfer limitations in ethanol hydro-amination.

Ethanol (99.9%) was supplied by Orion Chemicals, *n*-Propanol (99.5%) by Sigma Aldrich, *iso*-Propanol (99.7%) by Merck Laboratory Suppliers (PTY) Ltd and *n*-Butanol was purchased from SAARCHEM (Univar) (PTY) Ltd. Ammonia Hydrogen and Nitrogen were supplied by Air Products.

## 3.4. DATA EVALUATION

Sampling analysis produced a set of data consisting of GC traces with peak areas of different components of the reaction mixture, namely the reactant alcohol and the amine products. In order to ensure the reproducibility of the analytical results, at least two

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analyses were performed for each sample. Reproducibility in sample analysis was typically satisfactory and consequently the closest two data set per analysis were used in the results reported.

Selectivities for amines were calculated as amine content in the fraction of amines in carbon weight percent, so their values correspond to area (or area-%) of given amine divided by the total area (or area-%) of amines. Yield is calculated as a product between selectivity and ethanol conversion. Ethanol conversion is calculated in carbon percent by correcting the areas using response factors.

$$X_{ROH} = \left(1 - \frac{Area_{ROH} \cdot RF}{Area_{ROH} \cdot RF + Area_{RNH_2} + Area_{R_2NH} + Area_{R_3N}}\right) \cdot 100\%, \quad \text{in C} - \%$$

(Equation 3.1)

The calculated Response Factors (RF) for ethanol, propanol and butanol are respectively $\frac{1}{0.775}$, $\frac{1}{0.85}$ and $\frac{1}{0.8875}$.

In mol-% the conversion can be calculated as:

$$X_{ROH} = \frac{\frac{100 \cdot RF}{CN} - \frac{\%Area_{ROH} \cdot RF}{CN}}{\frac{100 \cdot RF}{CN}} \cdot 100\% = \frac{100 - \%Area_{ROH}}{100} \cdot 100\%, \quad \text{in mol} - \%$$

(Equation 3.2)

The denominator CN represents the number of carbon atoms existent in an alcohol molecule.

It can be seen, by comparing Equations 3.1 and 3.2, that the numerical value of ethanol conversion either in C-% or in mol-% should always be the same. However, they do differ in certain initial data points where ethanol has been consumed but none of the amines has been formed yet.

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Ammonia conversion has been calculated based on the consecutive reactions (1) to (3), below, as follows:

$$EtOH + NH_3 = MEA + H_2O \quad (1)$$

$$EtOH + MEA = DEA + H_2O \quad (2)$$

$$EtOH + DEA = TEA + H_2O \quad (3)$$

Defining $X_1$, $X_2$ and $X_3$ the degree of conversion of ethanol in the reactions (1), (2) and (3), respectively, the stoichiometric table for the system will be:

**Table 3.4** Stoichiometric Table

| **Compound** | **In** | **Reaction / Yield** | **Out** |
|---|---|---|---|
| EtOH | 1 | $-X_1-X_2-X_3$ | $1-X_1-X_2-X_3$ |
| $NH_3$ | a | $-X_1$ | $a-X_1$ |
| MEA | | $X_1-X_2$ | $X_1-X_2$ |
| DEA | | $X_2-X_3$ | $X_2-X_3$ |
| TEA | | $X_3$ | $X_3$ |
| $H_2O$ | | $X_1+X_2+X_3$ | $X_1+X_2+X_3$ |

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Ethanol conversion is defined as: $X_{EtOH} = X_1 + X_2 + X_3$

and ammonia conversion as: $X_{NH_3} = 1 - \frac{a - X_1}{a} = \frac{X_1}{a}$

Since $X_1 = Y_{MEA}$ (yield of mono-ethylamine), $X_{NH_3} = \frac{Y_{MEA}}{a}$

Because, as shown in Table 3.3, for all reactions, the rate EtOH : $NH_3$ = 2 : 1, then $X_{NH_3} = 2 \cdot Y_{MEA}$

# 4. RESULTS

## 4.1. EXTERNAL MASS TRANSFER LIMITATIONS

It is of interest to assess whether the reaction at the chosen conditions is in the kinetically or the mass-transfer controlled regime, since they play an important role on the global reaction rate. For his purpose, ethanol amination reactions were carried out at four different stirrer speed rates and the change of catalyst activity as a function of reaction time was measured.

The results, depicted by the Figure 4.1 below, showed no change in activity when the stirrer speed rate was increased. This is a clear indication that the amination of ethanol is not mass transfer controlled. Only kinetic effects govern the reaction.

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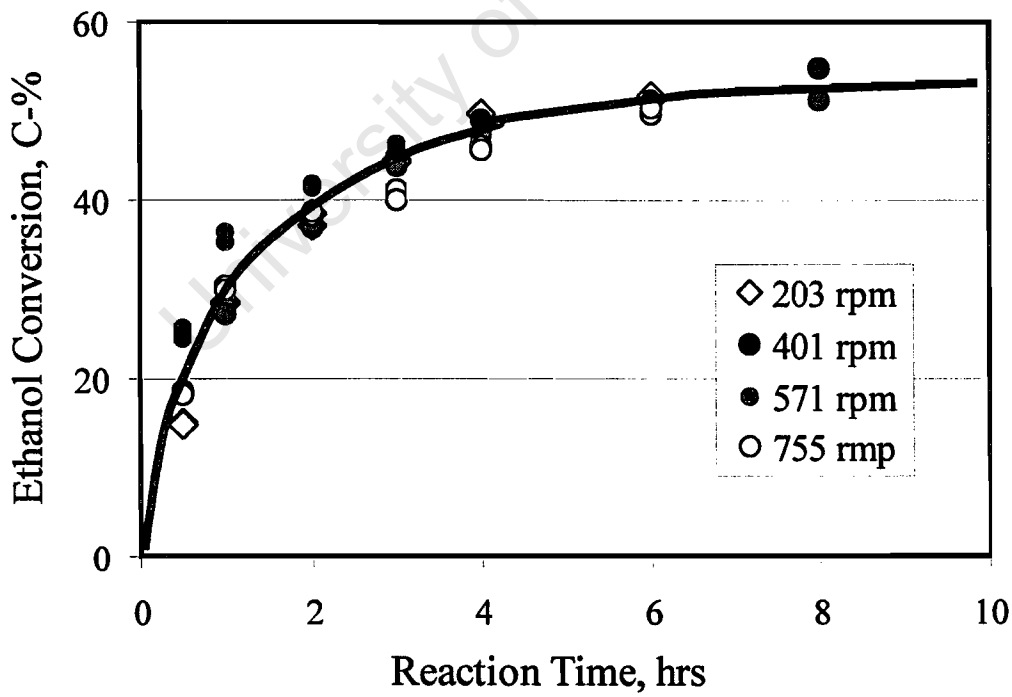


**Figure 4.1** Ethanol conversion as a function of reaction time at four different stirrer speed rate. **Reaction Conditions**: $T_{reaction}$: 200°C; $P_{H2}$: 30 bar; molar ratio: $H_2$ : EtOH : $NH_3$ = 0.29 : 1 : 0.5.

## 4.2. ETHANOL AMINATION

Following the failure of the mechanism proposed by Baiker (1983) for alcohol amination and subsequently proposed pathway by Freese (2001), an investigation on influence of hydrogen on amine distribution was undertaken.

As referred in Section 3.3, amination reaction were performed with loads of 10 and 1 g of the same catalyst with the aim of getting corresponding data for low reaction times. Reaction time was then normalised for 10 g of catalyst. This was based on the assumption that reducing catalyst weight by ten times the reaction time necessary to achieve same conversion will also be reduced by ten times. For instance a reaction time of one hour with 1 g of catalyst correspond to 0.1 hour of reaction time when the catalyst load is 10 g. The results have shown acceptable correlations between data collected both with 1 and 10 g of catalyst. Figures 4.2 and 4.3 as examples demonstrate these trends in ethanol and ammonia conversions and in amines selectivities versus normalised reaction time.

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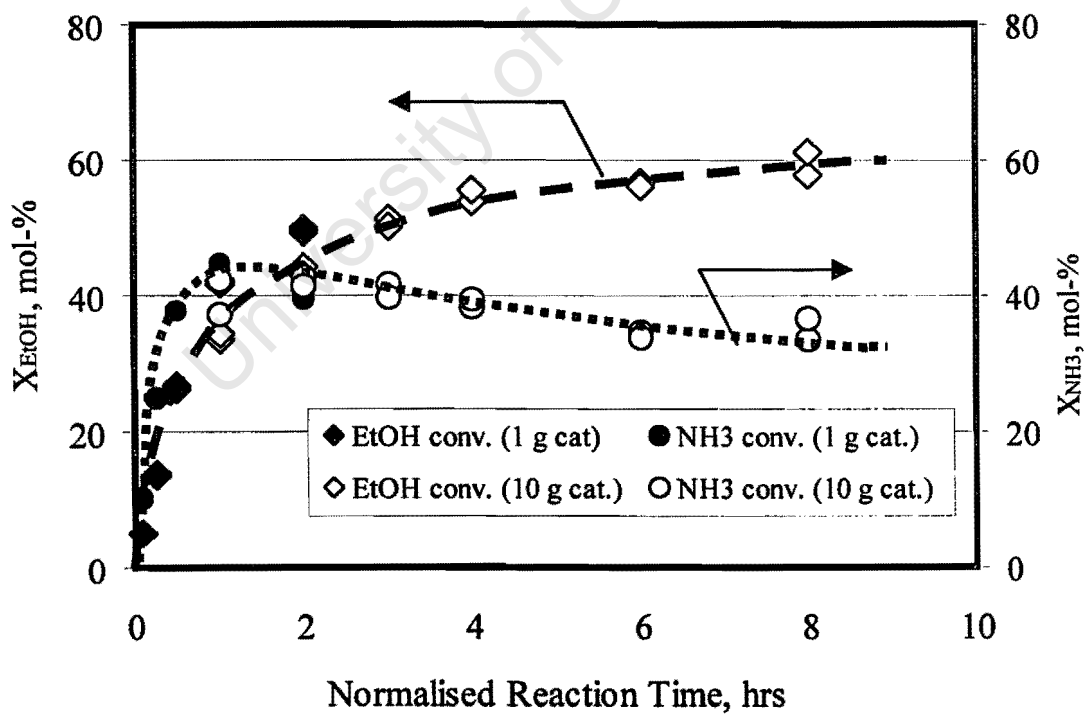


**Figure 4.2** Ethanol and ammonia conversions as a function of normalised reaction time (normalised with respect to the reaction time for 10 g catalyst) **Conditions**: $T_{reaction}$: 200°C; $P_{H2}$: 30 bar; $H_2$: EtOH: $NH_3$ = 0.29: 1: 0.5

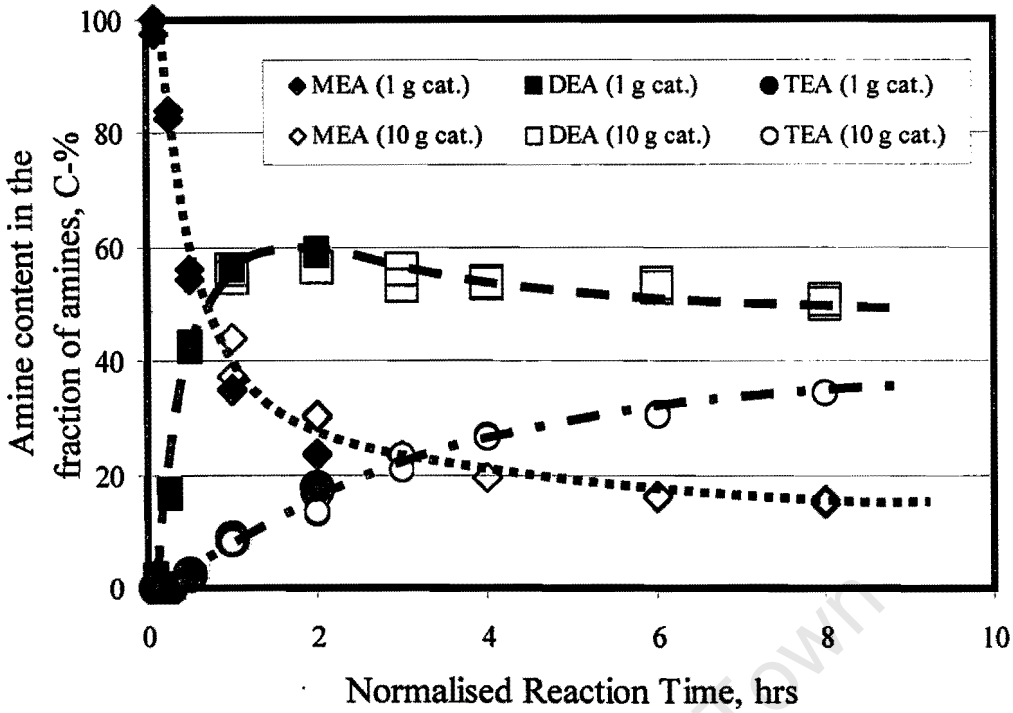


**Figure 4.3** Amines selectivity as a function of normalised reaction time (normalised with respect to the reaction time for 10 g catalyst). **Conditions**: $T_{reaction}$: 200°C; $P_{H2}$: 30 bar; $H_2$: EtOH: $NH_3$ = 0.29: 1: 0.5

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### 4.2.1. INFLUENCE OF HYDROGEN ON ETHANOL AND AMMONIA CONVERSION

The influence of hydrogen on ethanol and ammonia conversion during ethanol amination was investigated by carrying out this reaction at six different hydrogen partial pressures including the absence of it. Figures 4.4 and 4.5 show the ethanol and ammonia conversion profiles obtained.

Ethanol conversion showed a regular increase throughout the reaction time. At high reaction times the conversion increases faster as the hydrogen partial pressure increases, meanwhile in some cases, at low residence times the dependency of conversion rate with hydrogen content is not clear. At hydrogen pressure of 10 bar the conversion seems to be maximum only in the initial stages of the reaction. Nevertheless, there is an indication that the reaction rate of ethanol amination is influenced by the hydrogen partial pressure.

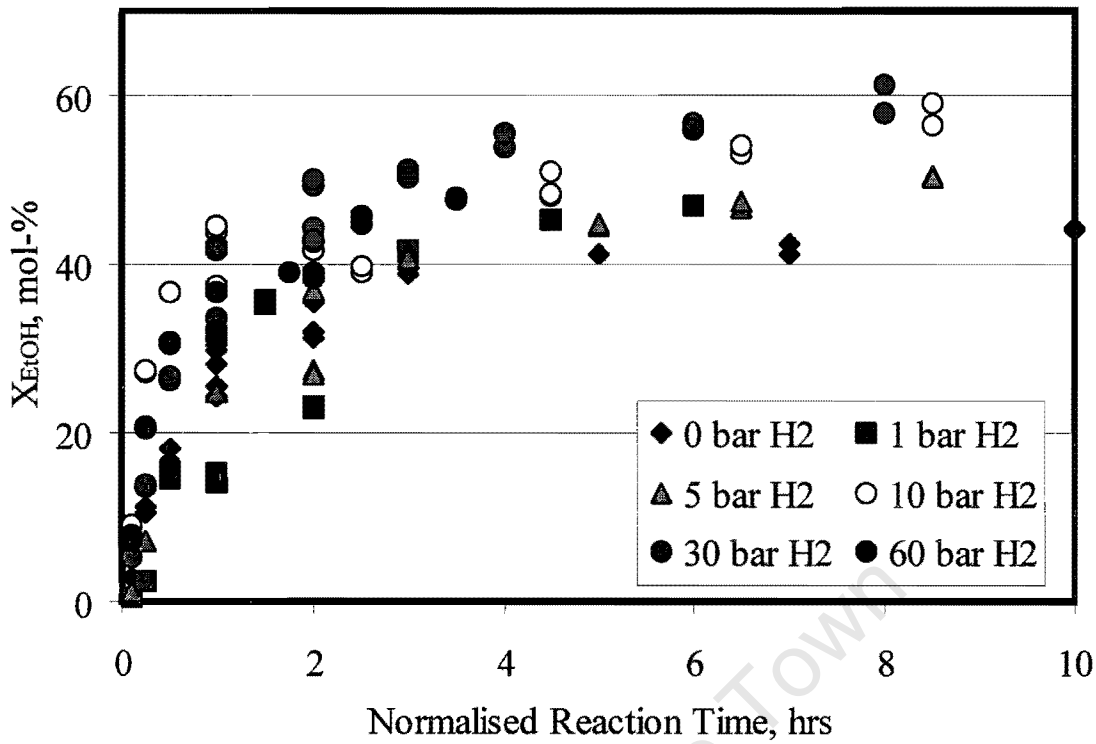


**Figure 4.4** Ethanol conversion profile at different hydrogen partial pressures

Contrasting that of ethanol, the ammonia conversion goes steeply to a maximum, at reaction time between 1 and 1.5 hours, following a smooth decrease. The highest maximum is reached when the reaction was carried out with 1 bar of hydrogen followed by zero and 10 bar. Ammonia profile is suggestive that it is initially consumed to yield MEA. In successive steps the formation of DEA and TEA from MEA and DEA release ammonia:

$$2\ MEA = DEA + NH_3\ ,\ \text{and}$$

$$MEA + DEA = TEA + NH_3$$

In fact, it has been shown that DEA and TEA are formed in consecutive reactions (see Figure 5.4).

An important observation is that even with no hydrogen, the reaction occurs and both ethanol and ammonia conversion follow the same profile as in reactions with hydrogen. The rate of variation of ethanol and ammonia conversion change as the hydrogen partial pressure is changed. These observations will seem to link the amine product distribution with the hydrogen partial pressure through the ammonia consumption.

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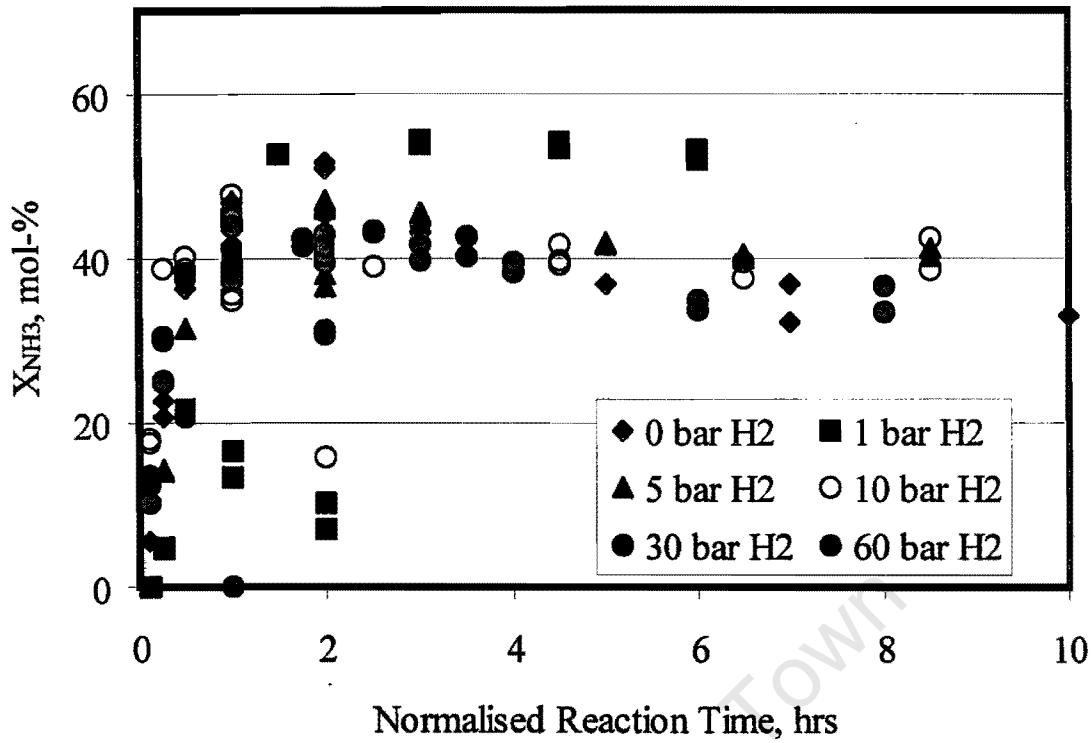


**Figure 4.5** Ammonia conversion profile at different hydrogen partial pressures

Figures 4.6 to 4.11 show the variation of the ethanol and ammonia conversion as a function of reaction time, separately at each hydrogen partial pressure. The ratio of ethanol to ammonia as well as the amount of catalyst and other reaction temperatures were kept unchanged.

The occurrence of ethanol amination in absence of hydrogen here can be ascribed to the fact that this is a closed system. Once the catalyst is activated and introduced into the reactor and since there is no flow in/out the catalyst activity remains unaffected. The fact that ethanol conversion takes place even in absence of hydrogen and the selectivities following the same profile as if hydrogen was present may imply that there is another role played by hydrogen other than preventing catalyst deactivation. Sewell (1996) observed an increasing in rate of ethanol conversion with increasing hydrogen partial pressure. He found that the reaction order with respect to hydrogen was 1.91. Hydrogen may facilitate adsorption species favouring thus the rate of the reaction. Another role of hydrogen in ethanol amination is what has been proposed by Freese (2001), which is the hypothesis presented by this research.

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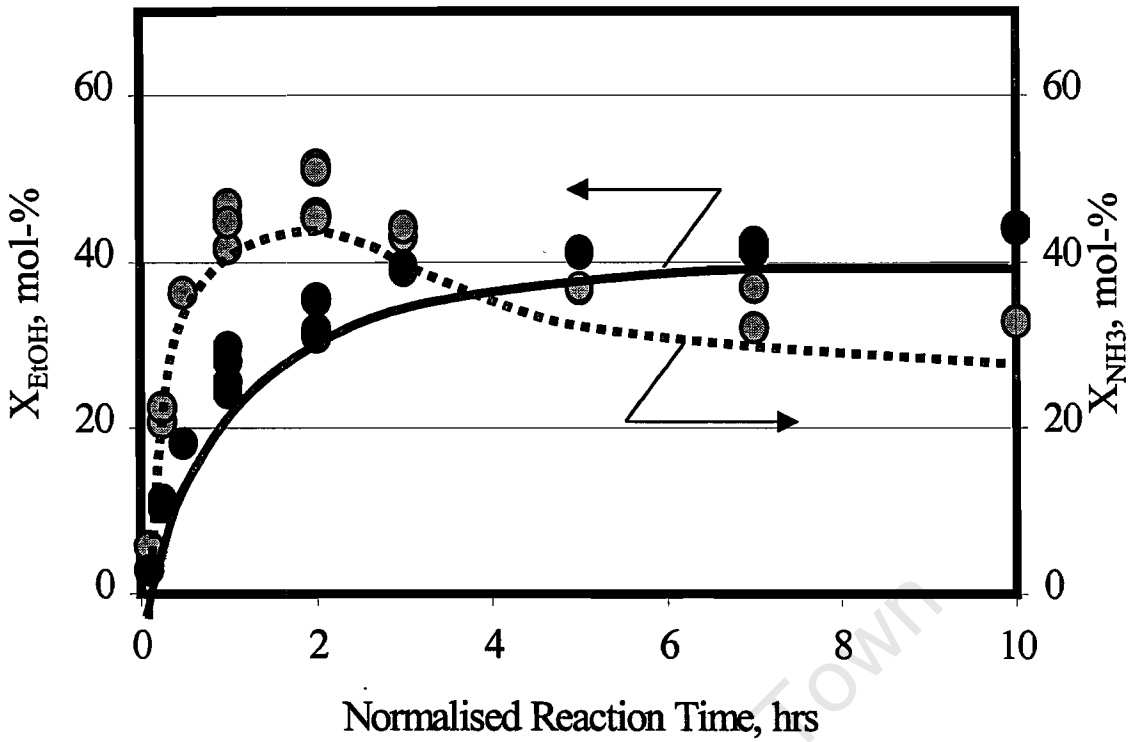


**Figure 4.6** Ethanol and ammonia conversion profile on ethanol amination carried out with no hydrogen

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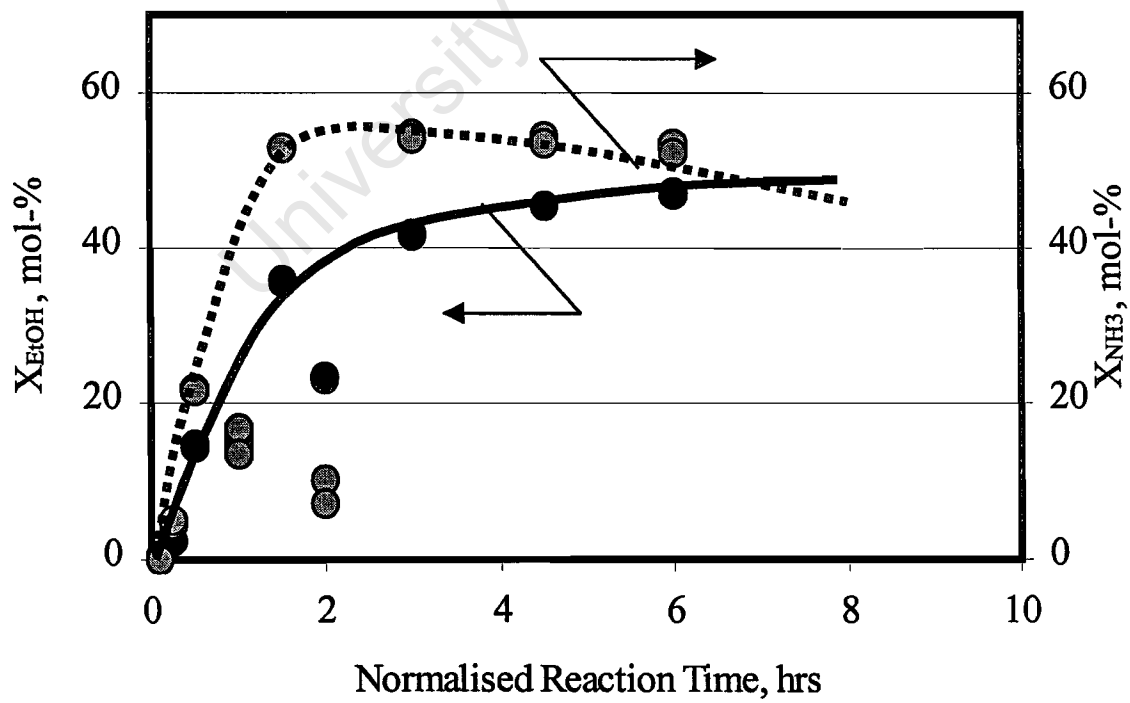


**Figure 4.7** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 1 bar

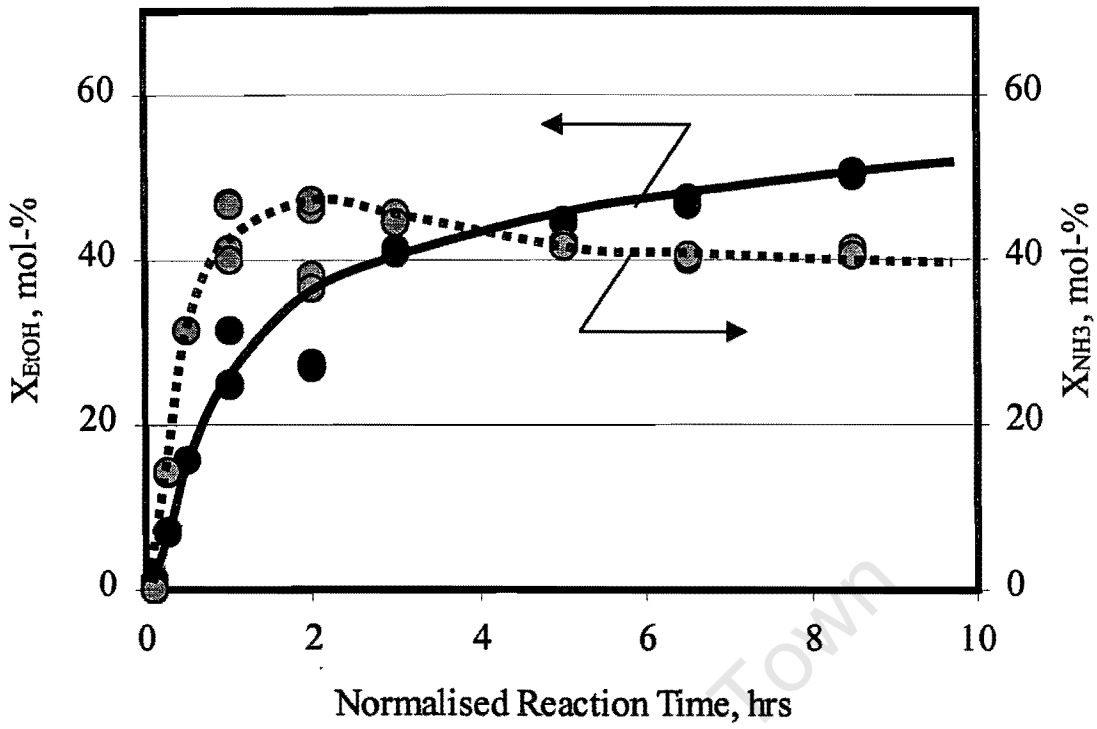


**Figure 4.8** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 5 bar

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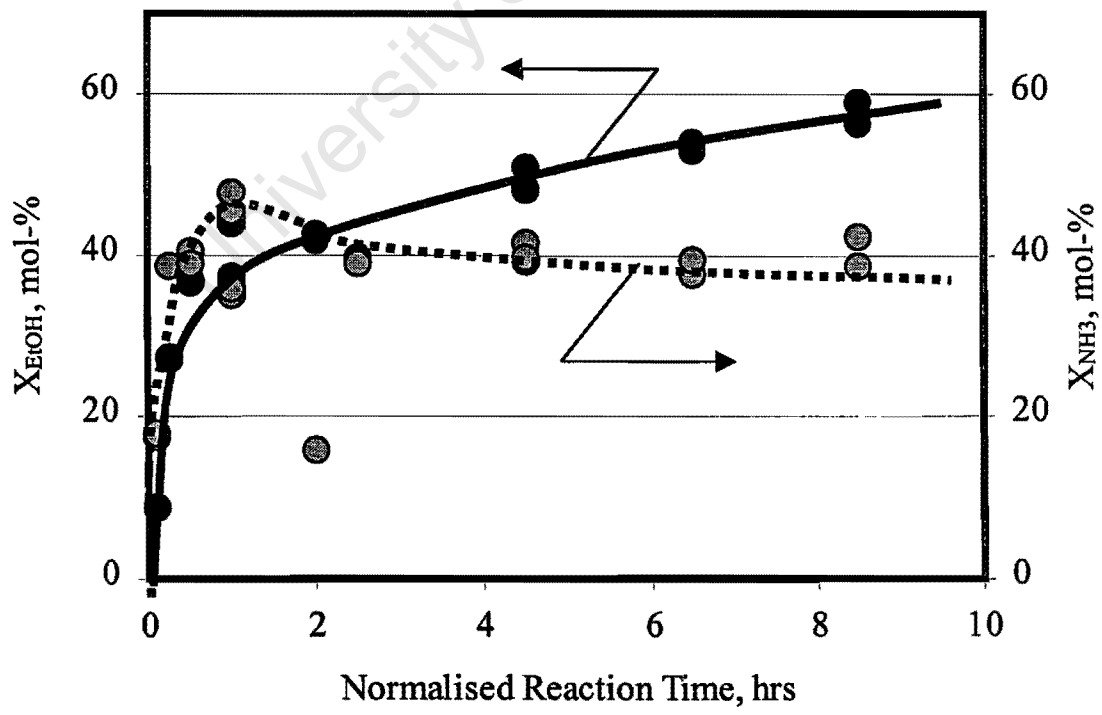


**Figure 4.9** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 10 bar

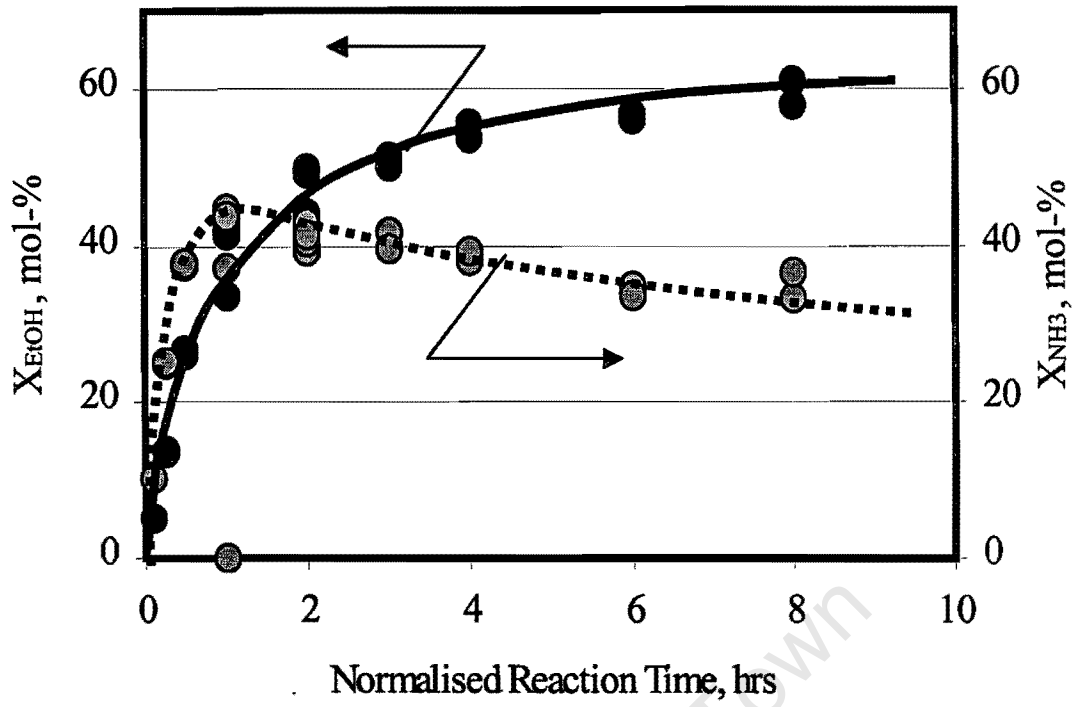


**Figure 4.10** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 30 bar

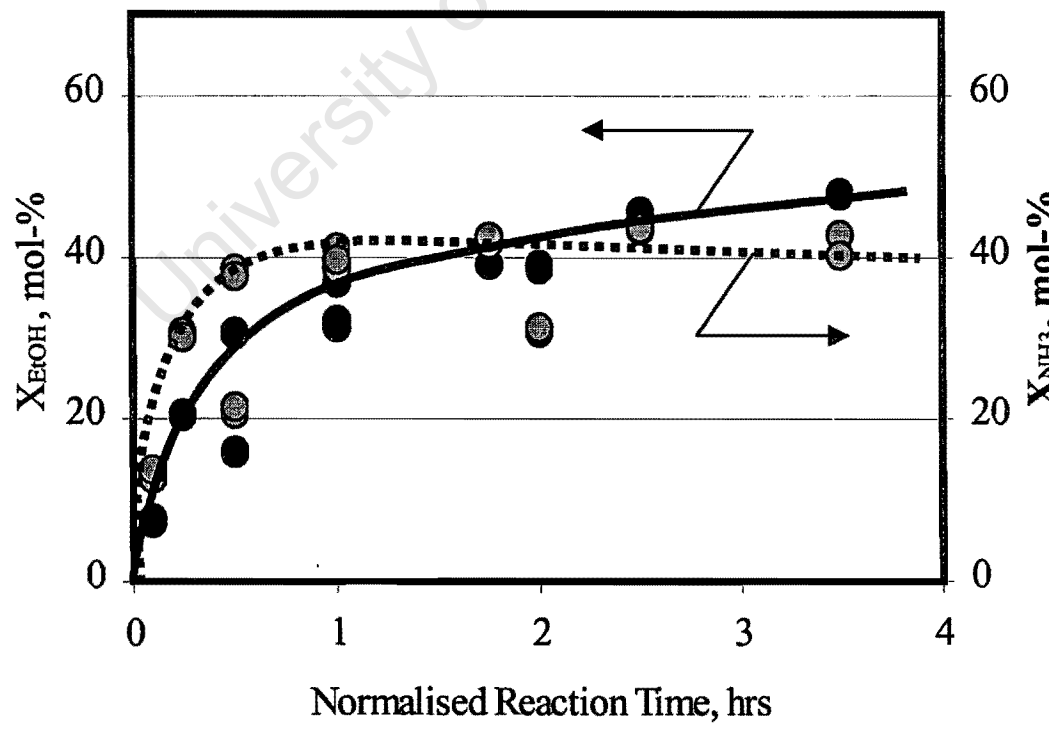


**Figure 4.11** Ethanol and ammonia conversion profile on ethanol amination carried out with hydrogen partial pressure of 60 bar

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## 4.2.2. INFLUENCE OF HYDROGEN ON AMINE SELECTIVITY

The selectivity profile is influenced by hydrogen partial pressure, despite it is not linear. This is depicted by the Figures 4.3 (for hydrogen partial pressure of 30 bar) and 4.12 - 4.15. The rate of consumption of MEA is more pronounced when hydrogen pressure is 10 bar. This led to lower selectivity of MEA and highest selectivity to DEA (above 60 C-%) at low reaction time. This trend is not obvious when hydrogen partial pressure was changed from zero to one bar. DEA and TEA contents seem to be higher and MEA be lower at zero bar hydrogen compared with the values obtained when the reaction was carried with hydrogen partial pressure of 1 bar.

GC-MS analysis was performed and no side product could be identified. Carrying out experiments in ethanol hydro-amination in a tubular reactor over this $Co/SiO_2$ catalyst, Freese (2001) found selectivities to ethylamines of around 100%.

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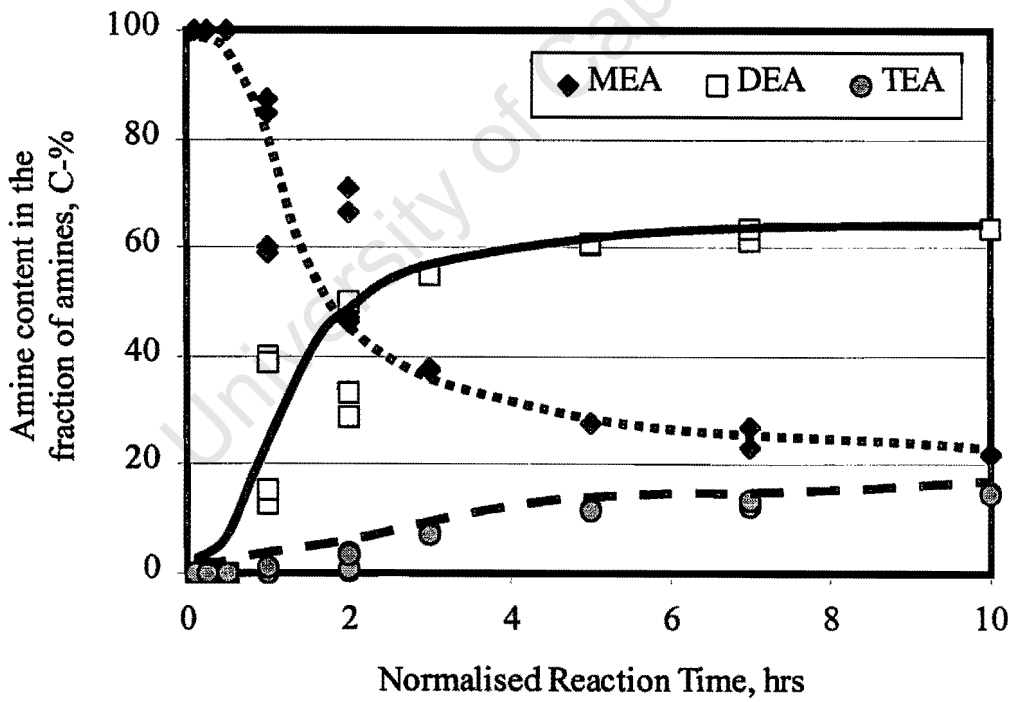


**Figure 4.12** Amine selectivity from ethanol hydro-amination in the absence of hydrogen

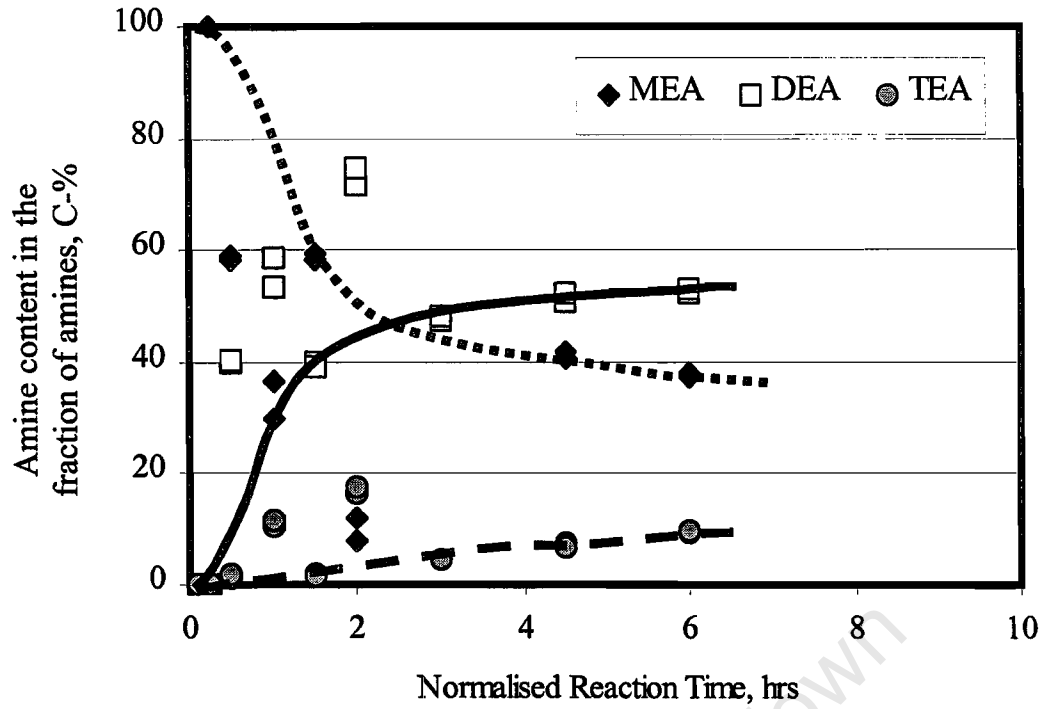


**Figure 4.13** Amine selectivity from ethanol hydro-amination with 1 bar of hydrogen partial pressure

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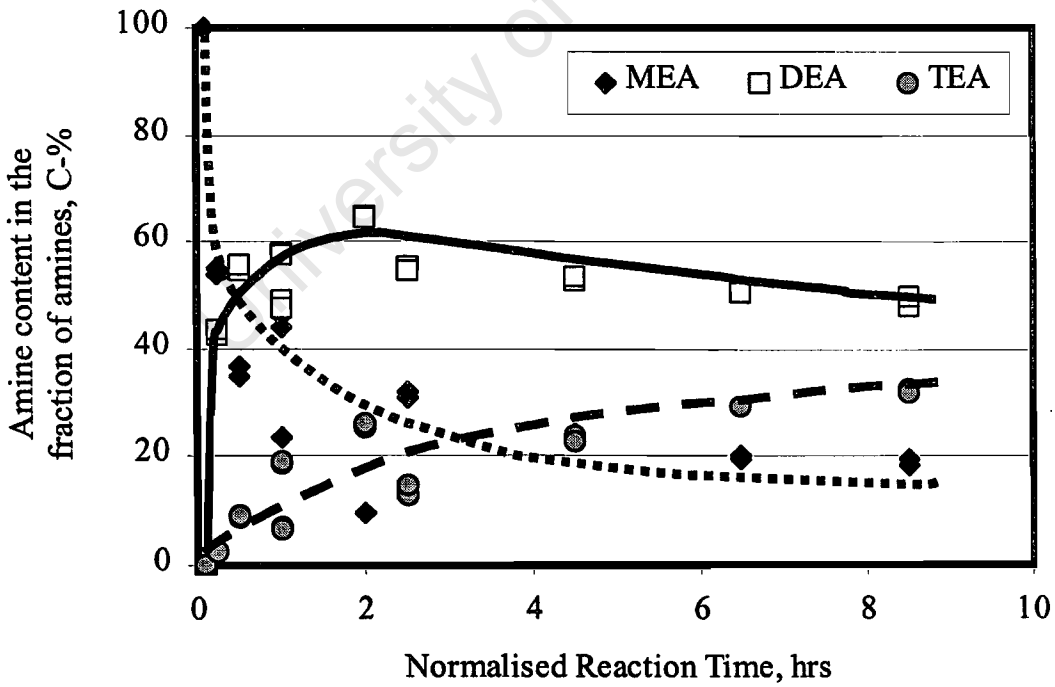


**Figure 4.14** Amine selectivity from ethanol hydro-amination carried out with 10 bar of hydrogen partial pressure

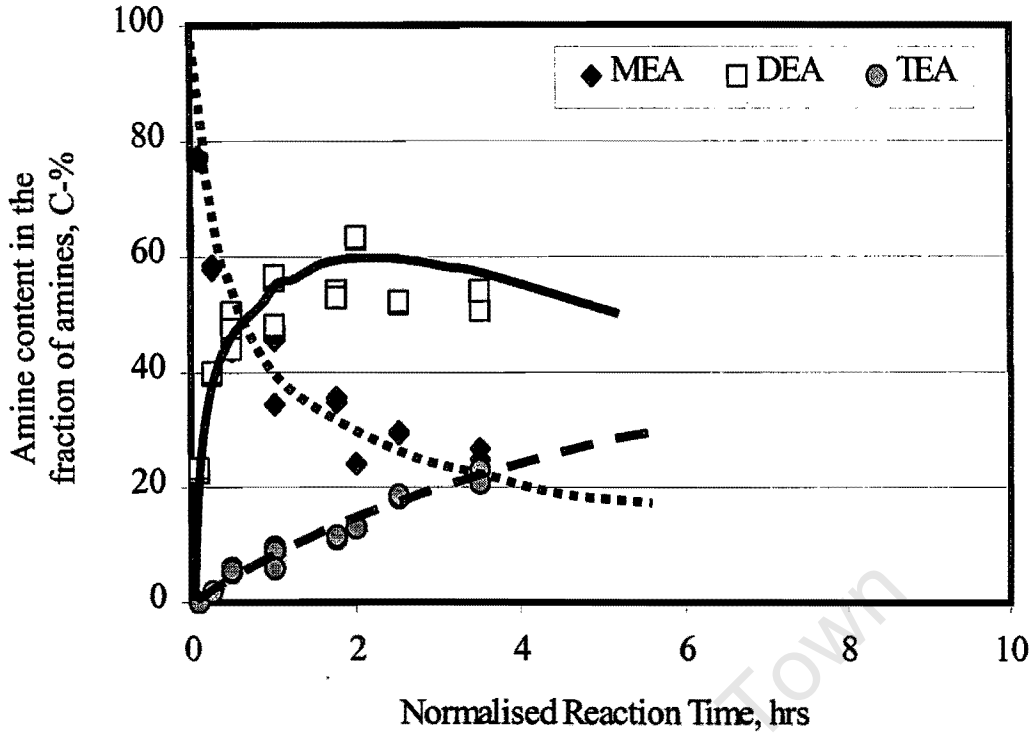


**Figure 4.16** Amine selectivity from ethanol hydro-amination performed with 60 bar of hydrogen partial pressure

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### 4.2.3. INFLUENCE OF HYDROGEN ON AMINES YIELD

The yield of MEA increases fast and passes through a maximum at reaction times around 1 to 1.5 hours. DEA and TEA yields increase in time. The rate of DEA formation is far higher than the rate of formation of TEA. At high reaction times, the yield of DEA increase with hydrogen partial pressure. In the other hand, increasing the partial pressure of hydrogen the changes in amine yield become more pronounced. This is shown in Figures 4.16 – 4.21.

The magnitude of maximum MEA yield is associated with that of ammonia conversion. Typically, the higher the maximum of ammonia conversion the higher the maximum of MEA yield.

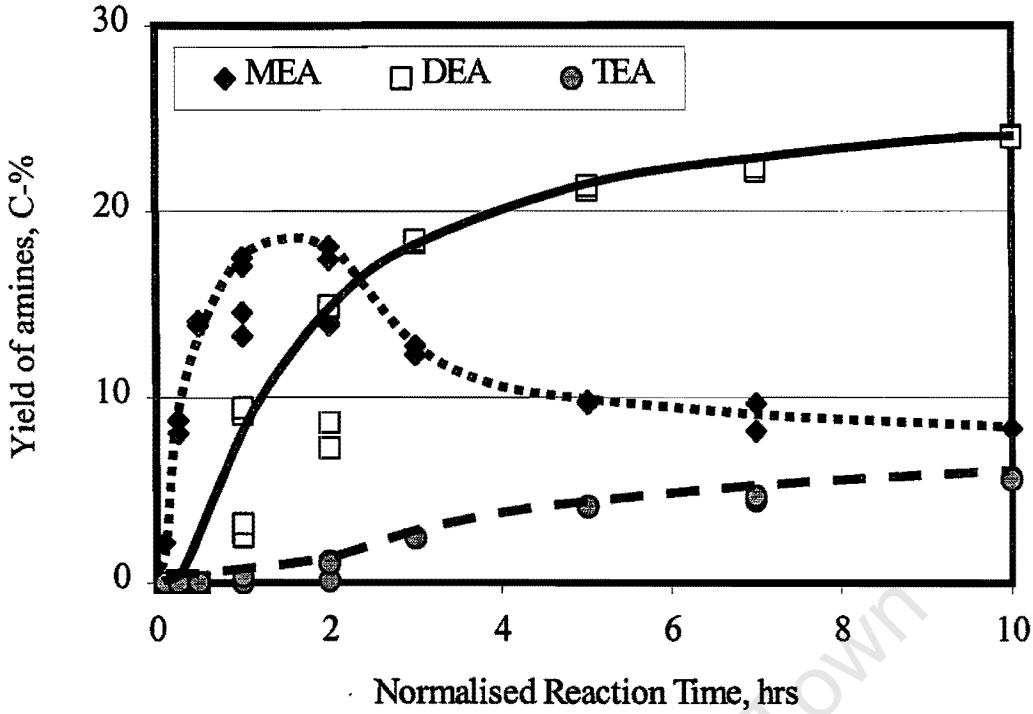


**Figure 4.16** Yield of Amines in a Ethanol Amination Reaction performed in absence of hydrogen

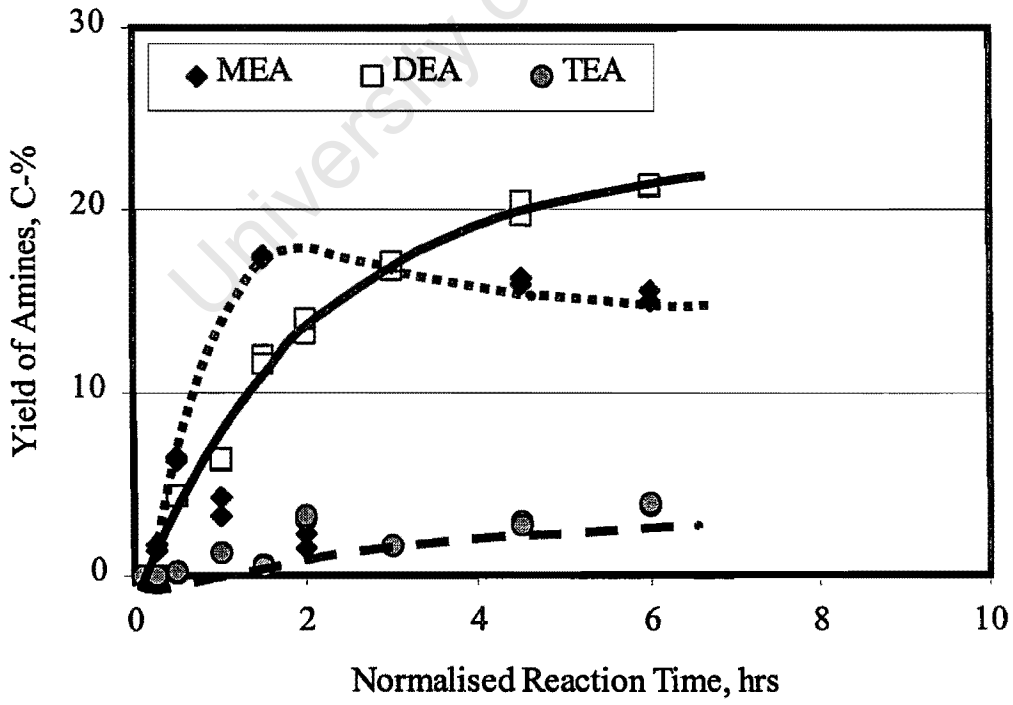


**Figure 4.17** Yield of amines in reaction performed with 1 bar hydrogen

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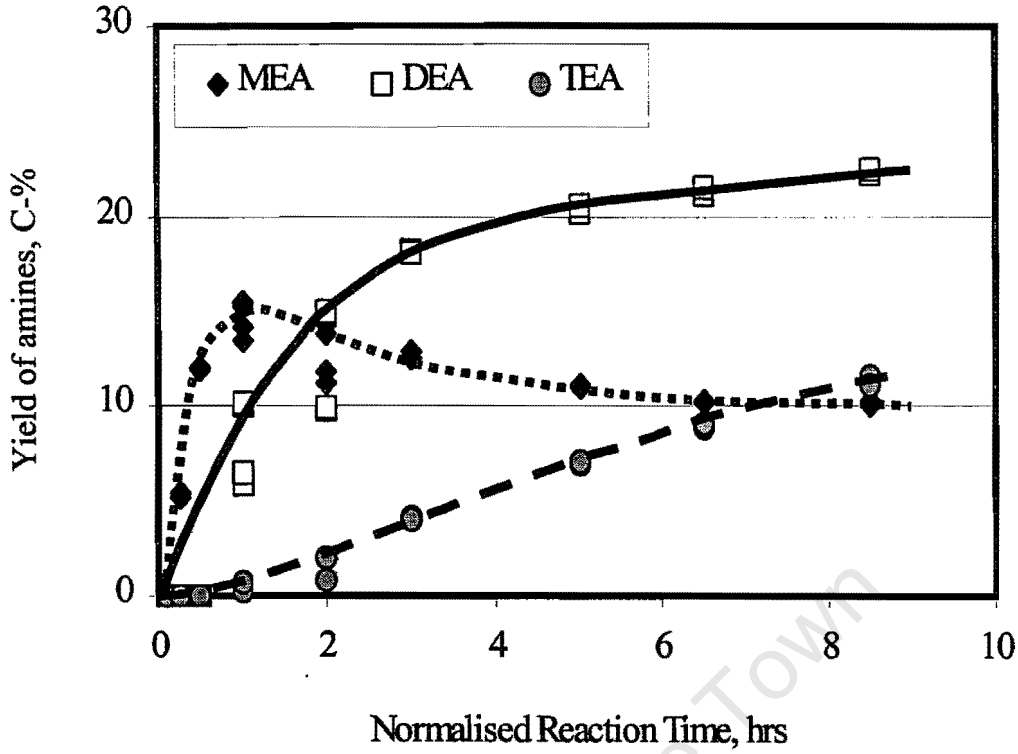


**Figure 4.18** Yield of Amines in a Ethanol Amination performed with 5 bar $H_2$

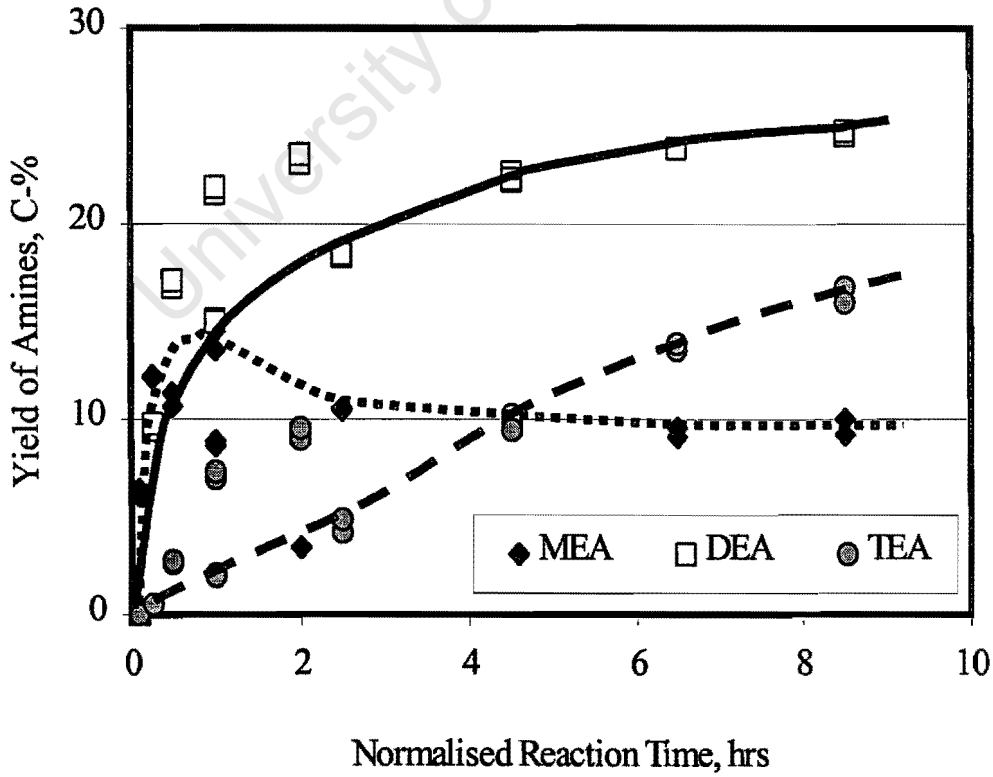


**Figure 4.19** Yield of Amines in a Ethanol Amination carried out at 10 bar $H_2$

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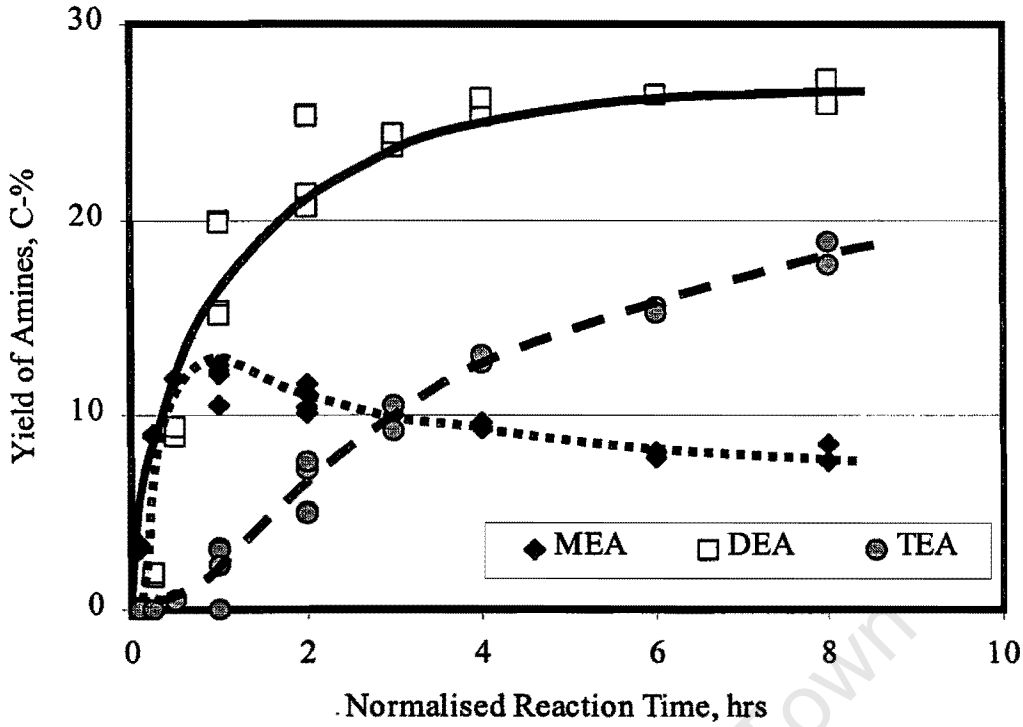


**Figure 4.20** Yield of Amines in a Ethanol Amination performed at 30 bar $H_2$

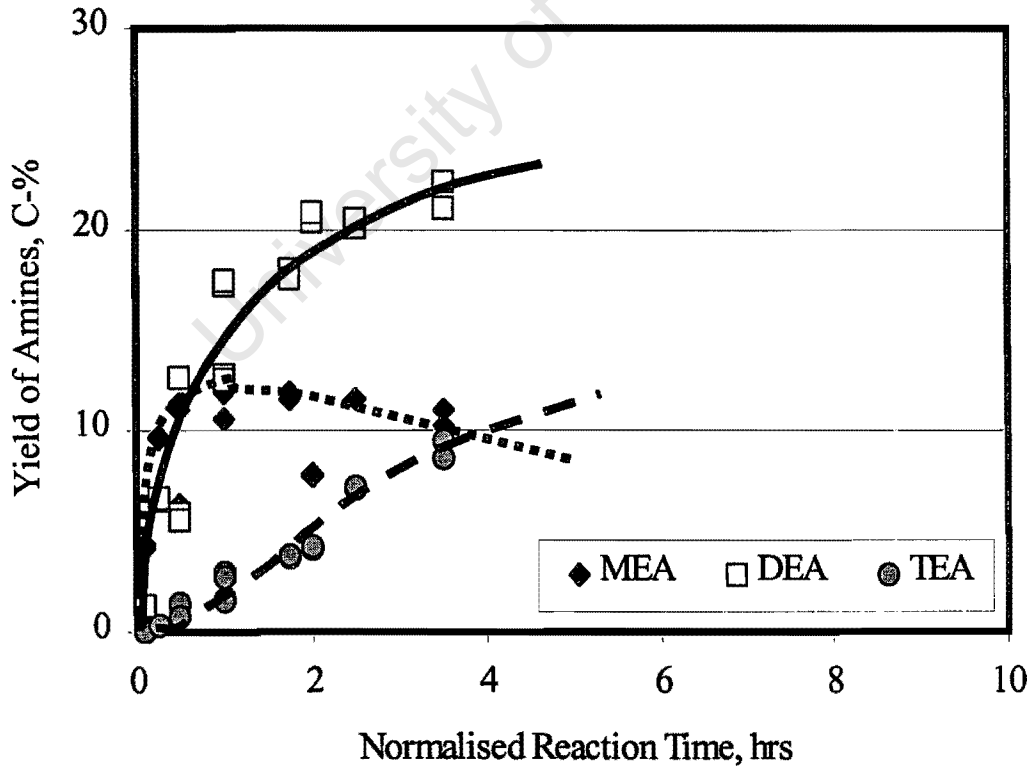


**Figure 4.21** Yield of Amines in a Ethanol Amination performed at 60 bar $H_2$

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Table 4.1 shows the maximums of ammonia conversion and MEA yield for all selected hydrogen partial pressures. These values are derived from the Figures 4.16 – 4.21.

**Table 4.1** Maximums of ammonia conversion as a function of hydrogen pressure

| **$H_2$ Partial Pressure, bar** | 0 | 1 | 5 | 10 | 30 | 60 |
|---|---|---|---|---|---|---|
| **Maximum $X_{NH_3}$, mol-%** | 52 | 55 | 48 | 47 | 45 | 42 |
| **Maximum $Y_{MEA}$, C-%** | 19 | 18 | 16 | 14 | 13 | 13 |
| **Time, hrs** | 1.5 | 1.5 | 1 | 1 | 1 | 1 |

It can be seen that from 1 bar hydrogen upward, the higher the hydrogen partial pressure applied the lower the maximum in ammonia conversion and thus the lower the maximum in MEA yield. This leads to high yields of DEA and TEA.

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## 4.3. *NORMAL*-PROPANOL AMINATION

Similarly to ethanol, *n*-propanol amination was carried out with 1 and 10 g of catalyst. Analysis of samples collected from the reaction performed with the catalyst load of 10 g was difficult. This was due to the formation of two non-miscible phases on the samples, as a consequence of high concentration of less soluble components on the reaction mixture. Mixing by shaking was tried with no success. The shaken sample mixture contained bubbles, showing that complete miscibility was not achieved. This phenomenon was less pronounced in the samples resulting from 1 g catalyst runs. In this case analysis were possible, but the level of reproducibility was low.

The Figure 4.22 depicts n-propanol and ammonia conversion as a function of reaction time. Ammonia conversion goes through to a maximum of around 1.5 mol-%, whereas *n*-propanol conversion increases and seems to go to a maximum little above 30 mol-%.

Amine selectivity is presented in the Figure 4.23. It is shown that mono-propylamine (MPA) is the primary product. Di-propylamine (DPA) and tri-propylamine (TPA) are partly formed by consumption of MPA.

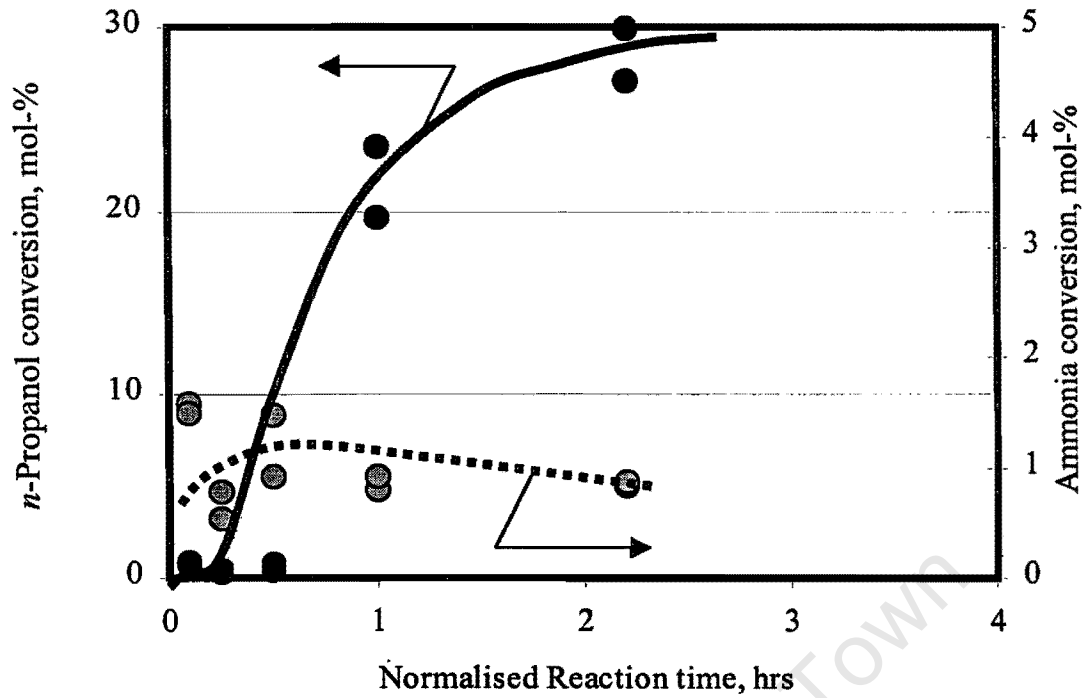


**Figure 4.22** *n*-Propanol and ammonia conversion as a function of reaction time. $P_{H2}$ : 25 bar

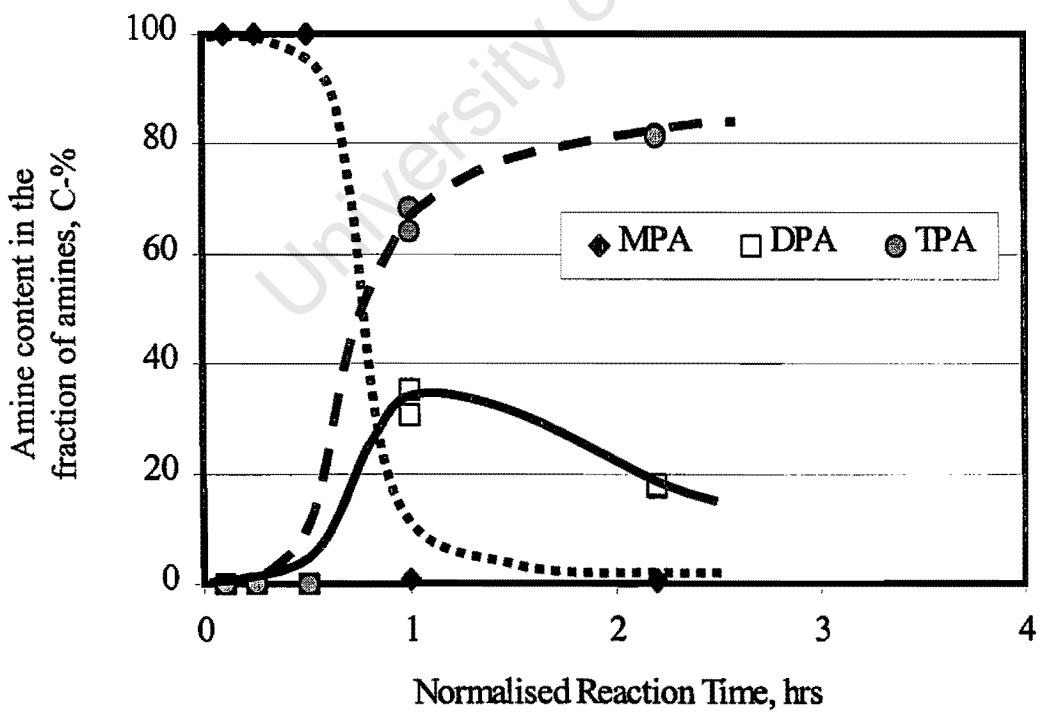


**Figure 4.23** Amine Selectivity in *n*-propanol amination. $P_{H2}$: 25 bar

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The ammonia conversion – time profile presents a quite lower conversion than the stoichiometrically expected, even considering the higher selectivities to TPA and DPA. This is not a true ammonia conversion and is a consequence of the above mentioned difficulties in sample analysis.

## 4.4. *ISO*-PROPANOL AMINATION

*Iso*-propanol hydro-amination reactions were performed at a hydrogen partial pressure of 25 bar. The molar ratio *iso*-propanol: ammonia was 2 : 1. *Iso*-propanol and ammonia conversion showed different trends to those of ethanol and *n*-propanol amination (Figure 4.24). Over a period of 8 hours time the ammonia conversion was always higher than alcohol conversion and both seem to become constant in considerably short reaction time.

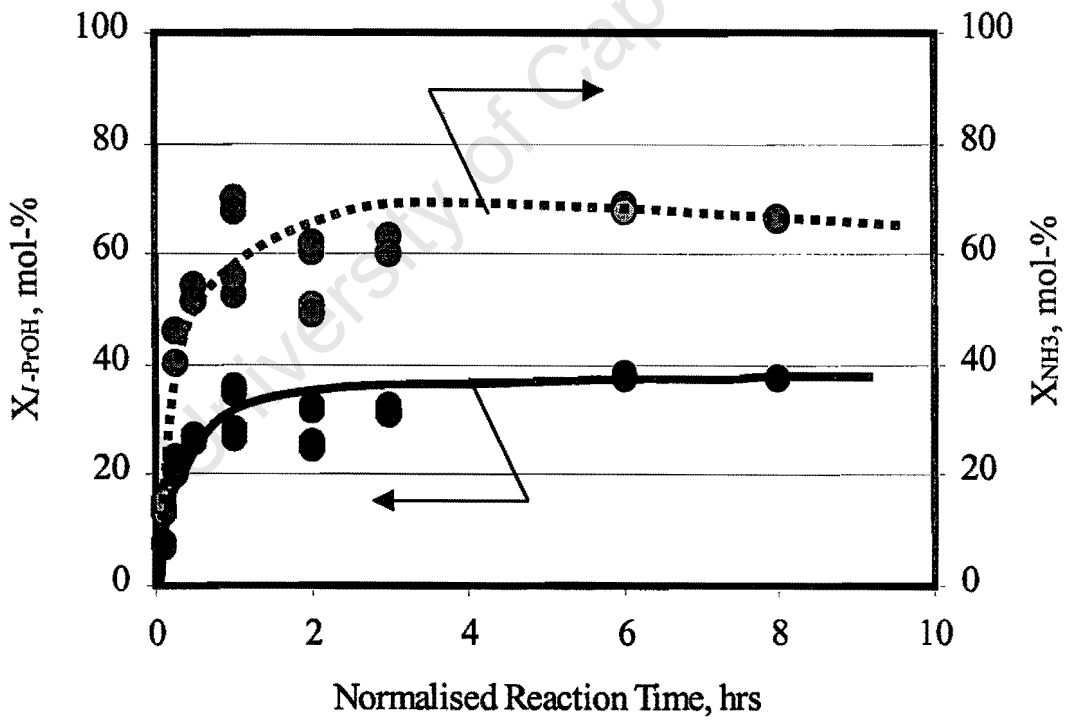


**Figure 4.24** *I*-propanol and ammonia conversion in *i*-propanol amination. $P_{H2}$: 25 bar

As derived in Section 3.4, ammonia conversion is twice the yield of the mono-amine. Contrasting in ethanol and n-propanol amination, the *iso*-propanol amination showed a

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very high selectivity to mono-*iso*-propylamine (MIPA) (see Figure 4.25) which remains higher, compared to the other amines, throughout the reaction time considered. This makes the ammonia conversion higher than that of *iso*-propanol.

The plot of amine selectivity as a function of normalised reaction time shows that both mono-*iso*-propylamine and di-*iso*-propylamine (DIPA) are the primary formed products, being the last one produced in small amounts. Tri-*iso*-propylamine (TIPA) formation occurs via the consumption of MIPA and DIPA.

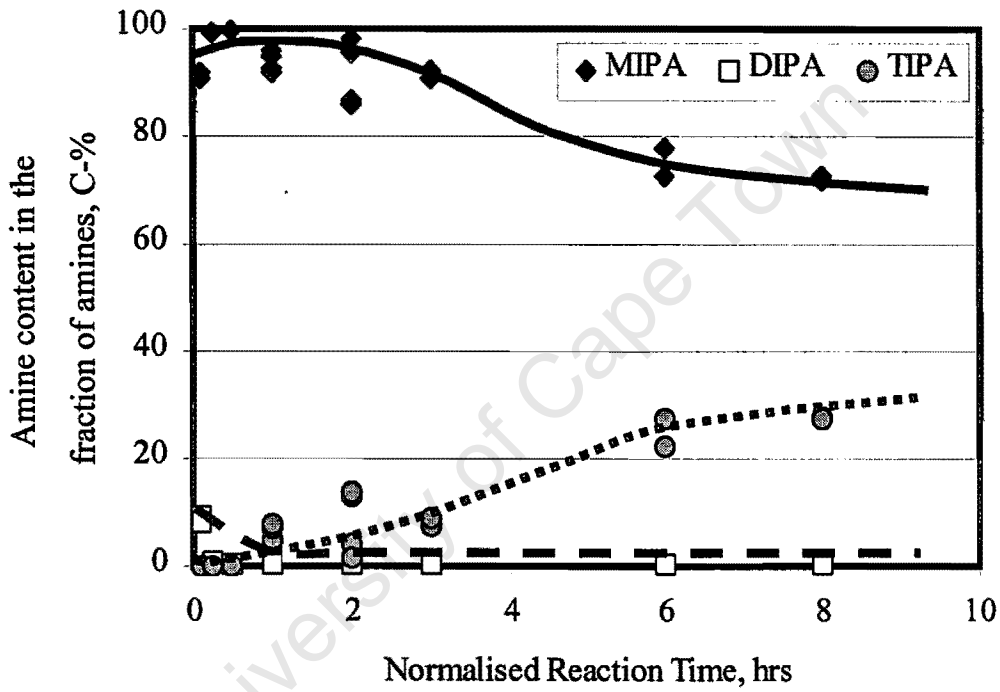


**Figure 4.25** Amine selectivity in *iso*-propanol amination. $P_{H2}$: 25 bar

## 4.5. *NORMAL*-BUTANOL AMINATION

Equally to other alcohols investigated, *n*-butanol amination was performed with catalyst loads of 1 and 10 g. Due to the formation of two immiscible phases, was not possible to analyse samples of the first run. Thus, the available data are too high to ascertain the initial selectivity, conversion and yield. Additionally the reproducibility of the results was affected by this phenomena.

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Under the reaction conditions only two products were formed, namely mono-butylamine (MBA) and di-butylamine (DBA). Tri-butylmine (TBA) was not formed. The samples underwent to GC-MS analysis. No secondary product could be identified. MBA is the primary product.

Like in *iso*-propanol amination case, here ammonia showed higher conversion as a function of the reaction time than that of n-butanol (Figure 4.26). Figure 4.27 depicts amine selectivity as a function of reaction time, showing that in the reaction time considered, MBA has higher selectivity than DBA.

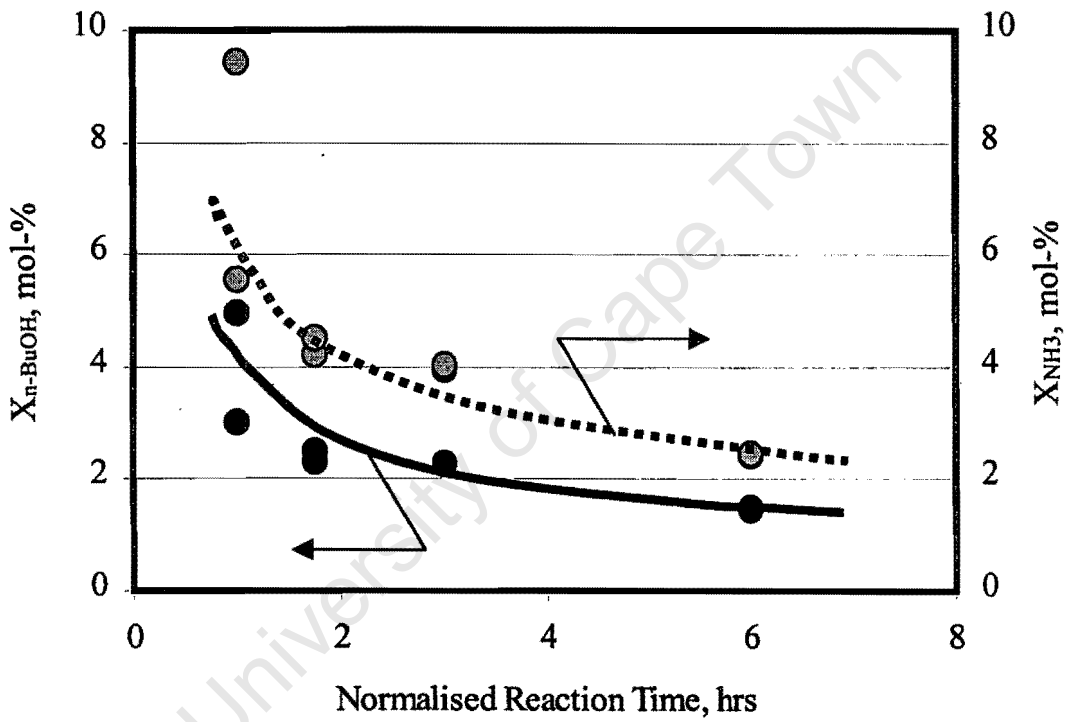


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**Figure 4.26** *n*-Butanol and ammonia conversion in *n*-butanol amination. $P_{H2}$: 20 bar

An increase in conversion both for *n*-butanol and ammonia, at least initially, was to be expected as a normal trend in a batch reactor. That is not observed here due to the impossibility of getting well-mixed samples for GC analysis, which led to non true conversions.

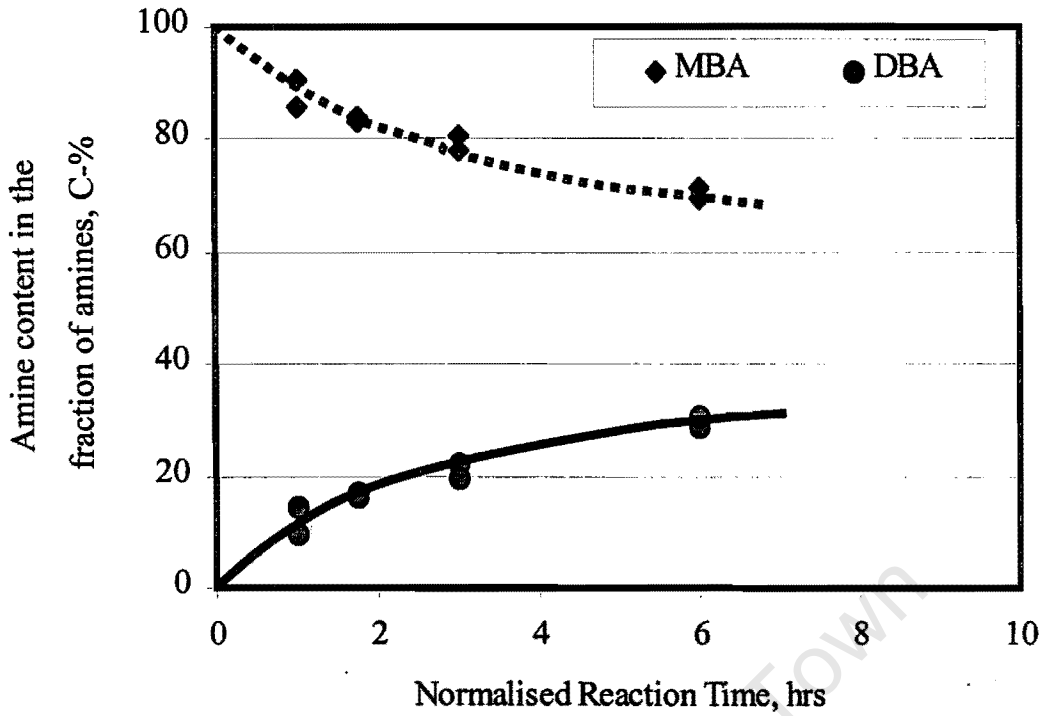


**Figure 4.27** Amine selectivity in *n*-butanol amination. $P_{H2}$: 20 bar

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# 5. DISCUSSION

## 5.1. CATALYST ACTIVITY

In ethanol amination, although the overall ethanol thermodynamic equilibrium conversion reaches values of around 99%, the observed ethanol conversion seams to reach a maximum of approximately 60 mol-% irrespective to the hydrogen partial pressure. This is an indication that ethanol amination under the conditions here investigated is not due to equilibrium limitation. This also holds for propanol and butanol amination, despite in these cases the observed maximum conversions were lower: ca 30 mol-% for *n*-propanol, 40 mol-% for *iso*-propanol and les than 10 mol-% for *n*-butanol. The difference between the overall equilibrium conversion and the maximum observed conversion must be ascribed to the catalyst loss of activity occurring during the reaction and/or losses of reactants due to sampling. Five to six samples of around 10 ml volume each are taken every run.

The catalyst deactivation might be attributed to the effect of water formed, which is a co-product of the reaction. It has been referred by Kliger *et al.*, (1975) in his study of octanol amination in gas phase, that the addition of water to the original mixture sharply slows the reaction rate. Decreases in reaction rate are caused by a modification of the catalyst surface (Sewell, 1996). Ethanol hydro-amination performed with hydrogen pressure of 30 bar at four different stirrer speed rate (Figure 4.1) proved that the catalyst is active within the range of conditions tested.

In order to visualise the influence of hydrogen on catalyst activity, the first data points of ethanol and ammonia conversion were plotted against the hydrogen partial pressure (Figures 5.1 and 5.2). These points correspond to 0.1 and 1 hr respectively for reactions performed with 1 and 10 g of catalyst. Their choice was based on the fact that at these reaction times there are no losses of material due to sampling.

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Although some deviations were observed, the results typically indicate that hydrogen enhances the catalyst activity, being 10 bar hydrogen the pressure that yields the maximum initial ethanol conversion, within the pressure range considered in this study. This tendency has been shown much more clearly by comparing the entire conversion profiles at different hydrogen partial pressures (Figures 4.4 and 4.5). It can be seen that in the first ca 1 hr of reaction ethanol and ammonia conversion remain the highests at hydrogen pressure of 10 bar. As it can also be observed in Figures 4.4, 4.5, 5.1 and 5.2, the catalyst is still active even in total absence of hydrogen.

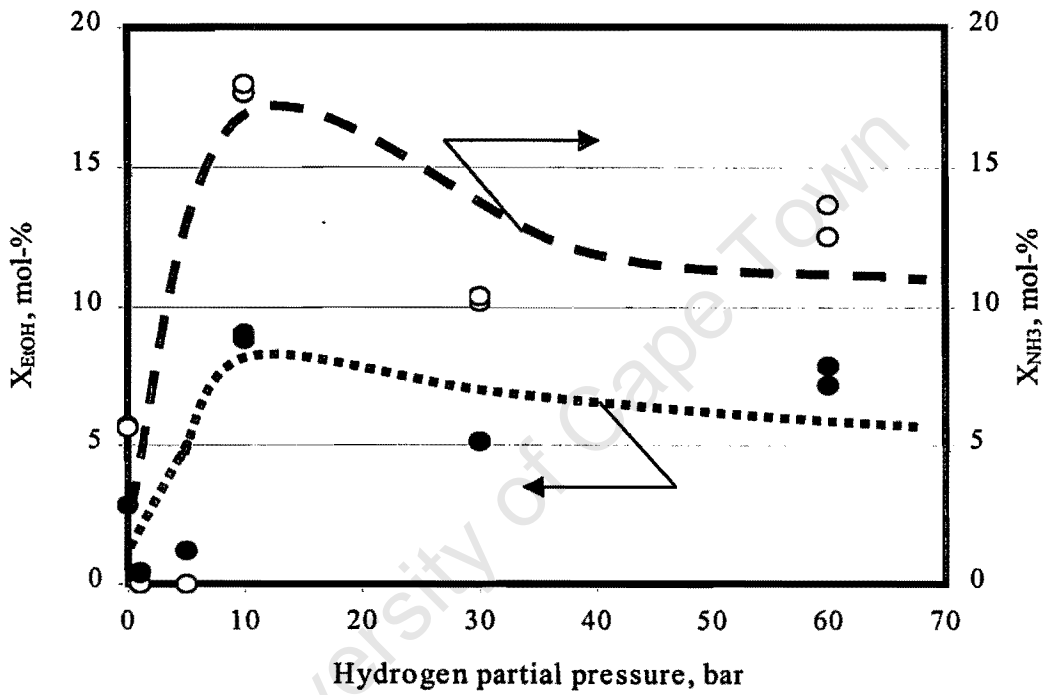


**Figure 5.1** Ethanol and ammonia conversion as a function of hydrogen partial pressure at 0.1 hr (first data points). Mass of catalyst: 1 g

The influence of hydrogen on the initial ethanol conversion contrasts with the way it influences the conversion at high reaction times. At high reaction times, the higher the hydrogen partial pressure, the higher the ethanol and ammonia conversion. This means that at higher concentrations of ethanol and ammonia, the conversion is favoured neither by low nor high hydrogen pressure. Once ethanol and ammonia concentration are reduced by conversion into products, the rate of conversion is favoured by high hydrogen pressure.

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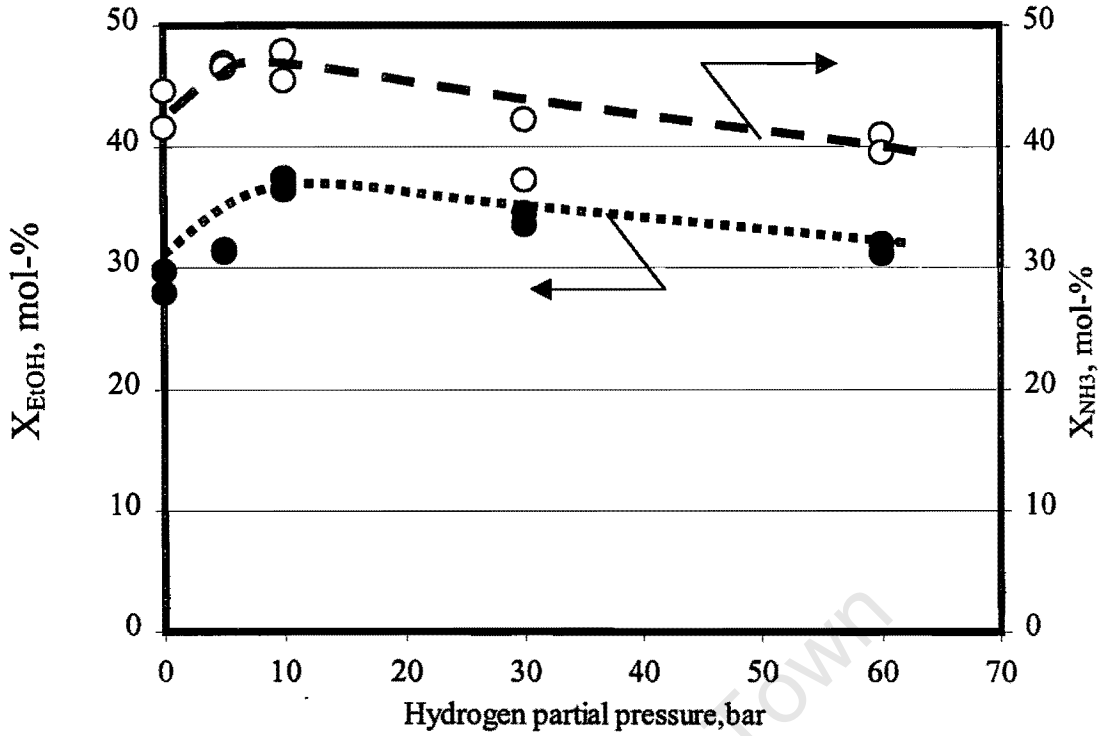


**Figure 5.2** Ethanol and ammonia conversion as a function of hydrogen partial pressure at 1.0 hr (first data points). Mass of catalyst: 10 g.

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Deviations can be explained by variations in distribution of cobalt over the support $SiO_2$. This was evaluated by the heterogeneity of the catalyst showed by its coloration and could be observed in Electron Microscopy Analysis (Appendix A.I). The variations in dispersion can be ascribed to the different degrees of interaction of the metal precursor compounds with the support. As cited by Sewell (1996), the strong interaction between cobalt and $SiO_2$ support results in incomplete reduction by activation in hydrogen. As a consequence, a significant proportion of cobalt atoms are unavailable for the reduction since only zero-valent cobalt is active for hydro-amination reactions under these conditions. This also explains the less good correlation, in some cases, between the runs performed with 1 and 10 g catalyst, in addition to inaccuracies in reactants loading. In addition, the estimated initial composition based on fugacities of the initial reactants mixture (Table 5.1), with binary interaction coefficients ($k_{ij}$) taken as zero, show a deviation from the charge composition.

**Table 5.1** Estimated fugacities based on the Peng-Robinson equation of the state ($k_{ij}$ = 0) and the pressure in the reactor at 200°C at the start of the reaction.

| $P_{H2}$ at 200°C, bar | | 0 | 1 | 5 | 10 | 30 | 60 |
|---|---|---|---|---|---|---|---|
| 1 g catalyst | $P_0$ at 200°C, bar | 39 | 40 | 45 | 48 | 71 | 111 |
| | $f_{EtOH}$, bar | 18.46 | 18.63 | 19.51 | 19.72 | 21.61 | 22.60 |
| | $f_{NH3}$, bar | 12.72 | 12.95 | 14.07 | 14.36 | 17.92 | 21.51 |
| | $f_{H2}$, bar | 0.00 | 0.35 | 0.20 | 4.14 | 17.23 | 48.90 |
| 10 g catalyst | $P_0$ at 200°C, bar | 38 | 40 | 45 | 48 | 72 | 110 |
| | $f_{EtOH}$, bar | 18.17 | 18.63 | 19.51 | 19.72 | 21.69 | 22.59 |
| | $f_{NH3}$, bar | 12.39 | 12.95 | 14.07 | 14.36 | 18.15 | 21.36 |
| | $f_{H2}$, bar | 0.00 | 0.35 | 0.20 | 4.14 | 17.63 | 48.20 |

Although it could not be measured, the reproducibility of reduction process is guaranteed by the extent of reduction time (16 hours) and relatively high hydrogen flow (60 ml (NTP)/min). Same batch of catalyst was used in all experiments.

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## 5.2. SEQUENCE OF ETHYLAMINES PRODUCTS FORMATION

Contrasting predictions initially made, based on Freese (2001) observations on the sequence of amine products formation, independently of the hydrogen partial pressure applied, ethanol hydro-amination produced here consecutively mono-ethylamine (MEA), di-ethylamine (DEA) and tri-ethylamine (TEA). This is demonstrated by the fact that plots of $\frac{\text{MEA selectivity}}{(\text{MEA}+\text{DEA}+\text{TEA})\text{ selectivity}}$ and $\frac{\text{DEA selectivity}}{(\text{DEA}+\text{TEA})\text{ selectivity}}$ both as a function of residence time (Figures 5.3 and 5.4) show a tendency to 100% at very low residence time. The Figures present results obtained from ethanol hydro-amination performed with 0; 1; 10; and 60 bar of hydrogen. Very similar results are obtained in when experiments were executed with 5 and 30 bar of hydrogen partial pressure.

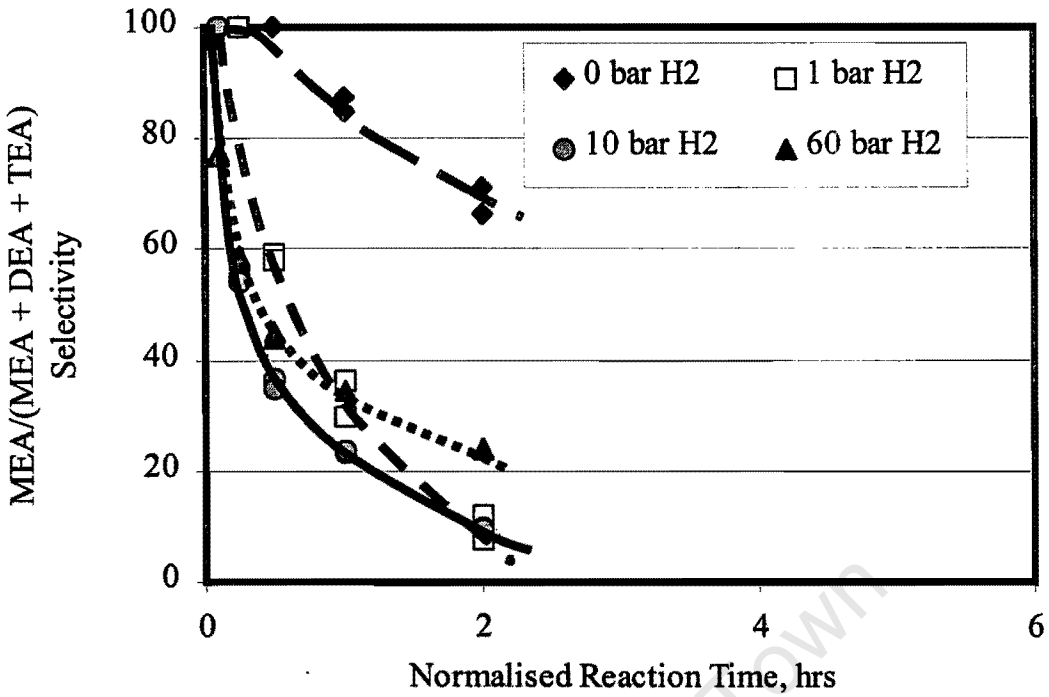


**Figure 5.3** Sequence of product formation in ethanol hydro-amination. Ratio MEA/(MEA+DEA+TEA) selectivity as function of reaction time

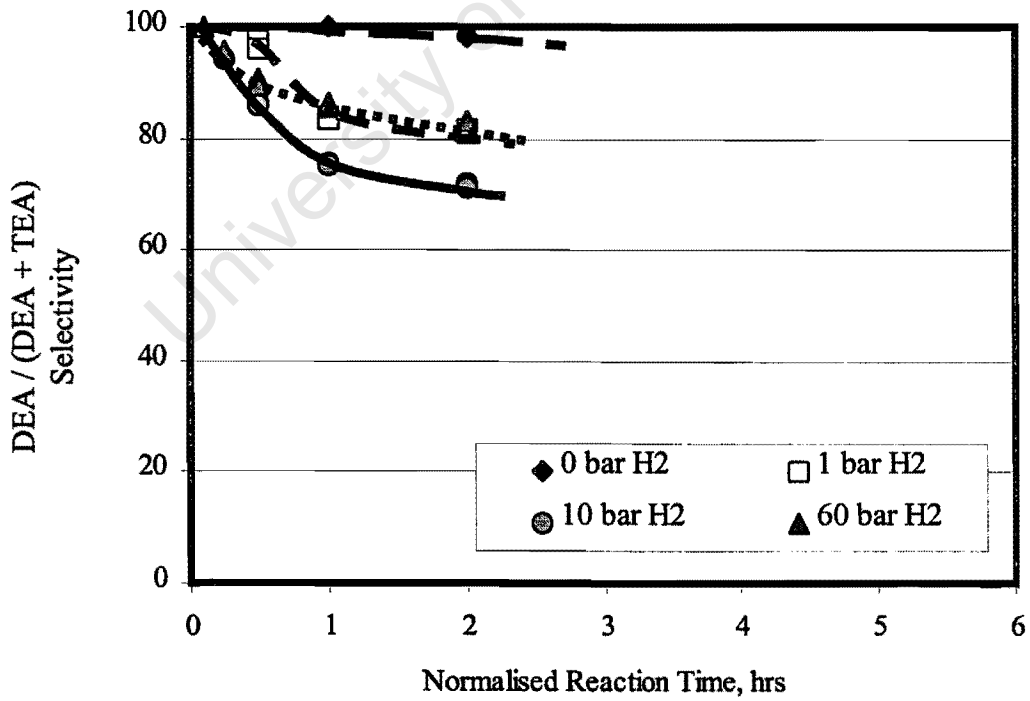


**Figure 5.4** Sequence of product formation in ethanol hydro-amination. Ratio DEA/(DEA+TEA) selectivity as function of reaction time

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The selectivity – time profiles depicted in the Figures 4.12 - 4.15 support this conclusion. They showed the formation of MEA as the primary product. Then DEA is formed through the consumption of MEA. This process is initially fast and progressively smooth. TEA starts appearing at relatively longer reaction times and increases smoothly. The continue decreasing on MEA selectivity and the quasi steadiness of DEA selectivity against the increasing of TEA selectivity suggest that this is formed through MEA conversion. At late stage of the reaction, the selectivity of the amine products are ordered as follow: DEA > TEA > MEA. This order is in accordance with the calculated thermodynamic equilibrium composition for the gas phase (see Table 2.3).

## 5.3. INFLUENCE OF HYDROGEN PARTIAL PRESSURE ON REACTION KINETICS AND SELECTIVITY

The mechanism proposed by Freese (2001) predicts that hydrogen shifts the equilibrium in the ammonia activation step. Hence, it was expected that with increasing partial pressure of hydrogen the MEA content in the fraction of ethylamines increased. This is not observed here. Nevertheless, it was observed that with increasing partial pressure of hydrogen the secondary transformation of the primarily formed amines is favoured. From the final product distribution it can be inferred that to produce more MEA, less hydrogen partial pressure has to be applied. With increase on hydrogen pressure, the final selectivity of MEA and DEA reduce, whereas the selectivity of TEA increases (Figures 4.2, 4.12 – 4.15).

The hydrogen partial pressure's role on increasing the rate of ethanol amination is in accordance with observations by Baiker and Kijenski (1985) and Sewell (1996). However, the results are contrasting with regard to the effect of total absence of hydrogen. In experiments performed absolutely with no hydrogen was observed the formation of the same products as in other experiments where hydrogen was added. Meanwhile, different selectivities and conversions were observed. It has been reported by Baiker *et al.* (1983), and Baiker and Kijenski (1985) that hydrogen was vital for alcohol amination since it prevents catalyst deactivation. They showed, in Figure 2.7,

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that a replacement of hydrogen by nitrogen in a continuous reactor (1-octanol amination with DMA over $Cu/Al_2O_3$), led to decrease in alcohol conversion and amines selectivity. It has also been reported (Baiker, 1983) that increasing hydrogen pressure (above the minimum necessary to prevent catalyst deactivation) has no effect on the rate of alcohol conversion, but increased the selectivity to di-methyloctylamine. Increase in DEA selectivity was observed, but the alcohol conversion showed a slight (at high reaction times).

Figures 5.5 and 5.6 compare the yield of amines (MEA, DEA and TEA) at first data points for experiments performed both with catalyst loads of 1 and 10 g as a function of hydrogen partial pressure. In both catalyst loads, initial MEA yield goes to a maximum a hydrogen pressure of 10 bar. The initial yields of DEA and TEA seems not being influenced by hydrogen at low catalyst loading, whereas with 10 g catalyst DEA registered a maximum also at 10 bar hydrogen.

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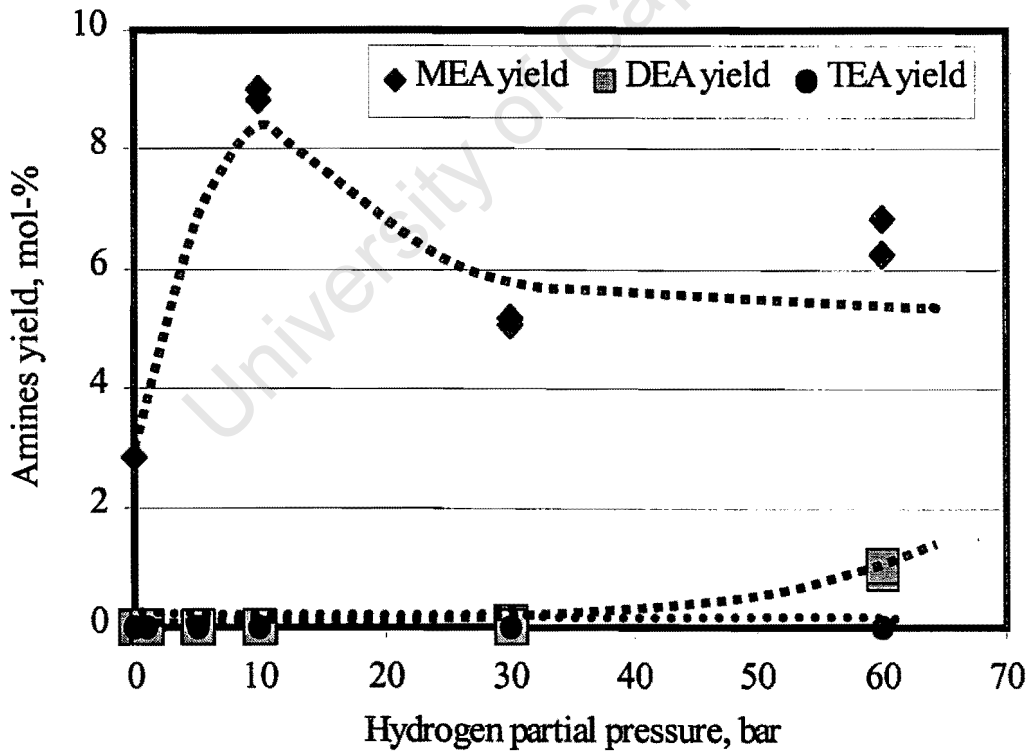


**Figure 5.5** Yield of amines as a function of hydrogen partial pressure at 0.1 hr. Mass of catalyst: 1 g.

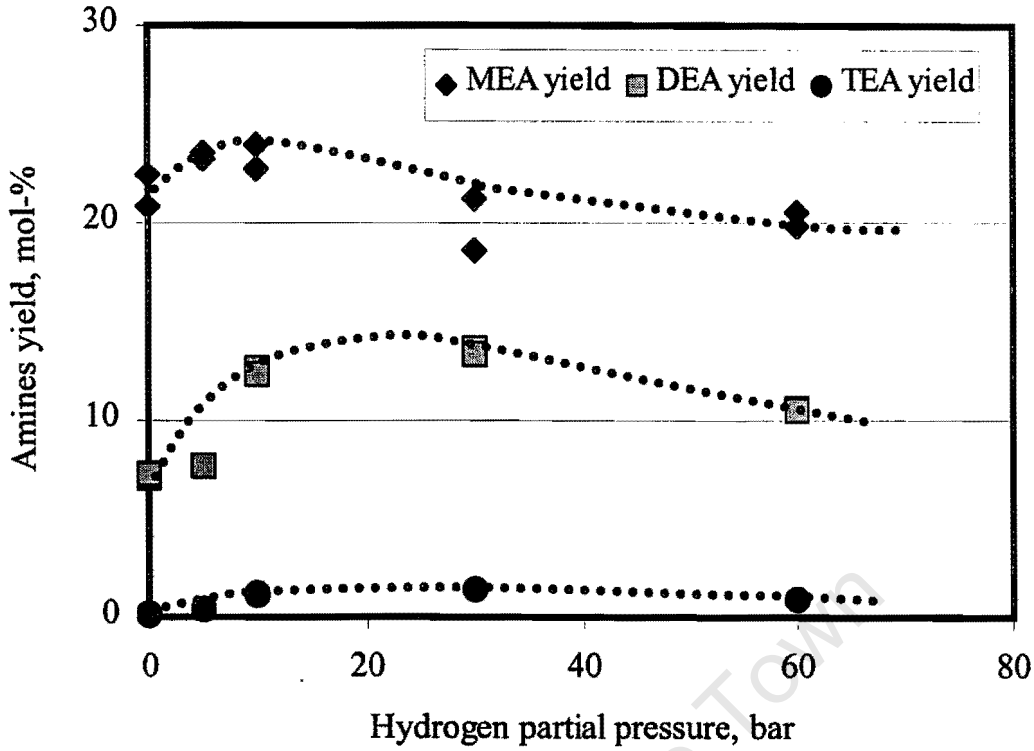


**Figure 5.6** Yield of amines as a function of hydrogen partial pressure at 1.0 hrs. Mass of catalyst: 10 g.

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Investigations in ethanol amination reported in literature have shown occurrence of secondary products, such as aldehydes, ketones, nitriles and alcanes/alkenes. The Freese (2001) proposed mechanism predicts the formation of ethane, acetaldehyde and acetonitrile and Baiker (1983) observed the formation of aldehyde (octanal) and 1-(N,N-dimethylamino)-octene-1 in his investigation on octanol amination. However, in this study any secondary product could be identified, as referred before in Section 4, despite the GC spectra showed some peaks other than amine products. It was always observed a peak at residence time of around 2.2 minutes. This retention time is not comparable neither to any of predicted secondary products above mentioned. Generally the total area-% taken by those peaks is very small (ca. 2 area-% in the worst cases), hence the possible occurrence of secondary products does not seem to have any influence in amine products yield and does not seem to be a function of hydrogen partial pressure.

## 5.4. INFLUENCE OF ALCOHOL LENGTH ON ALCOHOL AND AMMONIA CONVERSION AND AMINES DISTRIBUTION

The influence of alcohol length on alcohol and ammonia conversion and on amines distribution is here investigated by comparing conversions and selectivities resulting from ethanol, *n*-propanol and *n*-butanol amination. These reactions were carried out with the same molar ratio of *n*-ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3, corresponding to hydrogen partial pressure of 30, 25 and 20 respectively for ethanol, *n*-propanol and *n*-butanol amination. Reaction temperature was 200°C for all runs.

A common characteristic of these reactions is the consecutive formation of the mono-, and di-amine, despite in *n*-propanol amination the tri-amine selectivity increases more steeply than di-amine. The following Figures (5.6 – 5.10) depict separately the obtained profiles of alcohol conversion, ammonia conversion and mono-, di- and tri-amines selectivities in time for the above mentioned normal alcohols. The lack of data for n-butanol amination at reaction time lower than 1 hour makes a much clear comparison difficult.

With respect to alcohol and ammonia conversion the graphs show that there is no clearly logic trends. Nevertheless, the profile shapes show some similarities.

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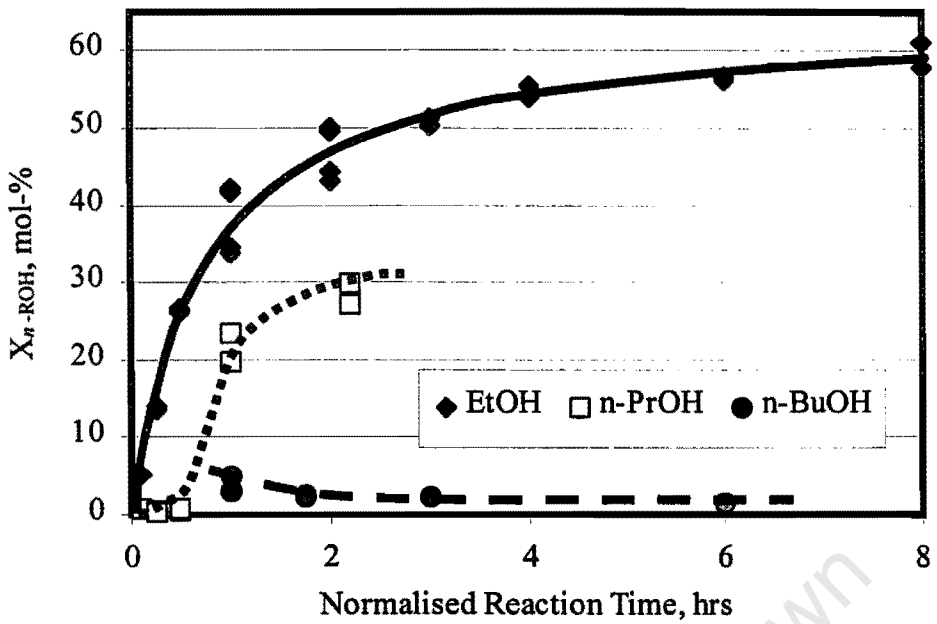


**Figure 5.7** Alcohol conversion as a function of reaction time. **Conditions:** Molar ratio, *n*-ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{reaction}$, 200°C; $P_{H2,EtOH}$ = 30 bar, $P_{H2,n\text{-}PrOH}$ = 25 bar and $P_{H2,n\text{-}BuOH}$ = 20 bar.

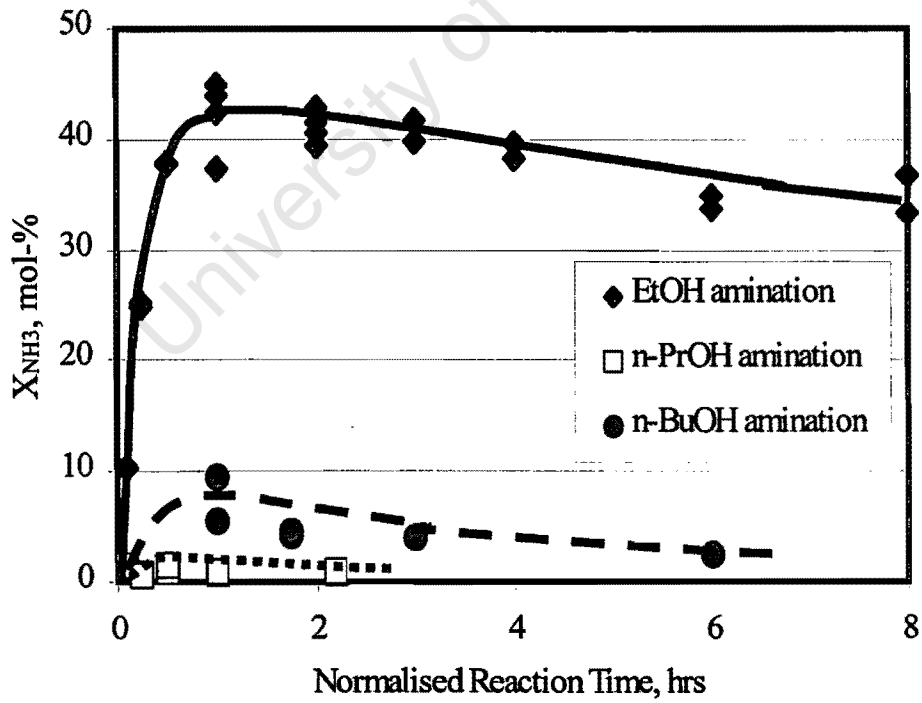


**Figure 5.8** Ammonia conversion in n-alcohols amination as a function of reaction time. **Conditions:** Molar ratio, *n*-ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{reaction}$, 200°C; $P_{H2,EtOH}$ = 30 bar, $P_{H2,n\text{-}PrOH}$ = 25 bar and $P_{H2,n\text{-}BuOH}$ = 20 bar.

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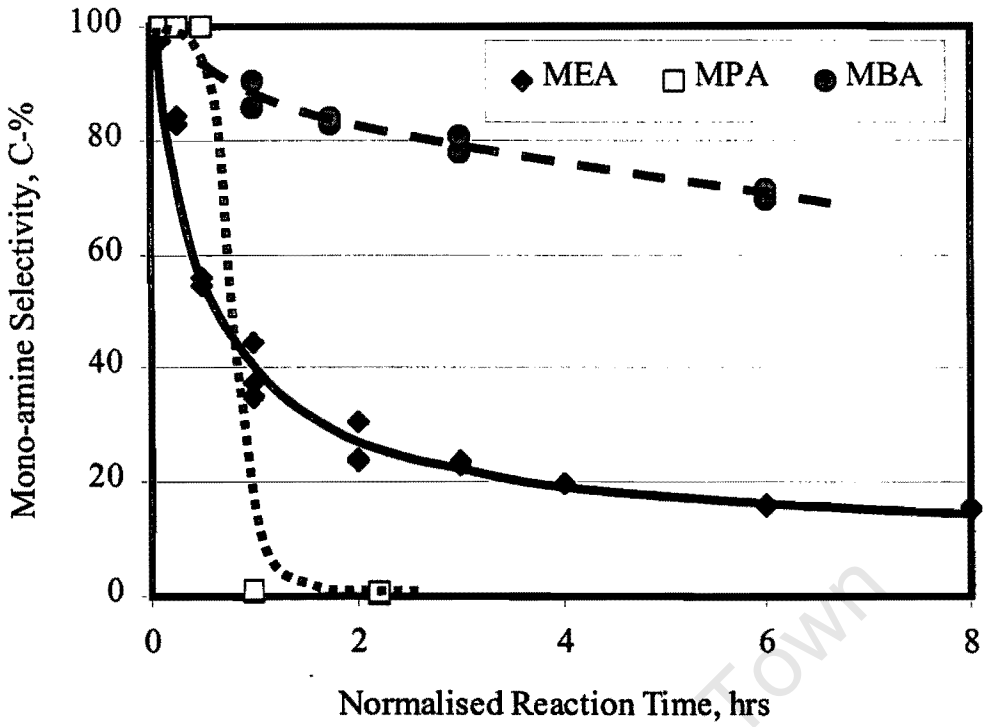


**Figure 5.9** Mono-amine selectivity-time profile in *n*-alcohols amination

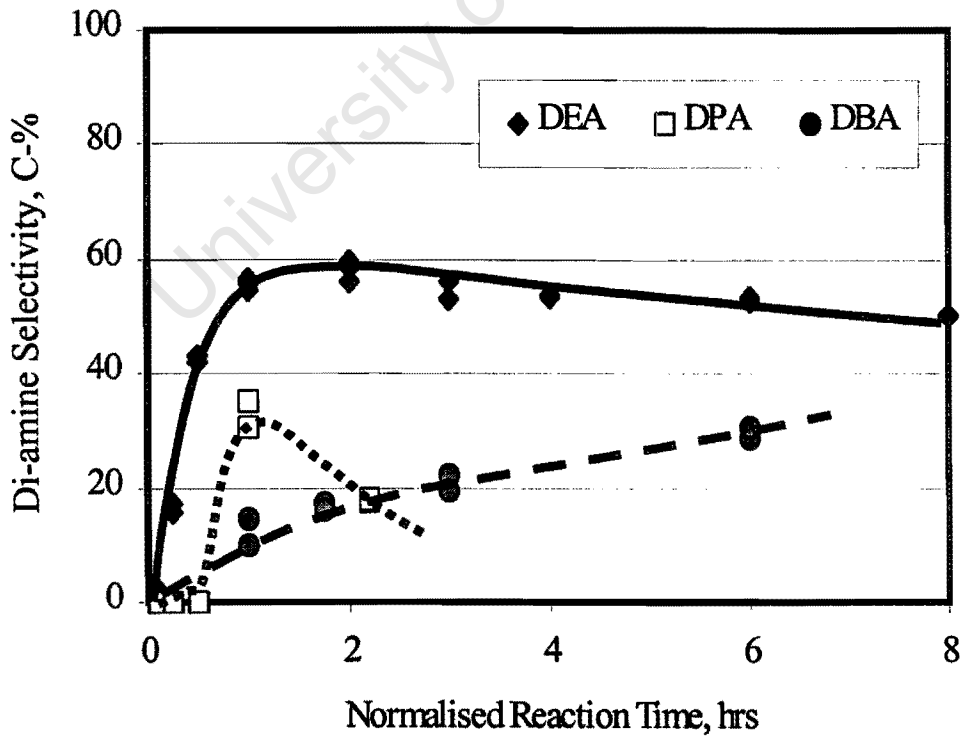


**Figure 5.10** Di-amine selectivity-time profile in *n*-alcohol amination

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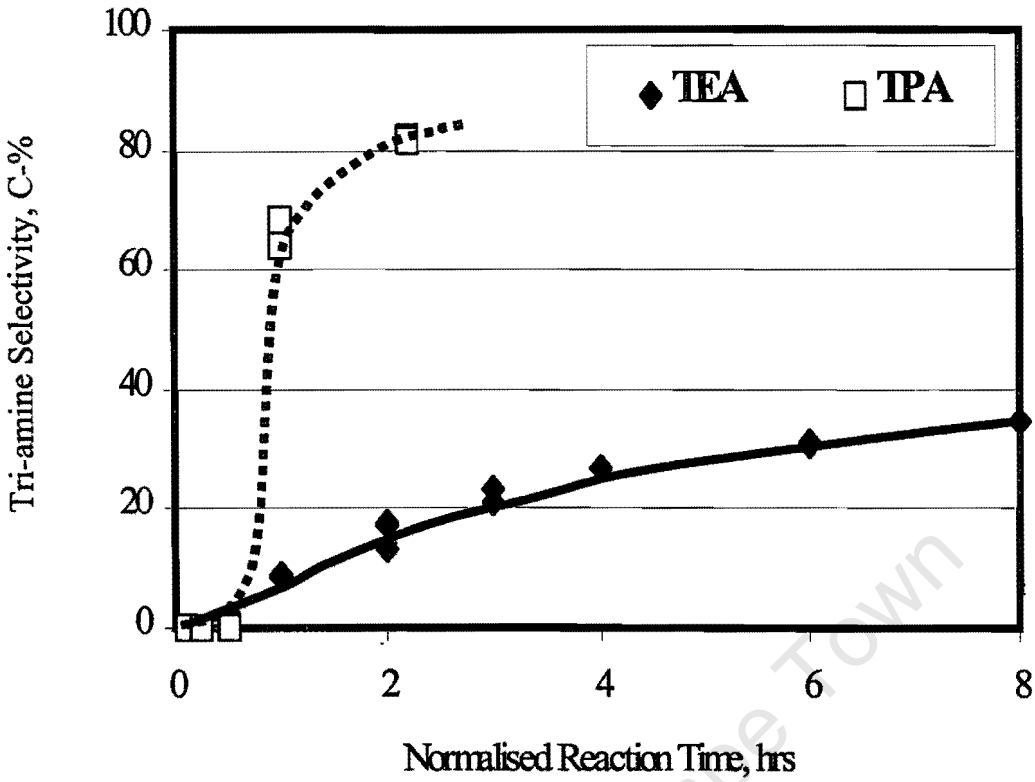


**Figure 5.11** Tri-amine selectivity-time profile in *n*-alcohol amination

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The alcohol conversion – time profile follows the order $X_{EtOH} > X_{n\text{-}PrOH} > X_{n\text{-}BuOH}$ whereas the ammonia conversion –time profile shows $X_{EtOH} > X_{n\text{-}BuOH} > X_{n\text{-}PrOH}$. These differences might be ascribed to differences in reactivity of mono- and di-amines to the consecutive reaction. The consequences are seen in Figures 5.8 – 5.10 illustrating amines selectivity – time profiles.

Despite the observed differences, the results suggest that hydro-amination of ethanol, *n*-propanol and *n*-butanol might be explained a same or similar reaction mechanism.

## 5.5. INFLUENCE OF OH POSITION ON AMMONIA CONVERSION AND AMINES DISTRIBUTION

By comparing the alcohol and ammonia conversion – time profiles for *n*-propanol and *iso*-propanol amination (Figures 5.12 and 5.13), similarities can be observed in trends. The difference resides in the fact that alcohol and ammonia conversion is always higher in *i*-propanol amination than in *n*-propanol amination. This is in accordance with the results of thermodynamic calculations (Table 2.5) and shows that *i*-propanol reactivity is higher than the reactivity of *n*-propanol. The electronic effect of alkyl groups on the α-carbon is stronger in *iso*-propanol (two adjacent methyl groups) than in *n*-propanol (only one ethyl group). This must enhance the adsorption of *iso*-propanol leading to its higher reactivity.

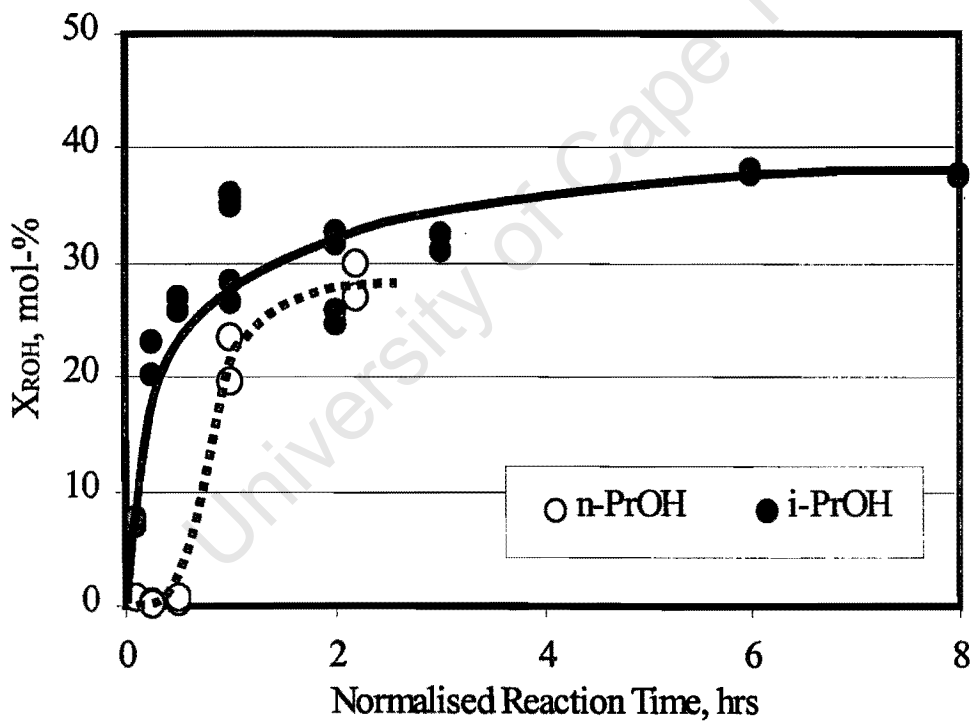


**Figure 5.12** *n*-Propanol and *iso*-propanol conversion as a function of reaction time. **Conditions:** Molar ratio ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{recation}$, 200°C; $P_{H2,n\text{-}PrOH} = P_{H2,i\text{-}PrOH}$ = 25 bar.

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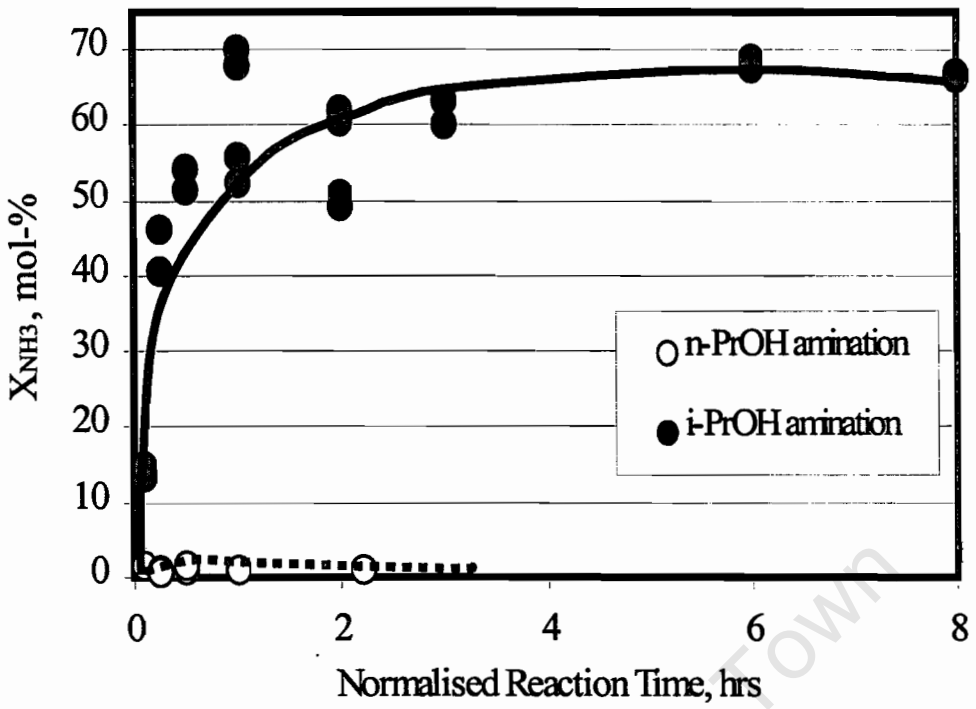


**Figure 5.13** Ammonia conversion in *n*-Propanol and *iso*-propanol amination as a function of reaction time. **Conditions:** Molar ratio ROH : $NH_3$ : $H_2$ = 1 : 0.5 : 0.3; $T_{recation}$, 200°C; $P_{H2,n\text{-PrOH}} = P_{H2,i\text{-PrOH}}$ = 25 bar.

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## 5.6. REACTION PATHWAY

As referred in Section 2.4, the main points raised by Freese (2001) in her proposal were based on her observations that DEA and TEA were the primary products and that the amine formation was not consecutive. These facts contrasted the observations by other researchers. The experimental results obtained in the current study object Freese's observations. Given that the new proposed reaction pathway was based on the mentioned observations, it seems plausible to reject it.

# 6. CONCLUSIONS

Hydrogen does have influence on hydro-amination of ethanol over $Co/SiO_2$ catalyst, despite the reaction takes place even in absence of hydrogen, yielding the same amine products and producing the same distribution. Catalyst activity does not seem to be significantly affected by the absence of hydrogen, contrasting its reported effect of catalyst activity restorer. The influence of hydrogen changes from high to low ethanol and ammonia concentrations. At high reactant concentrations experiments carried out with 10 bar of hydrogen displayed the maximum ethanol and ammonia conversion, compared to other hydrogen pressures, whereas at advanced reaction time, the higher the hydrogen partial pressure, the higher the conversion. From the available results it is still not possible to ascertain about the exact or different roles of hydrogen in this reaction.

Whatever the hydrogen content, the amines formation was consecutive: MEA, DEA and TEA. Additionally, contrasting prediction of the Freese (2001) proposed mechanism, the increase in hydrogen content reduces the MEA selectivity. Based in these evidences, it can be concluded that the mechanism under investigation does not fit the experimental observations, thus it seems not to be valid under the present conditions. The fact that no side product was identified reduces possible terms of comparison, since one of the fundamental characteristics of any proposed pathway is the type of intermediates/side products formed.

The reaction is kinetically controlled. The selectivity in ethanol hydro-amination at high reaction times follows the order: DEA>TEA>MEA irrespective to the hydrogen pressure. This is in accordance to the calculated equilibrium composition for the gas phase. The calculated equilibrium compositions order change from liquid to gas phase. For the other low alcohols investigated the selectivities at high reaction times do also change: TPA>DPA>MPA for *n*-propanol; MIPA>TIPA>DIPA for *iso*-propanol; and

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MBA>DBA for *n*-butanol amination. TBA formation was not observed under the reaction conditions.

The number of carbon atoms and the position of OH group in the alcohol molecule seem to slightly determine the hydro-amination pathway. This is explained by the small differences in conversion, selectivity and yield – time profiles.

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# APPENDICES

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# APPENDIX A.I

## THERMODYNAMIC EQUILIBRIUM IN AMINATION OF ALCOHOLS

### A.I-1 STEPS OF CALCULATION

Ethanol equilibrium calculations were done taking into consideration the following independent reactions taking place:

(1) $CH_3CH_2OH + NH_3 = CH_3CH_2NH_2 + H_2O$ ; $K_{a1}$

(2) $CH_3CH_2OH + CH_3CH_2NH_2 = (CH_3CH_2)_2NH + H_2O$ ; $K_{a2}$

(3) $CH_3CH_2OH + (CH_3CH_2)_2NH = (CH_3CH_2)_3N + H_2O$ ; $K_{a3}$

Definition of conversion:

$X_1$ : amount of ethanol converted in reaction (1) related to the amount of ethanol fed;

$X_2$ : amount of MEA ($CH_3CH_2NH_2$) converted in reaction (2) related to the amount of ethanol fed;

$X_3$ : amount of DEA ($(CH_3CH_2)_2NH$) converted in reaction (3) related to the amount of ethanol fed.

Stoichiometric table

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**Table A.I-1** Stoichiometric table for ethanol amination

| Specie | In | Reaction | Equilibrium |
|---|---|---|---|
| Ethanol | $N_{EtOH,0}$ | $-N_{EtOH,0}\cdot(X_1-X_2-X_3)$ | $N_{EtOH,0}\cdot(1-X_1-X_2-X_3)$ |
| Ammonia | $N_{NH3,0}$ | $-N_{EtOH,0}\cdot X_1$ | $N_{NH3,0}- N_{EtOH,0}\cdot X_1$ |
| MEA | 0 | $N_{EtOH,0}\cdot X_1$- Netoh,0*$X_2$ | $N_{EtOH,0}\cdot(X_1-X_2)$ |
| DEA | 0 | $N_{EtOH,0}\cdot X_2$-Netoh,0*$X_3$ | $N_{EtOH,0}\cdot(X_2-X_3)$ |
| TEA | 0 | $N_{EtOH,0}\cdot X_3$ | $N_{EtOH,0}\cdot X_3$ |
| Water | 0 | $N_{EtOH,0}\cdot(X_1+X_2+X_3)$ | $N_{EtOH,0}\cdot(X_1+X_2+X_3)$ |
| Hydrogen | $N_{H2,0}$ | - | $N_{H2,0}$ |
| TOTAL | $N_{T,0}$ | - | $N_T = N_{T,0}$ |

In all cases $N_{EtOH,0}$ = 1.89 moles and $N_{NH3,0}$ = 0.94 moles. $N_{H2,0}$ was varied and corresponded to the hydrogen partial pressure applied.

Equilibrium Constants:

$$K_{a_1} = \frac{a_{MEA}\cdot a_{H_2O}}{a_{EtOH}\cdot a_{NH_3}} = \frac{y_{MEA}\cdot y_{H_2O}}{y_{EtOH}\cdot y_{NH_3}}$$

$$K_{a_2} = \frac{a_{DEA}\cdot a_{H_2O}}{a_{EtOH}\cdot a_{MEA}} = \frac{y_{DEA}\cdot y_{H_2O}}{y_{EtOH}\cdot y_{MEA}}$$

$$K_{a_3} = \frac{a_{TEA}\cdot a_{H_2O}}{a_{EtOH}\cdot a_{DEA}} = \frac{y_{TEA}\cdot y_{H_2O}}{y_{EtOH}\cdot y_{DEA}}$$

Where activity is: $a_i = \frac{\bar{f}_i^V}{f_i^V(1\,\text{bar})} = \frac{y_i\cdot P_{total}\cdot \Phi_i^V}{1\,\text{bar}}$

Number of moles of each component in liquid phase

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$$N_{EtOH} = N_{EtOH,0}(1 - X_1 - X_2 - X_3) = N^L_{EtOH} + N^V_{EtOH}; \quad N^L_{EtOH} = N_{EtOH,0}(1 - X_1 - X_2 - X_3) - N^V_{EtOH}$$

$$N_{NH_3} = N_{NH_3,0} - N_{EtOH,0} \cdot X_1 = N^L_{NH_3} + N^V_{NH_3}; \quad N^L_{NH_3} = N_{NH_3,0} - N_{EtOH,0} \cdot X_1 - N^V_{NH_3}$$

$$N_{MEA} = N_{EtOH,0}(X_1 - X_2) = N^L_{MEA} + N^V_{MEA}; \quad N^L_{MEA} = N_{EtOH,0}(X_1 - X_2) - N^V_{MEA}$$

$$N_{DEA} = N_{EtOH,0}(X_2 - X_3) = N^L_{DEA} + N^V_{DEA}; \quad N^L_{DEA} = N_{EtOH,0}(X_2 - X_3) - N^V_{DEA}$$

$$N_{TEA} = N_{EtOH,0} \cdot X_3 = N^L_{TEA} + N^V_{TEA}; \quad N^L_{TEA} = N_{EtOH,0} \cdot X_3 - N^V_{TEA}$$

$$N_{H_2O} = N_{EtOH,0}(X_1 + X_2 + X_3) = N^L_{H_2O} + N^V_{H_2O}; \quad N^L_{H_2O} = N_{EtOH,0}(X_1 + X_2 + X_3) - N^V_{H_2O}$$

$$N_{H_2} = N_{H_2,0} = N^L_{H_2} + N^V_{H_2}; \quad N^L_{H_2O} = N_{H_2} - N^V_{H_2}$$

Total number of moles in liquid phase

$$N^L = N^L_{EtOH} + N^L_{NH_3} + N^L_{MEA} + N^L_{DEA} + N^L_{TEA} + N^L_{H_2O} + N^L_{H_2}$$

$$N^L = N_{EtOH,0} + N_{NH_3,0} - N^V_{EtOH} - N^V_{NH_3} - N^V_{MEA} - N^V_{DEA} - N^V_{TEA} - N^V_{H_2O} - N^V_{H_2}$$

Phase equilibrium relation: $\bar{f}_i^L = \bar{f}_i^V$

$$\gamma_i^L \cdot P_i^{VAP} \cdot X_i = \Phi_i^V \cdot P \cdot y_i$$

Where:

$\gamma_i^L$: Activity coefficient of componet i

$P_i^{VAP}$: Vapor pressure of component i

$X_i$: Molar fraction of component i in liquid phase

$\Phi_i^V$: Fugacity coefficient of component i

P: Total pressure of system

$Y_i$: Molar fraction of component i in vapor phase

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For instance, for ethanol:

$$\gamma^{L}_{EtOH} \cdot P^{VAP}_{EtOH} \cdot X_{EtOH} = \Phi^{V}_{EtOH} \cdot P \cdot Y_{EtOH}$$

$$\frac{N^{V}_{EtOH}}{N^{V}} = \left(\frac{\gamma^{L}}{\Phi^{V}}\right)_{EtOH} \cdot \frac{P^{VAP}_{EtOH}}{P} \cdot \frac{N^{L}_{EtOH}}{N^{L}}$$

Analogously for other components:

Ammonia: $$\frac{N^{V}_{NH_3}}{N^{V}} = \left(\frac{\gamma^{L}}{\Phi^{V}}\right)_{NH_3} \cdot \frac{P^{VAP}_{NH_3}}{P} \cdot \frac{N^{L}_{NH_3}}{N^{L}}$$

Monomethylamine: $$\frac{N^{V}_{MEA}}{N^{V}} = \left(\frac{\gamma^{L}}{\Phi^{V}}\right)_{MEA} \cdot \frac{P^{VAP}_{MEA}}{P} \cdot \frac{N^{L}_{MEA}}{N^{L}}$$

Diethylamine: $$\frac{N^{V}_{DEA}}{N^{V}} = \left(\frac{\gamma^{L}}{\Phi^{V}}\right)_{DEA} \cdot \frac{P^{VAP}_{DEA}}{P} \cdot \frac{N^{L}_{DEA}}{N^{L}}$$

Trimethylamine: $$\frac{N^{V}_{TEA}}{N^{V}} = \left(\frac{\gamma^{L}}{\Phi^{V}}\right)_{TEA} \cdot \frac{P^{VAP}_{TEA}}{P} \cdot \frac{N^{L}_{TEA}}{N^{L}}$$

Water: $$\frac{N^{V}_{H_2O}}{N^{V}} = \left(\frac{\gamma^{L}}{\Phi^{V}}\right)_{H_2O} \cdot \frac{P^{VAP}_{H_2O}}{P} \cdot \frac{N^{L}_{H_2O}}{N^{L}}$$

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Because the vapor pressure of hydrogen is very high at reaction conditions its solubility in the reaction system is very low and consequently the number of moles of hydrogen in the liquid phase ($N^{L}_{H2}$) will be assumed to be zero.

## A.I-2 POLYMATH PROGRAM FOR CALCULATION OF EQUILIBRIUM CONVERSION AND COMPOSITION

**Nonlinear equations**

[1] f(NVetoh) = (PVAPetoh/P)*(Aetoh/Fetoh)*NLetoh/NL-NVetoh/NV = 0
[2] f(NVnh3) = (PVAPnh3/P)*(Anh3/Fnh3)*NLnh3/NL-NVnh3/NV = 0
[3] f(NVmea) = (PVAPmea/P)*(Amea/Fmea)*NLmea/NL-NVmea/NV = 0

[4] f(NVdea) = (PVAPdea/P)*(Adea/Fdea)*NLdea/NL-NVdea/NV = 0

[5] f(NVtea) = (PVAPtea/P)*(Atea/Ftea)*NLtea/NL-NVtea/NV = 0

[6] f(NVh2o) = (PVAPh2o/P)*(Ah2o/Fh2o)*NLh2o/NL-NVh2o/NV = 0

[7] f($X_1$) = (NVmea*NVh2o)/NV^2-Ka1*(NVetoh*NVnh3)/NV^2 = 0

[8] f($X_2$) = (NVdea*NVh2o)/NV^2-Ka2*(NVetoh*NVmea)/NV^2 = 0

[9] f($X_3$) = (NVtea*NVh2o)/NV^2-Ka3*(NVetoh*NVdea)/NV^2 = 0

**Explicit equations**

[1] NVh2 = [Enter the number of moles of $H_2$]

[2] Netoh0 = [Enter the initial number of moles of EtOH]

[3] Nnh30 = [Enter the initial number of moles of $NH_3$]

[4] NLetoh = Netoh0*(1-$X_1$-$X_2$-$X_3$)-NVetoh

[5] NLmea = Netoh0*($X_1$-$X_2$)-NVmea

[6] NLdea = Netoh0*($X_2$-$X_3$)-NVdea

[7] NLtea = Netoh0*$X_3$-NVtea

[8] NLnh3 = Nnh30-Netoh0*$X_1$-NVnh3

[9] NV = NVetoh+NVnh3+NVmea+NVdea+NVtea+NVh2o+NVh2

[10] P = [Enter the initial total pressure at 200°C, in kPa]

[11] Aetoh = [Enter the activity coefficient of EtOH]

[12] Anh3 = [Enter the activity coefficient of $NH_3$]

[13] Amea = [Enter the activity coefficient of MEA]

[14] Adea = [Enter the activity coefficient of DEA]

[15] Atea = [Enter the activity coefficient of TEA]

[16] Ah2o = [Enter the activity coefficient of $H_2O$]

[17] Fetoh = [Enter the fugacity coefficient of EtOH]

[18] Fnh3 = [Enter the fugacity coefficient of $NH_3$]

[19] Fmea = [Enter the fugacity coefficient of MEA]

[20] Fdea = [Enter the fugacity coefficient of DEA]

[21] Ftea = [Enter the fugacity coefficient of TEA]

[22] Fh2o = [Enter the fugacity coefficient of $H_2O$]

[23] Fh2 = [Enter the fugacity coefficient of $H_2$]

[24] NLh2o = Netoh0*($X_1$+$X_2$+$X_3$)-NVh2o

[25] NL = Netoh0+Nnh30-NVetoh-NVnh3-NVmea-NVdea-NVtea-NVh2o

[26] yetoh = NVetoh/NV

[27] ynh3 = NVnh3/NV

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[28] ymea = NVmea/NV

[29] ydea = NVdea/NV

[30] ytea = NVtea/NV

[31] yh2o = NVh2o/NV

[32] yh2 = NVh2/NV

[33] xetoh = NLetoh/NL

[34] xnh3 = NLnh3/NL

[35] xmea = NLmea/NL

[36] xdea = NLdea/NL

[37] xtea = NLtea/NL

[38] xh2o = NLh2o/NL

[39] Ntequil = NV+NL

[40] PVAPetoh = [Enter the vapor pressure of EtOH, in kPa]

[41] PVAPnh3 = [Enter the vapor pressure of $NH_3$, in kPa]

[42] PVAPmea = [Enter the vapor pressure of MEA, in kPa]

[43] PVAPdea = [Enter the vapor pressure of DEA, in kPa]

[45] PVAPtea = [Enter the vapor pressure of TEA, in kPa]

[46] PVAPh2o = [Enter the vapor pressure of $H_2O$, in kPa]

[47] Ka1 = [Enter the equilibrium constant of reaction 1 (formation of MEA)]

[48] Ka2 = [Enter the equilibrium constant of reaction 2 (formation of DEA)]

[49] Ka3 = [Enter the equilibrium constant of reaction 3 (formation of TEA)]

**Conditions for solution**

[1] NVetoh : Physically Positive

[2] NVnh3 : Physically Positive

[3] NVmea : Physically Positive

[4] NVdea : Physically Positive

[5] NVtea : Physically Positive

[6] NVh2o : Physically Positive

[7] $X_1$ : Physically Positive

[8] $X_2$ : Physically Positive

[9] $X_3$ : Physically Positive

The program is comprised of 9 non-linear equations and 49 explicit equations.

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# APPENDIX A.II

## CATALYST PREPARATION AND CHARACTERISATION

### A.II – 1 CATALYST PREPARATION

The catalyst was prepared by wetness impregnation technique. The calculations done to determine the amount of the precursor cobalt nitrate, support silica gel and water used are presented below:

**Steps of catalyst preparation:**

1. Distribution of the precursor component over the support surface by incipient wetness impregnation;
2. Drying and calcinations of the catalyst precursor;
3. Activation of the metallic component b reduction using hydrogen.

**Amount of catalyst to be prepared:**

It has been planed to perform over 20 amination reactions, using a total of around 200 g of reduced catalyst with 10 wt-% cobalt content.

**Procedures and calculations:**

- Dry some amount of $Co(NO_3)_2.6H_2O$ in a cupboard (oven) at 100°C overnight;

- Determination by mean of Atom Absorption Spectroscopy the true cobalt content in the precursor. In the current case the result was 24.98 wt-%;

- Dry $SiO_2$ (pore volume: 2.25 ml/g) in a cupboard at 100°C during 20 hrs. The limiting factor of the amount of catalyst to be prepared is the volume of a

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volumetric flask chosen to measure the catalyst prcursor solution. A 250 ml volumetric flask was chosen.

- Mass of SiO2 to be used: $\frac{\text{Volume of solution}}{SiO_2 \text{ pore volume}} = \frac{250 \text{ ml}}{2.25 \text{ ml/g}} = 111.11 \text{ g of } SiO_2$

- In the reduced catalyst 111.11 g of silica correspond to90 Wt-% of cobalt, so the mass of cobalt in the reduced catalyst will be: $\frac{0.1 \cdot 111.11 \text{ g}}{0.9} = 12.34 \text{ g of Co}$;

- Since the Co content in $Co(NO_3)_2.6H_2O$ is 24.98 wt-%, the mass of cobalt nitrate needed to produce 12.34 g of cobalt is: $\frac{100\,\% \cdot 12.34 \text{ g}}{24.98\,\%} = 49.42 \text{ g of dried } Co(NO_3)_2.6H_2O$

- The 42.42 g of $Co(NO_3)_2.6H_2O$ are transferred into the 250 ml volumetric flask and it is filled up to the meniscus with de-ionised water. This volume exactly corresponds to the total pore volume of the 111.11 g of $SiO_2$ weighted;

- In a porcelan dish the solution is mixed with the dried silica and placed in a drying cupboard at 100°C for 16 hrs.

**Activation (reduction):**

- The catalyst transferring must be performed in total absence of air, thus there is no chance to weight the catalyst after its reduction. Therefore, the unreduced catalyst that lead to the required amount of unreduced catalyst has to be weighted prior to he reduction;

- In a load of 10 g of reduced catalyst (10 wt-% Co content) we have 1 g of Co and 9 g of SiO2. Then the amount of $Co(NO_3)_2.6H_2O$ will be: $\frac{100}{24.98} = 4.00 \text{ g of } Co(NO_3)_2.6H_2O$. Thus, the amount of unreduced catalyst to

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be activated corresponds to 9 g $SiO_2$ + 4 g $Co(NO_3)_2.6H_2O$ = **13 g of unreduced catalyst**

- For loading of 1 g of reduced catalyst, 1.3 g of unreduced catalyst was used.

## A.II – 2 CATALYST CHARACTERISATION

The catalyst used in all reactions has been characterised by two techniques:

1. Adsorptive (BET)

   BET surface area : 275.16 $m^2/g$

   Average pore diameter: 135.20 Å

2. Electron Microscopic Spectroscopy

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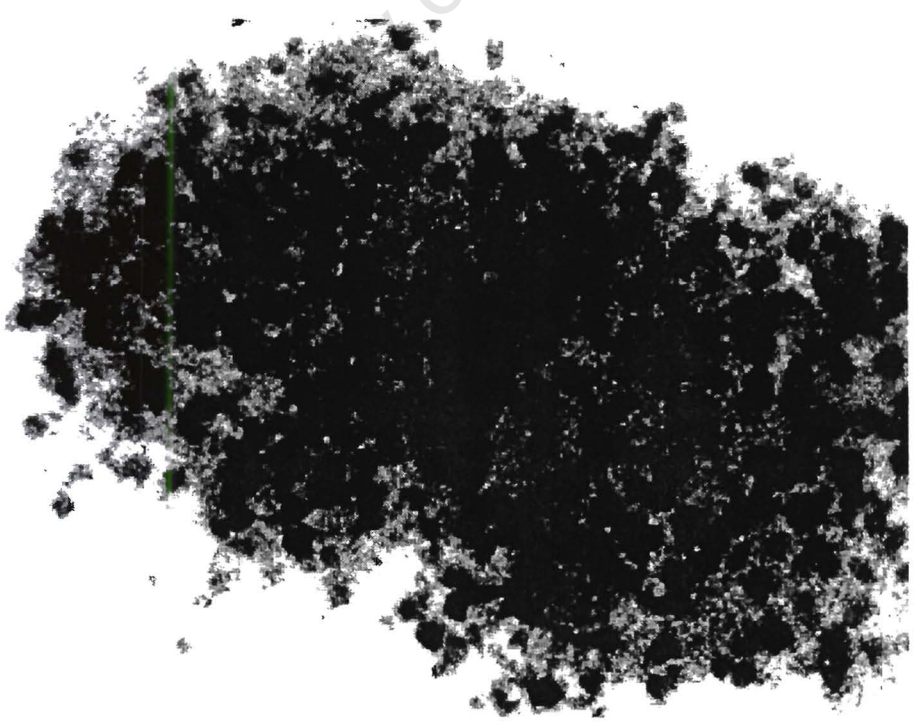

**Figure A.II-1** Non calcined catalyst - electron microscope illustration

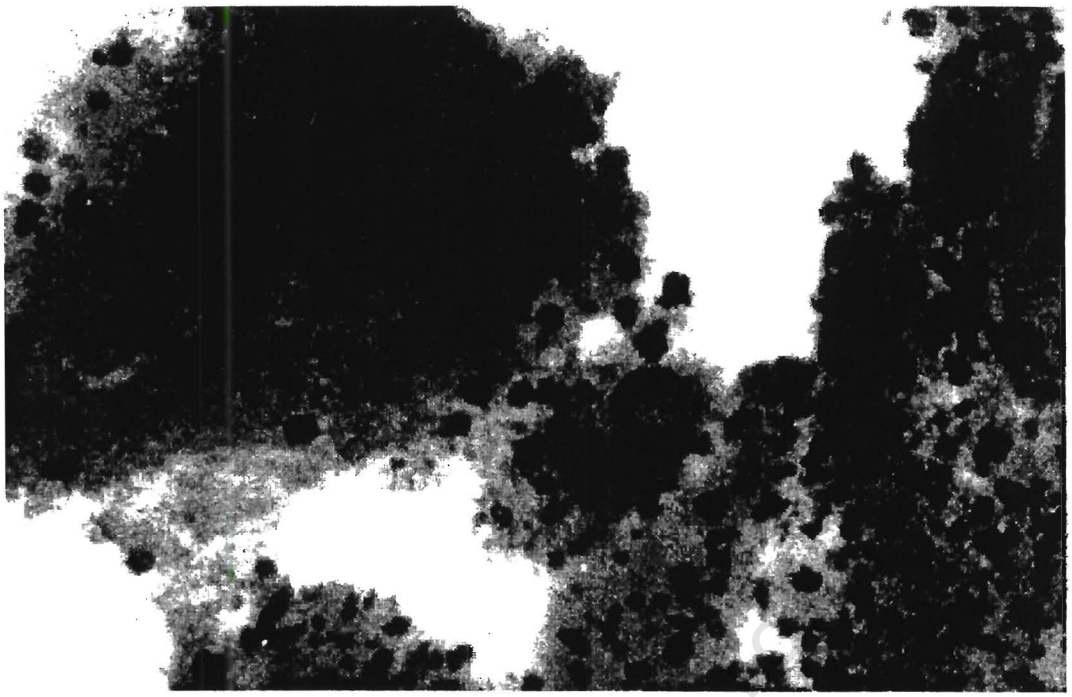

**Figure A.II-2** Calcined catalyst - electron microscope illustration

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# APPENDIX A.III

## REACTION DATA FOR LOW ALCOHOLS HYDRO-AMINATION

### A.III-1 GAS-CHROMATOGRAMS

The following Figures (A.III-1 to A.III-4) depict typical chromatograms obtained.

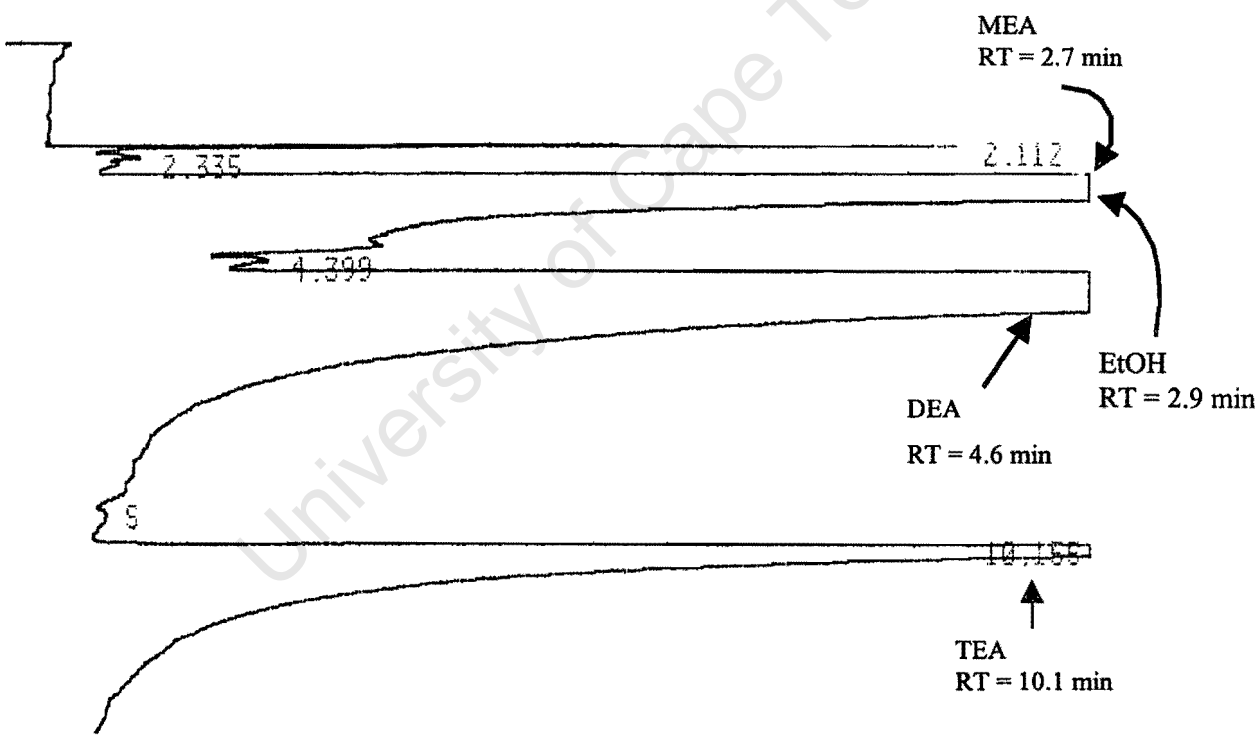


**Figure A.III-1** A typical chromatogram of ethanol hydro-amination

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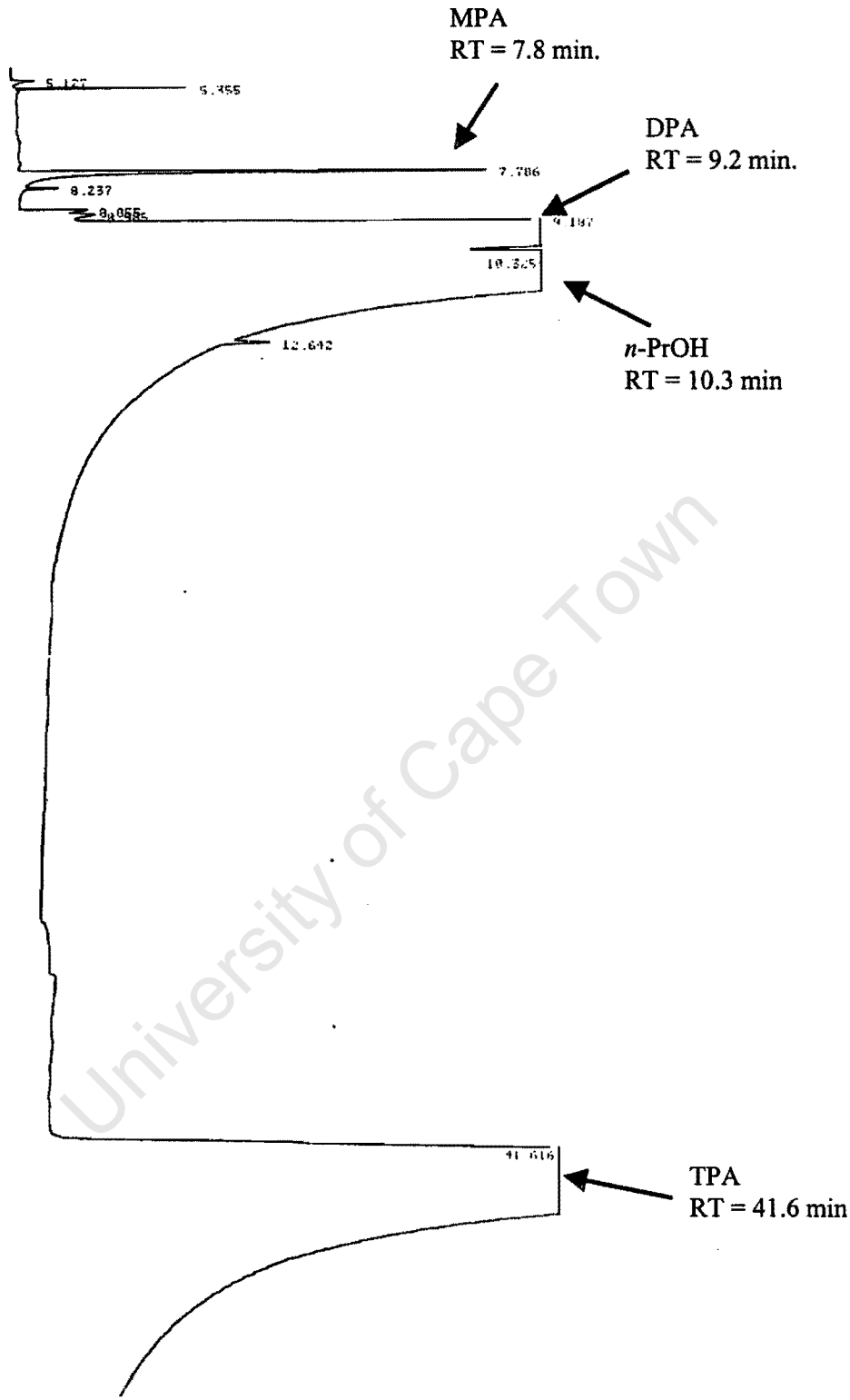


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**Figure AIII-2** A typical chromatogram of *n*-propanol hydro-amination

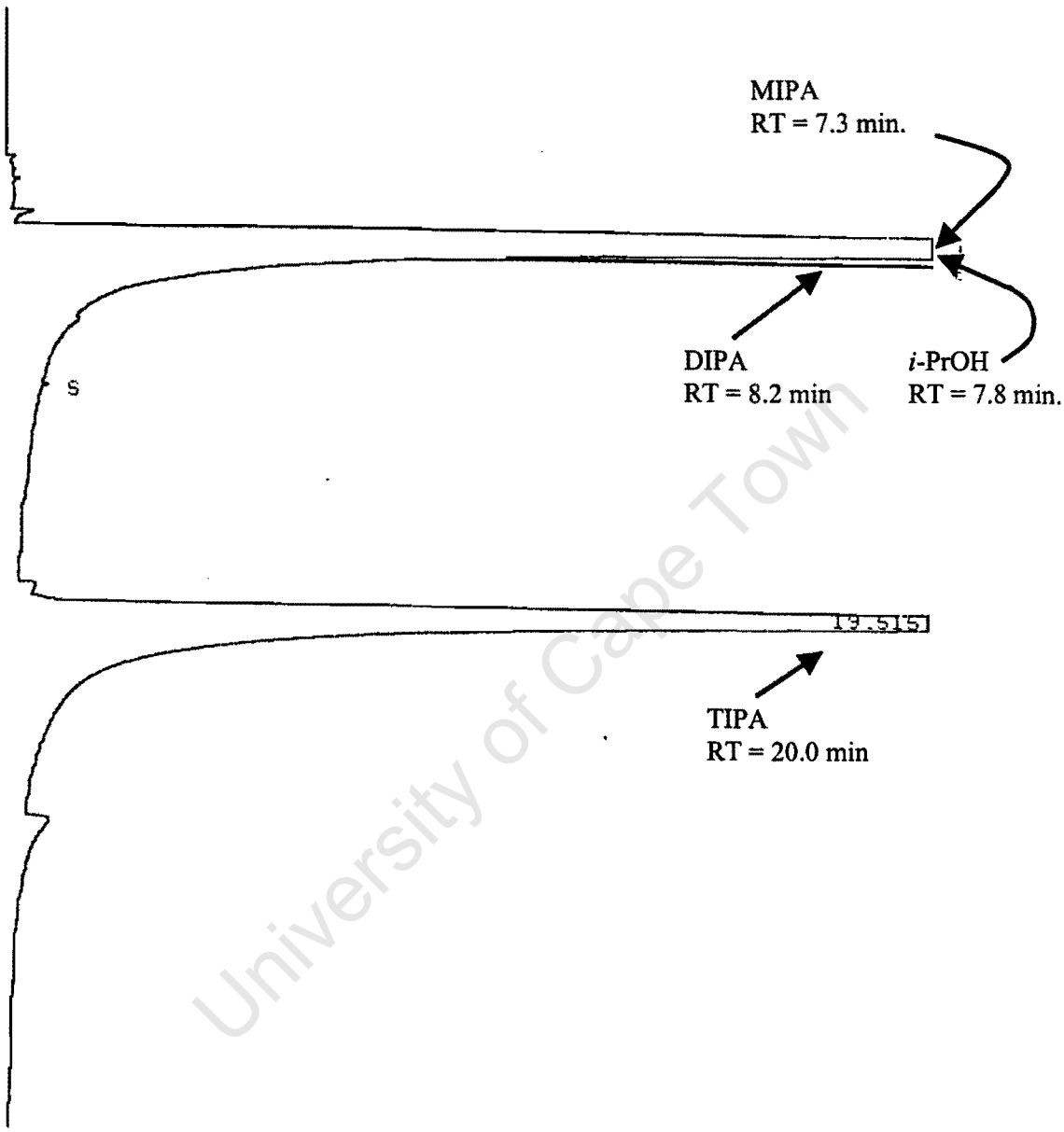


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**Figure A.III-3** A typical chromatogram of *i*-propanol hydro-amination

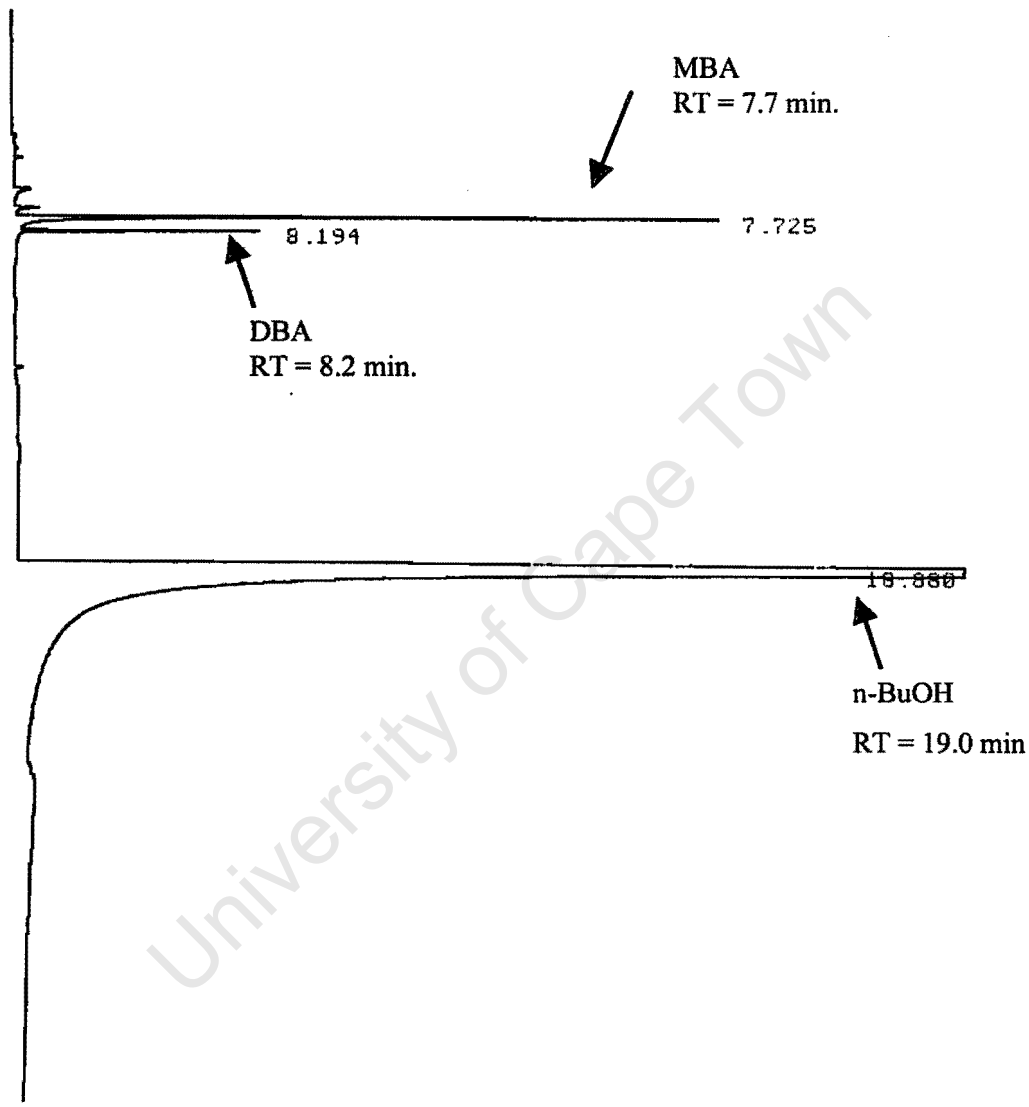


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**Figure A.III-4** A typical chromatogram of *n*-Butanol hydro-amination

## A.III-2 REACTION DATA AND SELECTIVITY, YIELD AND CONVERSION CALCULATIONS

**Table A.III-1** Approximate compound retention times (RT) in minutes

| **Ethanol** | | ***n*-Propanol** | | ***Iso*-Propanol** | | ***n*-Butanol** | |
|---|---|---|---|---|---|---|---|
| **Compound** | **RT** | **Compound** | **RT** | **Compound** | **RT** | **Compound** | **RT** |
| EtOH | 2.9 | *n*-PrOH | 10.3 | *i*-PrOH | 7.8 | *n*-BuOH | 19.0 |
| MEA | 2.7 | MPA | 7.8 | MIPA | 7.3 | MBA | 7.7 |
| DEA | 4.6 | DPA | 9.2 | DIPA | 8.2 | DBA | 8.2 |
| TEA | 10.1 | TPA | 41.6 | TIPA | 20.1 | TBA | NF |

**NF:** Not formed under the reaction conditions

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**Table A.III-2 RUN G1 (Ethanol amination)**

**Hydrogen partial pressure: 0 bar (at 20°C)**

**Mass of catalyst:** **1 g**

**Volume of ethanol:** **110 mL**

**Mass of ammonia:** **16.04 g**

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 20 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1 | | 2 | |
| MEA area % | 2.72 | 2.70 | 10.17 | 11.02 | 17.32 | 17.05 | 20.68 | 21.16 | 21.56 | 20.78 |
| Ethanol area % | 97.16 | 97.16 | 89.60 | 88.72 | 81.80 | 81.85 | 75.67 | 74.47 | 68.92 | 68.12 |
| DEA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.05 | 3.78 | 8.74 | 10.35 |
| TEA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.12 | 0.19 |
| MEA selectivity, C-% | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 87.15 | 84.83 | 70.87 | 66.34 |
| DEA selectivity, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 12.85 | 15.17 | 28.72 | 33.05 |
| TEA selectivity, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.41 | 0.61 |
| MEA yield, C-% | 2.13 | 2.11 | 8.09 | 8.78 | 14.09 | 13.90 | 17.04 | 17.48 | 18.06 | 17.43 |
| DEA yield, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 2.51 | 3.13 | 7.32 | 8.68 |
| TEA yield, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | 0.16 |
| Ethanol conversion, C-% | 2.13 | 2.11 | 8.09 | 8.78 | 14.09 | 13.90 | 19.55 | 20.61 | 25.49 | 26.27 |
| Ethanol conversion, mol-% | 2.84 | 2.84 | 10.40 | 11.28 | 18.20 | 18.15 | 24.33 | 25.53 | 31.08 | 31.88 |
| MEA yield, mol-% | 2.84 | 2.84 | 10.40 | 11.28 | 18.20 | 18.15 | 22.66 | 23.44 | 25.80 | 25.46 |
| Ammonia conversion, mol-% | 5.69 | 5.67 | 20.79 | 22.57 | 36.40 | 36.30 | 45.32 | 46.87 | 51.60 | 50.93 |

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## Table A.III-3 RUN G2 (Ethanol amination)

**Hydrogen partial pressure:** 0 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2 | | 3 | | 5 | | 7 | | 10 | |
| Normalised rxn time, hrs | 1 | | 2 | | 3 | | 5 | | 7 | | 10 | |
| MEA area % | 16.03 | 17.43 | 16.56 | 16.38 | 14.47 | 14.89 | 11.35 | 11.38 | 11.27 | 9.51 | 9.57 | 9.59 |
| Ethanol area % | 71.98 | 70.24 | 64.45 | 64.55 | 61.10 | 60.49 | 58.91 | 58.72 | 57.66 | 58.80 | 55.81 | 56.01 |
| DEA area % | 10.87 | 11.26 | 17.49 | 17.69 | 21.47 | 21.61 | 24.77 | 25.01 | 25.81 | 26.16 | 27.91 | 27.84 |
| TEA area % | 0.35 | 0.36 | 1.30 | 1.23 | 2.83 | 2.83 | 4.85 | 4.76 | 5.16 | 5.47 | 6.53 | 6.43 |
| MEA selectivity, C-% | 58.84 | 59.99 | 46.84 | 46.40 | 37.33 | 37.85 | 27.70 | 27.65 | 26.69 | 23.12 | 21.74 | 21.86 |
| DEA selectivity, C-% | 39.89 | 38.76 | 49.47 | 50.11 | 55.38 | 54.95 | 60.47 | 60.77 | 61.11 | 63.59 | 63.42 | 63.48 |
| TEA selectivity, C-% | 1.27 | 1.25 | 3.69 | 3.49 | 7.29 | 7.20 | 11.83 | 11.57 | 12.21 | 13.29 | 14.84 | 14.66 |
| MEA yield, C-% | 13.35 | 14.56 | 13.98 | 13.81 | 12.30 | 12.68 | 9.70 | 9.74 | 9.66 | 8.13 | 8.25 | 8.26 |
| DEA yield, C-% | 9.05 | 9.41 | 14.76 | 14.92 | 18.25 | 18.41 | 21.18 | 21.39 | 22.13 | 22.35 | 24.06 | 23.98 |
| TEA yield, C-% | 0.29 | 0.30 | 1.10 | 1.04 | 2.40 | 2.41 | 4.14 | 4.07 | 4.42 | 4.67 | 5.63 | 5.54 |
| Ethanol conversion, C-% | 22.68 | 24.27 | 29.84 | 29.77 | 32.96 | 33.51 | 35.02 | 35.20 | 36.21 | 35.15 | 37.94 | 37.77 |
| Ethanol conversion, mol-% | 28.02 | 29.76 | 35.55 | 35.45 | 38.90 | 39.51 | 41.09 | 41.28 | 42.34 | 41.20 | 44.19 | 43.99 |
| MEA yield, mol-% | 20.82 | 22.38 | 22.87 | 22.65 | 21.53 | 22.08 | 18.40 | 18.44 | 18.43 | 16.05 | 16.45 | 16.44 |
| Ammonia conversion, mol-% | 41.63 | 44.75 | 45.75 | 45.30 | 43.06 | 44.17 | 36.79 | 36.89 | 36.86 | 32.10 | 32.91 | 32.88 |

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## Table A.III-4 RUN H1 (Ethanol amination)

**Hydrogen partial pressure:** 1 bar (at 20°C)

**Mass of catalyst:** 1 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 20 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1 | | 2 | |
| MEA area % | 0.00 | 0.00 | 1.78 | 2.11 | 8.00 | 7.80 | 5.26 | 4.01 | 2.68 | 1.77 |
| Ethanol area % | 99.55 | 99.60 | 97.74 | 97.50 | 85.42 | 85.57 | 84.76 | 85.90 | 77.15 | 76.82 |
| DEA area % | 0.00 | 0.00 | 0.00 | 0.00 | 5.41 | 5.39 | 7.71 | 7.93 | 16.04 | 16.99 |
| TEA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.14 | 0.23 | 1.49 | 1.57 | 3.65 | 4.00 |
| MEA selectivity, C-% | - | - | 100.00 | 100.00 | 59.08 | 58.12 | 36.40 | 29.68 | 11.97 | 7.76 |
| DEA selectivity, C-% | - | - | 0.00 | 0.00 | 39.92 | 40.15 | 53.32 | 58.73 | 71.73 | 74.66 |
| TEA selectivity, C-% | - | - | 0.00 | 0.00 | 1.00 | 1.73 | 10.28 | 11.59 | 16.30 | 17.58 |
| MEA yield, C-% | 13.35 | 14.56 | 13.98 | 13.81 | 12.30 | 12.68 | 9.70 | 9.74 | 9.66 | 8.13 |
| DEA yield, C-% | 9.05 | 9.41 | 14.76 | 14.92 | 18.25 | 18.41 | 21.18 | 21.39 | 22.13 | 22.35 |
| TEA yield, C-% | 0.29 | 0.30 | 1.10 | 1.04 | 2.40 | 2.41 | 4.14 | 4.07 | 4.42 | 4.67 |
| Ethanol conversion, C-% | 0.00 | 0.00 | 1.39 | 1.65 | 10.95 | 10.84 | 11.67 | 10.86 | 18.35 | 18.67 |
| Ethanol conversion, mol-% | 0.45 | 0.40 | 2.26 | 2.50 | 14.58 | 14.43 | 15.24 | 14.10 | 22.85 | 23.18 |
| MEA yield, mol-% | - | - | 2.26 | 2.50 | 10.86 | 10.65 | 8.34 | 6.65 | 5.14 | 3.53 |
| Ammonia conversion, mol-% | - | - | 4.53 | 5.00 | 21.71 | 21.30 | 16.68 | 13.30 | 10.27 | 7.06 |

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## Table A.III-5 RUN H2 (Ethanol amination)

**Hydrogen partial pressure:** 1 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | |
|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1.5 | | 3 | | 4.5 | | 6 | |
| Normalised rxn time, hrs | 1.5 | | 3 | | 4.5 | | 6 | |
| MEA area % | 20.45 | 20.64 | 19.79 | 19.61 | 18.76 | 18.43 | 17.90 | 17.30 |
| Ethanol area % | 64.26 | 64.68 | 58.52 | 58.44 | 54.83 | 54.70 | 53.01 | 53.16 |
| DEA area % | 14.08 | 13.71 | 19.46 | 19.97 | 22.78 | 23.66 | 24.48 | 24.63 |
| TEA area % | 0.60 | 0.53 | 1.82 | 1.79 | 3.30 | 3.06 | 4.43 | 4.54 |
| MEA selectivity, C-% | 58.21 | 59.17 | 48.19 | 47.40 | 41.84 | 40.82 | 38.24 | 37.23 |
| DEA selectivity, C-% | 40.08 | 39.30 | 47.39 | 48.27 | 50.79 | 52.40 | 52.29 | 53.00 |
| TEA selectivity, C-% | 1.71 | 1.53 | 4.42 | 4.33 | 7.37 | 6.78 | 9.47 | 9.77 |
| MEA yield, C-% | 17.32 | 17.44 | 16.98 | 16.80 | 16.23 | 15.93 | 15.54 | 15.03 |
| DEA yield, C-% | 11.93 | 11.58 | 16.70 | 17.10 | 19.71 | 20.44 | 21.25 | 21.40 |
| TEA yield, C-% | 0.51 | 0.45 | 1.56 | 1.53 | 2.86 | 2.65 | 3.85 | 3.95 |
| Ethanol conversion, C-% | 29.76 | 29.48 | 35.23 | 35.43 | 38.80 | 39.02 | 40.63 | 40.38 |
| Ethanol conversion, mol-% | 35.74 | 35.32 | 41.48 | 41.56 | 45.17 | 45.30 | 46.99 | 46.84 |
| MEA yield, mol-% | 26.40 | 26.34 | 27.25 | 27.00 | 27.12 | 26.69 | 26.60 | 26.03 |
| Ammonia conversion, mol-% | 52.79 | 52.68 | 54.50 | 53.99 | 54.24 | 53.38 | 53.21 | 52.06 |

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## Table A.III-6 RUN E1 (Ethanol amination)

**Hydrogen partial pressure:** 5 bar (at 20°C)

**Mass of catalyst:** 1 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 20 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1 | | 2 | |
| MEA area % | 0.00 | 0.00 | 6.64 | 6.80 | 14.91 | 14.78 | 17.16 | 16.30 | 14.21 | 13.49 |
| Ethanol area % | 98.82 | 98.80 | 92.96 | 92.82 | 84.23 | 84.26 | 75.02 | 75.15 | 72.65 | 73.10 |
| DEA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 7.19 | 7.94 | 11.80 | 12.03 |
| TEA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.28 | 0.25 | 0.94 | 0.99 |
| MEA selectivity, C-% | - | - | 100.00 | 100.00 | 100.00 | 100.00 | 69.65 | 66.57 | 52.72 | 50.88 |
| DEA selectivity, C-% | - | - | 0.00 | 0.00 | 0.00 | 0.00 | 29.19 | 32.41 | 43.79 | 45.37 |
| TEA selectivity, C-% | - | - | 0.00 | 0.00 | 0.00 | 0.00 | 1.15 | 1.02 | 3.50 | 3.74 |
| MEA yield, C-% | - | -! | 5.25 | 5.38 | 12.06 | 11.97 | 14.13 | 13.42 | 11.78 | 11.16 |
| DEA yield, C-% | - | - | 0.00 | 0.00 | 0.00 | 0.00 | 5.92 | 6.53 | 9.78 | 9.95 |
| TEA yield, C-% | - | - | 0.00 | 0.00 | 0.00 | 0.00 | 0.23 | 0.21 | 0.78 | 0.82 |
| Ethanol conversion, C-% | 0.00 | 0.00 | 5.25 | 5.38 | 12.06 | 11.97 | 20.29 | 20.16 | 22.34 | 21.94 |
| Ethanol conversion, mol-% | 1.18 | 1.20 | 7.04 | 7.18 | 15.77 | 15.74 | 24.98 | 24.85 | 27.35 | 26.90 |
| MEA yield, mol-% | - | - | 7.04 | 7.18 | 15.77 | 15.74 | 20.56 | 19.90 | 19.03 | 18.29 |
| Ammonia conversion, mol-% | - | - | 14.07 | 14.36 | 31.53 | 31.48 | 41.12 | 39.81 | 38.06 | 36.58 |

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## Table A.III-7 RUN E2 (Ethanol amination)

**Hydrogen partial pressure:** 5 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2 | | 3 | | 5 | | 6.5 | | 8.5 | |
| Normalised rxn time, hrs | 1 | | 2 | | 3 | | 5 | | 6.5 | | 8.5 | |
| MEA area % | 18.50 | 18.30 | 16.36 | 16.84 | 15.01 | 14.62 | 12.84 | 12.68 | 11.75 | 11.89 | 11.74 | 11.50 |
| Ethanol area % | 68.48 | 68.64 | 63.36 | 63.02 | 58.67 | 59.32 | 55.44 | 55.21 | 53.37 | 52.74 | 49.51 | 49.88 |
| DEA area % | 12.08 | 12.14 | 17.82 | 17.67 | 21.26 | 21.21 | 23.37 | 23.76 | 24.40 | 24.75 | 25.30 | 25.66 |
| TEA area % | 0.86 | 0.85 | 2.39 | 2.39 | 4.87 | 4.64 | 8.14 | 8.17 | 10.27 | 10.42 | 13.28 | 12.74 |
| MEA selectivity, C-% | 58.85 | 58.48 | 44.73 | 45.63 | 36.48 | 36.12 | 28.95 | 28.42 | 25.31 | 25.27 | 23.33 | 23.05 |
| DEA selectivity, C-% | 38.43 | 38.82 | 48.72 | 47.90 | 51.68 | 52.41 | 52.69 | 53.27 | 52.56 | 52.59 | 50.28 | 51.42 |
| TEA selectivity, C-% | 2.72 | 2.70 | 6.54 | 6.47 | 11.84 | 11.46 | 18.36 | 18.31 | 22.13 | 22.14 | 26.38 | 25.53 |
| MEA yield, C-% | 15.45 | 15.27 | 13.82 | 14.24 | 12.84 | 12.49 | 11.08 | 10.94 | 10.19 | 10.33 | 10.28 | 10.07 |
| DEA yield, C-% | 10.09 | 10.13 | 15.06 | 14.95 | 18.20 | 18.13 | 20.17 | 20.51 | 21.16 | 21.50 | 22.16 | 22.46 |
| TEA yield, C-% | 0.71 | 0.71 | 2.02 | 2.02 | 4.17 | 3.97 | 7.03 | 7.05 | 8.91 | 9.05 | 11.63 | 11.15 |
| Ethanol conversion, C-% | 26.25 | 26.10 | 30.90 | 31.21 | 35.21 | 34.59 | 38.28 | 38.50 | 40.26 | 40.88 | 44.06 | 43.67 |
| Ethanol conversion, mol-% | 31.52 | 31.36 | 36.64 | 36.98 | 41.33 | 40.68 | 44.56 | 44.79 | 46.63 | 47.26 | 50.49 | 50.12 |
| MEA yield, mol-% | 23.49 | 23.27 | 22.99 | 23.52 | 22.75 | 22.21 | 21.01 | 20.81 | 20.01 | 20.26 | 20.57 | 20.17 |
| Ammonia conversion, mol-% | 46.98 | 46.55 | 45.99 | 47.04 | 45.50 | 44.42 | 42.01 | 41.62 | 40.02 | 40.53 | 41.15 | 40.35 |

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## Table A.III-8 RUN A1 (Ethanol amination)

**Hydrogen partial pressure:** 10 bar (at 20°C)

**Mass of catalyst:** 1 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 20 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1 | | 2 | |
| MEA area % | 7.72 | 8.16 | 14.73 | 14.62 | 13.34 | 12.61 | 10.07 | 10.28 | 4.02 | 4.02 |
| Ethanol area % | 91.19 | 91.00 | 72.91 | 72.54 | 63.23 | 63.31 | 56.19 | 55.38 | 58.33 | 57.43 |
| DEA area % | 0.00 | 0.00 | 11.36 | 11.77 | 19.84 | 20.14 | 24.94 | 25.28 | 26.96 | 27.44 |
| TEA area % | 0.00 | 0.00 | 0.69 | 0.70 | 3.15 | 3.33 | 8.10 | 8.41 | 10.55 | 11.09 |
| MEA selectivity, C-% | 100.00 | 100.00 | 55.01 | 53.97 | 36.72 | 34.94 | 23.35 | 23.37 | 9.69 | 9.44 |
| DEA selectivity, C-% | 0.00 | 0.00 | 42.40 | 43.44 | 54.61 | 55.82 | 57.86 | 57.50 | 64.91 | 64.49 |
| TEA selectivity, C-% | 0.00 | 0.00 | 2.59 | 2.59 | 8.68 | 9.24 | 18.79 | 19.12 | 25.40 | 26.07 |
| MEA yield, C-% | 6.16 | 6.50 | 12.19 | 12.11 | 11.31 | 10.71 | 8.71 | 8.90 | 3.45 | 3.44 |
| DEA yield, C-% | 0.00 | 0.00 | 9.40 | 9.75 | 16.83 | 17.10 | 21.57 | 21.91 | 23.08 | 23.52 |
| TEA yield, C-% | 0.00 | 0.00 | 0.57 | 0.58 | 2.67 | 2.83 | 7.01 | 7.29 | 9.03 | 9.51 |
| Ethanol conversion, C-% | 6.16 | 6.50 | 22.16 | 22.44 | 30.81 | 30.64 | 37.29 | 38.10 | 35.56 | 36.48 |
| Ethanol conversion, mol-% | 8.81 | 9.00 | 27.09 | 27.46 | 36.77 | 36.69 | 43.81 | 44.62 | 41.67 | 42.57 |
| MEA yield, mol-% | 8.81 | 9.00 | 19.33 | 19.36 | 20.18 | 19.45 | 17.47 | 17.83 | 7.98 | 7.98 |
| Ammonia conversion, mol-% | 17.62 | 17.99 | 38.67 | 38.72 | 40.36 | 38.89 | 34.94 | 35.66 | 15.96 | 15.96 |

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## Table A.III-9 RUN A2 (Ethanol amination)

**Hydrogen partial pressure:** 10 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 4.5 | | 6.5 | | 8.5 | | 10.50 | |
| Normalised rxn time, hrs | 1 | | 2.5 | | 4.5 | | 6.5 | | 8.5 | | 10.5 | |
| MEA area % | 16.04 | 17.17 | 12.38 | 12.23 | 11.28 | 11.49 | 10.25 | 10.82 | 10.89 | 10.36 | 9.47 | 8.80 |
| Ethanol area % | 63.44 | 62.61 | 60.94 | 60.24 | 51.85 | 51.76 | 46.93 | 46.01 | 40.93 | 43.53 | 43.31 | 44.65 |
| DEA area % | 17.86 | 17.67 | 21.59 | 21.63 | 25.46 | 25.55 | 27.02 | 26.98 | 26.71 | 27.89 | 30.51 | 30.88 |
| TEA area % | 2.50 | 2.39 | 4.97 | 5.76 | 11.10 | 10.84 | 15.35 | 15.69 | 18.21 | 17.91 | 16.09 | 15.15 |
| MEA selectivity, C-% | 44.06 | 46.11 | 31.79 | 30.86 | 23.57 | 24.00 | 19.48 | 20.23 | 19.51 | 18.45 | 16.89 | 16.05 |
| DEA selectivity, C-% | 49.07 | 47.46 | 55.45 | 54.59 | 53.22 | 53.36 | 51.34 | 50.44 | 47.86 | 49.66 | 54.42 | 56.33 |
| TEA selectivity, C-% | 6.86 | 6.43 | 12.76 | 14.55 | 23.21 | 22.64 | 29.17 | 29.33 | 32.63 | 31.89 | 28.69 | 27.63 |
| MEA yield, C-% | 13.56 | 14.55 | 10.53 | 10.42 | 9.83 | 10.02 | 9.06 | 9.59 | 10.02 | 9.22 | 8.46 | 7.82 |
| DEA yield, C-% | 15.11 | 14.97 | 18.36 | 18.43 | 22.19 | 22.28 | 23.87 | 23.91 | 24.59 | 24.83 | 27.25 | 27.46 |
| TEA yield, C-% | 2.11 | 2.03 | 4.23 | 4.91 | 9.68 | 9.45 | 13.56 | 13.90 | 16.76 | 15.95 | 14.37 | 13.47 |
| Ethanol conversion, C-% | 30.78 | 31.55 | 33.12 | 33.76 | 41.69 | 41.76 | 46.49 | 47.39 | 51.38 | 50.00 | 50.08 | 48.76 |
| Ethanol conversion, mol-% | 36.56 | 37.39 | 39.06 | 39.76 | 48.15 | 48.24 | 53.07 | 53.99 | 59.07 | 56.47 | 56.69 | 55.35 |
| MEA yield, mol-% | 22.72 | 23.95 | 19.47 | 19.48 | 19.60 | 19.88 | 18.84 | 19.78 | 21.22 | 19.33 | 17.84 | 16.63 |
| Ammonia conversion, mol-% | 45.45 | 47.90 | 38.95 | 38.95 | 39.19 | 39.76 | 37.67 | 39.55 | 42.44 | 38.65 | 35.69 | 33.25 |

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## Table A.III-10 RUN B1 (Ethanol amination)

**Hydrogen partial pressure:** 30 bar (at 20°C)

**Mass of catalyst:** 1 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 20 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1 | | 2 | |
| MEA area % | 3.89 | 4.27 | 11.11 | 11.28 | 14.37 | 14.30 | 14.62 | 14.34 | 11.51 | 11.79 |
| Ethanol area % | 94.86 | 94.83 | 86.39 | 86.08 | 73.86 | 73.29 | 57.83 | 58.41 | 50.61 | 50.05 |
| DEA area % | 0.10 | 0.00 | 2.08 | 2.35 | 10.80 | 11.38 | 23.25 | 23.23 | 29.07 | 28.84 |
| TEA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.55 | 0.62 | 3.74 | 3.53 | 8.29 | 8.69 |
| MEA selectivity, C-% | 97.58 | 100.00 | 84.22 | 82.76 | 55.87 | 54.39 | 35.14 | 34.89 | 23.55 | 23.91 |
| DEA selectivity, C-% | 2.42 | 0.00 | 15.78 | 17.24 | 41.97 | 43.27 | 55.88 | 56.52 | 59.49 | 58.47 |
| TEA selectivity, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 2.16 | 2.34 | 8.98 | 8.60 | 16.96 | 17.62 |
| MEA yield, C-% | 3.08 | 3.37 | 8.91 | 9.05 | 11.88 | 11.83 | 12.58 | 12.31 | 10.08 | 10.35 |
| DEA yield, C-% | 0.08 | 0.00 | 1.67 | 1.88 | 8.92 | 9.42 | 20.00 | 19.94 | 25.46 | 25.32 |
| TEA yield, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.46 | 0.51 | 3.21 | 3.03 | 7.26 | 7.63 |
| Ethanol conversion, C-% | 3.15 | 3.37 | 10.58 | 10.93 | 21.26 | 21.76 | 35.79 | 35.29 | 42.80 | 43.30 |
| Ethanol conversion, mol-% | 5.14 | 5.17 | 13.61 | 13.92 | 26.14 | 26.71 | 42.17 | 41.59 | 49.39 | 49.95 |
| MEA yield, mol-% | 5.07 | 5.17 | 12.44 | 12.61 | 18.83 | 18.91 | 22.43 | 21.98 | 19.73 | 20.23 |
| Ammonia conversion, mol-% | 10.15 | 10.34 | 24.88 | 25.21 | 37.66 | 37.83 | 44.85 | 43.96 | 39.47 | 40.47 |

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## Table A.III-11 RUN B2 (Ethanol amination, also used as RUN D2)

**Hydrogen partial pressure:** 30 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2 | | 3 | | 4 | | 6 | | 8 | |
| Normalised rxn time, hrs | 1 | | 2 | | 3 | | 4 | | 6 | | 8 | |
| MEA area % | 12.49 | 13.98 | 13.47 | 12.94 | 12.00 | 11.45 | 10.48 | 10.85 | 9.13 | 8.83 | 8.56 | 9.50 |
| Ethanol area % | 66.34 | 65.50 | 55.76 | 57.03 | 48.73 | 49.83 | 46.12 | 44.52 | 43.33 | 43.96 | 42.14 | 38.92 |
| DEA area % | 18.32 | 17.59 | 24.79 | 24.01 | 27.09 | 27.96 | 28.63 | 29.51 | 29.65 | 29.73 | 29.00 | 30.26 |
| TEA area % | 2.75 | | 5.81 | 5.70 | 11.91 | 10.48 | 14.36 | 14.66 | 17.42 | 17.11 | 19.82 | 20.97 |
| MEA selectivity, C-% | 37.22 | 44.28 | 30.56 | 30.34 | 23.54 | 22.95 | 19.60 | 19.73 | 16.25 | 15.87 | 14.92 | 15.64 |
| DEA selectivity, C-% | 54.59 | 55.72 | 56.25 | 56.29 | 53.12 | 56.05 | 53.54 | 53.63 | 52.75 | 53.40 | 50.54 | 49.83 |
| TEA selectivity, C-% | 8.19 | 0.00 | 13.19 | 13.37 | 23.34 | 21.00 | 26.86 | 26.64 | 31.00 | 30.73 | 34.54 | 34.53 |
| MEA yield, C-% | 10.48 | 12.04 | 11.61 | 11.13 | 10.54 | 10.03 | 9.28 | 9.65 | 8.15 | 7.86 | 7.66 | 8.56 |
| DEA yield, C-% | 15.37 | 15.15 | 21.37 | 20.65 | 23.79 | 24.49 | 25.34 | 26.24 | 26.44 | 26.45 | 25.95 | 27.28 |
| TEA yield, C-% | 2.31 | 0.00 | 5.01 | 4.91 | 10.46 | 9.17 | 12.71 | 13.03 | 15.54 | 15.22 | 17.73 | 18.90 |
| Ethanol conversion, C-% | 28.16 | 27.20 | 37.99 | 36.69 | 44.79 | 43.69 | 47.32 | 48.93 | 50.13 | 49.54 | 51.34 | 54.74 |
| Ethanol conversion, mol-% | 33.66 | 34.50 | 44.24 | 42.97 | 51.27 | 50.17 | 53.88 | 55.48 | 56.67 | 56.04 | 57.86 | 61.08 |
| MEA yield, mol-% | 18.63 | 21.18 | 21.43 | 20.71 | 20.85 | 19.86 | 19.09 | 19.75 | 17.39 | 16.84 | 16.70 | 18.35 |
| Ammonia conversion, mol-% | 37.27 | 42.36 | 42.86 | 41.43 | 41.70 | 39.72 | 38.18 | 39.50 | 34.78 | 33.68 | 33.39 | 36.69 |

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## Table A.III-12 RUN C1 (Ethanol amination)

**Hydrogen partial pressure:** 60 bar (at 20°C)

**Mass of catalyst:** 1 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 20 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1 | | 2 | |
| MEA area % | 5.28 | 5.56 | 11.99 | 11.74 | 13.64 | 13.22 | 12.51 | 12.51 | 9.08 | 9.21 |
| Ethanol area % | 92.82 | 92.14 | 79.38 | 79.56 | 69.37 | 69.59 | 63.42 | 63.39 | 61.57 | 61.00 |
| DEA area % | 1.55 | 1.69 | 8.10 | 8.14 | 15.24 | 15.22 | 20.37 | 20.55 | 23.99 | 24.37 |
| TEA area % | 0.00 | 0.00 | 0.35 | 0.39 | 1.56 | 1.75 | 3.44 | 3.27 | 4.93 | 4.96 |
| MEA selectivity, C-% | 77.37 | 76.68 | 58.64 | 57.93 | 44.81 | 43.80 | 34.45 | 34.42 | 23.90 | 23.91 |
| DEA selectivity, C-% | 22.63 | 23.32 | 39.63 | 40.16 | 50.07 | 50.40 | 56.08 | 56.58 | 63.13 | 63.23 |
| TEA selectivity, C-% | 0.00 | 0.00 | 1.73 | 1.91 | 5.11 | 5.80 | 9.47 | 9.00 | 12.97 | 12.87 |
| MEA yield, C-% | 4.17 | 4.41 | 9.76 | 9.55 | 11.37 | 11.02 | 10.59 | 10.59 | 7.73 | 7.86 |
| DEA yield, C-% | 1.22 | 1.34 | 6.60 | 6.62 | 12.71 | 12.68 | 17.24 | 17.40 | 20.42 | 20.78 |
| TEA yield, C-% | 0.00 | 0.00 | 0.29 | 0.31 | 1.30 | 1.46 | 2.91 | 2.77 | 4.20 | 4.23 |
| Ethanol conversion, C-% | 5.39 | 5.75 | 16.64 | 16.48 | 25.38 | 25.16 | 30.74 | 30.76 | 32.35 | 32.87 |
| Ethanol conversion, mol-% | 7.18 | 7.86 | 20.62 | 20.44 | 30.63 | 30.41 | 36.58 | 36.61 | 38.43 | 39.00 |
| MEA yield, mol-% | 6.27 | 6.82 | 15.30 | 15.05 | 19.19 | 18.78 | 19.20 | 19.18 | 15.37 | 15.59 |
| Ammonia conversion, mol-% | 12.54 | 13.65 | 30.60 | 30.11 | 38.37 | 37.55 | 38.39 | 38.35 | 30.73 | 31.18 |

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## Table A.III-13 RUN C2 (Ethanol amination)

**Hydrogen partial pressure:** 60 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 0.5 | | 1 | | 1.75 | | 2.5 | | 3.5 | |
| Normalised rxn time, hrs | 0.5 | | 1 | | 1.75 | | 2.5 | | 3.5 | |
| MEA area % | 7.18 | 7.91 | 14.75 | 14.20 | 13.57 | 13.94 | 13.35 | 13.38 | 12.66 | 11.85 |
| Ethanol area % | 83.91 | 84.14 | 67.94 | 68.85 | 60.86 | 60.90 | 55.15 | 54.39 | 52.15 | 52.46 |
| DEA area % | 7.29 | 6.93 | 15.30 | 14.99 | 21.14 | 20.64 | 23.28 | 23.78 | 24.24 | 25.69 |
| TEA area % | 0.90 | 0.88 | 1.95 | 1.88 | 4.37 | 4.46 | 8.16 | 8.39 | 10.91 | 9.93 |
| MEA selectivity, C-% | 46.71 | 50.29 | 46.10 | 45.70 | 34.72 | 35.71 | 29.81 | 29.37 | 26.48 | 24.96 |
| DEA selectivity, C-% | 47.43 | 44.08 | 47.82 | 48.24 | 54.09 | 52.86 | 51.98 | 52.21 | 50.71 | 54.12 |
| TEA selectivity, C-% | 5.86 | 5.63 | 6.09 | 6.06 | 11.18 | 11.43 | 18.22 | 18.41 | 22.81 | 20.92 |
| MEA yield, C-% | 5.81 | 6.36 | 12.32 | 11.84 | 11.54 | 11.85 | 11.51 | 11.56 | 11.00 | 10.29 |
| DEA yield, C-% | 5.90 | 5.58 | 12.78 | 12.50 | 17.97 | 17.54 | 20.08 | 20.55 | 21.06 | 22.31 |
| TEA yield, C-% | 0.73 | 0.71 | 1.63 | 1.57 | 3.72 | 3.79 | 7.04 | 7.25 | 9.47 | 8.62 |
| Ethanol conversion, C-% | 12.44 | 12.65 | 26.74 | 25.91 | 33.23 | 33.19 | 38.63 | 39.36 | 41.54 | 41.23 |
| Ethanol conversion, mol-% | 16.09 | 15.86 | 32.06 | 31.15 | 39.14 | 39.10 | 44.85 | 45.61 | 47.85 | 47.54 |
| MEA yield, mol-% | 10.38 | 10.75 | 20.51 | 19.81 | 20.75 | 21.17 | 21.61 | 21.74 | 21.32 | 20.12 |
| Ammonia conversion, mol-% | 20.76 | 21.50 | 41.03 | 39.63 | 41.50 | 42.35 | 43.21 | 43.48 | 42.64 | 40.23 |

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## Table A.III-14 RUN D1 (Ethanol amination at stirrer speed of 203 RPM)

**Hydrogen partial pressure:** 30 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 0.5 | | 1 | | 2 | | 3 | | 4 | | 6 | |
| Normalised rxn time, hrs | 0.5 | | 1 | | 2 | | 3 | | 4 | | 6 | |
| MEA area % | 6.95 | 7.00 | 10.75 | 10.47 | 9.43 | 8.15 | 6.97 | 6.80 | 6.07 | 6.06 | 4.76 | 4.74 |
| Ethanol area % | 81.35 | 81.58 | 65.85 | 66.14 | 55.40 | 56.78 | 49.07 | 49.21 | 44.00 | 44.00 | 42.33 | 41.97 |
| DEA area % | 9.42 | 9.11 | 18.92 | 19.08 | 26.47 | 26.96 | 31.04 | 31.04 | 29.46 | 29.67 | 29.22 | 29.38 |
| TEA area % | 2.15 | 2.19 | 4.38 | 4.19 | 8.58 | 8.04 | 12.81 | 12.82 | 20.35 | 20.22 | 23.63 | 23.84 |
| MEA selectivity, C-% | 37.54 | 38.26 | 31.57 | 31.04 | 21.20 | 18.89 | 13.72 | 13.42 | 10.87 | 10.83 | 8.26 | 8.18 |
| DEA selectivity, C-% | 50.84 | 49.79 | 55.57 | 56.56 | 59.50 | 62.48 | 61.07 | 61.27 | 52.72 | 53.03 | 50.72 | 50.69 |
| TEA selectivity, C-% | 11.62 | 11.95 | 12.87 | 12.41 | 19.29 | 18.62 | 25.21 | 25.31 | 36.42 | 36.14 | 41.02 | 41.14 |
| MEA yield, C-% | 5.63 | 5.67 | 9.03 | 8.79 | 8.13 | 7.00 | 6.11 | 5.96 | 5.39 | 5.38 | 4.24 | 4.23 |
| DEA yield, C-% | 7.63 | 15.15 | 21.37 | 20.65 | 23.79 | 24.49 | 25.34 | 26.24 | 26.44 | 26.45 | 25.95 | 27.28 |
| TEA yield, C-% | 1.74 | 1.77 | 3.68 | 3.52 | 7.40 | 6.90 | 11.22 | 11.23 | 18.06 | 17.94 | 21.05 | 21.27 |
| Ethanol conversion, C-% | 15.00 | 14.81 | 28.61 | 28.34 | 38.36 | 37.07 | 44.52 | 44.38 | 49.60 | 49.64 | 51.33 | 51.69 |
| Ethanol conversion, mol-% | 18.65 | 18.42 | 34.15 | 33.86 | 44.60 | 43.22 | 50.93 | 50.79 | 56.00 | 56.00 | 57.67 | 58.03 |
| MEA yield, mol-% | 10.47 | 10.50 | 16.94 | 16.57 | 16.48 | 14.49 | 13.27 | 12.99 | 12.33 | 12.28 | 10.07 | 10.04 |
| Ammonia conversion, mol-% | 20.95 | 21.00 | 33.88 | 33.13 | 32.96 | 28.99 | 26.53 | 25.97 | 24.65 | 24.56 | 20.15 | 20.09 |

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## Table A.III-15 RUN D3 (Ethanol amination at stirrer speed of 571 RPM)

**Hydrogen partial pressure:** 30 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 0.5 | | 1 | | 2 | | 3 | | 4 | | 6 | |
| Normalised rxn time, hrs | 0.5 | | 1 | | 2 | | 3 | | 4 | | 6 | |
| MEA area % | 12.51 | 11.93 | 12.27 | 13.22 | 9.77 | 10.05 | 7.65 | 7.89 | 6.62 | 7.33 | 6.36 | 5.38 |
| Ethanol area % | 69.17 | 70.36 | 58.71 | 57.44 | 52.38 | 51.93 | 47.29 | 47.96 | 44.82 | 44.46 | 42.12 | 42.46 |
| DEA area % | 16.32 | 15.80 | 24.03 | 24.34 | 28.97 | 29.35 | 28.93 | 27.82 | 29.92 | 28.54 | 29.59 | 30.32 |
| TEA area % | 1.89 | 1.80 | 4.90 | 4.91 | 8.79 | 8.59 | 16.07 | 16.26 | 18.56 | 19.57 | 21.85 | 21.80 |
| MEA selectivity, C-% | 40.73 | 40.39 | 29.78 | 31.12 | 20.56 | 20.95 | 14.53 | 15.18 | 12.01 | 13.23 | 11.00 | 9.36 |
| DEA selectivity, C-% | 53.13 | 53.51 | 58.33 | 57.32 | 60.95 | 61.15 | 54.95 | 53.53 | 54.30 | 51.48 | 51.20 | 52.73 |
| TEA selectivity, C-% | 6.15 | 6.09 | 11.89 | 11.56 | 18.50 | 17.90 | 30.52 | 31.30 | 33.69 | 35.29 | 37.80 | 37.91 |
| MEA yield, C-% | 10.43 | 9.91 | 10.49 | 11.34 | 8.49 | 8.74 | 6.73 | 6.93 | 5.86 | 6.50 | 5.67 | 4.79 |
| DEA yield, C-% | 13.61 | 13.13 | 20.55 | 20.88 | 25.16 | 25.52 | 25.45 | 24.43 | 26.49 | 25.30 | 26.38 | 27.00 |
| TEA yield, C-% | 1.57 | 1.50 | 4.19 | 4.21 | 7.64 | 7.47 | 14.13 | 14.29 | 16.44 | 17.34 | 19.48 | 19.41 |
| Ethanol conversion, C-% | 25.61 | 24.54 | 35.23 | 36.42 | 41.29 | 41.74 | 46.31 | 45.65 | 48.79 | 49.15 | 51.53 | 51.21 |
| Ethanol conversion, mol-% | 30.83 | 29.64 | 41.29 | 42.56 | 47.62 | 48.07 | 52.71 | 52.04 | 55.18 | 55.54 | 57.88 | 57.54 |
| MEA yield, mol-% | 18.11 | 17.30 | 19.55 | 20.81 | 17.11 | 17.52 | 14.68 | 15.08 | 13.15 | 14.48 | 12.94 | 11.14 |
| Ammonia conversion, mol-% | 36.21 | 34.61 | 39.10 | 41.63 | 34.23 | 35.03 | 29.35 | 30.16 | 26.30 | 28.96 | 25.88 | 22.27 |

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## Table A.III-16 RUN D4 (Ethanol amination) at stirrer speed of 755 RPM

**Hydrogen partial pressure:** 30 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 16.04 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | | 6 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 0.5 | | 1 | | 2 | | 3 | | 4 | | 6 | |
| Normalised rxn time, hrs | 0.5 | | 1 | | 2 | | 3 | | 4 | | 6 | |
| MEA area % | 11.30 | 11.36 | 13.75 | 13.42 | 11.59 | 11.08 | 8.93 | 7.76 | 8.67 | 8.01 | 7.47 | 7.53 |
| Ethanol area % | 77.23 | 77.54 | 63.94 | 64.42 | 55.65 | 55.04 | 52.46 | 53.69 | 47.58 | 47.89 | 44.03 | 43.35 |
| DEA area % | 10.27 | 9.84 | 19.70 | 19.10 | 26.29 | 26.97 | 29.30 | 29.26 | 28.44 | 29.06 | 29.57 | 30.12 |
| TEA area % | 1.14 | 1.18 | 2.53 | 2.96 | 6.36 | 6.72 | 9.21 | 9.18 | 15.21 | 14.96 | 18.83 | 18.91 |
| MEA selectivity, C-% | 49.75 | 50.78 | 38.22 | 37.83 | 26.20 | 24.75 | 18.83 | 16.80 | 16.58 | 15.40 | 13.37 | 13.32 |
| DEA selectivity, C-% | 45.25 | 43.96 | 54.75 | 53.82 | 59.42 | 60.24 | 61.77 | 63.33 | 54.35 | 55.84 | 52.93 | 53.25 |
| TEA selectivity, C-% | 5.00 | 5.26 | 7.04 | 8.35 | 14.38 | 15.01 | 19.41 | 19.87 | 29.07 | 28.76 | 33.70 | 33.43 |
| MEA yield, C-% | 9.23 | 9.28 | 11.61 | 11.32 | 9.99 | 9.57 | 7.76 | 6.72 | 7.63 | 7.04 | 6.63 | 6.69 |
| DEA yield, C-% | 8.40 | 8.03 | 16.63 | 16.10 | 22.65 | 23.29 | 25.45 | 25.34 | 25.01 | 25.53 | 26.24 | 26.77 |
| TEA yield, C-% | 0.93 | 0.96 | 2.14 | 2.50 | 5.48 | 5.80 | 8.00 | 7.95 | 13.38 | 13.15 | 16.71 | 16.81 |
| Ethanol conversion, C-% | 18.55 | 18.28 | 30.37 | 29.92 | 38.12 | 38.66 | 41.20 | 40.01 | 46.02 | 45.71 | 49.58 | 50.28 |
| Ethanol conversion, mol-% | 22.77 | 22.46 | 36.06 | 35.58 | 44.35 | 44.96 | 47.54 | 46.31 | 52.42 | 52.11 | 55.97 | 56.65 |
| MEA yield, mol-% | 15.30 | 15.31 | 20.29 | 19.93 | 19.14 | 18.58 | 15.93 | 14.12 | 16.26 | 15.17 | 14.66 | 14.77 |
| Ammonia conversion, mol-% | 30.60 | 30.61 | 40.57 | 39.87 | 38.28 | 37.16 | 31.86 | 28.24 | 32.52 | 30.34 | 29.31 | 29.53 |

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## Table A.III-17 RUN NP1 (*n*-Propanol amination)

**Hydrogen partial pressure:** 25 bar (at 20°C)

**Mass of catalyst:** 1 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 12.53 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 22 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1.0 | | 2.2 | |
| MPA area % | 0.64 | 0.68 | 0.23 | 0.23 | 0.22 | 0.22 | 0.16 | 0.18 | 0.15 | 0.16 |
| DPA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 8.22 | 6.01 | 5.25 | 4.85 |
| n-Propanol area % | 99.21 | 99.25 | 99.61 | 99.73 | 99.54 | 99.26 | 76.51 | 80.30 | 70.13 | 72.94 |
| TPA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 15.02 | 13.40 | 24.39 | 21.96 |
| MPA selectivity, C-% | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 0.68 | 0.91 | 0.51 | 0.59 |
| DPA selectivity, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 35.13 | 30.70 | 17.64 | 17.98 |
| TPA selectivity, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 64.19 | 68.39 | 81.86 | 81.43 |
| MPA yield, C-% | 0.55 | 0.58 | 0.20 | 0.19 | 0.19 | 0.19 | 0.14 | 0.16 | 0.13 | 0.14 |
| DPA yield, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 7.25 | 5.27 | 4.68 | 4.30 |
| TPA yield, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 13.24 | 11.75 | 21.72 | 19.47 |
| n-Propanol conversion, C-% | 0.55 | 0.58 | 0.20 | 0.19 | 0.19 | 0.19 | 20.63 | 17.17 | 26.53 | 23.91 |
| n-Propanol conversion, mol-% | 0.79 | 0.75 | 0.39 | 0.27 | 0.46 | 0.74 | 23.49 | 19.70 | 29.87 | 27.06 |
| MPA yield, mol-% | 0.79 | 0.75 | 0.39 | 0.27 | 0.46 | 0.74 | 0.40 | 0.46 | 0.41 | 0.43 |
| Ammonia conversion, mol-% | 1.58 | 1.49 | 0.79 | 0.54 | 0.92 | 1.48 | 0.80 | 0.92 | 0.83 | 0.87 |

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## Table A.III-18 RUN IP1 (*iso*-Propanol amination)

**Hydrogen partial pressure: 25 bar (at 20°C)**

**Mass of catalyst:** 1 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 12.30 g

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2.5 | | 5 | | 10 | | 20 | |
| Normalised rxn time, hrs | 0.1 | | 0.25 | | 0.5 | | 1 | | 2 | |
| MIPA area % | 6.31 | 7.17 | 23.01 | 20.14 | 27.00 | 25.72 | 25.53 | 27.01 | 27.23 | 27.79 |
| I-Propanol area % | 93.03 | 92.16 | 76.82 | 79.68 | 72.86 | 74.16 | 73.33 | 71.53 | 68.29 | 67.36 |
| DIPA area % | 0.65 | 0.65 | 0.17 | 0.17 | 0.13 | 0.12 | 0.09 | 0.09 | 0.06 | 0.07 |
| TIPA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 1.05 | 1.37 | 4.09 | 4.44 |
| MIPA selectivity, C-% | 90.69 | 91.72 | 99.28 | 99.17 | 99.51 | 99.53 | 95.75 | 94.86 | 86.76 | 86.04 |
| DIPA selectivity, C-% | 9.31 | 8.28 | 0.72 | 0.83 | 0.49 | 0.47 | 0.32 | 0.32 | 0.21 | 0.22 |
| TIPA selectivity, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.93 | 4.81 | 13.03 | 13.75 |
| MIPA yield, C-% | 5.42 | 6.17 | 20.26 | 17.66 | 23.93 | 22.75 | 22.61 | 23.98 | 24.37 | 24.91 |
| DIPA yield, C-% | 0.56 | 0.56 | 0.15 | 0.15 | 0.12 | 0.11 | 0.08 | 0.08 | 0.06 | 0.06 |
| TIPA yield, C-% | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.93 | 1.22 | 3.66 | 3.98 |
| I-Propanol conversion, C-% | 5.97 | 6.73 | 20.41 | 17.81 | 24.04 | 22.85 | 23.61 | 25.28 | 28.09 | 28.96 |
| I-Propanol conversion, mol-% | 6.97 | 7.84 | 23.18 | 20.32 | 27.14 | 25.84 | 26.67 | 28.47 | 31.71 | 32.64 |
| MIPA yield, mol-% | 6.63 | 7.50 | 23.09 | 20.23 | 27.07 | 25.78 | 26.26 | 27.95 | 30.17 | 30.95 |
| Ammonia conversion, mol-% | 13.27 | 15.00 | 46.18 | 40.47 | 54.14 | 51.56 | 52.53 | 55.90 | 60.33 | 61.90 |

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## Table A.III-19 RUN IP2 (*iso*-Propanol amination)

**Hydrogen partial pressure: 25 bar (at 20°C)**

**Mass of catalyst: 10 g**

**Volume of ethanol: 110 mL**

**Mass of ammonia: 12.30 g**

| Sample number | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 2 | | 3 | | 6 | | 8 | |
| Normalised rxn time, hrs | 1 | | 2 | | 3 | | 6 | | 8 | |
| MIPA area % | 33.26 | 32.16 | 24.42 | 24.11 | 29.94 | 28.20 | 29.31 | 27.62 | 26.88 | 27.15 |
| I-Propanol area % | 63.99 | 65.04 | 74.12 | 75.23 | 67.51 | 68.91 | 62.21 | 61.80 | 62.41 | 62.31 |
| DIPA area % | 0.14 | 0.12 | 0.14 | 0.12 | 0.12 | 0.11 | 0.12 | 0.12 | 0.11 | 0.11 |
| TIPA area % | 2.60 | 2.68 | 1.04 | 0.34 | 2.43 | 2.78 | 8.36 | 10.45 | 10.43 | 10.26 |
| MIPA selectivity, C-% | 92.39 | 91.99 | 95.41 | 98.15 | 92.15 | 90.71 | 77.57 | 72.32 | 71.82 | 72.38 |
| DIPA selectivity, C-% | 0.40 | 0.35 | 0.54 | 0.48 | 0.36 | 0.35 | 0.31 | 0.31 | 0.30 | 0.28 |
| TIPA selectivity, C-% | 7.22 | 7.66 | 4.05 | 1.37 | 7.49 | 8.93 | 22.12 | 27.37 | 27.88 | 27.34 |
| MIPA yield, C-% | 29.89 | 28.85 | 21.65 | 21.33 | 26.76 | 25.14 | 26.41 | 24.91 | 24.25 | 24.50 |
| DIPA yield, C-% | 0.13 | 0.11 | 0.12 | 0.10 | 0.11 | 0.10 | 0.10 | 0.11 | 0.10 | 0.09 |
| TIPA yield, C-% | 2.34 | 2.40 | 0.92 | 0.30 | 2.17 | 2.48 | 7.53 | 9.43 | 9.41 | 9.26 |
| I-Propanol conversion, C-% | 32.35 | 31.36 | 22.69 | 21.73 | 29.04 | 27.72 | 34.05 | 34.44 | 33.76 | 33.85 |
| I-Propanol conversion, mol-% | 36.01 | 34.96 | 25.88 | 24.77 | 32.49 | 31.09 | 37.79 | 38.20 | 37.59 | 37.69 |
| MIPA yield, mol-% | 35.02 | 33.96 | 25.45 | 24.60 | 31.58 | 30.04 | 34.45 | 33.85 | 33.23 | 33.42 |
| Ammonia conversion, mol-% | 70.04 | 67.91 | 50.90 | 49.20 | 63.15 | 60.09 | 68.89 | 67.71 | 66.45 | 66.84 |

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## Table A.III-20 RUN NB1 (*n*-Butanol amination)

**Hydrogen partial pressure:** 20 bar (at 20°C)

**Mass of catalyst:** 10 g

**Volume of ethanol:** 110 mL

**Mass of ammonia:** 10.23 g

| Sample number | 1 | | 2 | | 3 | | 4 | |
|---|---|---|---|---|---|---|---|---|
| Reaction time, hrs | 1 | | 1.75 | | 3 | | 6 | |
| Normalised rxn time, hrs | 1 | | 1.75 | | 3 | | 6 | |
| MBA area % | 2.55 | 2.03 | 1.71 | 1.77 | 1.76 | 1.82 | 1.04 | 1.05 |
| DBA area % | 0.28 | 0.34 | 0.35 | 0.34 | 0.50 | 0.44 | 0.41 | 0.46 |
| n-Butanol area % | 95.03 | 96.99 | 97.67 | 97.51 | 97.74 | 97.73 | 98.55 | 98.49 |
| TBA area % | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| MBA selectivity, C-% | 90.26 | 85.67 | 82.95 | 83.78 | 77.92 | 80.49 | 71.48 | 69.42 |
| DBA selectivity, C-% | 9.74 | 14.33 | 17.05 | 16.22 | 22.08 | 19.51 | 28.52 | 30.58 |
| MBA yield, C-% | 2.32 | 1.82 | 1.52 | 1.58 | 1.57 | 1.62 | 0.92 | 0.93 |
| DBA yield, C-% | 0.25 | 0.30 | 0.31 | 0.31 | 0.44 | 0.39 | 0.37 | 0.41 |
| n-Butanol conversion, C-% | 2.57 | 2.13 | 1.84 | 1.88 | 2.01 | 2.02 | 1.29 | 1.34 |
| n-Butanol conversion, mol-% | 4.97 | 3.01 | 2.33 | 2.49 | 2.26 | 2.27 | 1.45 | 1.51 |
| MBA yield, mol-% | 4.71 | 2.78 | 2.11 | 2.27 | 1.98 | 2.02 | 1.21 | 1.23 |
| Ammonia conversion, mol-% | 9.43 | 5.56 | 4.22 | 4.53 | 3.96 | 4.04 | 2.42 | 2.47 |

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# APPENDIX A.IV

## STANDARD PROCEDURES FOR REACTOR OPERATION

### I. PRE-ASSEMBLING

Make sure that pressure gauge installed is adequate (200 bar).

Make sure that adequate pressure relief valve (BAFFEL) is installed (218 bar is the operation pressure limit at reaction temperature 200°C according to operating instructions manual).

De-oil the reactor and reactor lid including installations.

### II. ASSEMBLING AND OPERATION

1. Continuously flush the reactor with $N_2$ to remove $O_2$
   Fill in alcohol into the reactor.

2. Flush reduced catalyst with $N_2$.
   Transfer reduced catalyst into the reactor in $N_2$.

3. Close the reactor.
   Tighten it up following the prescribed methodology.
   Ensure the screws are equally tight.

4. Make sure the fan in the fume cupboard is on.

5. The transference of $NH_3$ from the gas cylinder into the reactor is made via a metallic U shape tube container:
   Place the U tube container (previously weighted) in a plastic bucket.
   Connect one of the sides of the U tube to the $NH_3$ supply.
   Fill the bucket with dry ice and add methanol.
   Place the bucket on a balance.

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Zero the balance

Open the $NH_3$ supply valve and monitor the weight on the balance.

When the weight displayed is the required close the supply valve.

Remove the U tube from the bucket with ice and place the reactor into it.

Disconnect the U tube from the $NH_3$ supply and connect it to the reactor to cool down the reactor.

Place the U tube into a cup with warm water.

Open both the gas inlet valve of the reactor and the U tube valve.

Allow all $NH_3$ move from the U tube into the reactor.

After wile close all the valves (first close one of the reactor, followed by U tube valve).

Disconnect the U tube.

6. Remove reactor from bucket.

Dry outside the reactor.

Insert reactor into the heating mantel.

7. Connect the cooling water loops for the reactor.

Connect the cooling water loops for the magnetic stirrer drive.

Connect thermocouple.

Connect the inlet pipes for $H_2$ supply to the reactor.

8. Let reactor warm up to ambient temperature (room temperature).

9. Pressurise with $H_2$ until the pressure reached corresponds to 200 bar at reaction temperature (200°C).

10. Close all valves in $H_2$ supply line.

Disconnect pipes for $H_2$ supply.

11. Open cooling water for magnetic stirred drive.

Ensure that cooling water is running through the loop.

Switch the stirrer on.

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12. Set the heating controller to 200°C. Stagger temperature rise to prevent over shooting of the set point.
Heat the reactor up to reaction temperature (200°C).

13. Ensure that temperature does not exceed 200°C.
Ensure that pressure does not exceed 200 bar.

14. Let the reaction run.

15. From time to time, previously established, cool down to room temperature in order to take samples in liquid phase as described in the following:
- Switch off heating unit.
- Open water supply to reactor cooling.
- Cool down to ambient temperature (the stirrer should remain activated, to ensure good heat transfer).
- Collect samples using appropriate system.

16. Close reactor cooling water valve.
Go back to step 13 and repeat the circle.

17. When the experiment shall be terminated:
- Switch off heating mantel.
- Open water supply to reactor cooling
- Cool down to ambient temperature.
- Collect a final sample.

## III. SHUT DOWN THE EXPERIMENT

Check if the heating mantel is switched off.
Depressurise reactor slowly.
Switch off the stirrer.
Close cooling water (reactor first and stirrer 5 minutes later).

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