

Partial Oxidation
of Methanol to Formaldehyde
over Sb-Mo Oxide Catalysts

By
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Dedication

A mis padres

Rafael y Haidée Irma

A mis hermanos

Rosana, Carlos Alberto, Irma Teresa y Adriana Patricia

A mi sobrina

Andani Rosana

Date tiempo para trabajar,
es el precio del triunfo.

Date tiempo para pensar,
es la fuente de poder.

Date tiempo para jugar,
es el secreto de la eterna juventud.

Date tiempo para leer,
es el fundamento de la sabiduría.

Date tiempo para ser amigo,
es el camino de la felicidad.

Date tiempo para soñar,
no atar tu carreta a una estrella.

Date tiempo para amar y ser amado,
es el privilegio de los dioses.

Date tiempo para mirar alrededor,
el día es muy corto para ser egoísta.

Date tiempo para reír,
es la música del alma.

Anónimo

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Nomenclature

Various symbols, superscripts, subscripts and abbreviations used in this work are summarized below. All notation is fully defined when it first arises in the text.

Symbols

a, b, c	Parameters for fractional factorial design models
a, b, c	Lattice parameters
a, b, c, d	Molar quantities of the chemical species in a chemical reaction
a_m	Area of particle per unit mass
a_p	Average surface area per particle
a_v	Area of particle per unit volume of bed
A, B, R, S, X, Y	Chemical species
A, B, C	Antoine Constants
C	Conversion , %
C	Constant for equation 2.58
C_{A_0}	Bulk concentration
C_{As}	External pellet surface concentration

C_p°, C_p	Heat capacity
d	Interplanar angle
d_t	reactor diameter (tubular)
D_p, d_p	Effective particle diameter
D_a	Effective axial dispersion
$\mathcal{D}_e$	Effective diffusivity
$\mathcal{D}_{mi}$	Mean diffusion coefficient of component i in a multicomponent system
$\mathcal{D}_{K_{eff}}$	Effective Knudsen diffusivity
e	Estimated random error
e	Electron charge
E	Potential difference
ΔE	Energy field strength
F	Flow rate of feed, moles/h
F	Formaldehyde concentration (by weight)
F	Moles of formaldehyde in liquid product (Appendix D)
g	Splitting factor
g_{mA}	Molal heat transfer rate per unit mass of bed
G	Mass velocity of fluid based on total cross section of bed
G_m	Molal mass velocity of gas
ΔG_f°	Standard free energy
h	Plank's constant
h_G	Heat transfer coefficient in gas phase
H	Heat of reaction
$\mathcal{H}$	The Zeeman Hamiltonian
H	Magnetic field strength
ΔH_f°	Heat of formation
ΔH_v	Heat of vaporization
I	Defining relation as defined on page 61
j_D	Mass transfer number (Colburn factor)
j_H	Heat transfer number (Colburn factor)

k	Indicates number of operating variables
k	Thermal conductivity of fluid
k_c	Mass transfer coefficient
k_{Gi}	Mass transfer coefficient in gas phase of component i
k_i	Forward reaction rate constant i, from left to right
K, k	Equilibrium constants
L	Reactor length
$L(r)$	Pore size distribution function
m	Mass of electron at rest
m_s	Momentum of electron spin
M	Compensating cation in a zeolite cage
M	Molecular weight of gas mixtures
M	Methanol concentration (by weight)
M	Moles of methanol in the liquid product (Appendix D)
M_A	Overall rate of reaction
n	Refractive index
n	Order of reflexion
p	Momentum of the particle
P	Partial pressure
P_i	Partial pressure of component i
P_s	Saturation pressure
Pe	Peclet number
Pr	Prandtl number
Q	Defined as per equation 2.38
r	Rate of reaction
$\bar{r}$	Average pore size
r_o	Initial rate
r_{mA}	Molal reaction rate per unit mass of bed
R	Universal gas constant
$\bar{R}$	Methanol to air flow ratio, $100 \times \text{mol}_{\text{CH}_3\text{OH}}\text{h}^{-1} / \text{mol}_{\text{air}}\text{h}^{-1}$
$\dot{R}$	Defined as per equation 2.39

R	Catalyst particle radius
Re	Reynolds number defined as per equation 2.41
Re	Reynolds number defined as per equation 2.29
S	Selectivity, %
S	Electron spin operator
S°	Entropy
S_a	Surface area per mass of catalyst
S_g	Specific surface area of catalyst
S_{ox}	Oxidized site, active site on lattice or adsorbed oxygen on catalyst
S_{red}	Reduced site of lattice oxygen or the empty site on catalyst
Sc	Schmidt number
t, t	Temperature, °C
t	Defined as per equation 2.60
T	Temperature, K
T	Total moles of liquid product (Appendix D)
$\bar{u}$	Mean fluid velocity
V	Volume
V_a	Volume of gas adsorbed
V_c	Volume of liquid remaining condensed
V_m	Volume adsorbed equivalent to a monolayer of gas
V_p	Total pore volume
W	Weight of catalyst, g
W	Moles of water in the liquid product (Appendix D)
x	Independent variable
x	Conversion
x	Conversion at equilibrium
X_1, X_2, X_3	Variables defined as per equations 3.4 to 3.6
y	Measured response variable
y_1	Defined as conversion for first-order model

y_2	Defined as selectivity for first-order model
Y	Random variable
Y	Yield, %
Y_{fA}	Defined as per equation 2.40
z	Critical compressibility factor

Abbreviations

BET	(Brunauer, Emmet and Teller) Method for surface area determination
CRT	Cathode Ray Tube
EPR	Electron Paramagnetic Resonance
ESR	Electron Spin Resonance
SEM	Scanning Electron Microscopy
W.H.M.I.S.	Workplace Hazardous Materials Information System

Greek Symbols

α	Number of oxygen molecules required to convert one molecule of methanol
α, β	Electron spin states
β	Electron Bohr magnaton
β_0, β_1	Parameters of equations for Least Squares Estimates in Appendix H
δ_A	Defined as per equation 2.35
ϵ	Random error estimate
ϵ	Porosity of catalyst
ϵ_b	Bed void fraction
ϵ_p	Pellet porosity
η	Internal effectiveness factor
θ	Glacing angle
θ	Contact angle
Θ_i	Fraction of the catalyst surface that is covered by adsorbed component i
λ	Wavelength
μ	Viscosity
Π	Total pressure
ρ	Density
ρ_p	Catalyst particle density
ρ_s	Catalyst bed density
σ	Constriction factor
σ	Surface tension
τ	Tortuosity of catalyst
ϕ	Shape factor
Φ	Thiele modulus
Ω	Overall efectiveness factor

Superscripts

[*]	Indicates selected values (for the parameters)
[*]	Indicates least squares estimates (for the parameters)
^m	Reaction order
ⁿ	Reaction order
^T	Indicates a transpose

Subscripts

—	indicates a matrix
•	placed before a symbol means in the feed
air	air
cat	catalyst
f	film average conditions
(g)	gas
i	component i
M	methanol
O ₂	oxygen
u	indicates value for datum u

Abstract

The kinetics of the vapor phase air oxidation of methanol to formaldehyde over molybdenum oxide catalysts, antimony oxide catalyst, and their mixtures (both supported and unsupported), at atmospheric pressure and different operating conditions, has been studied in a fixed-bed integral reactor heated by a fluidized sand bath.

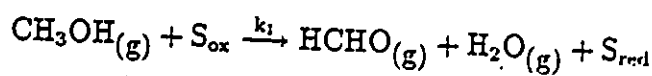
The effect of various process variables, namely the process temperature (T), the ratio of catalysts to feed flow rate or space time (W/F), and the ratio of methanol fed to air ($\bar{R}$), on conversion and yield have been determined.

A screening study at varying operating conditions was performed to determine the optimum composition of a Sb_2O_3 - MoO_3 mixture. On the basis of this study a catalyst containing 67% Sb_2O_3 -33% MoO_3 was selected for the detailed kinetic study of oxidation of methanol to formaldehyde.

The operating conditions studied were as follows: temperatures in the range 623 to 698 K, space times from 5 to 50 $\text{g}_{\text{cat}}/\text{mol}_{\text{CH}_3\text{OH}}\text{h}^{-1}$, and methanol to air ratios in the range 0.04 to 0.10 $\text{mol}_{\text{CH}_3\text{OH}}\text{h}^{-1}/\text{mol}_{\text{air}}\text{h}^{-1}$.

This catalyst proved to be highly active and selective to formaldehyde formation. Yields up to ~100% were obtained. Best operating conditions found were obtained at a space time of 27.5 for a methanol/air ratio of 0.06 and a temperature of 698 K.

The rate equation for the oxidation of methanol to formaldehyde was derived on the basis of a two-stage redox mechanism



where S_{ox} represents an active site of lattice oxygen and S_{red} represents a reduced site of lattice oxygen. The rate equation for the temperature of 648 to 698 K which correlated the data was

$$r = \frac{k_1 P_M}{1 + \frac{k_1 P_M}{2k_2 P_{O_2}}}$$

where k_1 and k_2 are the temperature dependent rate constants of steps one and two. The equations relating k_1 and k_2 with temperature were

$$\ln k_1 = -6.4039 - \frac{6.9153 \times 10^3}{T}$$

$$\ln k_2 = -3.0154 + \frac{1.8809 \times 10^3}{T}$$

Several spectroscopic and analytical techniques, viz, electron spin resonance (ESR), x-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), and adsorption studies were used to characterize the catalysts. The surface area of the catalyst used in the kinetic study was 6.1 m²/g as determined by the BET method.

A preliminary study of the Sb-Mo oxide mixture (load of ~ 5 wt%) supported on Y zeolite was also carried out. Maximum yield obtained was comparable to that obtained with pure MoO₃.

A new catalyst has been developed that gave nearly 100 % conversion and 100 % yield. The industrial potential of this catalyst is very promising.

Contents

Dedication	ii
Acknowledgement	iv
Nomenclature	v
Abstract	xiii
1 Introduction	1
1.1 Formaldehyde Manufacture	2
1.2 Oxide Catalysts	6
1.3 Motivation	8
2 Theoretical Aspects	11
2.1 Basis of Catalyst Preparation	11
2.1.1 Components of the Catalyst Formulation	12
2.1.2 Carbon Formation	14
2.2 Development of Metal Oxide Catalysts	15
2.2.1 Reaction Mechanisms for MoO_3	16
2.3 Theory of Kinetic Analysis	18
2.3.1 Steps in Heterogeneous Catalytic Reactions	20
2.3.2 Langmuir-Hinshelwood Mechanism	21
2.3.3 Modified Langmuir-Hinshelwood Mechanism	21
2.4 Initial Reaction Rate	28

2.5	Heat and Mass Transfer Effects	30
2.5.1	Axial Dispersion and Channeling	34
2.6	Diffusion	35
2.6.1	Molecular Diffusion	35
2.6.2	Knudsen Diffusion	36
2.6.3	Effectiveness Factor	37
2.7	Zeolites	39
2.7.1	Structure	40
2.7.2	Properties	41
2.7.3	Acid Sites	46
2.7.4	Uses in Catalytic Processes	46
2.7.5	Zeolite Used in this Study	48
2.8	Surface Chemistry	48
2.8.1	Electron Spin Resonance	49
2.8.2	X-Ray Diffraction	52
2.8.3	Scanning Electron Microscopy	52
2.8.4	Adsorption	54
3	Methodology	57
3.1	Design of Experiments	57
3.1.1	Design of Screening Study	57
3.2	Kinetic Experiments	63
3.2.1	Experimental Scheme for Kinetic Study	64
3.2.2	Experimental Design for Supported Catalyst	64
3.3	Selection of Rate Equation	65
3.3.1	Initial Rate Method	66
3.3.2	General Methodology	66
3.4	Correlation of Conversion Data	68
3.5	Surface Chemistry Analyses	68
3.5.1	Electronic Spin Resonance	68
3.5.2	X-Ray Diffraction	70

3.5.3	Scanning Electron Microscopy	72
3.5.4	Adsorption	72
4	Properties of Materials	74
4.1	Formaldehyde	74
4.1.1	Physical Properties	75
4.1.2	Chemical Properties	76
4.1.3	Specifications	79
4.1.4	Health and Safety Factors	81
4.2	Methanol	81
4.2.1	Physical Properties	82
4.2.2	Chemical Properties	82
4.2.3	Specifications	84
4.2.4	Health and Safety Factors	84
5	Experimental Aspects	87
5.1	Chemicals and Equipment	87
5.1.1	Preparation of Catalyst	88
5.2	Experimental Apparatus	90
5.2.1	Analysis Procedure	94
5.2.2	Operating Procedure	95
5.3	Surface Characterization Studies	99
5.3.1	ESR	99
5.3.2	SEM	100
5.3.3	XRD	100
5.4	Adsorption Studies	101
6	Results and Discussion	102
6.1	Preliminary Study	103
6.1.1	Results with Molybdenum Trioxide	103
6.1.2	Results with Inert Medium	105
6.1.3	Results with Antimony Oxide	107

6.2	Screening Study	109
6.2.1	Model Building with MoO_3	109
6.2.2	Model Building with Sb_2O_4	112
6.2.3	Results with Mo-Sb Oxide Mixtures	113
6.2.4	ESR Spectra	119
6.2.5	XRD Spectra	123
6.3	Kinetic Analysis of Data	124
6.3.1	Factors Affecting Rate Mechanism	124
6.3.2	Effect of Process Variables	127
6.3.3	Initial Rates	132
6.3.4	Correlation of Data	145
6.4	Results on Supported Catalyst	148
6.4.1	Adsorption Studies	150
6.5	Results of SEM	152
6.6	Discussion	155
7	Conclusions & Recommendations	164
7.1	Conclusions	164
7.2	Recommendations	165
	Bibliography	167
A	Calibration Curves	186
B	Computer Programs	189
B.1	Programs for Mass Balance	189
B.1.1	Main Program: MBAL FORTRAN	189
B.1.2	Exec (Main program): MB EXEC	191
B.2	Programs for Experimental Modelling	191
B.2.1	Main Program: MODEL FORTRAN	191
B.2.2	Exec (Main Program) : MD EXEC	199
B.3	Program for Kinetic Constants	199

B.3.1	Main Program: REAC FORTRAN	199
B.3.2	Exec (Main Program): REAC EXEC	204
C	Kinetic Analysis Graphs	205
C.1	Temperature Effect of Conversion and Yield of HCHO	205
C.2	W/F Effect on Conversion and Yield of HCHO	226
C.3	$\bar{R}$ Effect on Conversion and Yield of HCHO	243
D	Mass Balance	264
D.1	Sample Calculation	264
D.2	Results from Computer Program	267
D.3	Rate Constants for Several Reaction Mechanisms	284
E	Thermodynamic Aspects	297
E.1	Dehydrogenation Method	298
E.2	Oxidation Method	298
F	Heat and Mass Transfer Effects	302
F.1	Mass Transfer Effects	302
F.2	Heat Transfer Effects	304
G	Factorial Design Model	307
G.1	Sample Calculation of Model Building	307
G.2	Replicate Runs for Kinetic Analysis	310
H	Least Squares Criterion	312
H.1	Fitting a Straight Line	312
H.2	Fitting Linear Models	315
I	X-Ray Diffraction	318
J	Electronic Spin Resonance	320

List of Tables

1.1	Properties of Monomeric Formaldehyde	4
2.1	Development of Metal Oxide Catalysts for the Oxidation of Methanol to Formaldehyde	19
2.2	Two-Stage Redox Mechanism	23
2.3	Three-Stage Redox Mechanism (a)	25
2.4	Three-Stage Redox Mechanism (b)	26
2.5	Three-Stage Redox Mechanism (c)	27
2.6	Details of Zeolite Material	48
3.1	Catalysts' Composition	58
3.2	A 2^{3-1} Fractional Factorial Design for Preliminary Catalysts	61
3.3	2^3_{III} Experimental Design	65
3.4	Correlated y and x Relations for Two-Stage Redox Mechanism	69
4.1	Vapor Composition of Formaldehyde-Methanol Mixtures	75
4.2	Formaldehyde Specifications	80
4.3	Specifications of Commercial Formaldehyde-Alcohol Solutions	80
4.4	Health and Safety Factors	81
4.5	Physical Properties of Methanol	83
4.6	Specifications of Pure Methanol	85
4.7	Estimated Tolerance Values for Methanol	86
6.1	Effect of Temperature on Conversion, Selectivity and Yield with MoO ₃ as Catalyst	105
6.2	Effect of Temperature on Inert Medium	107

6.3	Effect of Temperature on Conversion, Selectivity and Yield with Sb ₂ O ₄ as Catalyst	109
6.4	Fractional Factorial Design Runs with MoO ₃	111
6.5	Runs at Centre Point with MoO ₃	111
6.6	Fractional Factorial Design Runs with Sb ₂ O ₄	113
6.7	Catalysts' Composition	114
6.8	Statistical Models for Conversion	115
6.9	Statistical Models for Selectivity	115
6.10	Statistical Models for Yield	116
6.11	ESR Catalysts' Activity	119
6.12	Reaction Rate Constant Values	146
6.13	Results with Sb-Mo Supported on Y zeolite	148
6.14	Best Operating Conditions for Catalyst: 67% Sb ₂ O ₄ -33% MoO ₃ . . .	160
E.1	Thermodynamic Equilibrium Constants	298
E.2	Heats of Reaction	300
E.3	Heat Contents	301
F.1	Data for Mass Transfer Effects	304
F.2	Data for Heat Transfer Effects	305
G.1	Replicate Runs for Kinetic Analysis	311
H.1	Collected Data for Least Squares Criterion	315
I.1	Crystalline Structure of Different Oxides	319

List of Figures

2.1	Dual Dioxo Site Mechanism	42
2.2	Zeolite X and Y (Faujasite) Structure	42
2.3	Faujasite Structures	43
2.4	Sodalite Cages	43
2.5	Electronic Zeeman Hamiltonian	51
3.1	Fractional Factorial Design for 3 Operating Variables	60
5.1	Experimental Apparatus	91
5.2	Reactor and Pre-heater	92
5.3	Typical Analysis of Gas Products	96
5.4	Typical Analysis of Liquid Products	97
6.1	Effect of Temperature on Conversion, Selectivity and Yield with MoO ₃ as Catalyst	104
6.2	Formation of Carbon Oxides with Temperature with MoO ₃	106
6.3	Conversion of Methanol on Inert Medium	108
6.4	Conversion of Methanol on Antimony Oxide	110
6.5	Effect of Catalyst Composition on Conversion	118
6.6	ESR Signal Intensity vs Composition of MoO ₃ in Catalyst	120
6.7	ESR Paramagnetic Spins per gram vs. Composition of MoO ₃ in Catalyst	121
6.8	Effect of Feed Velocity on Conversion	128
6.9	Catalyst Size Effect on Conversion	129
6.10	Effect of Temperature on Conversion, Selectivity and Yield at W/F of 27.5 and $\bar{R}$ of 6	130

6.11 Effect of Temperature on Conversion, Selectivity and Yield at W/F of 50.0 and $\bar{R}$ of 6	131
6.12 Effect of Space Time on Conversion, Selectivity and Yield at T of 673 K and $\bar{R}$ of 6	133
6.13 Effect of Space Time on Conversion, Selectivity and Yield at T of 698 K and $\bar{R}$ of 8	134
6.14 Effect of Methanol-Air Flow Ratio at T of 648 K and W/F of 38.75	135
6.15 Effect of Methanol-Air Flow Ratio at T of 698 K and W/F of 27.5 .	136
6.16 W/F Effect on Yield of HCHO at 623 K	137
6.17 W/F Effect on Yield of HCHO at 648 K	138
6.18 W/F Effect on Yield of HCHO at 673 K	139
6.19 W/F Effect on Yield of HCHO at 698 K	140
6.20 Initial Rates vs. Moles % CH ₃ OH at 623 K	141
6.21 Initial Rates vs. Moles % CH ₃ OH at 648 K	142
6.22 Initial Rates vs. Moles % CH ₃ OH at 673 K	143
6.23 Initial Rates vs. Moles % CH ₃ OH at 698 K	144
6.24 Effect of Temperature on the Rate Constants k_1 and k_2	147
6.25 Adsorption-Desorption Isotherm for Catalyst: 67% Sb ₂ O ₄ -33% MoO ₃ on Y-zeolite	151
6.26 Pore Volume Distribution	153
6.27 Unsupported Sb ₂ O ₄ -MoO ₃ (2:1)	154
6.28 Rare-Earth Exchanged Y Zeolite	156
6.29 Sb ₂ O ₄ -MoO ₃ Supported on Y Zeolite	157
A.1 Calibration Curve for Air	187
A.2 Calibration Curve for Gas Mixture	188
C.1 Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 4	206
C.2 Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 6	207
C.3 Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 8	208

C.4	Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 10	209
C.5	Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 4	210
C.6	Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 6	211
C.7	Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 8	212
C.8	Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 10	213
C.9	Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 4	214
C.10	Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 6	215
C.11	Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 8	216
C.12	Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 10	217
C.13	Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 4	218
C.14	Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 6	219
C.15	Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 8	220
C.16	Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 10	221
C.17	Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 4	222
C.18	Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 6	223

C.19 Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 8	224
C.20 Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 10	225
C.21 W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 4	227
C.22 W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 6	228
C.23 W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 8	229
C.24 W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 10	230
C.25 W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 4	231
C.26 W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 6	232
C.27 W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 8	233
C.28 W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 10	234
C.29 W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 4	235
C.30 W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 6	236
C.31 W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 8	237
C.32 W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 10	238
C.33 W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 4	239

C.34 W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 6	240
C.35 W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 8	241
C.36 W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 10	242
C.37 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 5	244
C.38 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 16.25	245
C.39 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 27.5	246
C.40 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 38.75	247
C.41 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 50	248
C.42 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 5	249
C.43 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 16.25	250
C.44 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 27.5	251
C.45 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 38.75	252
C.46 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 50	253
C.47 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 5	254
C.48 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 16.25	255

C.49 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 27.5	256
C.50 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 38.75	257
C.51 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 50	258
C.52 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 5	259
C.53 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 16.25	260
C.54 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 27.5	261
C.55 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 38.75	262
C.56 $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 50	263
J.1 ESR Spectrum of MoO ₃	321
J.2 ESR Spectrum of Sb ₂ O ₄	321
J.3 ESR Spectrum of Catalyst Composition: 67% Sb ₂ O ₄ -33% MoO ₃	322

Chapter 1

Introduction

Chemical kinetics is the study of the factors influencing the rate of a chemical reaction. Chemical engineering allows considerable freedom of choice in reactor design; this could involve the adoption of a continuous or batch process, the variation of the initial concentration of reactants or operating conditions, or the alterations of these variables during the course of the reaction.

In a kinetic study, the aim is to attain a high yield and good selectivity. In many cases, the use of an empirical rate expression is adequate in order to design the equipment for such reactions. However, it is desirable to obtain a model that would accurately predict the reaction behaviour, since it may then be safer to extrapolate outside the range of experimental data.

The term *catalysis* describes a process in which the rate of reaction is influenced by a substance which remains theoretically unaffected; this substance is called the *catalyst*. In 1902, Ostwald [150] defined catalyst as “any substance that alters the velocity of a chemical reaction without appearing in the end product of the reaction”. This insight provided a basis for scientific inquiry into the subject and paved the way for widespread investigation of catalytic phenomena. Since the time of Ostwald, the science of catalysis has progressed steadily. The scientific progress has been accompanied by enormous technological advances, ranging from the Haber process for ammonia synthesis to present-day processes for the catalytic cracking and reforming of petroleum fractions, to the creation of tailor-made catalysts for greater efficiency

in a very specific process, such as those for hydrodenitrogenation of quinoline and pyridine [10,173] or those for methane coupling [15,57,93,119,124,125,141]

It is handy to classify catalytic reactions according to the number of phases in which they occur. Homogeneous reactions are those that occur when only a single phase is involved in the process, whereas heterogeneous reactions are those that occur when there are two or more phases involved. Heterogeneous reactions occur at the interface between the two phases. An important group of heterogeneous reactions, the oxidation of oxygenated hydrocarbons, is the subject of the present investigation.

There are several methods available [97] to measure reaction rates. These involve either a differential or an integral reactor, and yet none is entirely satisfactory. In the differential method the reactor operates at a low conversion so that the reaction rate may be assumed constant. The integral method is carried out with a steady state process making the experimental accuracy greater. However, the latter method presents difficulties in the integration of the rate equation since there are several hidden parameters.

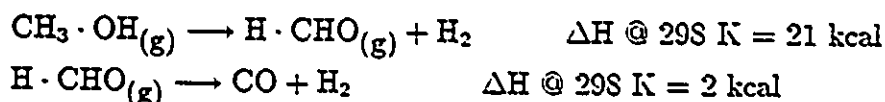
A fixed-bed integral reactor operating at atmospheric pressure is used in this investigation. Since we are more interested in yield and selectivity, and the most common industrial process uses a mixture of methanol and air over a heated stationary catalyst at atmospheric pressure, care is taken to minimize the drawbacks inherent in this choice.

1.1 Formaldehyde Manufacture

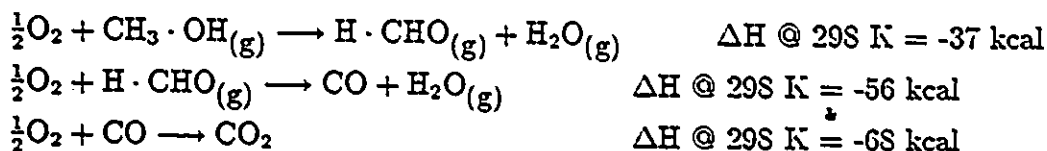
Formaldehyde was discovered by the Russian chemist Butlerov in 1859 [86] as the product of attempted synthesis of methylene glycol. It is the first of the series of aliphatic aldehydes. At ordinary temperatures, pure formaldehyde is a colourless gas with a pungent, suffocating odor. It is produced and sold as water solutions containing variable amounts of methanol. It is noted for its reactivity and versatility as a chemical intermediate. Formaldehyde is used in the form of anhydrous monomer, solutions, polymers and derivatives. Physical properties are summarized

in Table 1.1. Further information about its physical and chemical properties is given in Chapter 4.

There are two stages of practical importance in the pyrolytic decomposition of methanol:



and three stages of importance in its pyrolytic oxidation:



It is to be noted that the dehydrogenation reactions are endothermic and the oxidation reaction exothermic. Consequently, if one aims to manufacture formaldehyde by the dehydrogenation of methanol, heat must be supplied at a rate of 21 kcal per mole of formaldehyde; if one chooses the oxidation process, provision must be made for the removal of 37 kcal of heat per mole of formaldehyde. It would then be obvious that if the two reactions could be combined in such a way that there would not be heat generated or absorbed, i.e. zero heat reaction, the temperature would be independent of the throughput, and the only factor limiting output would be the reaction rate.

At ambient temperatures, the rates of these reactions are insignificant, so steps must be taken to accelerate them. Since the rate of a chemical process is normally an exponential function of the temperature, the logical course is to operate at elevated temperatures. Unfortunately when this happens new problems show up. The first and second stages in the pyrolytic decomposition of methanol, and the first and second oxidation stages, occur in temperature ranges which overlap; the result is that, under ordinary operating conditions, the formaldehyde is destroyed almost as quickly as it is formed. To freeze the formaldehyde, a way must be found to induce

Table 1.1: Properties of Monomeric Formaldehyde

Property	Value
density, g/cm ³	
at 193 K	0.9151
at 253 K	0.8153
boiling point at 101.3 kPa, K	254
melting point, K	155
vapor pressure, Antoine constants, Pa†	
A	9.28176
B	959.43
C	243.392
heat of vaporization, ΔH _v	
at 292 K, kJ/mol	23.3
at 164 to 251 K, J/mol	27,234 + 14.56 T - 0.1207 T ²
heat of formation, ΔH _f [°] at 298 K, kJ/mol	-115.9
std free energy, ΔG _f [°] at 298 K, kJ/mol	-109.9
heat capacity, Cp [°] , J/(mol·K)	35.4
entropy, S [°] , J/(mol·K)	218.8
heat of combustion, kJ/mol	561-571
critical constants	
temperature, K	410.2-414.2
pressure, MPa	6.784-6.637
flammability in air	
lower/upper limits, mol%	7.0/73
ignition temperature, K	703

$$\dagger \log_{10} P_{\text{Pa}} = A - B/(C + t); t = [^{\circ}\text{C}]$$

the primary decomposition, or the primary oxidation, of methanol to take place at a lower temperature level. This calls for the use of a catalyst.

Subject to the reservation that the size and depth of the catalyst in the reactor are adjustable parameters, the problem of producing formaldehyde from methanol seems capable of solution by thermodynamic methods. Jones and Fowlie [80] analyzed this possibility which is summarized in Appendix E.

From this analysis and the knowledge that methanol decomposition starts at 773 K, it is seen that the tendency towards dehydrogenation increases rapidly with rising temperature and will be virtually complete at or above 1000 K. This means that if there was only one stage in the pyrolysis of methanol, formaldehyde could be produced simply by heating methanol vapour at some temperature above 1000 K, and, to avoid methanol regeneration, rapidly condensing the formaldehyde.

However, analyzing the second stage one finds several drawbacks. As its equilibrium constant has values between 10^5 and 10^6 the reaction is highly irreversible and will go virtually to completion. It is also known that formaldehyde vapours start decomposing at 573 K, so that at 1000 K, the formaldehyde would be liable to be destroyed almost as quickly as it is formed. Thus, straight dehydrogenation is not attractive and experience has also proven so.

In the straight oxidation method, the aim is, with the aid of a catalyst, to induce the primary stage in the oxidation of methanol to take place rapidly at temperatures below those at which the second stage occurs at an appreciable rate. This is possible because the primary stage becomes a heterogeneous reaction whereas the second stage remains homogeneous.

After performing the thermodynamic analysis using air (20 vol% O_2), Jones and Fowlie found that the temperature range 573–673 K corresponds to working mixtures in the range 5.5–8 % of methanol, i.e. $\bar{R}$ of 5.8 to 8.7. The straight oxidation method is subject to a wide number of patents [32,49,91,92,113,117]. Its working temperatures are given as 523–723 K and the gas composition as 5–10 % of methanol in air.

The conclusion drawn by these researchers exclusively from this thermodynamic

analysis, is that a 'composite' method (dehydrogenation and oxidation) would operate more efficiently near the upper explosive limit and the straight oxidation method would do it in the region of the lower explosive limit of methanol vapour/air mixtures.

Production in Canada reached an estimated level of 99.88×10^3 metric tons in 1980 [156]. In that same year world production was estimated at about 12×10^6 metric tons [86]. The U.S. is by far the largest producer, 3.055×10^6 metric tons were produced in 1988 [132]. From January to April 1990 Canada exported, mainly to the U.S., 4,166,971 kg valued at \$ 1,613,000 [1]. It imported 371,318 kg valued at \$260,000 [2].

Though formaldehyde is mainly produced today by the partial oxidation of methanol, it is also manufactured from the direct oxidation of hydrocarbon gases. Unfortunately this method requires an energy-intensive plant. This makes it more expensive [43,86]. Because of its relatively low cost, higher purity and variety of chemical reactions, formaldehyde has become one of the world's most important industrial and research chemicals.

1.2 Oxide Catalysts

For years, several metal catalysts had been used for the production of formaldehyde. However, metal oxide catalysts have proven to give better yields. Further details about metallic catalysts can be found in a comprehensive bibliographic review on formaldehyde research until 1963 published by J. F. Walker [164].

Initial studies with oxide catalyst mixtures were performed by Adkins and Peterson [7]. They investigated the oxidation of methanol to formaldehyde using ferric trioxide and molybdenum trioxide and mixtures of the two. The most satisfactory catalyst was found to be an equimolar mixture of both oxides. Conversion reached 91 % at 646 K and $\bar{R}$ of 7.5. Jiru *et al.* [79] carried out a very extensive study on the oxidation of methanol to formaldehyde. His catalyst was composed of 17.5 wt% ferric trioxide and 82.5 wt% molybdenum trioxide. Based on this study, Jiru and co-workers [78,79] have postulated a two-stage oxidation reduction mechanism.

Klissurski and Bliznakov [89] extended the investigations by E. Fields [49] further and studied the effect of manganese dioxide-molybdenum trioxide ratios on conversion. They found that a catalyst containing 20 wt% of MnO_2 to 80 wt% MoO_3 gave the best results. Later Bliznakov *et al.* [24] investigated the rate mechanism of the oxidation of methanol to formaldehyde over this catalyst. They derived an expression similar to that obtained by Jiru *et al.* [79] for a Fe_2O_3 - MoO_3 catalyst. However they did not study the effect of the process variables. Mann and Hahn [107,108] carried out a kinetic analysis based on this catalyst (MnO_2 - MoO_3) as well. They analyzed the effect of process variables, temperature (T), space time (W/F), methanol-air ratio ($\bar{R}$), and methanol feed rate, and found the best results (conversion 84%, selectivity $\sim 100\%$) at 638 K, W/F of 22 and $\bar{R}$ of 8. They also confirmed that the model that correlated the data more satisfactorily was one derived from a two-stage irreversible redox process.

Mann *et al.* [109] investigated the catalytic oxidation of methanol over molybdenum trioxide-tungsten trioxide catalyst. From a preliminary study by Dosi [76,105], a 45 wt% WO_3 -55 wt% MoO_3 catalyst was found to give maximum yield. After analyzing process variables, operating conditions that gave highest yield were found. A 94.9% selectivity and a 95.6% conversion were obtained at 699 K with W/F of 48 and $\bar{R}$ of 10. Again a two-stage redox mechanism was found to fit the data satisfactorily.

Several other catalysts have been studied in the catalytic oxidation of methanol to formaldehyde. Bliznakov *et al.* [26] used BiO - MoO_3 mixtures as catalysts. Maximum selectivity was obtained for a catalyst containing Bi_2O_3 -4 MoO_3 . Selectivity increased up to Mo-Bi oxide ratio of 1:1; beyond which no change was observed. Fedevich and Zhiznevskii [47] performed experiments using TeO_2 - MoO_3 . They found that these catalysts were not suitable for obtaining a very high yield of formaldehyde. Koval *et al.* [96] utilized V_2O_5 - Cr_2O_3 in their catalytic studies. They suggested that the reaction mechanism depended upon the oxide catalysts composition. The activity of the catalyst increased with decrease in the strength of the oxygen bond on the catalyst surface. Oxides in which an exchange of lattice oxygen with $\text{O}_2(\text{g})$ was slow were found to be more selective. Bhattacharyya

et al. [22] used pure V_2O_5 as catalyst. It was found that V_2O_5 gives about 60% formaldehyde yield at about 625 K, but as temperature increases selectivity decreases increasing CO production. Mann and Dosi [109] studied the kinetics of vapor-phase oxidation of methyl alcohol on vanadium pentoxide-molybdenum trioxide catalysts. They found that a two-stage redox mechanism fitted the data satisfactorily for these catalysts. Bliznakov and co-workers [24,25] studied such catalyst mixtures finding similar results as well. Recently more complex mixtures have been tried out. Bliznakov *et al.* [24,25] studied the activity and selectivity of V_2O_5 - MoO_3 - TeO_2 catalysts. They found that the selectivity of V_2O_5 catalyst for conversion of methanol to formaldehyde was increased by adding TeO_2 and MoO_3 . The binary system V_2O_5 - TeO_2 gave an unsatisfactory degree of conversion, while the three-component V_2O_5 - MoO_3 - TeO_2 catalyst had a stable activity and oxidized methanol with a specific rate comparable with industrial iron-molybdenum catalyst. It must be noticed that the difficulties already found in analyzing a two-component catalyst are multiplied when analyzing a three-component catalyst. A complementary survey of the effect of metal oxide catalysts in oxidation reactions in the last few years is given in Section 2.2.

1.3 Motivation

It is known that there is abundant literature regarding the use of MoO_3 as catalyst for the oxidation of methanol to formaldehyde [7,35,63,88,101,115,116,128]. Several mixtures of MoO_3 with other oxides [7,22,25,26,78,79,96,107] have been tried out. However, little information is available regarding antimony oxide as a catalyst for this reaction. Its characteristics as such have been studied by Abadzhieva and Klisurski [6]. They concluded that Sb_2O_4 was a very selective catalyst but its activity was one order of magnitude less than that of MoO_3 . Information on the use of mixtures of antimony oxide with molybdenum trioxide as a catalyst is even more scarce. Antimony oxide often promotes the activity of catalysts used for selective partial oxidations and for related reactions such as oxidative coupling. Although various starting materials can be used, the calcined catalyst will usually contain the

most stable oxide, i.e. Sb_2O_4 . Normally, the tetroxide appears in the orthorhombic α -form, but in the presence of molybdenum, vanadium or iron it can undergo transformation to monoclinic β - Sb_2O_4 [62]. It has been shown [18,19,20,123] that there is a synergistic effect between Sb_2O_4 and SnO_2 . The Sb_2O_4 seems to trap O_2 and generate ions, and then "spill" these ions so that remote centres on the SnO_2 become activated. Similar effects have been observed for Sb_2O_4 - MoO_3 mixtures.

Several researchers have used mixtures of Sb-Mo oxides as catalysts for oxidation and dehydration reactions. Ruiz *et al.* [138] studied the catalytic effect of mechanical oxide mixtures of Sb_2O_4 and MoO_3 in two reactions: N-ethyl formamide dehydration and isobutylene oxidation. They propose that the former reaction is controlled by a remote control mechanism that included the formation of active sites and a catalytic cycle. It was also found that a synergetic effect is obtained on utilizing a mixture of these oxides in both reactions. Such findings were latter confirmed by Zhou *et al.* [174]. Wang and co-workers [165] studied the oxidative esterification of ethanol on a mechanical mixture of the same oxides mentioned above, which is not selective for the ester formation. However, in the course of the oxidation of ethanol, some reduced phases such as $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$ were formed in the catalyst, accompanied with an increase of ester formation. As part of a broader study on oxidation of alcohols, Fedevich *et al.* [48] used mixtures of Fe-Sb-Mo catalysts. They found that primary alcohols effectively oxidized to the corresponding aldehydes. There is no reference to any possible mechanism or kinetic study on the effect of Sb-Mo catalyst in such a reaction. Some studies on surface characterization have been carried out in the last few years [115], but with a broader base of molybdenum oxide mixtures, and with only a specific study in mind. There is no reference to the effects of any specific support on the behaviour of the above mentioned catalyst.

In order to understand the changes that occur on the catalyst surface several analytical techniques and spectroscopic analyses were carried out, namely, electron spin resonance (ESR), x-ray diffraction spectroscopy (XRD), scanning electron microscopy (SEM), and adsorption and surface area analyses. These studies have helped in determining some of the changes that occur on the catalyst surface due to the activation itself as well as those due to the interactions between the oxide

catalysts and the support. They have helped to shed some light on the postulation of a possible mechanism for this specific reaction.

The purposes of the present investigation were: (i) to study the effect of operating variables, i.e. temperature, space time (W/F), methanol to oxygen in air ratio ($\bar{R}$), air flow rate and catalyst composition, on yield and selectivity of formaldehyde production; (ii) to characterize some of the changes that occur on the surface of the oxide catalyst (both supported and unsupported) that give the highest yield and selectivity, through surface studies; (iii) to study the kinetics and postulate a possible mechanism for the oxidation of methanol to formaldehyde over an improved oxide catalyst and (iv) to develop a suitable rate expression, which would represent the data satisfactorily.

Chapter 2

Theoretical Aspects

In order to properly perform a kinetic analysis on a specific chemical reaction one has to consider a broad variety of theoretical aspects related with the science of catalysis, from the how and the why of selection of the catalyst used in this investigation, to its mass and heat transfer related properties, to the way it affects the reaction mechanism, to its interaction with its support and how it differs from the unsupported catalyst, and finally to the theory behind the techniques used to study the phenomena that occur on the catalyst surface.

2.1 Basis of Catalyst Preparation

Chemical composition is clearly the major factor in determining the catalyst properties. However, with a constant chemical composition, the catalytic characteristics may vary over a wide range depending on the conditions and methods of catalyst preparation, owing to the change in the nature of interaction of catalyst components, dispersion, pore structure, crystallochemical changes and other factors which may greatly influence catalytic reactions.

The catalytic properties of a catalyst are measured by the following characteristics [28] :

1. Catalytic activity determined by the amount of a substance reacting per unit volume of the catalyst per unit time under given conditions.

2. Selectivity characterized by the ratio of the formation rate of the required product to the overall rate of conversion of the initial product at a certain temperature and reaction mixture composition.
3. Stability (thermal stability, resistance to poisoning, stable operation over a long period of time).
4. Mechanical strength.
5. Hydrodynamic characteristics determined by the size, shape and density of the catalyst grains.

The task of the theory of catalyst preparation is to find out:

1. What properties of a catalyst other than its chemical composition influence these basic characteristics?
2. What are the optimum values of these properties, or more exactly, what is the optimum combination of these values that will provide high quality of a catalyst for a particular reaction?
3. How can these properties be varied during the catalyst preparation in order to achieve their optimum value?

2.1.1 Components of the Catalyst Formulation

In general, the catalyst formulation (be it a pellet, extrusion or grain) consists of: (a) the support, usually porous Al_2O_3 , SiO_2 , or $\text{SiO}_2\text{--Al}_2\text{O}_3$, upon which is deposited; (b) the catalytic agent; (c) promoters. Andrew [12], and Boreskov [28] give some guide about scientific steps to follow in heterogeneous catalyst preparation.

Supports

Since catalytic activity may be proportional to the concentration of active sites, supports of high area are commonly employed. Porous solids provide areas ranging from one to several hundred square meters per gram. In the silica-alumina catalyst

the active site is formed when one aluminum atom shares four oxygen atoms which in turn are shared by four silicon atoms. An acidic hydrogen ion is thought to be associated with the four oxygen atoms surrounding the aluminum atom. The catalytic activity is ascribed to this acidic hydrogen [158].

Thermal deactivation is a sintering process; i.e. the deposited crystallites grow in size, with the consequence that the number of surface atoms per unit mass of deposited metal decreases. This sintering is minimized with high dispersion, hence the advantages of high area supports. A high area support is characterized by pores of small diameter, which invites diffusional intrusions. In general, a porous support is desirable, but the absolute magnitude of total area sought depends upon the particular reaction and operating conditions.

The support should not be assumed to be inert in the catalytic process for it may endow the deposited catalyst with certain properties (state of oxidation, valence) and may exhibit the ability to adsorb reactants and/or atomic species dissociated by the deposited catalytic agents. Some of these effects are discussed by de Beer [38], and Lo Jacono and Schiavello [100]. Also, an overall review on this subject is given by Topsøe *et al.* [160].

Catalytic Agents

Usually deposited agents are metals and semiconductors, while insulator catalysts are unsupported. The supported catalytic ingredients are generally deposited upon the support from solution. It is to be noted that total impregnation of the support by the catalyst bearing solution is not readily realized, nor, in fact, is it always desirable [31]. Kotera *et al.* [94] found that, in the preparation of Co/Mo supported on alumina catalyst, impregnated catalysts exhibited higher catalytic activities than kneaded ones and that a different optimum Co/Mo ratio existed for both preparation methods.

Promoters

Promoters are classified as physical or chemical. Additives which serve to maintain the physical integrity of the support and/or deposited catalytic agent are termed

physical promoters. Chemical promoters are those which increase the intrinsic activity of the crystallites, and are also those which inhibit undesirable products formation. Thus promoters can be added during catalyst preparation or during reaction. Dosi [43] studied the oxidation of methane to formaldehyde using a catalyst of palladium supported on alumina. This catalyst was modified by a constant and continuous supply of small amounts of chlorine, bromine and iodine compounds. These promoters enhanced, each one differently, the reaction yield.

2.1.2 Carbon Formation

Carbonaceous deposits (coke) can be formed on catalysts under a wide variety of conditions in a reducing environment. The factors involved in carbon formation on nonmetallic catalysts, such as acid catalysts, are substantially different than those involved with metals. On non-metallic catalysts the deposit may contain considerable hydrogen, represented by an empirical formula CH_x in which x may vary between about 0.5 and 1. Carbon deposits on metals generally contain little or no hydrogen, depending in part on the reaction temperature. Many reactions can cause carbon deposits, but the process can be visualized in terms of the decomposition of CO ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$), of CH_4 ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$), or of other gaseous reactions (for example, $2\text{H}_2 + \text{CO}_2 \rightarrow \text{C} + 2\text{H}_2\text{O}$).

The thermodynamic equilibrium conditions under which solid carbon forms assume that the carbon is present as β -graphite. This has been questioned by Manning and co-workers [111] in a study of carbon deposition using nickel and cobalt catalysts where they postulate carbon deposits as a metastable metal-carbide intermediate.

Carbon is often formed as filaments that appear in some cases like hollow tubes, termed *filamentous carbon*. The carbon deposition mechanism causes attack on the metal and disperses it through a mass of finely divided carbon, which thus becomes very catalytically active because the metal is finely divided. With time the fibrous carbon structure may sinter and become more compact, whereupon it becomes less reactive. This phenomenon is a mechanism of attack on bulk metal and supported metal catalysts that can have serious consequences, such as rapid deactivation of the catalyst. Recently Klingman and Lee [87] have proposed a kinetic model of

catalyst deactivation by multilayer coking.

2.2 Development of Metal Oxide Catalysts

Recently the oxide catalyst process for formaldehyde production has assumed increased importance. This process differs from the 'classical' procedure in that it employs lower temperatures, leaner methanol-air mixtures, and can produce formaldehyde that is virtually free of methanol. Manufacturing yields are said to be higher with metallic oxides than with pure metals - silver, copper [86]. The 'classical' process is described in texts, such as those by Walker [164], Hartley [65] and Tataryn [156]. Nonetheless there are still several plant sites worldwide where formaldehyde is still produced from methanol using metallic catalyst and several improvements in performance and equipment have been attained [81,95,99,122,130,135,136,146,155]. Economical reasons are mentioned as the main factor on why these facilities still operate with metallic catalyst.

As previously mentioned in Section 1.2 the first comprehensive study on a metal oxide catalyst, MoO_3 , Fe_2O_3 and their mixtures, for the oxidation of methanol to formaldehyde was carried out by Adkins and Peterson in 1931 [7]. Since then several other researchers have studied, in more or less depth, the use of other metal oxides as catalyst for the manufacture of methanol from formaldehyde. Table 2.1 illustrates the development of this field of research since 1931. It relates the researcher with the catalyst - as a single metal oxide or as a mixture of two or more components. It is observed that MoO_3 has proven to be an extremely good catalyst with high selectivity for this reaction. The other metal oxide added to it in most cases acts as a promoter. Its purpose is to enhance conversion without sacrificing the selectivity gained by the MoO_3 . In most cases the mixtures have a synergetic effect, sometimes due to the formation of a new phase between the oxides. Popov *et al.* [131] studied the physicochemical properties of Cr_2O_3 - MoO_3 catalysts for methanol oxidation. They found that two phases are formed during the catalyst preparation, $\text{Cr}_2(\text{MoO}_4)_3$ and MoO_3 . Gasser and Baiker [56] using amorphous V_2O_5 as catalyst found that after thermal activation the final catalyst exhibited a crystalline structure consisting

of V_2O_5 and V_3O_7 .

Bliznakov *et al.*[26] studied the selectivity of V_2O_5 catalyst and its mixtures with TeO_2 and MoO_3 for conversion of methanol to formaldehyde. The selectivity of V_2O_5 was increased by adding TeO_2 and MoO_3 . In most cases it reached 100% for temperatures between 573 and 673 K. The reason for the high selectivity of V_2O_5 - MoO_3 - TeO_2 catalyst could be associated with the increased surface concentration of V^{4+} ions in the tellurium-containing catalysts. It is generally accepted that the V^{4+} sites are the catalytically active centres of V_2O_5 -containing catalysts. Khulbe *et al.*[55] found that the increase in concentration of V^{4+} ions, which play the role of lattice defects, affects the activity of a catalyst, enhancing its selectivity. The modifying effect of TeO_2 consists in stabilization of the surface concentration of vanadium in the V^{4+} valence state which is probably maintained during the process. Unfortunately Bliznakov and co-workers provided little information regarding conversion of methanol to formaldehyde. The highest conversion achieved was 63.8 % at 613 K for a V_2O_5 -10% TeO_2 catalyst. No information regarding conversion is given for the three-component catalyst making comparisons difficult.

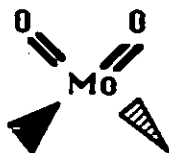
Estévez *et al.*[46] experimented at mild temperatures with iron-molybdenum oxide catalysts in which chromium was added as promoter. They found that the addition of Cr in even small quantities produces a significant rise in formaldehyde yield surpassing that of the industrial catalyst used for comparison. At 548 K the catalyst doped with Cr gave a yield close to 35% whereas the industrial catalyst reached only 20%.

2.2.1 Reaction Mechanisms for MoO_3

The effect of MoO_3 on the oxidation of methanol to formaldehyde has been, as already mentioned, subject of great study. Most of the information concerning the mechanism of reaction with such a catalyst has been extracted with a variety of infrared spectroscopy, mass spectroscopy, and kinetic isotope studies. The following concepts are generally accepted regarding the oxidation of methanol to formaldehyde over MoO_3 .

- (a) The first step consists of dissociative adsorption of methanol to yield surface methoxy and surface hydroxyl species.
- (b) The rate-determining step is the breaking of a C-H bond of the surface methoxy species.
- (c) The activation energies for oxidation of methanol over MoO_3 and $\text{Fe}_2(\text{MoO}_4)_3$ are in the range 16–20 kcal/mol [61].
- (d) The catalysis by both supported and unsupported single crystals of MoO_3 crystals having a variety of geometries indicated that the basal crystal face[(010) surface] of MoO_3 is responsible for forming formaldehyde, while the side surface [(100)] and apical surfaces [(001) and (110)] lead to methylal and dimethyl ether, respectively [9,101,115,116].
- (e) Mo=O centres have been identified by a number of workers as possible dehydrogenation centres believed to be important in mild oxidation [35,101]

Allison and Goddard [9] found that surface *dioxo* sites



are critical to activating methanol. They concluded that an important catalytic site involves two adjacent surface dioxo units, with each dioxo site extracting one H in a sequence of steps. The required dual dioxo site exists on the [(010)] surface of MoO_3 but does not exist on the other low index surfaces.

Chung *et al.*[35] propose that the oxidation of methanol to formaldehyde over MoO_3 can be represented by a mechanism involving methoxy intermediates chemisorbed on oxygen vacancy sites. Formaldehyde and CO are mainly produced from methoxy

on terminal oxygen ($\text{Mo}=\text{O}$) vacancy sites while bridged oxygen ($\text{Mo}-\text{O}-\text{Mo}$) vacancy sites are responsible for the production of dimethyl ether, dimethoxy methane, and methyl formate. The bond strength of chemisorbed methoxy is greatly affected by the electronic state of the oxygen vacancy. Reduced oxygen vacancy sites weaken the C-H bond but strengthen the C-O and chemisorption bonds in the methoxy, resulting in the formation of more hydrogen-abstracted products. They also found that the decrease in the formation of high-order products, dimethyl ether, dimethoxy methane, and methyl formate, at high reaction temperatures is caused by the decrease in the concentration of bridged oxygen vacancy sites by formation of shear planes in the surface layers of MoO_3 .

Louis and co-workers [101] studied two types of MoO_3 on SiO_2 catalyst for the oxidation of methanol -one prepared by the classical impregnation method, the other by the grafting method. They found that there is a dependence of the formation of formaldehyde and methyl formate on the molybdenum content for grafted catalysts, with higher selectivity for methyl formate. This could not be clearly found for the impregnated catalyst. For this catalyst they proposed a mechanism which involves the formation of formaldehyde from methanol on Mo sites, followed by its migration on silica, where it further reacts with methoxy groups to form methyl formate via hemiacetal intermediate.

It is clear that the $[(010)]$ face of MoO_3 is highly selective for the formation of formaldehyde, also that the sites on other face ought to be deactivated in order to keep high selectivity. What is not clear yet is the effect of some other oxides, other than Fe_2O_3 and V_2O_5 , on the $\text{Mo}=\text{O}$ sites. Gasser and Baiker [56] confirmed, in a study of methanol oxidation on vanadium oxide catalyst, that the active sites were considered to be the $\text{V}^{5+}=\text{O}$ species located on the $[(010)]$ face, in accordance with what was said in the previous section.

2.3 Theory of Kinetic Analysis

The relationship between reaction rate and operating variables is a very important factor in the design of any catalytic process. In heterogeneous catalysis it is generally

Table 2.1: Development of Metal Oxide Catalysts for the Oxidation of Methanol to Formaldehyde

Author	Catalyst	Year	Reference
Adkins & Peterson	MoO ₃ -Fe ₂ O ₃	1931	[7]
Jiru <i>et al.</i>	MoO ₃ -Fe ₂ O ₃	1964	[79]
Klissurski & Bliznakov	MnO ₂ -Fe ₂ O ₃	1965	[89]
Bhattacharyya <i>et al.</i>	V ₂ O ₅	1967	[22]
Mann & Hahn	MnO ₂ -MoO ₃	1969	[107,108]
Fedevich & Zhiznevskii	TeO ₂ -MoO ₃	1970	[47]
Bliznakov <i>et al.</i>	BiO-MoO ₃	1973	[26]
Koval <i>et al.</i>	V ₂ O ₅ -Cr ₂ O ₃	1974	[96]
Mann <i>et al.</i>	V ₂ O ₅ -MoO ₃	1973	[106]
Mann <i>et al.</i>	MoO ₃ -WO ₃	1977	[109]
Bliznakov <i>et al.</i>	V ₂ O ₅ -MoO ₃ -TeO ₂	1987	[25]
Gasser & Baiker	V ₂ O ₅	1988	[56]
Louis <i>et al.</i>	MoO ₃ /SiO ₂	1988	[101]
Chung <i>et al.</i>	MoO ₃	1988	[35]
Estévez <i>et al.</i>	MoO ₃ -Fe ₂ O ₃ /Cr	1989	[46]

desired to derive rate expressions based on the *Langmuir-Hinshelwood* theory [97] which may ultimately be used in the design of reactors.

2.3.1 Steps in Heterogeneous Catalytic Reactions

The sequence of physical and chemical steps which occur in an heterogeneous reaction are [151]:

1. Transport of reactants from the bulk fluid to the fluid-solid interface (external surface of catalyst particle)
2. Intraparticle transport of reactants into the catalyst particle (if it is porous)
3. Adsorption of reactants at sites of the catalyst particle
4. Chemical reaction between adsorbed reactants to produce adsorbed products (surface reaction-the intrinsic chemical step)
5. Desorption of adsorbed products
6. Transport of products from the interior sites to the outer surface of the catalyst particle (if it is porous)
7. Transport of products from the fluid-solid interface into the bulk-fluid stream

The rate of reaction is generally a function of temperature, pressure, and composition of the reactants. The actual kinetics may sometimes be hidden by several factors, e.g. catalytic activity of the reactor system, stability of the catalyst, diffusion, and catalyst surface temperature effects. In order to derive a "true" rate equation, the preceding factors, which may affect the mechanism significantly, must be minimized as much as possible. The importance of the resistance of the various steps varies greatly, depending upon operating conditions. Steps 1 and 7, being physical processes, can be minimized by having highly turbulent flow and by making active sites easily accessible to reactants. The effects of steps 2 and 6 can be reduced by having a small particle size thereby making the effectiveness factor ~ 1 . Therefore, in most cases only steps 3 to 5 are considered to offer resistance. Usually only one of these steps is rate controlling.

2.3.2 Langmuir-Hinshelwood Mechanism

This mechanism is based on the concept of monolayer chemisorption on the surface of the catalyst. The theory assumes that adsorption and desorption processes are in equilibrium at constant pressure, and that the reaction takes place between either an adsorbed molecule and a gaseous reactant molecule, or between two chemisorbed molecules on adjacent sites.

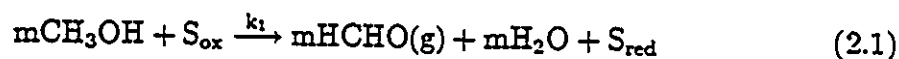
A rate equation is derived by assuming a rate mechanism and selecting one of the reaction steps as rate controlling. The slowest step controls the reaction. Further details are given by Smith [151], Yang and Hougen [168] and by Hahn [83]. This mechanism is not favored for oxygenated hydrocarbons.

2.3.3 Modified Langmuir-Hinshelwood Mechanism

The assumption of adsorption equilibrium in the original Langmuir-Hinshelwood theory is not valid if the rate of adsorption of reactants offers significant resistance. The modified theory considers that reactants adsorbed on the surface increase by adsorption and decrease by reaction. The equilibrium conditions are established when the two rates are equal. Mechanisms following this are generally termed *Redox Mechanisms*. Oxidation of oxygenated hydrocarbons can be treated as an irreversible two or three stage oxidation-reduction reaction. Two and three stage redox mechanisms are briefly described here. Further details can be found elsewhere [31,61,76,98,143,151,168].

Two stage redox mechanism

A steady state is assumed between the following two steps, with the equilibrium shifted to the right side.



The rate of reaction for relations 2.1 and 2.2 are:

$$r_1 = k_1 P_M^m \Theta \quad (2.3)$$

$$r_2 = k_2 P_{O_2}^n (1 - \Theta) \quad (2.4)$$

$$\alpha r_1 = r_2 \quad (2.5)$$

where Θ is defined as the fraction of catalyst surface covered by adsorbed or lattice oxygen and α is the number of oxygen molecules required to convert one molecule of methanol, i.e. 0.5 in the present case. Based on equations 2.3, 2.4 and 2.5, the following expressions can be derived:

$$\Theta = \frac{1}{1 + \frac{\alpha k_1 P_M^m}{k_2 P_{O_2}^n}} \quad (2.6)$$

$$r = r_1 = \frac{k_1 P_M^m}{1 + \frac{\alpha k_1 P_M^m}{k_2 P_{O_2}^n}} \quad (2.7)$$

where r is the rate of oxidation of methanol to formaldehyde. The integrated forms of the rate equation with different values of m and n are given in Table 2.2, where

$$P_M = {}^0P_M(1 - x)$$

$$P_{O_2} = {}^0P_{O_2} - \frac{1}{2} {}^0P_M x$$

Three stage redox mechanism

The oxidation of methanol to formaldehyde taking place by a three stage redox mechanism, can be visualized to occur through the following sequences:

1. Methanol in gaseous state is adsorbed on the catalyst surface at an oxidized site. It is then decomposed to yield gaseous formaldehyde, water and a reduced site. Oxygen reacts with the reduced site to yield an oxidized site.
2. Methanol in gaseous state reacts on the catalyst surface with an oxidized site to produce water and adsorbed formaldehyde. The adsorbed formaldehyde desorbs and it then yields gaseous formaldehyde and a reduced site. Oxygen reacts with the reduced site to yield an oxidized site.

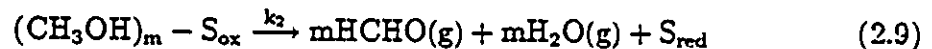
Table 2.2: Two-Stage Redox Mechanism

No.	Reaction Order		Integrated Rate Equation
	m CH ₃ OH	n O ₂	
1	1	0.5	$\frac{W}{F} \frac{{}_oP_M}{\ln(1-x)} = -\frac{1}{k_1} - \frac{4\alpha({}_oP_{O_2} - 0.5{}_oP_Mx)^{0.5}}{\ln(1-x)}$
2	1	0	$\frac{W}{F} \frac{1}{x} = -\frac{1}{k_1} \frac{\ln(1-x)}{{}_oP_Mx} + \frac{\alpha}{k_2}$
3	0.5	0	$\frac{W}{F} \frac{1}{x} = -\frac{2}{k_1} \frac{(1-x)^{0.5}}{{}_oP_M^{0.5}x} + \frac{\alpha}{k_2}$
4	1	1	$\frac{W}{F} \frac{{}_oP_M}{\ln(1-x)} = -\frac{1}{k_1} - \frac{2\alpha \ln({}_oP_{O_2} - 0.5{}_oP_Mx)}{\ln(1-x)}$
5	0.5	0.5	$\frac{W}{F} \frac{{}_oP_M^{0.5}}{2(1-x)^{0.5}} = -\frac{1}{k_1} - \frac{2\alpha({}_oP_{O_2} - 0.5{}_oP_Mx)^{0.5}}{{}_oP_M^{0.5}(1-x)^{0.5}}$
6	2	0.5	$\frac{W}{F} {}_oP_M^2(1-x) = \frac{1}{k_1} - \frac{4\alpha{}_oP_M(1-x)}{k_2}({}_oP_{O_2} - 0.5{}_oP_Mx)^{0.5}$
7	2	1	$\frac{W}{F} {}_oP_M^2(1-x) = \frac{1}{k_1} - \frac{2\alpha{}_oP_M(1-x)}{k_2} \ln({}_oP_{O_2} - 0.5{}_oP_Mx)$
8	2	0	$\frac{W}{F} \frac{1}{x} = \frac{1}{k_1 {}_oP_M^2 x(1-x)} + \frac{\alpha}{k_2}$
9	1.5	0	$\frac{W}{F} \frac{1}{x} = \frac{1}{k_1 {}_oP_M^{1.5} x(1-x)^{0.5}} + \frac{\alpha}{k_2}$
10	1.5	0.5	$\frac{W}{F} {}_oP_M^{1.5}(1-x)^{0.5} = \frac{1}{k_1} - \frac{4\alpha{}_oP_M^{0.5}(1-x)^{0.5}}{k_2}({}_oP_{O_2} - 0.5{}_oP_Mx)^{0.5}$
11	1.5	1	$\frac{W}{F} {}_oP_M^{1.5}(1-x)^{0.5} = \frac{1}{k_1} - \frac{2\alpha{}_oP_M^{0.5}(1-x)^{0.5}}{k_2} \ln({}_oP_{O_2} - 0.5{}_oP_Mx)$

3. Methanol in gaseous state reacts on the catalyst surface with an oxidized site to produce gaseous formaldehyde and adsorbed water. The adsorbed water subsequently desorbs to yield gaseous water and a reduced site. Oxygen reacts with the reduced site to yield an oxidized site.
4. Methanol in gaseous state reacts on the catalyst surface with an oxidized site producing gaseous formaldehyde, water and a reduced site. Oxygen is then adsorbed at the reduced site, reacting with it to form an oxidized site.
5. Methanol in gaseous state reacts on the catalyst surface with an oxidized site forming water and adsorbed formaldehyde. The latter enters in equilibrium with the reduced site and the desorbed formaldehyde. Oxygen reacts with the reduced site to yield an oxidized site.

The rate equations, with their respective m and n values for the above mentioned three-stage redox mechanism for various sequences are shown in Tables 2.3 to 2.5.

The rate equation for the first case of the three-stage redox mechanism can be derived as follows: Methanol in gaseous state is adsorbed on the catalyst surface on an oxidized site to produce gaseous formaldehyde, water and a reduced site. Oxygen then reacts with the reduced site to give the oxidized site. The rate equations for this mechanism can be derived as follows:



From these relations we can write the rate equations as:

$$r_1 = k_1 \Theta_1 P_M^m \quad (2.11)$$

$$r_2 = k_2 \Theta_2 \quad (2.12)$$

$$r_3 = k_3 \Theta_3 P_{\text{O}_2}^n \quad (2.13)$$

$$r_1 = r_2 \quad (2.14)$$

Table 2.3: Three-Stage Redox Mechanism (a).

No.	Reaction Order	Reaction Mechanism
m CH_3OH	n O_2	
1	1, 2	0.5
$m\text{CH}_3\text{OH}(\text{g}) + \text{S}_{\text{ox}} \xrightarrow{k_1} (\text{CH}_3\text{OH})_m - \text{S}_{\text{ox}}$ $(\text{CH}_3\text{OH})_m - \text{S}_{\text{ox}} \xrightarrow{k_2} m\text{HCHO}(\text{g}) + m\text{H}_2\text{O}(\text{g}) + \text{S}_{\text{red}}$ $\text{S}_{\text{red}} + n\text{O}_2(\text{g}) \xrightarrow{k_3} \text{S}_{\text{ox}}$		
Rate Equation		
$r = \frac{k_1 P_M^m}{1 + \frac{k_1 P_M^m}{k_2} + 0.5 \frac{k_1 P_M^m}{k_3 P_{\text{O}_2}}}$		
2	1, 2	0.5
$m\text{CH}_3\text{OH}(\text{g}) + \text{S}_{\text{ox}} \xrightarrow{k_1} (\text{HCHO})_m - \text{S}_{\text{red}} + m\text{H}_2\text{O}(\text{g})$ $(\text{HCHO})_m - \text{S}_{\text{red}} \xrightarrow{k_2} m\text{HCHO}(\text{g}) + \text{S}_{\text{red}}$ $\text{S}_{\text{red}} + n\text{O}_2(\text{g}) \xrightarrow{k_3} \text{S}_{\text{ox}}$		
Rate Equation		
$r = \frac{k_1 P_M^m}{1 + \frac{k_1 P_M^m}{k_2} + 0.5 \frac{k_1 P_M^m}{k_3 P_{\text{O}_2}}}$		

Table 2.4: Three-Stage Redox Mechanism (b)

No.	Reaction Order		Reaction Mechanism
	$\frac{m}{\text{CH}_3\text{OH}}$	$\frac{n}{\text{O}_2}$	
3	1, 2	0.5	$m\text{CH}_3\text{OH}(\text{g}) + \text{S}_{\text{ox}} \xrightarrow{k_1} m\text{HCHO}(\text{g}) + (\text{H}_2\text{O})_m - \text{S}_{\text{red}}$ $(\text{H}_2\text{O})_m - \text{S}_{\text{red}} \xrightarrow{k_2} m\text{H}_2\text{O}(\text{g}) + \text{S}_{\text{red}}$ $\text{S}_{\text{red}} + n\text{O}_2(\text{g}) \xrightarrow{k_3} \text{S}_{\text{ox}}$
			Rate Equation
			$r = \frac{k_1 P_M^m}{1 + \frac{k_1}{k_2} P_M^m + 0.5 \frac{k_1 P_M^m}{k_3 P_{\text{O}_2}^n}}$
4	1, 2	0.5	$m\text{CH}_3\text{OH}(\text{g}) + \text{S}_{\text{ox}} \xrightarrow{k_1} m\text{HCHO}(\text{g}) + m\text{H}_2\text{O}(\text{g}) + \text{S}_{\text{red}}$ $\text{S}_{\text{red}} + n\text{O}_2(\text{g}) \xrightarrow{k_2} (\text{O}_2)_n - \text{S}_{\text{red}}$ $(\text{O}_2)_n - \text{S}_{\text{red}} \xrightarrow{k_3} \text{S}_{\text{ox}}$
			Rate Equation
			$r = \frac{k_1 P_M^m}{1 + 0.5 \frac{k_1}{k_3} P_M^m + 0.5 \frac{k_1 P_M^m}{k_2 P_{\text{O}_2}^n}}$

Table 2.5: Three-Stage Redox Mechanism (c)

No.	Reaction Order		Reaction Mechanism
	$\frac{m}{\text{CH}_3\text{OH}}$	$\frac{n}{\text{O}_2}$	
5	1, 2	0.5	$m\text{CH}_3\text{OH}(\text{g}) + \text{S}_{\text{ox}} \xrightarrow{k_1} m\text{H}_2\text{O}(\text{g}) + (\text{HCHO})_m - \text{S}_{\text{red}}$ $(\text{HCHO})_m - \text{S}_{\text{red}} \xrightleftharpoons{K_2} m\text{HCHO}(\text{g}) + \text{S}_{\text{red}}$ $\text{S}_{\text{red}} + n\text{O}_2(\text{g}) \xrightarrow{k_3} \text{S}_{\text{ox}}$
			Rate Equation
			$r = \frac{k_1 P_M^m}{1 + 0.5 \frac{k_1 P_M^m}{k_3 P_{\text{O}_2}^n} + 0.5 \frac{k_1 P_M^m P_F^m}{K_2 k_3 P_{\text{O}_2}^n}}$

$$\Theta_2 = \frac{k_1 \Theta_1 P_M^m}{k_2} \quad (2.15)$$

$$r_2 = 2r_3 \quad (2.16)$$

$$\Theta_3 = \frac{k_2 \Theta_2}{2k_3 P_{O_2}^n} = \frac{k_1 P_M^m \Theta_1}{2k_3 P_{O_2}^n} \quad (2.17)$$

$$\sum_{i=1}^3 \Theta_i = 1 \quad (2.18)$$

Where Θ_1 , Θ_2 , and Θ_3 represent the fractions of the catalyst surface that are bare, covered by methanol, and the reduced sites respectively, and Θ_i is the fraction of the surface covered by the i th species. Combining equations 2.11 to 2.18 we obtain:

$$\Theta_1 = \frac{1}{1 + \frac{k_1 P_M^m}{k_2} + \frac{k_1 P_M^m}{2k_3 P_{O_2}^n}} \quad (2.19)$$

If r_1 is the rate-controlling step then,

$$r = r_1 = \frac{k_1 P_M^m}{1 + \frac{k_1 P_M^m}{k_2} + \frac{k_1 P_M^m}{2k_3 P_{O_2}^n}} \quad (2.20)$$

Similarly if r_2 or r_3 are rate controlling steps then,

$$r = r_2 = k_1 \Theta_1 P_M^m \quad (2.21)$$

and

$$r = r_3 = \frac{k_1 \Theta_1 P_M^m}{2} \quad (2.22)$$

2.4 Initial Reaction Rate

In a steady state flow system, the relationship between conversion, flow rate and reaction rate is given by the equation

$$F dx = r dW \quad (2.23)$$

which on integration yields

$$\frac{W}{F} = \int_0^x \frac{dx}{r} \quad (2.24)$$

where

r	=	Moles of reactants converted per (unit time) (unit mass of catalyst)
F	=	Flow rate of feed, moles per unit time
W	=	Mass of catalyst
x	=	Moles of reactant converted per mol of feed

Values of the reaction rate should be correlated against the conditions of composition and temperature which prevail at the surface of the catalyst where the catalytic reaction actually takes place. From equations for mass and heat transfer (see Section 2.5) the film gradients for partial pressure of each component gas and temperature can be evaluated. If the rate of catalytic reaction is plotted against mass velocity the rate increases progressively from a certain value at zero mass velocity to an asymptotic value at high mass velocity. It is desirable to operate at sufficiently high mass velocity so that film gradients become negligible. The value of r at zero mass velocity is the reaction rate obtained in a nonflow system.

After the effects of heat and mass transfer, diffusion, fouling and deactivation have been minimized, eliminated or accounted for, selection of the rate-determining chemical step is in order. For gaseous reactions catalyzed by solid surfaces each separate molecular change usually consists of one or two rate-controlling chemical steps such as chemisorption with or without association of one or both reactants; surface reaction between adsorbed reactants and products, and impact of a nonadsorbed reactant with one that is adsorbed.

Mathematical expressions for rate equations can be derived by considering the principles mentioned earlier. In general these rates may be expressed by a combination of three terms; the kinetic term, the potential term and the adsorption term. Detailed expressions for these general rate equations can be found in a paper by Yang and Hougen [168]. In the same paper one finds several curves that in a general way show the effects of total pressure and feed composition for zero percentage conversion. To show the effects of conversion each of these curves would be replaced by a family of curves, one for each percentage. Each curve would be of a similar shape to the parent curve at zero conversion but would drop progressively with increase in percentage conversion and reach a zero rate curve at equilibrium.

In general where adsorption is controlling, the rate curve plotted against conversion at constant pressure and temperature is concave downwards and where surface reaction is controlling is concave upwards. For reversible reactions the same effects are observed but the falling off in rate is more marked.

2.5 Heat and Mass Transfer Effects

In the rate equations for reactions catalyzed by solid surfaces the partial pressure and temperature changes at the gas-solid interface should not be necessarily assumed to have negligible effect in the interpretation of the catalytic reaction-rate data. It is usually assumed that the surface conditions are the same as those of the ambient gas stream. If this assumption is not verified there can be an erroneous interpretation of the reaction model.

The values at the gas-solid interface can usually be calculated from measurements of the bulk-stream values. Because of resistances imposed by heat and mass transfer, the interfacial and bulk-stream values are different. It is desirable to eliminate these transfer resistances to simplify the correlation of experimental data on reaction rates. The effect of heat and mass transfer can be seen from the following relations:

$$r_{mA} = k_{GA} a_m \phi (P_A - P_{Ai}) \quad (2.25)$$

$$g_{mA} = r_{mA} \Delta H_A = h_G a_m \phi (T - T_i) \quad (2.26)$$

where

r_{mA}	=	Molal reaction rate of component A per unit mass of bed
g_{mA}	=	Molal heat transfer rate of component A per unit mass of bed
ΔH_A	=	Molal heat of reaction of component A
k_{GA}	=	Mass transfer coefficient in gas phase of component A
h_G	=	Heat transfer coefficient in gas phase
a_m	=	Area of particle per unit mass
ϕ	=	Shape factor, assumed to be 0.9 for irregular granules
P_A	=	Partial pressure of component A in ambient fluid

P_{Ai}	=	Partial pressure of component A at catalyst surface
T	=	Temperature of the ambient stream
T_i	=	Temperature of catalyst surface

The transfer coefficients h_G and k_{GA} can be calculated from the dimensionless Chilton-Colburn j factors [34].

$$j_H = \frac{h_G}{C_p G} \left(\frac{C_p \mu}{k} \right)_f^{\frac{2}{3}} \quad (2.27)$$

$$j_D = \frac{k_{GA} P_{fA}}{G_m} \left(\frac{\mu}{\rho D_{mA}} \right)_f^{\frac{2}{3}} \quad (2.28)$$

where

j_H	=	Heat transfer number
j_D	=	Mass transfer number
C_p	=	Heat capacity per unit mass at constant pressure
G_m	=	Molal mass velocity of gas based on total cross section of bed
μ	=	Viscosity of fluid
k	=	Thermal conductivity of fluid
$\frac{C_p \mu}{k}$	=	Prandtl number (Pr)
P_{fA}	=	Film pressure factor, defined by equation 2.34
ρ	=	Density of fluid
D_{mA}	=	Mean diffusion coefficient of component A in a multicomponent system
$\frac{\mu}{\rho D_{mA}}$	=	Schmidt number (Sc)
f	=	Properties evaluated at film average conditions

The j factors can be evaluated from expressions developed by Gamson *et al.* [55] and by Wilke and Hougen [167] in different ranges of Reynolds number. Such modified Reynolds number is defined as

$$Re = \frac{D_p G}{\mu} \quad (2.29)$$

where G is the mass velocity of fluid based on total cross section of bed, and D_p is the effective particle diameter. The effective particle diameter is, as well, defined as $\sqrt{a_p/\pi}$; where a_p is the average surface area per particle.

For $Re > 350$ j_H and j_D can be obtained from [55]:

$$j_H = 1.06 Re^{-0.41} \quad (2.30)$$

$$j_D = 0.99 Re^{-0.41} \quad (2.31)$$

For $Re \leq 350$ the heat and mass transfer numbers are obtained from [167]:

$$j_H = 1.95 Re^{-0.51} \quad (2.32)$$

$$j_D = 1.82 Re^{-0.51} \quad (2.33)$$

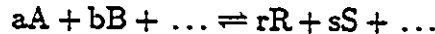
The film pressure factor for component A, P_{fA} , in equation 2.28 is defined by:

$$P_{fA} = \frac{(\Pi + \delta_A P_A) - (\Pi + \delta_A P_{Ai})}{\ln \left(\frac{\Pi + \delta_A P_A}{\Pi + \delta_A P_{Ai}} \right)} \quad (2.34)$$

where Π is the total pressure and δ_A is

$$\delta_A = \frac{r + s + \dots - a - b \dots}{a} \quad (2.35)$$

where $r, s, \dots a, b, \dots$ are the coefficients of components R, S, ... A, B, ..., respectively, in the reaction



It is observed that P_{fA} is the log-mean value of $(\Pi + \delta_A P_A)$ across the gas film. Similar equations can be obtained for components B, S, etc.

Based on the above equations Yoshida *et al.* [172] developed a method for calculating drops in temperature and partial pressure between the bulk gas stream and the exterior surface of the catalyst. This method can be used as well for surfaces on the inside of the catalyst.

Pressure (ΔY) and temperature (ΔT) gradients can be determined from charts and equations proposed by Yoshida *et al.* [172]. Such charts make use of calculated

values for constants and dimensionless numbers for a given system. The equations developed follow:

$$\Delta T = Q(j_H)^{-1}(Pr)_f^{\frac{2}{3}} \quad (2.36)$$

$$\frac{\Delta P_A}{P_A} = \Delta Y_A = \dot{R}(j_D)^{-1}Y_{fA}(Sc)_f^{\frac{2}{3}} \quad (2.37)$$

where

$$Q = \frac{r_{mA}\Delta H_A}{a_m\phi C_p G_m} \quad (2.38)$$

$$\dot{R} = \frac{r_{mA}}{a_m\phi G_m} \quad (2.39)$$

$$Y_{fA} = \frac{P_{fA}}{\Pi} \quad (2.40)$$

For ease of calculation the values of j factors can be correlated with a modified Reynolds number, $\dot{Re}$. This modified Reynolds number is a function of the shape factor and the area of particle per unit volume:

$$\dot{Re} = \frac{G}{a_v\phi\mu} \quad (2.41)$$

where a_v is the area of particle per unit volume of bed, which is defined as $a_v = a_m\rho_s$, where ρ_s is the catalyst bed density.

The values of j factors to be associated with $\dot{Re}$ are [172]:

For $0.01 < \dot{Re} \leq 50$

$$j_D = 0.84\dot{Re}^{-0.51} \quad (2.42)$$

For $50 < \dot{Re} < 1000$

$$j_D = 0.57\dot{Re}^{-0.41} \quad (2.43)$$

And for both cases

$$j_H = 0.076j_D \quad (2.44)$$

The gradients are found to fall in a narrow band either on a ΔY_A versus $\dot{R}$ or a ΔT versus Q plot, which indicates that the parameters $\dot{R}$ and Q are the most important factors in this method in controlling the pressure and temperature drops, respectively.

From Yoshida's mathematical development it can be inferred that both the temperature and partial pressure differences across the film are proportional to

$r_A D_p^{m+1} G^{m-1}$. Since m is either 0.51 or 0.41, by decreasing the particle size and increasing the flow rate, heat and mass transfer resistances are practically eliminated. Several other researchers have arrived at similar findings [45,67,68,69,139,143].

A sample calculation based on the method of Yoshida *et al.* [172] that estimates the temperature and pressure drop from the bulk phase to the catalyst surface is shown in Appendix F.

2.5.1 Axial Dispersion and Channeling

Deviations from plug flow may be caused by one or more of several effects. The void fraction of a packed bed next to the wall is higher than in the center. Because of the lower resistance at the wall, the linear velocity near the wall is greater. The contribution of wall flow to the total flow may be significant for low ratios of $\frac{d_p}{D_a}$, for example 10 or less. The extent to which this may affect reactor performance, however, depends on several factors such as the value of Re , the bed length, and the conversion. At low Reynolds numbers, molecular diffusion may cause a significant axial dispersion. Regardless of the cause, axial dispersion, also called back-mixing, is usually represented by a Peclet number, $Pe = \frac{\bar{u} d_p}{D_a}$, where D_a is the effective axial dispersion and $\bar{u}$ the mean fluid velocity.

Usually, axial dispersion is of negligible importance, except for very short beds and high conversions at low flow rates. Since this can usually be overcome by lengthening the bed, the following criterion [143] is presented for the minimum reactor length necessary to avoid a significant dispersion effect.

$$\frac{L}{d_p} > \frac{20n}{Pe} \ln \frac{C_f}{C_i} \quad (2.45)$$

Here n is the order of reaction, and $\frac{C_f}{C_i}$ is the fractional conversion. The Peclet number is about 2 for gases at Reynolds numbers above about 2 if the ratio $\frac{d_p}{D_a}$ is sufficiently large that wall bypassing is not serious. According to this criterion, for axial dispersion effect on reactor performance to be less than 5 %, the reactor length to particle diameter ratio ($\frac{L}{d_p}$) should be more than 350.

Almost all the information on the effect of the Reynolds number on the Peclet number has been obtained from nonreacting, isothermal systems. At low values of Re , convection effects in laboratory reactors may be a far more important source of deviation from plug-flow than is generally recognized; for example, if an exothermic reaction is studied in a down-flow reactor, convection effects may be suspected, especially in short, squat types of configuration. It is difficult to predict such effects, but experimentally, if a fairly coarse catalyst is being studied and dispersion by convection is suspected, filling the void with an inert material may be an effective diagnostic procedure. If dispersion by convection is indeed significant, this would reduce convection and likely increase conversion.

2.6 Diffusion

When catalysts are porous their external surface area constitutes a small fraction of the total surface area on which the reaction takes place. The diffusion of reactants into and that of products out of the pores could become an important factor in controlling the reaction rate. Depending on whether the mean free path between intermolecular collisions is small or large compared with the pore radii, either one of the two kinds of diffusion, molecular or Knudsen, in pores is possible. If the mean free path of the diffusing molecule is small with respect to the pore radius, the collisions between molecules control diffusion and the unusual molecular or bulk diffusion is applicable. On the other hand, if the pore size of catalyst is small, collisions between molecules and pore wall control the diffusion process and Knudsen diffusion prevails.

2.6.1 Molecular Diffusion

It predominates with all catalysts -porous and nonporous- at very high pressures (> 101.3 MPa) or at atmospheric pressure with very large pores ($> 50\mu\text{m}$ radius). The effect of molecular diffusion is minimized by using high velocity of gas stream passing through the catalyst bed, and its extent can be evaluated by varying the

feed rate while the space time is kept constant.

2.6.2 Knudsen Diffusion

The Knudsen diffusivity depends on the molecular velocity and the pore radius, and it is independent of pressure. Since the mean free path for gases is of the order of $10\ \mu\text{m}$ at atmospheric pressure, diffusion in micropores of catalysts will be predominantly of the Knudsen type. Some restrictions apply, though, when zeolites are used as supports for metal or oxide catalysts, as explained in Section 2.7.2.

The effective Knudsen diffusivity is given as [143]

$$D_{K_{eff}} = 19400 \frac{\varepsilon^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}} \quad (2.46)$$

where

ε	=	Porosity of catalyst
τ	=	Tortuosity of catalyst
S_g	=	Specific surface area of catalyst
ρ_p	=	Catalyst particle density
T	=	Absolute temperature
M	=	Molecular weight of gas mixture

The effect of Knudsen diffusion is evaluated from the knowledge of the *effectiveness factor* of the catalyst. This factor is defined as the ratio of actual reaction rate per unit mass of catalyst to the rate which would exist if the concentration at all interior interfaces were the same as those at the exterior surface. Details of the effectiveness factor are described in Section 2.6.3.

Although several researchers [43,76,83] have correlated effectiveness factor with physical properties of systems such as the one here investigated, there is still much work to be done in this field. An estimate of the effectiveness factor for catalysts such as the ones used in this study can be calculated using a modified Thiele method [143].

2.6.3 Effectiveness Factor

The magnitude of the effectiveness factor -generally ranging from 0 to 1- indicates the relative importance of diffusion and reaction limitations. The internal effectiveness factor, η , is defined as the ratio of the actual overall rate of reaction to the rate of reaction that would result if the entire surface were exposed to the external pellet surface concentration C_{As} .

After performing the proper substitutions and assuming a first-order reaction (see Fogler [51] and Smith [151] for the general case) one obtains

$$\eta = \frac{3}{\Phi_1^2}(\Phi_1 \coth \Phi_1 - 1) \quad (2.47)$$

where Φ_1 is the *Thiele modulus* for a first-order reaction. The Thiele modulus is defined as

$$\Phi_1 = \mathcal{R} \left(\frac{k_1 \rho_p S_a}{\mathcal{D}_e} \right)^{0.5} \quad (2.48)$$

where

$\mathcal{R}$	=	Catalyst particle (pellet) radius
k_1	=	Rate constant for a first-order reaction
S_a	=	Surface area per mass of catalyst
$\mathcal{D}_e$	=	Effective diffusivity

The effective diffusivity, $\mathcal{D}_e$, is related to either the molecular or Knudsen diffusivity as follows

$$\mathcal{D}_e = \frac{\mathcal{D} \varepsilon_p \sigma}{\tau} \quad (2.49)$$

where ε_p is the pellet porosity and σ is the constriction factor.

When the particle diameter becomes very small, Φ decreases, so that the effectiveness factor approaches one and the reaction is surface reaction limited. On the other hand; when Φ is large (~ 30), the internal effectiveness factor η is very small, (i.e. $\ll 1$), and the reaction is diffusion limited within the pellet. Consequently, factors influencing the rate of external mass transport will have a negligible effect on

the overall reaction rate. For large values of the Thiele modulus, the effectiveness factor can be rewritten as

$$\eta \simeq \frac{3}{\Phi_1} = \frac{3}{\mathcal{R}} (\mathcal{D}_e k_1 \rho_p S_a)^{0.5} \quad (2.50)$$

Therefore, in order to increase the overall rate of reaction, M_A , for a specified mass of catalyst one might

1. decrease the radius $\mathcal{R}$, i.e. make pellet smaller,
2. increase temperature,
3. increase the concentration of reactants,
4. increase internal surface area.

It is obvious that these are general guidelines and might not necessarily apply in all cases. For reactions of order n , when generalizing equation 2.48 one obtains

$$\Phi_n^2 = \frac{k_n \mathcal{R}^2 S_a \rho_p C_{A_s}^{n-1}}{\mathcal{D}_e} \quad (2.51)$$

If there happens to be a situation where external and internal resistances to mass transfer and within the pellet are of the same order of magnitude the internal effectiveness factor alone will not describe completely the effect of mass transfer to the surface of the catalyst. In such a case it is convenient to define an overall effectiveness factor that is based on the bulk concentration. This overall effectiveness factor, Ω , is the ratio of the actual overall rate to the rate that would result if the entire surface were exposed to the bulk concentration C_{A_o} . Both effectiveness factors are related as follows

$$\Omega = \frac{\eta}{1 + \frac{\eta S_a}{k_c a_c}} \quad (2.52)$$

where

- | | | |
|--------------|---|--------------------------------------|
| k_c | = | Mass transfer coefficient |
| a_c | = | $\frac{6(1-\epsilon_b)}{\rho_b d_p}$ |
| ϵ_b | = | Bed void fraction |

Several treatises deal with this subject in much more detail (see Fogler [51], Smith [151], Carberry [31], and Chen [33]).

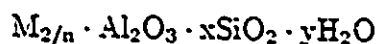
2.7 Zeolites

Zeolites are highly crystalline, hydrated aluminosilicates that upon dehydration develop into an ideal crystal having a uniform pore structure having minimum channel diameters (apertures) of from about 0.3 to 1.0 nm. The size depends primarily upon the type of zeolite and secondarily upon the cations present and the nature of treatments such as calcination and leaching. Zeolites have been of intense interest as catalysts for some two decades because of the high activity and unusual selectivity they provide in a variety of acid-catalyzed types of reactions. In many cases, but not all, the unusual selectivity is associated with the extremely fine pore structure. This permits only certain molecules to penetrate into the interior of the catalyst particles, or only certain products to escape from the interior. Further descriptions of zeolites are given by Bolton [27], Scott [148], Gottardi [64] and Jacobs [75].

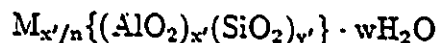
Zeolites are of practical interest for a variety of reasons. The fine pore structure permits adsorption separation to be carried out on the basis of molecular size and shape, so-called *molecular sieving*, as in the separation of n-paraffins from isoparaffins. The ability to alter zeolite properties by ion exchange permits the synthesis of adsorbents of unusual selectivity, even when all molecules have free access to the interior pores of the zeolite. The ion-exchange properties also allow a high degree of flexibility in synthesizing catalysts, for example the ability to produce a highly dispersed metal. From the catalytic point of view zeolites are of special interest in that they exhibit unusual high activity for various acid-catalyzed reactions such as cracking, the ability to combine a molecular sieving property with catalysis, and unusual selectivity behaviour.

2.7.1 Structure

The structure of a zeolite consists of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra, each of which contains a silicon or aluminum atom in the centre. The oxygen atoms are shared between adjoining tetrahedra, which can be present in various ratios and arranged in a variety of ways. Zeolites may be represented by the empirical formula



or by the structural formula



where M is the compensating cation for the net negative charge that is the result of isomorphic substitution of Si by Al, and the bracketed term is the crystallographic unit cell. The metal cation (of valence n) is present to produce electrical neutrality, since for each aluminum tetrahedron in the lattice there is an overall charge of -1. Access to the channels is limited by apertures consisting of a ring of oxygen atoms of connected tetrahedra. There may be 4, 5, 6, 8, 10, or 12 oxygen atoms in the ring. The largest apertures occur in the faujasite-type zeolites (types X and Y) and mordenite, which are of high current interest as catalysts. Zeolites are often prepared in the sodium form; the sodium can then be replaced by various other cations or by hydrogen ions.

Pore Structure

During dehydration some movement of cation may occur; the cation may also move by interaction with adsorbed species and thus alter the structure. Hence the effective pore size of dehydrated zeolites cannot be directly inferred from that of the hydrated form. The effective pore diameter may also vary with the nature of the cation present, for example Na, Ca, H or the dehydroxylated form, and with other treatments. For use in reactions, such as catalytic cracking, high temperature stability is important, which is generally increased by minimum sodium content.

Zeolites Type X and Y

Types X and Y are structurally and topologically related to the mineral faujasite and frequently referred to as *faujasite-type* zeolites. They have three-dimensional intersecting channels in which the minimum free diameter is the same in each direction. They consist of an array of cavities having internal diameter of about 1.2 nm. Access to each cavity (also termed *supercage*) is through six equispaced necks having a diameter of about 0.74 nm. The X and Y zeolites have among the largest minimum aperture restrictions of any zeolite, and the highest void fractions. Their structure may be visualized by the line drawings of Figures 2.2, 2.3 and 2.4. In the foreground of Figure 2.2 is one of the necks, consisting of a ring of 12 oxygen atoms, through which may be seen slight portions of the three other necks. The rows of necks comprise an array of passageways perpendicular to one another in three dimensions.

2.7.2 Properties

In this section the properties of zeolites related to their use as catalysts are reviewed. Their ion-exchange capability, diffusion, thermal stability and molecular sieve effect are also described.

Ion-Exchange Capability

Owing to the isomorphic substitution of silicon by aluminum, the three-dimensional oxygen framework carries an excess negative charge, compensated by cations. The cations can be exchanged with other cations of different nature and valency, which permits the introduction of catalytically important elements. By changing the nature of the cation and the degree of exchange, a whole family of single cations can be exchanged, as well as complexes of cation such as $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Pt}(\text{NH}_3)_4^{2+}$. The only limitation to the nature of the cations that can be introduced by ion-exchange is the acid stability of the zeolite. Generally the zeolite is more stable in acidic solutions when the Si:Al ratio is higher. However, when the exchange solution is strongly acidic, one should bear in mind that, in addition to a given cation, protons

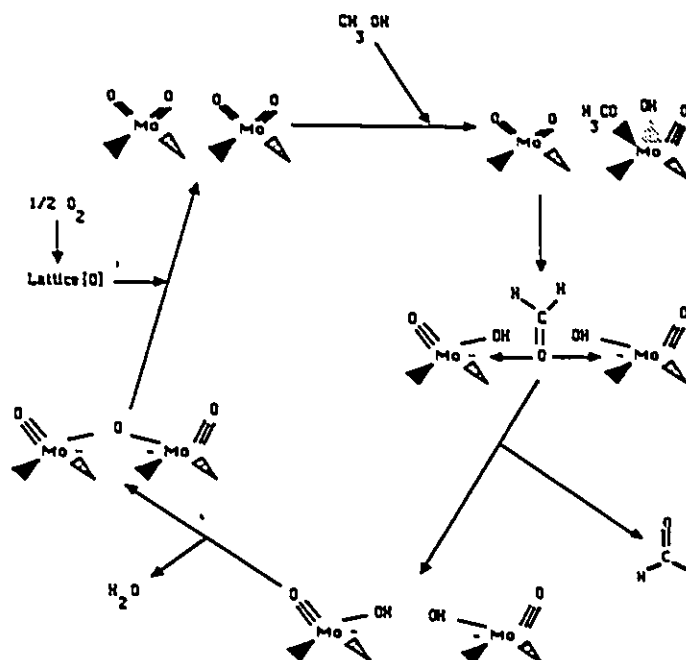


Figure 2.1: Dual Dioxo Site Mechanism

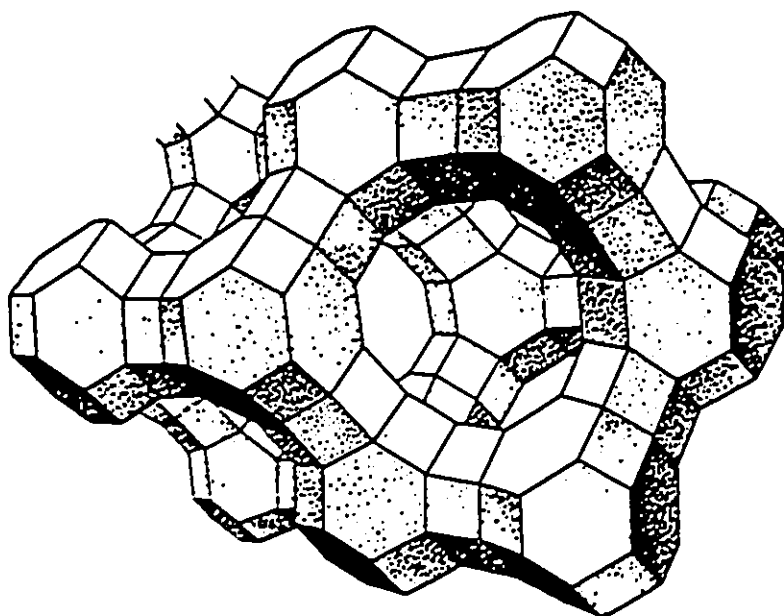


Figure 2.2: Zeolite X and Y (Faujasite) Structure

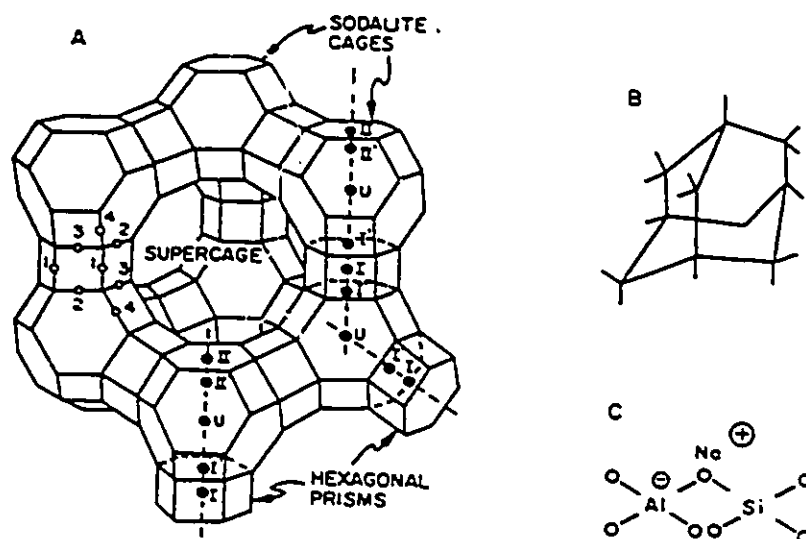


Figure 2.3: (A) Schematic of faujasite framework showing oxygen type (o) and non-framework (•) locations. (B) Adamantanoid pore structure in faujasite. (C) Basic unit of cation exchange/functionality

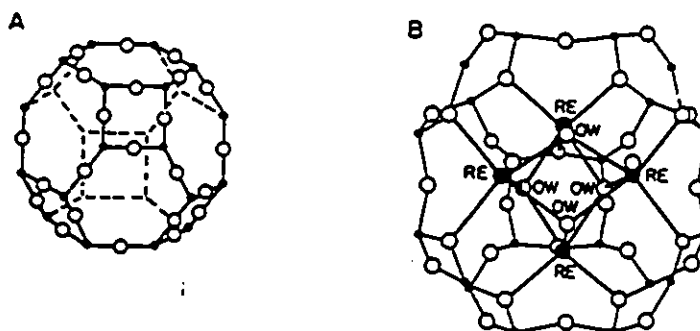


Figure 2.4: (A) Geometric representation of sodalite cage as a truncated octahedron. (B) Sodalite cage complex containing four rare earth cations. (•)=Si,Al; (o)=oxygen; (•)=rare earth

are also exchanged in the zeolite. In this way, a solid with strong acid sites in the pores is created.

Diffusion

Diffusion in zeolites is more complex than Knudsen diffusion or bulk diffusion, and the activation energy is usually substantially greater than that for Knudsen or bulk diffusion. Diffusion in zeolite pores of roughly 1 to 5 nm diameter, in which Knudsen diffusion merges with configurational diffusion, is essentially unexplored, but surface diffusion may well play a significant role under these circumstances.

In the configurational diffusion regime, the increase in diffusivity with change in zeolite generally parallels the increase in pore size, as determined by sorption measurements with different-sized molecules. For a specific zeolite, the activation energy generally increases with increasing molecular size of diffusing species, within a series of similar types of molecules. However, adsorption phenomena and the interaction energy between diffusing molecules and pore walls are also significant variables.

Unlike Knudsen diffusion, in which the fluxes of oppositely moving molecules are independent of one another, the diffusion in zeolites is such that the flux in one direction is markedly hindered by the opposing flux. Such counter diffusion is inevitable in catalytic reactions. Diffusivities can also be markedly affected by slight variation in zeolite structure, including the nature of the cations and the presence of impurities, and by the size and polarity of counter-diffusing molecules. The apparent activation energy for zeolite diffusion is greater than that for bulk or Knudsen diffusion. The few values that have been reported are relatively uncertain because of the limited temperature range covered and other difficulties such as deviations from Fick's law, sorption effects, and questions concerning the difference between unidirectional and counter-diffusion. Generally, the smaller the diffusion coefficient, the higher the activation energy.

In their commercial form zeolite catalysts are incorporated into a gel matrix, but diffusivities are much greater in the pores of the matrix than in the zeolite pores. Diffusion limitation inside the zeolite pores may not be significant in commercial

catalytic processes. However, it depends on the feedstock, amount of carbon present on the catalyst, and several other factors.

Haynes *et al.*[66] investigated the effects of hydrocracking mixtures of two-, three-, and four-ring structures over a nickel-tungsten sulfide ultrastable zeolite Y catalyst. They found that when diffusion is in the configurational zone, differences of the order of several picometers in molecular size can have drastic influences on the zeolite diffusivity.

Thermal Stability

The structural stability of the less stable zeolites (X and Y) is increased after exchange with polyvalent ions such as Ca, Mg and La. The thermal stability of hydrogen zeolites, obtained by proton exchange or after decomposition of the ammonium-exchanged form, is several hundred degrees lower than that of the parent zeolite. For high-temperature reactions catalyzed by these acidic forms of zeolite, it is necessary to stabilize the zeolite structure; one way is by prior exchange with polyvalent cations. In this way, rare earth-exchanged NH_4 Y-zeolites after dehydration are suitable cracking catalysts in terms of thermal stability and acidity of the solid. Thermal stability is also increased after gradually leaching out aluminum atoms from the lattice.

The practical use of zeolites as catalysts also requires a high hydrothermal stability. The structural resistance against steam treatment is also higher for zeolites with higher thermal stability and lower aluminum content.

Molecular Sieve Effect

Sieving of one type of molecule out of a feed containing a mixture of molecules with different shapes and/or sizes is possible as the free apertures of the zeolites have molecular dimensions. From the catalytic point of view, such a system constitutes a very selective catalyst if the sites responsible for the catalytic action are located inside the cavities or pores. The zeolite component is expected to be more selective than the matrix for the desired product. Similarly, the matrix may be considered more selective for other products [36].

2.7.3 Acid Sites

The discovery that silica-alumina catalysts were active for cracking reactions stimulated research to elucidate the nature of the active sites on the surface. It was found that acid sites were responsible for the cracking activity. The existence of those sites is readily demonstrated by the affinity of basic molecules such as ammonia, pyridine, or quinoline for the surface of silica-alumina. Further description of such structures can be found elsewhere [17,75,150].

Both Brönsted and Lewis acid sites are found in zeolites. The former are protons attached to lattice oxygen atoms, while the latter can be the charge-compensating cations or triangular aluminum atoms at oxygen-deficient sites or at cation positions. Protons can be introduced into the structure through ion exchange, thermal decomposition of the NH_4 -exchanged form, hydrolysis of water of hydration of cations or reduction of cations to a lower valency state. If these structures are further dehydrated, this results in dehydroxylation and the formation of Lewis acid sites.

The ratio depends, then, on the temperature of pretreatment prior to the determination. As it is increased, the ratio of Lewis to Brönsted sites increases. A more in-depth study about zeolites as acidic catalysts is given by Barthomeuf [17].

2.7.4 Uses in Catalytic Processes

In the early 1960s, crystalline aluminosilicates or zeolites were introduced in catalytic cracking. Their use has been responsible for the dramatic improvement in cracking processes. The industrial use of these solids as heterogeneous catalysts has been nonetheless limited. Their use in industrial processes implies that they exhibit higher activity and/or selectivity than existing catalysts. Their major applications as catalysts are found in the petroleum industry and are related to two important zeolite properties: the molecular sieve effect and the extremely high acidity of these solids [75]. Both characteristics have already been described above. More recently, wide-pore zeolites have been used as supports for highly dispersed metals. Commercial catalysts are of the faujasite type (X and Y) or are synthetic mordenites and zeolites T (erionite type).

The most important industrial applications of zeolites up until now are in catalytic cracking, hydroisomerization, selective forming, hydrocracking and transformations of aromatic hydrocarbons [162]. A 100–10000 times improved activity [40,75], for zeolite was claimed as compared to amorphous silica-alumina. This fact, coupled with an improved hydrogen transfer capability (presumably a consequence of hydrogen mobility between cracked molecules), was indicative of important potential of zeolitic materials for increasing conversions to gasolines with low coke yields [39]. The activity of modern zeolite cracking catalysts has improved to the point where for the most part only 1 to 4 seconds of contact time are required to effect substantially complete conversion of the non-aromatic portion of the feed.

Results obtained by a variety of methods indicated that the density of Brønsted acid sites was much higher for the Y-type zeolites in hydrocracking than for amorphous silica-aluminas. The higher selectivity to aromatics and isoparaffins indicates that hydrogen-transfer reactions occur more readily with zeolites as catalysts.

The tendency of metals to induce nonselective cracking in amorphous catalysts has been extensively studied [37,143,160]. Zeolite cracking catalysts have excellent resistance to contamination by vanadium, nickel, and other heavy metals, and appear to be superior to amorphous catalysts in this respect. This is evidenced by the lower carbon producing factor of a given metal loading for zeolites. The faujasite catalysts are also more resistant to poisoning by organic nitrogen compounds.

The study of applications of zeolites to enhance the activity of catalysts continues. Examples of these are given by Goddard and Ruthven [59], who studied the adsorption of C_8 aromatics on Na Y-zeolites and by Kallo *et al.* [82] who studied the hydrosulfurization of the C=C bond on Me^{2+} -zeolites. Scott [148] updates until 1980 all the advances and developments of zeolite technology and its applications. Swabb and Gates [154] studied the rates of dehydration of methanol to dimethyl ether catalyzed within the straight tubular pores of H-mordenite crystallites. They found that the rates of catalyst activity loss were independent of crystallite size, also that the diffusion of methanol appears to be hindered more by interaction with pore walls than by interference with counterdiffusion reaction products. Nováková

Table 2.6: Details of Zeolite Material

Description : Type Y, molecular sieve rare-earth exchanged		
Composition :	SiO ₂	- 65 %
	Al ₂ O ₃	- 23 %
	Na ₂ O	- 2 %
	Rare-earth	- 11 %
Form	: Grains	(0.246 to 0.175 mm)
Surface Area	: Approx.	550 m ² /g
Catalogue no.	: 14-S910	
Manufacturer	: Sterm Chemicals	U.S.A.

et al.[121] studied the transformation of methanol to olefines on several types of zeolites. Schults and co-workers [147] made studies on coke formation during methanol conversion on zeolite catalysts. Inui *et al.*[73] investigated the catalyst deactivation caused by coking in methanol to aromatic conversion on Ga- and Zn-ion-exchanged H-ZSM-5 zeolite. Nishizawa *et al.*[120] and Aparicio [13] have studied, independently, the catalytic activity of several cation-exchanged zeolites as catalysts for redox reactions.

2.7.5 Zeolite Used in this Study

The rare-earth exchanged Y-type zeolite is the one of the best options for hydroprocessing applications. It has also proven efficient in several other processes [13,120,147]. This material was obtained from a commercial source. Some details of the zeolite material used in this study are listed in Table 2.6.

2.8 Surface Chemistry

Spectroscopy is the study of the interactions of electromagnetic radiation with matter. When light or electromagnetic radiation impinges on a material, it will be

absorbed if the energy of the light coincides with the energy required to excite some transition of the sample. The exact nature of this transition can range from changes in rotational energy to high-energy electronic transition, and beyond. In the simplest sense, spectroscopy provides a record of the amount of electromagnetic energy absorbed by a material as a function of the energy of the radiation employed. This record, termed the spectrum, is unique to the sample and can be utilized to identify or quantify constituents, establish or follow changes in structure, or perhaps provide insight into mechanistic and kinetic details of a chemical reaction [126].

2.8.1 Electron Spin Resonance

Those atoms, molecules, and solids which have unpaired electrons and exhibit some magnetic properties are termed paramagnetic. The unpaired electrons are most conveniently detected by electron spin resonance, or ESR. This technique employs both external magnetic fields and radiofrequency photons. The substance to be studied is placed in the magnetic field and absorption of electromagnetic energy, i.e. the radiofrequency photons, is observed. This is much like any other type of spectroscopy except that the energy levels are strongly modified by a magnetic field.

With electron spin resonance, also called electron paramagnetic resonance (EPR), one can identify modified crystal structures, free radicals which are naturally or artificially produced, conduction electrons in metals and acceptors or donors in semiconductors. ESR detects the type of radiation that classifies as microwave, that is those radiations with frequencies between 10^9 and 10^{11} Hz and wavelength of 30 cm to 3 mm. Detailed information on ESR can be found in several treatises [8,21,90,115].

The Zeeman Effect

When a paramagnetic material is placed in a magnetic field, the degeneracy of the two possible spin states of the unpaired electron is removed. This interaction, called the electronic Zeeman effect, is described by the Zeeman Hamiltonian.

$$\mathcal{H} = g\beta H S \quad (2.53)$$

where β is electron Bohr magnaton, H is the applied magnetic field strength, and S is the electron spin operator. The g -value, also termed splitting factor, is a unitless ratio of the magnetic moment to the total angular moment of an unpaired electron.

The Bohr magnaton is defined as

$$\beta = \frac{eh}{4\pi m} \quad (2.54)$$

where

e	=	Electron charge (4.083×10^{-10} statcoul)
h	=	Planck's constant (6.625×10^{-27} erg-sec)
m	=	Mass of electron at rest (9.108×10^{-28} g)
β	=	Bohr's constant (0.9273×10^{-20} erg/G)

The electronic Zeeman Hamiltonian operating on the electron spin states, α and β , yields the energies of these states as represented in Figure 2.5. In a magnetic field, the β state ($m_S = -\frac{1}{2}$) has its moment along the field, and is therefore of lower energy than the α state ($m_S = +\frac{1}{2}$), the moment of which opposes the field direction. The magnitude of the energy difference between the two states is directly proportional to the applied field strength.

$$\Delta E = g\beta H \quad (2.55)$$

Electromagnetic radiation corresponding to this energy difference can be absorbed by a paramagnetic centre, promoting the unpaired electron from the lower energy β state to the α state. In a magnetic field of several thousand gauss the spin system absorbs radiation in the microwave region.

The Spin Hamiltonian

Although the Zeeman interaction provides the basis for ESR, other energies of greater or lesser magnitudes affect the experiment. The total Spin Hamiltonian describes the energy of a species interacting with a magnetic field.

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_d + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_Z + \mathcal{H}_{hf} + \mathcal{H}_Q + \mathcal{H}_N \quad (2.56)$$

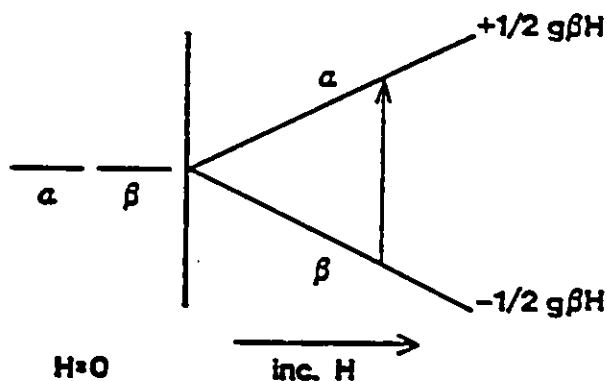


Figure 2.5: Electronic Zeeman Hamiltonian Operating on the Electron Spin States

The subscript notation indicates contribution from electronic effects, interactions with crystal field, spin-orbit coupling, spin-spin coupling, Zeeman interaction, hyperfine coupling, and nuclear quadrupolar and spin energies, respectively.

Anisotropy

The spin angular momentum vector of an unpaired electron in a magnetic field is aligned with the field. Therefore, the electronic Zeeman Hamiltonian is determined by the direction of the field. However, other interactions which perturb the energy of the unpaired spin, such as spin-orbit coupling and hyperfine coupling, are referenced to the coordinate system of the molecule or to the lattice.

Different orientations of the orbital motion of the electron, relative to the applied magnetic field, yield variations in the magnitude of the orbital angular momentum. The spin-orbit interactions which result vary with the orientation of the molecular coordinate frame relative to the magnetic field direction.

Similarly, for the hyperfine interaction, the nuclear spin moment aligns not with the applied magnetic field, but with the effective field that is the vector of the applied field and the local field induced by the electron orbital motion. The magnitude of the hyperfine coupling constant then also depends on the orientation of the molecule relative to the applied field.

In practice, however, some of the interactions perturb the unpaired spin only

slightly and can be neglected in an interpretation of results.

2.8.2 X-Ray Diffraction

All crystalline substances have a characteristic atomic structure with three-dimensional periodicity. In consequence of this and of the similarity in magnitude between inter-atomic distances and x-ray wavelengths, a crystal can function as a three-dimensional diffraction grating for x-rays and produce diffraction maxima in directions depending on the structural periodicities and x-rays wavelengths. When a beam of 'white' or polychromatic x-rays is diffracted by a stationary crystal, a characteristic *Laue* diffraction pattern is obtained, which, for certain special orientations, shows directly the symmetry of the crystal structure about the direction of the x-ray beam.

This method of analysis was first suggested by Bragg and may be expressed by the Bragg equation, which gives the requirement for a diffraction maximum as [152]

$$n\lambda = 2d \sin \theta \quad (2.57)$$

where

- n is the order of reflection,
- λ is the x-ray wavelength,
- d is the interplanar angle,
- θ is the glancing angle between the incident beam and the reflecting phase.

2.8.3 Scanning Electron Microscopy

In 1924 de Broglie proposed that with a moving particle was associated a wavelength λ ,

$$\lambda = \frac{h}{p}$$

where h is Plank's constant, and p the momentum of the particle.

Electrons, being charged, may be accelerated through a potential difference E , and the resulting wavelength is

$$\lambda = \frac{12.26}{E(1 + 0.9788 \times 10^{-6}E)^{1/2}} \text{ \AA}$$

where E is in volts.

The second term in the denominator is a relativistic correction, which becomes important at high voltages (>50 kV). At 100 kV, the operating voltage of most modern commercial instruments, $\lambda = 3.7$ pm. Thus, accelerating electrons provide a source of short-wavelength radiation capable of resolving small objects provided a lens system of sufficient quality can be provided.

The first scanning electron microscope using demagnifying lenses was constructed by von Ardenne in Berlin in 1938. This was a transmission instrument using photographic recording. In general, the resolution available from the early instruments was poor. After World War II, work at the Cambridge University Engineering Laboratories resulted in many improvements. The fraction of secondary electrons was high, and the current was amplified by an electron multiplier. The image was displayed on a cathode ray tube (CRT) and the electron beam scanned by two pairs of scanning coils. Further improvements resulted from the use of magnetic lenses in the column and the replacement of the electron multiplier system by a scintillator and photomultiplier.

Many features are common to several electron optical instruments. All contain an electron gun, with the required stabilized high-voltage supply, ability to vary the bias voltage, filament heating current, etc. Condenser lenses and apertures are required to provide a defocused image of the gun crossover at the specimen. The magnetic lenses require a stabilized current supply and cooling, with ability to vary the focal length of the lenses by varying the current in the lens solenoids. The column must be evacuated to $\sim 1.33 \times 10^{-3}$ Pa by a diffusion pump backed by a rotary pump. The latter is often isolated mechanically from the system to reduce vibration pickup at the specimen.

The scanning microscope differs from the transmission microscope in that the electron beam focused at the sample by the lens system is scanned over the sample

in a raster using a set of deflecting coils. The lens system gives a demagnified image of the electron source of the order of 10 to 25 nm in size when focused at the specimen.

The sample can be either thin enough for transmission of electrons to occur or massive, in which case the incident beam is converted into secondary electrons or some other form of energy such as optical radiation or characteristic X-rays. The basic concept in examining samples by scanning microscopy is that the intensity of the radiation emerging from each point on the surface is characteristic of the composition and topology at that point. Thus, by amplifying the detected signal and displaying it on a CRT scanned synchronously with the beam of the sample, a high resolution image of the surface can be displayed. The magnification is determined by the ratio of the distance that the beam is scanned on the specimen compared to the distance scanned on the CRT.

Sargent and Embury [142] provide extensive description of the operation of transmission and scanning electron microscopy. Sanders [140] describes some applications of electron microscopy in determining the surface characteristics of catalysts.

2.8.4 Adsorption

The molecules in the surface layer of a solid are bound on one side to the inner molecules of the solid but there is an imbalance of atomic and molecular forces on the surface side. The surface molecules attract gas, vapour, or liquid molecules in order to satisfy these unbalanced, bonding forces. The attraction may be either physical or chemical, depending on the system involved and the temperature employed.

Physical adsorption, frequently referred to as van der Waal's adsorption, is the result of a relatively weak interaction between a solid and a gas. This type of adsorption has one primary characteristic. Essentially all of a gas adsorbed can be removed by evacuation at the same temperature at which it was adsorbed.

Chemical adsorption, or chemisorption, is also an interaction between a solid and a gas but it is more energetic than physical adsorption. Evacuation at an elevated temperature is required for the removal of the adsorbed species. However, this may not be sufficient in some cases. The quantity of physically adsorbed gas at a

given pressure increases with decreasing temperature, whereas in chemisorption the quantity decreases as the temperature is decreased. Consequently, adsorption measurements for the purpose of determining surface area or pore distribution are made at low temperature; chemisorption studies usually involve elevated temperatures.

Physical Adsorption

While the first gas molecules to contact a clean solid are held more or less rigidly by van der Waal's forces, the forces active in the condensation of vapours become increasingly responsible for the binding energy in subsequent layer adsorption development. The expression

$$V_a = \frac{V_m CP}{P_s - P} \left[1 + \frac{(C + 1)P}{P_s} \right] \quad (2.58)$$

where V_a is the volume of gas adsorbed at pressure P , V_m the volume adsorbed when the entire adsorbing surface is covered by a monomolecular layer, C a constant, and P_s the saturation pressure of the gas, is obtained by equating the rate of condensation of gas molecules onto an adsorbed layer to the rate of evaporation from that layer and summing for an infinite number of layers.

The physical adsorption of a gas on a smooth surface will continue as the gas pressure is increased at a constant temperature until a condensed layer quite a few molecules thick is formed. If the surface contains cracks, crevices, or pores, the adsorbed layer will fill these as its thickness increases. When a pore fills, its contribution to the surface area very nearly ceases. Conversely, the pore surface contribution again comes into play as adsorbed gas layers are desorbed and pore walls are re-exposed.

Continuing the adsorption by incremental steps to, or nearly to, the saturation pressure yields a complete adsorption isotherm. Then reversing the procedure by subjecting the sample to stepwise reduction in pressure while continuing to record volumes and equilibrium pressures permits obtaining the desorption isotherm. Adsorption and desorption isotherms coincide precisely only when the solid is completely nonporous and there are no contact points among particles creating the

effect of pores. Both adsorption and desorption isotherms are employed in calculating pore size distribution of porous materials; there is no distinction in the mathematical treatment.

If a cylindrical pore in a solid of radius r_c is not filled with condensate but has its walls blanketed with a condensed layer of thickness t , the radius of the free space, r , is $r_c - t$. The opening radius is related to the relative pressure of the condensed liquid forming its boundary by the Kelvin equation. Thus,

$$r = r_c - t = -\frac{2\sigma M \cos \theta}{RT\rho \ln \frac{P}{P_s}} \quad (2.59)$$

where σ is the surface tension of the adsorbate, ρ the density of the adsorbate, M the adsorbate molecular weight, θ the contact angle, R the gas constant, T the absolute temperature, and $\frac{P}{P_s}$ the relative pressure. The t values are obtained from the Halsey-type expression

$$t = 3.54 \left[\frac{-5}{\ln \left(\frac{P}{P_s} \right)} \right]^{\frac{1}{3}} \quad (2.60)$$

Assuming condensation has filled all pores, the volume of gas desorbed when all pores smaller than r_c remain filled may be written from geometrical considerations as

$$V_p - V_c = \int_{r_c}^{\infty} \pi(r_c - t)^2 L(r) dr \quad (2.61)$$

where V_p is the total pore volume, V_c the volume of liquid remaining condensed, and $L(r)$ a pore size distribution function describing the total length of all pores of radius r per unit weight of adsorbent. A very commonly used expression that approximates $L(r)$ is

$$\Delta L = \frac{\Delta V_p}{\pi \bar{r}^2} \quad (2.62)$$

where $\bar{r}$ is the average pore radius. Further details and applications of this method are given in treatises by Smith [151], Carberry [31], Chen [33] and others.

Chapter 3

Methodology

Methodology is defined as a system of methods and rules applied to science [3]. Here, the strategies followed for the design of experiments, during the screening study for unsupported catalysts and for the final catalyst composition supported on Y zeolite are explained in detail. The description of the experimental scheme for the full kinetic study, as well as the methods for the selection of the rate equation and the correlation of conversion data are also given.

3.1 Design of Experiments

One of the objectives of this research, as outlined on page 2, is to study the effect of operating variables, i.e. temperature, space time, methanol to air ratio and catalyst composition, on yield and selectivity of formaldehyde production. It is observed that these four variables would require an extremely large number of experiments if all of them were to be analyzed in detail. Therefore the need for an experimental strategy that would allow one to obtain the most information possible out of a reduced but properly designed number of experiments.

3.1.1 Design of Screening Study

It is to be noted however, that the other objectives of this research (the kinetic study and the catalyst characterization) had to be carried out with the “best” catalyst

Table 3.1: Catalysts' Composition

Catalyst	Sb ₂ O ₄ (wt%)	MoO ₃ (wt%)
I	0	100
II	100	0
III	83.33	16.66
IV	66.66	33.33
V	50	50
VI	33.33	66.66
VII	16.66	83.33

catalyst -the one that gave the highest yield- prepared in our laboratory. In order to attain this goal of producing this "best" catalyst, a fractional factorial experimental design method [14] was utilized. This method was modified using a model-building technique suggested by Hunt and Jaworsky [72]. Also some suggestions by McLean [114], Ioffe *et al.*[74] and Fux and Ioffe [53] were considered.

Catalyst Design

It was considered that the catalyst composition, i.e. percentages of Sb₂O₄ and MoO₃, should be varied so as to give a significant coverage of the composition range. The catalysts' compositions are shown in Table 3.1.

These compositions are based on the preparation of Sb₂O₄ and MoO₃ alone, which is described in Section 5.1.1.

Fractional Factorial Design

It is widely known in experimental design that two level factorial designs are most useful for screening studies involving up to four variables [14]. In a two level factorial design the experimental strategy commands the distribution of n operating variables whose influence on the response variable is to be described by a first degree polynomial,

$$E(Y) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots \quad (3.1)$$

where $E(Y)$ denotes the expected value of a random variable Y , β_i is the parameter associated with the "independent" variable x_i .

Two level factorial designs are not intended to provide definitive models of process behaviour. The main use of such designs is as a *screening* tool. It is useful to help detect those operating variables that exert stronger influence on the response, either individually, i.e. $\beta_1 x_1$, or jointly, i.e. $\beta_{12} x_1 x_2$.

As mentioned above, one important feature of the factorial design is that it provides valuable information about the possible interactions between operating variables. Two operating variables interact when the size of the influence of one of them on the response depends upon the value of the other one.

A two level factorial design for k operating variables is denoted as a 2^k design. It indicates that k variables are being tested, and each one at two levels. This is also useful to identify the number of tests that the experimental design requires. The following "complete" model shows the estimates of each of the 2^k parameters.

$$\begin{aligned}
 E(Y) = & \beta_0 + \beta_1 x_1 + \cdots + \beta_k x_k \\
 & + \beta_{12} x_1 x_2 + \cdots + \beta_{k-1,k} x_{k-1} x_k \\
 & + \beta_{123} x_1 x_2 x_3 + \cdots + \beta_{k-2,k-1,k} x_{k-2} x_{k-1} x_k \\
 & + \cdots \\
 & + \beta_{12\dots k} x_1 x_2 \cdots x_k
 \end{aligned} \tag{3.2}$$

Generally those interaction terms that involve more than two operating variables are neglected since their influence most of the time is small. Also by deleting such terms residual information for testing model adequacy might be produced.

There are cases where circumstances do not allow one to carry out the complete set of 2^k tests in a two level factorial design for k operating variables. It is obvious that some information will be lost. However, by properly selecting a subset of the complete 2^k design, that is, an appropriate *fractional factorial design*, the most relevant pieces of information will be retained. Unfortunately this selection generally includes some *a priori* judgment about the relevance of some variables. If after analyzing the data produced from a fractional factorial design results are

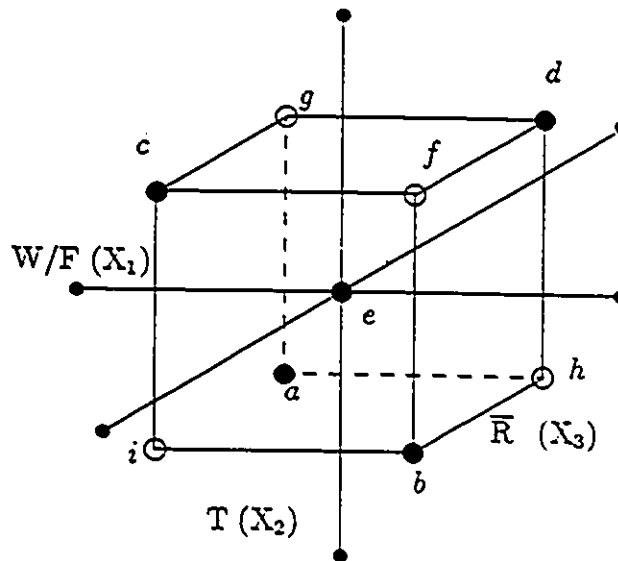


Figure 3.1: Fractional Factorial Design for 3 Operating Variables

still ambiguous, a further fractional factorial design, planned specifically to resolve those ambiguities, may be carried out.

In this screening study there are three operating variables of interest, i.e. temperature, space time, and ratio of methanol fed to air. According to our model-building technique above mentioned, each operating variable is tested at only two values, represented by -1 and 1 in the coded notation. A set of four tests is selected of the eight possible tests of a 2^3 design and denoted more concisely as a 2^{3-1} design. This set of runs makes the screening process faster. The complementary set of four tests would be carried out only if more discrimination is necessary.

There are 70 different subsets of four tests that can be selected from the eight tests of a 2^3 design, each yielding different mixtures of information. In the present case the subset chosen is that for which the three factor interaction terms $X_1X_2X_3$ have the value 1.

The positioning of the values for the operating variables to be used during the screening study is better shown in Figure 3.1.

Table 3.2: A 2^{3-1}_{III} Fractional Factorial Design for Preliminary Catalysts

Code†	Test code	X_1	X_2	X_3	T (K)	W/F	R
a	02	-1	-1	1	648	16.25	8
b	03	1	-1	-1	698	16.25	4
c	04	-1	1	-1	648	38.75	4
d	05	1	1	1	698	38.75	8
e	01, 06	0	0	0	673	27.5	6

†: Refer to Figure 3.1

When the experimental design is shown in a table-like format (as seen in Table 3.2), if a column consisting entirely of “1’s” is added and denoted as I, then because the values of the variable $X_1X_2X_3$ from the 2^{3-1} design are also ones this design can be identified by the *defining relation* $I = X_1X_2X_3$. As there is only one subset of four runs out of the 70 possible ones for which the interaction $X_1X_2X_3$ has the value 1 for all four runs, this design is unique. In Figure 3.1 those points are marked with a dot and labeled from a to d.

The complementary 2^{3-1} design for which $X_1X_2X_3$ has the value of -1 for all four runs, has the defining relation $I = -X_1X_2X_3$. This clearly indicates that corresponding elements of the I and $X_1X_2X_3$ columns have the same magnitude but opposite sign.

Bacon [14] explains that several other operations in experimental design can be carried out by properly handling the *defining relation*. However, such operations do not apply to the present design.

Two other concepts are important in defining the way operating variables are handled in a fractional factorial design. It is said that two variables, say x_1 and x_2x_3 , are *confounded* when one is an *alias* of the other and vice versa. Since in the four tests changes in the variable x_1 coincide exactly with changes in the variable x_2x_3 the resulting effect of those changes on the response is the sum of the individual effects of x_1 and x_2x_3 . Due to this perfect correlation between these two variables their effects are impossible to separate. It is a fact in all fractional factorial designs

that every variable is confounded with one or more other variables. The important feature of the design is to be able to isolate the effect of relevant operating variables.

The concept of *resolution* indicates the degree of confounding amongst the different operating variables. In this design resolution is set as type III, thus the complete denomination of the fractional factorial design is 2_{III}^{3-1} . Resolution III designs are those for which,

- i) no individual operating variable, such as x_1 , is confounded with any other individual operating variable, such as x_3 , and
- ii) at least one individual operating variable is confounded with a two variable interaction.

Another feature of this design is the utilization of a *centre point*. This location is shown as point *e* in Figure 3.1. At the centre point the value of all operating variables is zero, i.e. $(x_1, x_2, x_3) = (0, 0, 0)$. The parameter β_0 is an estimate of $E(Y)$ at the centre point of the experimental design. For this reason the centre point is favored to obtain replicates of the tests, which in this case indicate the catalyst stability with time.

Model Building

The 2_{III}^{3-1} design here utilized belongs to a generic group of resolution III designs known as *saturated designs* [14]. With this design k operating variables can be investigated simultaneously in $k + 1$ tests. The model used here follows the general formula

$$E(Y) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 \quad (3.3)$$

Frequently in model-building work, the most important independent variable is not measured directly but it is calculated from other quantities. As is the case here yield may be computed by multiplying the recorded values of conversion and selectivity. Let us define y_1 as conversion and y_2 as selectivity, and Y as yield. Also we define the variables for temperature, space time and methanol to air ratio:

$$X_1 = \frac{T - 673}{25} \quad (3.4)$$

$$X_2 = \frac{W/F - 27.5}{11.25} \quad (3.5)$$

$$X_3 = \frac{\bar{R} - 6}{2} \quad (3.6)$$

Defining conversion and selectivity as products of a first-order model we have,

$$y_1 = b_0 + b_1X_1 + b_2X_2 + b_3X_3 \quad (3.7)$$

$$y_2 = c_0 + c_1X_1 + c_2X_2 + c_3X_3 \quad (3.8)$$

multiplying them we obtain a second order model for yield,

$$\begin{aligned} Y = & b_0c_0 + (c_0b_1 + b_0c_1)X_1 + (c_0b_2 + b_0c_2)X_2 + (c_0b_3 + b_0c_3)X_3 + \\ & b_1c_1X_1^2 + (b_2c_1 + b_1c_2)X_1X_2 + (c_1b_3 + b_1c_3)X_1X_3 + \\ & b_2c_2X_2^2 + (c_2b_3 + b_2c_3)X_2X_3 + b_3c_3X_3^2 \end{aligned} \quad (3.9)$$

after substituting the model is,

$$\begin{aligned} Y = & a_0 + a_1X_1 + a_2X_2 + a_3X_3 + \\ & a_{11}X_1^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + \\ & a_{22}X_2^2 + a_{23}X_2X_3 + a_{33}X_3^2 \end{aligned} \quad (3.10)$$

3.2 Kinetic Experiments

These experiments consisted of analyzing the 'best' Mo:Sb oxide catalyst found under different operating conditions (temperature, space time and methanol/air ratio). A full experimental scheme was carried out with this optimum catalyst. Finally a complete 2_{III}^3 factorial design was performed on that optimum catalyst composition but supported on Y zeolite.

3.2.1 Experimental Scheme for Kinetic Study

The operating conditions studied were: 623 to 698 K for temperature, 0.04 to 0.10 mol_{CH₃OH}h⁻¹/mol_{air}h⁻¹ for methanol/air feed and 5 to 50 g_{cat}/mol_{CH₃OH}h⁻¹ for space time. Experimental temperatures were 623, 648, 673 and 698 K. Experimental space times were 5, 16.25, 27.5, 38.75 and 50 g_{cat}/mol_{CH₃OH}h⁻¹. Experimental methanol/air feeds ($\bar{R}$) were 4, 6, 8, and 10. These values were chosen to match those used in the factorial design. It is to be noticed that they are well scattered throughout the whole range of operating conditions that are of interest from an industrial perspective. All these experiments may provide complete information on how one variable interacts with the other two.

For every space time there were four replicates, at $X_1 = 0$ and $X_3 = 0$, i.e. $T = 673$ K and $\bar{R} = 6$. This had the purpose of testing the decay of catalyst's activity.

Some other characteristics of the reaction system were studied and/or verified during this research. Internal diffusion in a porous catalyst of this size has generally little effect on the reaction results. Knudsen and molecular diffusion were verified and are reported in Section 6.3.1. The external diffusion, determined by the drop in partial pressure through the reactor, was obtained using the method developed by Yoshida and Hougen [172]. Temperature effects, both temperature drop from catalyst particle to ambient gas stream and axial temperature gradient in the reactor were calculated in Appendix F and in Section 6.3.1.

3.2.2 Experimental Design for Supported Catalyst

Using the same Sb:Mo oxide ratio found for the highest yield catalyst, a catalyst supported on Y zeolite was prepared as described in Section 5.1.1. A complete 2³_{III} factorial design was carried out with this catalyst. Table 3.3 shows the experimental design performed. By carrying out these experiments the comparison between the supported and the unsupported catalysts is rather qualitative than quantitative. However it will establish a well supported background if future studies with such catalyst are deemed worth continuing. As mentioned before no study has been made of the oxidation of methanol to formaldehyde over a zeolite supported bimetallic

Table 3.3: 2_{III}^3 Experimental Design for Sb:Mo Oxide Catalyst Supported on Y Zeolite

Code †	Test code	X_1	X_2	X_3	T (K)	W/F	R
<i>i</i>	02	-1	-1	-1	64S	16.25	4
<i>b</i>	03	1	-1	-1	69S	16.25	4
<i>a</i>	04	-1	-1	1	64S	16.25	S
<i>h</i>	05	1	-1	1	69S	16.25	S
<i>c</i>	07	-1	1	-1	64S	38.75	4
<i>f</i>	08	1	1	-1	69S	38.75	4
<i>g</i>	09	-1	1	1	64S	38.75	S
<i>d</i>	10	1	1	1	69S	38.75	S
<i>e</i>	01, 06, 11	0	0	0	673	27.5	6

†: Refer to Figure 3.1

oxide catalyst.

3.3 Selection of Rate Equation

The correlation of initial rate data to obtain a rate expression for the reaction is always of primary importance for the kinetic study. The relationship between conversion, flow rate and reaction rate in a steady flow system is given by the equation

$$Fdx = rdW \quad (3.11)$$

which on integration yields

$$\frac{W}{F} = \int_0^x \frac{dx}{r} \quad (3.12)$$

As explained earlier, this is the general rate equation of a catalytic reaction in a flow system based on unit mass of catalyst. In order to obtain a rate equation that can accurately predict the reaction behaviour, the mechanism that controls the latter one must be obtained. An easy way to screen out several mechanisms is to use the initial rate method.

3.3.1 Initial Rate Method

Yang and Hougen [16S], who studied several reactions, have shown that by considering the effect of pressure on initial rate ($x = 0$) it is possible to reduce the number of reaction mechanisms and finally to test some of them for their suitability in representing the data. This method briefly envisages the plotting of the experimental data (conversion versus W/F ratio), and determining the slope of the curve as W/F approaches zero. This rate of reaction at zero conversion is defined as the initial rate. The initial rate equations are obtained by neglecting the partial pressures of the product. In equations 2.7 and 2.20 and most cases of the three-stage redox mechanism the initial rate equations are the same as the rate equations.

3.3.2 General Methodology

Although the initial rates may be quite helpful in the selection of a mechanism, they are not sufficient evidence in themselves to establish the mechanism or to evaluate the constants in the rate equation. The rates at finite values of conversion must be used as well. There are several methods for using the data to establish the true equation. They are:

1. Convert the rate equation for each mechanism to the linear form, and solve for rate constants.
2. Plot $F(r)$ as a function of rate vs. P_A , and observe the shape of the curve.
3. Evaluate the constants by "trial and error" until an equation is obtained which fits the data.
4. Use an integrated form of the rate equation and solve for the constants by the use of simultaneous equations.
5. Use the equation in the integrated form $W/F = af_1(x) + bf_2(x) + \dots$ and solve for the constants directly from the experimental data, using the method of least squares. In this equation the terms $f_1(x)$, $f_2(x)$, $\dots$, are functions of x

(conversion) that can be evaluated separately by either numerical or graphical integration.

In summary, the reaction mechanism and the rate controlling step and thereby the rate equation are determined through the following steps.

- Step 1: Either an integral or a differential reactor can be used. The reactor must be operated *isothermally*.
- Step 2: Make a check to see whether diffusion is a rate controlling factor.
- Step 3: In case of integral data, plot the data as W/F vs. x . All the points on the curve must be at *isothermal conditions*.
- Step 4: List all the possible mechanisms and derive the corresponding equations (an example of these is found in the Chemical Engineers' Handbook [129]).
- Step 5: Determine the initial rates, r_o , from the experimental data.
- Step 6: Plot the initial rate or an initial rate function vs. pressure or reactants ratio as the case may be. Using the method of Yang and Hougen [168], eliminate some of the proposed mechanisms.
- Step 7: Plot a function of the type $[P_A - (P_R P_S)/K]/r = R'$ against the pressure Π or reactants ratio.
- Step 8: Derive an equation of the type $P_A - (P_R P_S)/K = a + bP_A + cP_R$ and evaluate the remaining constants.
- Step 9: With the constants evaluated, one can calculate the plot x vs. W/F . Compare the calculated plot with the original data. If there is more than one possibility remaining, select the one that fits the data best.
- Step 10: Repeat the procedure at several other temperatures. One usually selects the equation that fits the data at most temperatures.
- Step 11: When the equation has been evaluated at several temperatures, make plots of $\log k$, K_A , K_R , etc. against $1/T$.

Step 12: Determine an equation of the form $\log k = a/T + b$ for each constant, in order to obtain their temperature dependance with an Arrhenius-type equation.

3.4 Correlation of Conversion Data

The integrated form of the rate equations in Table 2.2 can be rearranged into a new form, as shown in Table 3.4, where $y = \beta_0 + \beta_1 x$ represents a typical straight line, y being the dependent variable, x the independent variable, β_0 the intercept and β_1 the slope. The values for y and x in columns six and seven of the table are calculated from the experimental data by substituting the values of W/F and the respective partial pressures. The values of β_0 and β_1 may be determined from the intercept and slope of the line in the y versus x plot, using the method of least squares. This method is illustrated in Appendix H.

3.5 Surface Chemistry Analyses

3.5.1 Electronic Spin Resonance

ESR is used to identify electron acceptors or donors in semiconductors. In the present case this property is useful to help screen the catalysts used for the production of formaldehyde from methanol. When a catalyst made from two different metal oxides is analyzed, it yields a signal with a given intensity. As the composition (wt%) of these oxides varies, so does the intensity of the signal. The intensity of the signal may be related to the activity of the catalyst. The larger the intensity of the signal the larger the area registered in the spectrum.

ESR spectra were taken for each catalyst from Table 3.1. To measure the relative intensities the areas of the spectra were obtained for each catalyst.

Table 3.4: Correlated y and x Relations for Two-Stage Redox Mechanism

No.	Reaction Order	β_0	β_1	y	x
	m CH_3OH	n O_2			
1	1	0.5	$\frac{1}{k_1}$ $\frac{1}{k_2}$	$-\frac{W}{F} \frac{\alpha P_M}{\ln(1-x)}$	$\frac{4\alpha}{\ln(1-x)} (\alpha P_{\text{O}_2} - 0.5x\alpha P_M)^{0.5}$
2	1	0	$\frac{1}{k_2}$ $\frac{1}{k_1}$	$\frac{W}{F\alpha x}$	$-\frac{\ln(1-x)}{\alpha P_M x \alpha}$
3	0.5	0	$\frac{1}{k_2}$ $\frac{1}{k_1}$	$\frac{W}{F\alpha x}$	$\frac{2(1-x)^{0.5}}{\alpha P_M^{0.5} x \alpha}$
4	1	1	$\frac{1}{k_1}$ $\frac{1}{k_2}$	$-\frac{W\alpha P_M}{F \ln(1-x)}$	$-\frac{2\alpha \ln(\alpha P_{\text{O}_2} - 0.5x\alpha P_M)}{\ln(1-x)}$
5	0.5	0.5	$\frac{1}{k_1}$ $\frac{1}{k_2}$	$\frac{W\alpha P_M^{0.5}}{2F(1-x)^{0.5}}$	$\frac{2\alpha(\alpha P_{\text{O}_2} - 0.5x\alpha P_M)^{0.5}}{\alpha P_M^{0.5}(1-x)^{0.5}}$
6	2	0.5	$\frac{1}{k_1}$ $\frac{1}{k_2}$	$\frac{W\alpha P_M^2(1-x)}{F}$	$-4\alpha\alpha P_M(1-x)(\alpha P_{\text{O}_2} - 0.5\alpha P_M x)^{0.5}$
7	2	1	$\frac{1}{k_1}$ $\frac{1}{k_2}$	$\frac{W\alpha P_M^2(1-x)}{F}$	$-2\alpha\alpha P_M(1-x) \ln(\alpha P_{\text{O}_2} - 0.5\alpha P_M x)$
8	2	0	$\frac{1}{k_2}$ $\frac{1}{k_1}$	$\frac{W}{F\alpha x}$	$\frac{1}{\alpha P_M^2 \alpha x(1-x)}$
9	1.5	0	$\frac{1}{k_2}$ $\frac{1}{k_1}$	$\frac{W}{F\alpha x}$	$\frac{1}{\alpha P_M^{1.5} \alpha x(1-x)^{1.5}}$
10	1.5	0.5	$\frac{1}{k_1}$ $\frac{1}{k_2}$	$\frac{W\alpha P_M^{1.5}(1-x)^{0.5}}{F}$	$-4\alpha\alpha P_M^{0.5}(1-x)^{0.5}(\alpha P_{\text{O}_2} - 0.5\alpha P_M x)^{0.5}$
11	1.5	1	$\frac{1}{k_1}$ $\frac{1}{k_2}$	$\frac{W\alpha P_M^{1.5}(1-x)^{0.5}}{F}$	$-2\alpha\alpha P_M^{0.5}(1-x)^{0.5} \ln(\alpha P_{\text{O}_2} - 0.5\alpha P_M x)$

This was done by cutting out the areas (from the paper they were drawn) and weighing them. A catalyst with larger intensity than the others would give a larger (thereby "heavier") area. The intensities were then adjusted to a proper scale and plotted for comparison.

It was deemed important to measure the number of spins in a given catalyst to see if it related to the activity of such catalyst and to its performance in the oxidation of methanol to formaldehyde. The number of paramagnetic spins indicates the number of Mo^{+5} ions in the crystallite. To calculate the number of spins per gram for the catalysts, spectra of these were run along with a standard for each case. The standard used in every spectrum was *coke pitch Bruker* sample that produces a signal equal to 10^{14} spins. The signals produced by the catalysts were compared with that of the standard, and the number of spins per area was obtained for the catalysts' samples. Then the spins per area were adjusted to the sample's weight to obtain the number of spins per gram. The g -values were obtained using equation 2.55.

3.5.2 X-Ray Diffraction

The geometrical condition for a crystal to diffract radiation coherently with scattering angle 2θ is given by the Bragg equation (equation 2.57)

$$\lambda = 2d \sin \theta$$

here d is better defined as the spacing of a set of planes in the crystal which are oriented such that their normal bisects the angle between the incident and diffracted beams.

The techniques used for making diffraction measurements should ensure that during the experiment certain sets of planes within the crystal will be properly oriented. There are three classes of technique which are used. The moving-crystal technique includes all methods in which a single crystal is made to diffract radiation by moving it into the appropriate orientation. The *Laue* technique utilizes polychromatic radiation and a stationary crystal: it relies

on there being sets of planes in the crystal which are appropriately oriented to diffract some of the wavelengths within the primary beam. The third technique and the one used in this investigation, the powder method, is that in which a polycrystalline rather than a single-crystal specimen is used; in this case a large number of crystal orientations is present in the specimen and the Bragg condition for diffraction of the monochromatic radiation by each set of the planes should be fulfilled by some of the crystallites.

For the powder method the sample must be ground to fine powder, about $57/47\text{ }\mu\text{m}$, and mounted in such a way that it can be bathed in a monochromatic x-ray beam. In the simplest method for obtaining powder photographs the sample is shaped into the form of a cylinder of the order of 0.5 mm in diameter. The sample is mounted at the centre of the camera and is usually rotated about its own axis. A narrow strip of film is pressed against the inside of a cylindrical holder, the axis of which coincides with the axis of the sample; it has a hole or holes punched in it to allow the entry and/or exit of the primary beam. The Straumanis, or asymmetric film mounting is the one used in this analysis.

The x-ray reflections may be seen to occur as 'lines' on the photographs. Each of these lines corresponds to the reflections from all the planes of one form. This occurs because the crystal is a fine powder and, if the orientation of grains within the powder may be supposed to be random, there will be some particles oriented so as to diffract at the Bragg angle for every possible set of planes in the crystal. Considering a set of planes with spacing d , the spacing of all the other planes of the same form will also be d and these planes will diffract radiation of wavelength λ at an angle θ such that

$$\sin \theta = \frac{\lambda}{2d}$$

Since all orientations of the crystallites should be equally likely, the rays diffracted by these planes will lie along the surface of a cone of half-angle 2θ whose axis is the incident beam. The 'lines' on the powder photographs are the intersections of this cone with the cylindrical strip of film.

With this method, for the cubic system [29]

$$\sin^2 \theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) \quad (3.13)$$

so that the values of $\sin^2 \theta$ are proportional to integers which are the sum of squares of three-integers. Alternatively, values of $\sin^2 \theta$ may be plotted on a strip of paper and matched against a set of straight lines representing the orientation of $\sin^2 \theta$ with $\lambda^2/4a^2$ for different sets of hkl .

The indexing of powder photographs of non-cubic materials is straight forward so long as the dimensions of the unit cell are known. If the cell is not known, there is no simple way of indexing the lines directly.

3.5.3 Scanning Electron Microscopy

The scanning electron microscope was operated by a technician at the Chemistry department. The unsupported Sb_2O_4 - MoO_3 (2:1) catalyst, the Sb_2O_4 - MoO_3 (2:1) catalyst supported on rare-earth exchanged Y zeolite, and the Y zeolite itself were the object of this study. Three different magnifications were used for each specimen: 20 μm , 4 μm and 1 μm . The results of this study are given in Section 6.5.

3.5.4 Adsorption

These studies were performed using the *AccuSorb 2100E* Physical Adsorption Analyzer. Expression 2.5S describes the great majority of low temperature adsorption data. Physical measurements of the volume of gas adsorbed as a function of pressure at a fixed temperature, therefore, permit calculation of V_m , the volume of gas required to form a layer one molecule thick. Equation 2.5S can be rearranged to the linear form

$$\frac{P}{V_a(P_s - P)} = \frac{1}{V_m C} + \left[\frac{C - 1}{V_m C} \right] \frac{P}{P_s} \quad (3.14)$$

then a plot of data for $\frac{P}{V_a(P_s - P)}$ versus $\frac{P}{P_s}$ gives a straight line, the intercept and slope of which are $\frac{1}{V_m C}$ and $\frac{C-1}{V_m C}$, respectively. From this information and knowledge of the physical dimensions of single adsorbed molecules, the surface area of the adsorbing solid is computed.

After obtaining all the adsorption and desorption data as per Section 2.S.4, by solving equation 2.61 in a stepwise fashion from experimental data one would obtain the pore size distribution and a surface area lower or equal to the total BET surface area.

A computer program was implemented to carry out these calculations in a more expedient way. For further detailed calculations refer to several treatises [4,16,30,133,151].

Chapter 4

Properties of Materials

This chapter deals with the various properties of the main reactant material -methanol- and the main product of the reaction carried out in this research -formaldehyde. Their physical and chemical properties are given. In the case of formaldehyde its importance is stressed as raw material in the production of other specialty chemicals. Health and safety factors are related with their use, handling and storage are addressed as well. It is important to notice that the intent of this chapter is only to show the importance of the applications of these materials, and not in any manner to discuss them in any depth.

4.1 Formaldehyde

At ordinary temperatures, pure formaldehyde is a colourless gas with a pungent, suffocating odor. It is produced and sold as water solutions that contain variable amounts of methanol or other alcohols. These solutions are complex equilibrium mixtures of methylene glycol, $(\text{CH}_2(\text{OH})_2)$, poly(oxymethylene glycols), and hemiformals of these glycols.

Table 4.1: Vapor Composition of Formaldehyde-Methanol Mixtures at 101.3 kPa, mol%

Wt% HCHO to wt% CH ₃ OH, liquid	HCHO	CH ₃ OH
30 : 7.5	17.0	12.8
30 : 15	16.3	23.0
37 : 7.5	20.3	18.7
37 : 15	11.9	21.9
50 : 7.5	26.7	25.8
50 : 15	11.4	21.7

4.1.1 Physical Properties

Density and refractive index show a nearly linear dependance on concentration. Based on available data [S6], the density may be expressed as follows:

$$\rho = [1.110 + 0.003(F - 45) - 0.0027M][1.0 + 0.00055(55 - t)]\text{g/cm}^3$$

where F and M are the formaldehyde and methanol concentrations (by weight), respectively, and t is in $^{\circ}\text{C}$. Based on information from the same source the refractive index may be expressed, for solutions containing 30–50% HCHO and 0–15% CH₃OH, as:

$$n_D^{18} = 1.3295 + 0.00125F + 0.000113M$$

For the same compositions and with a temperature range of 298–313 K, viscosity may be approximated by

$$\mu = (1.28 + 0.039F + 0.05M - 0.024t) \text{ mPa}\cdot\text{s}$$

Table 4.1 gives the vapor compositions of formaldehyde-methanol mixtures. In this kind of solution increasing the concentration of either methanol or formaldehyde reduces the volatility of the other.

Formaldehyde solutions generally exist as a mixture of oligomers, $\text{HO}(\text{CH}_2\text{O})_n\text{H}$. Using 6–50 wt% HCHO solution with low methanol, the distribution of these oligomers has been determined using NMR and chromatographic techniques. This is expressed as follows :



The values given for the equilibrium constants are $K_2 = 7.1$, $K_3 = 4.7$, and $K_4 = 3.4$. These values appear to be independent of temperature over the range 303–328 K. Decreasing the average value of n helps methanol stabilize aqueous formaldehyde solutions. Thus, at room temperature methanolic solutions can be stored without risking polymerization.

For solutions containing 7–55 wt% formaldehyde and 0–14 wt% methanol the following approximation was derived from data at 298–353 K:

$$\text{monomer}(\text{mol}\%) = 100 - 12.3\sqrt{F} + (1.44 - 0.0164F)M$$

where the monomer is the mole percent of formaldehyde present as formaldehyde hemiformal and methylene glycol, F is the wt% HCHO, and M is the wt% CH_3OH . Above 289–294 K most commercial formaldehyde-alcohol solutions remain stable.

4.1.2 Chemical Properties

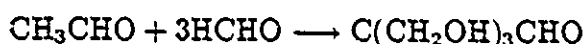
Formaldehyde is very reactive and versatile. The pure dry gas remains stable at temperatures above 353–373 K, below this range it starts to slowly polymerize. This action is greatly accelerated if there are traces of polar impurities. The polymerization reaction for liquid formaldehyde is an exothermic reaction (63 kJ/mol).

The decomposition of formaldehyde without a catalyst at temperatures below 573 K is a very slow process. The rate of decomposition increases with temperature. CO and H_2 are the main products of decomposition.

Formaldehyde reduces to methanol in a hydrogen atmosphere with several metal and metal oxide catalysts. It oxidizes to form either formic acid or CO_2 and H_2O . The Cannizzaro reaction gives methanol and formic acid.

In an aldol-type reaction formaldehyde condenses with itself yielding hydroxy compounds, such as hydroxy aldehydes and hydroxy ketones. This reaction occurs mostly under alkaline conditions.

Aldehydes containing α -hydrogen atoms undergo, in the presence of alkalis, aldol condensation with formaldehyde to form mono- and polymethylol derivatives. One such example is pentaerythritol:

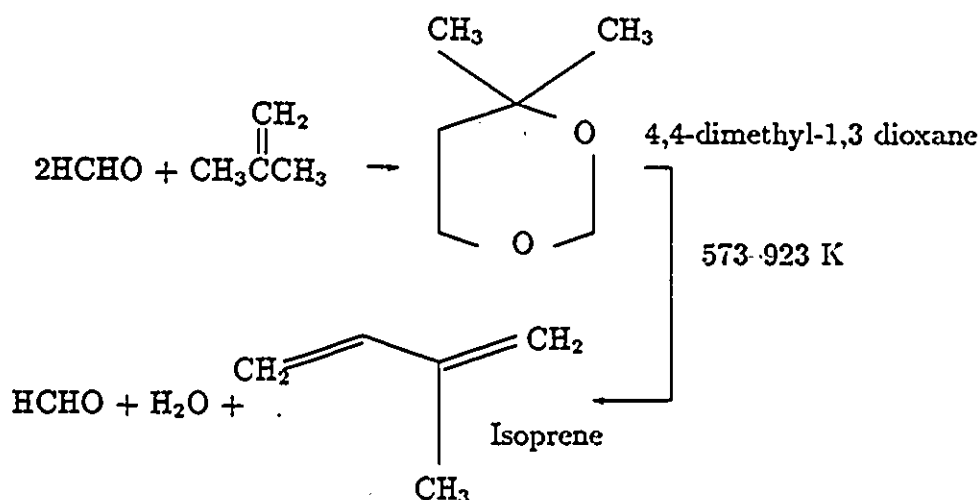


pentaerythritol

At 478 K, in the vapor phase, formaldehyde and acetaldehyde give acrolein:

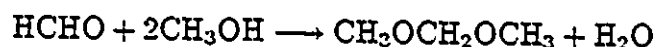


In aqueous acetic acid, formaldehyde and styrene give 1-phenyl-1, 3-propanediol diacetate, and with propylene one obtains 1,3-butanediol diacetate. Isoprene can be obtained from isobutene and formaldehyde:



From formaldehyde solutions and under strongly acidic conditions, hydrogen sulfide precipitates cyclic trithiane (trithioformaldehyde). Ketene reacts with anhydrous formaldehyde to give β -propiolactone. Hydrogen cyanide, in alkaline solution, yields glycolonitrile, HOCH_2CN .

Butadiene is obtained in the liquid-phase condensation of formaldehyde with propylene using BF_3 or H_2SO_4 as catalyst. Some formals like dimethoxymethane are produced from formaldehyde and alcohols with acidic catalysts in the liquid phase:



dimethoxymethane

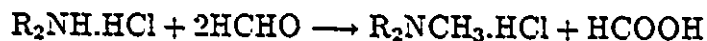
Compounds that have a hydrogen in the α position to an electron-withdrawing group, can be combined with formaldehyde in the vapor phase to form methylene derivatives.

Alkali and alkaline earths are effective catalysts for the production of acrylic and methacrylic acids or esters when acetic and propionic acids or esters, respectively, are reacted with formaldehyde at 573–698 K. Those same catalysts can be used to produce acrylonitrile from acetonitrile.

In the presence of formaldehyde and hydrogen chloride compounds containing active hydrogen atoms like phenolic esters or amide undergo chloromethylation.

With catalysts such as copper, mercury acetylide and silver monosubstituted acetylenes can add formaldehyde and produce acetylenic alcohols. Some amines also react with formaldehyde. Primary and secondary amines give alkyl-aminomethanols; whereas tertiary amines do not react. Those alkyl-aminomethanolic compounds, upon heating or under alkaline conditions yield substituted methylene-amines. These latter compounds can be treated with ammonia to produce hexamethylenetetramine (HMTA).

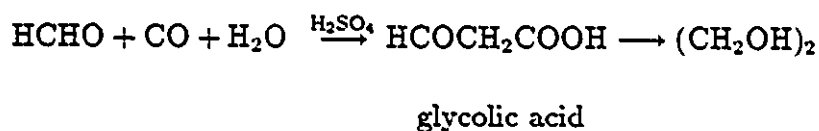
Under acid conditions amines and ammonium salts react to produce alkylamines:



Methylolureas undergo condensation to urea-formaldehyde resins under similar conditions.

Pyridine and 3-picoline can be produced when a mixture of formaldehyde, methanol, ammonia and acetaldehyde is passed over a silver-alumina catalysts at 773 K.

One very interesting reaction is that obtained by using formaldehyde and synthesis gas (CO, H₂O) as reactants for the synthesis of products such as ethylene glycol or glycolic acid



4.1.3 Specifications

Formaldehyde available commercially is sold in concentrations ranging from 30 to 56 wt%. Product specifications for typical grades are given in Table 4.2.

It is widely known that formaldehyde needs a stabilizer to facilitate its storage and handling [86]. Most of the time such stabilizer is methanol. Formaldehyde is sold as either low methanol (uninhibited) or as high methanol (inhibited) grades. Table 4.2 also indicates procedures for determining the quality of formaldehyde solutions as per ASTM methods. Specifications of commercial formaldehyde-alcohol solutions are given in Table 4.3. Nonetheless, for economical statistics all information on capacity, demand and prices is reported on a 37 wt% formaldehyde basis.

Despite the addition of stabilizing alcohols (methanol or *n*-butanol) or other stabilizing additives such as methyl cellulose or ethyl cellulose (up to 100 ppm

Table 4.2: Formaldehyde Specifications

	Methanol inhibited grades		Uninhibited, low methanol grades				ASTM Method
formaldehyde, wt%	37	44	37	44	50	56	D2194
methanol, wt% (max)†	5-8	6-7	1.8	2.0	2.0	2.0	D2380
acidity, wt% (max)‡	0.03	0.03	0.03	0.04	0.05	0.04	D2379
iron, ppm (max)	1	0.5	1	1	1	0.75	D2087
colour, APHA (max)	10	10	10	10	10	10	D1209

† For inhibited grades, range is the high and low specifications of producers surveyed

‡ As wt% formic acid

Table 4.3: Specifications of Commercial Formaldehyde-Alcohol Solutions

Assay	Methanol	n-Butanol	2-Methyl-1-propanol
alcohol, wt%	35	53	52
HCHO, wt%	55	40	40
H ₂ O, wt%	10	7	8
bp, K	375	380	377

Table 4.4: Health and Safety Factors for Formaldehyde Concentrations

Factor	Value
exposure time	
8-h time-weighted average, ppm	3
ceiling	5
max peak above ceiling, ppm for 30 min	10
minimum levels for sensory detection	
air borne, odor detectable at ppm	1
in water, odor detectable at mg/l	20-50
profuse lachrymation, ppm	20
eye irritation, ppm	0.05-0.5

of the additive), formaldehyde solutions are somewhat unstable. Concentrations of formic acid and paraformaldehyde increase with time and depend on temperature. Formic acid concentration increases at a rate of 1.5–3 ppm/day at 308 K. Storage at low temperature minimizes acidity but increases polymerization, the latter one being controlled by the addition of stabilizing agents.

4.1.4 Health and Safety Factors

Data regarding health and safety factors are given in Table 4.4. Although formaldehyde is suspected of being a carcinogenic agent, no definitive proof has been presented.

4.2 Methanol

Methanol is a clear, water-like liquid with a mild odor at ambient temperature. From its discovery in the 1600s, it has grown to become the 21st largest commodity chemical [86] with over 12×10^6 metric tons produced annually in the world. Methanol is also called wood alcohol because it was obtained commercially from the destructive distillation of wood during the

1800s. However, true wood alcohol contained some contaminants (acetone, acetic acid, allyl alcohol) that the chemical-grade methanol available today did not. From January to April 1990 Canada exported 323,972 metric tons valued at \$ 52,282,000, mainly to the U.S., Japan and South Korea [1]. It imported 953,796 kg valued at \$ 237,000 [2].

For many years the largest use for methanol has been as a feedstock in the production of formaldehyde, consuming almost half of all methanol produced. However, alternative uses such as the production of acetic acid and methyl-tert-butyl ether are increasing.

4.2.1 Physical Properties

The physical properties of methanol are given in Table 4.5 [86].

The vapour pressure of methanol, P_{Me} , from 288 to 337.5 K is given by the following equation

$$\ln P_{Me} = 15.76 - 2.846 \times 10^3 T^{-1} - 3.743 \times 10^5 T^{-2} + 2.189 \times 10^7 T^{-3}$$

Density and viscosity values are reported for aqueous methanol from 183 to 323 K [58,118,171]. Azeotropic data for several compounds with methanol are also available [71].

4.2.2 Chemical Properties

Methanol undergoes reactions that are typical of alcohols as a chemical class (e.g. see Vollhardt [163]). The reactions of particular interest from an industrial standpoint are dehydrogenation and oxidative dehydrogenation to formaldehyde (see Sections E.1 and E.2) usually over silver or molybdenum-iron oxide catalysts and carbonylation to acetic acid catalyzed by cobalt or rhodium. Dimethylether can be formed by the acid catalyzed elimination of water. Several other reactions of industrial importance use methanol as

Table 4.5: Physical Properties of Methanol

Property	Value
freezing point, K	175.47
boiling point, K	337.85
critical temperature, K	512.58
critical pressure, kPa	8096
critical volume, mL/mol	118
critical compressibility factor z in $PV=znRT$	0.224
heat of formation (liquid) at 298 K, kJ/mol	-239.03
free energy of formation (liquid) at 298 K, kJ/mol	-166.81
heat of fusion, J/g	103
heat of vaporization at boiling point, J/g	1129
heat of combustion at 298 K, J/g	22,662
flammable limits in air	
lower, vol%	6.0
upper, vol%	36.0
autoignition temperature, K	743
flash point, closed cup, K	289
surface tension, mN/m	22.6
specific heat	
of vapour at 298 K, J/(g·K)	1.37
of liquid at 298 K, J/(g·K)	2.533
vapour pressure at 298 K, kPa	16.96
solubility in water	total
density at 298 K, g/cm ³	0.78663
refractive index, n_D^{20}	1.3284
viscosity of liquid at 298 K, mPa·s	0.541
dielectric constant at 298 K	32.7
thermal conductivity at 298 K, W/(m·K)	0.202

their raw material. The acid catalyzed reaction of isobutylene and methanol to form methyl-tert-butyl ether, an important gasoline-octane improver, has become of great importance. Methyl esters of carboxylic acids can be prepared by acid-catalyzed reactions with azeotropic removal of water to force the reaction to completion. Methyl hydrogen sulfate, methyl nitrite, methyl nitrate, and methyl halides are formed by reaction with the appropriate inorganic acids. Mono-, di-, and trimethylamine result from the direct reaction of methanol with ammonia.

4.2.3 Specifications

Methanol is sold in two U.S. Federal Grades, A and AA. Requirements for each grade are shown in Table 4.6.

The tests to be used are ASTM methods:

- D-1087 distillation range
- D-1209 colour (platinum-cobalt scale)
- D-1296 odor
- D-1353 nonvolatile constituents
- D-1363 permanganate time
- D-1612 acetone
- D-1613 acidity, as acetic acid

4.2.4 Health and Safety Factors

Methanol may be stored and handled in clean carbon-steel equipment. Storage tanks must be constructed with an internal floating roof with an inert gas pad to minimize vapour emissions. Because of the flammability of the product, tanks are usually enclosed by a dike and protected by a foam-type fire-extinguishing system.

Table 4.6: Specifications of Pure Methanol

Property	Grade A	Grade AA
methanol content, wt%, min	99.85	99.85
acetone and aldehydes, ppm max.	30	30
acetone, ppm max.		20
ethanol, ppm max.		10
acid, ppm max.	30	30
water content, ppm max.	30	30
specific gravity, 20/20 °C	0.7928	0.7928
permanganate time, min	30	30
odor	characteristic	characteristic
distillation range at 101 kPa	1 K, must include 337.6 K	1 K, must include 337.6 K
colour, platinum-cobalt scale, max.	5	5
appearance	clear-colourless	clear-colourless
residual on evaporation, g/100 mL	0.001	0.001
carbonizable impurities; colour	30	30
platinum-cobalt scale, max.		

Table 4.7: Estimated Tolerance Values for Methanol

Duration	Concentration, ppm
single but not repeated exposure	
1 h	1000
8 h	500
24 h	200
5 × 8 h work/d	200
168 h	50
30 d	10
60 d	5
90 d	3

All shipping containers must be of carbon-steel and in a clean and dry condition prior to loading. Air pressure should never be used to load and unload methanol. Pumping is preferred but inert gas must be used when pressure loading or unloading is done. Each shipping container should bear the red label for flammable liquids and follow all W.H.M.I.S. safety standards accordingly.

The most generally known health hazard associated with methanol is blindness, usually as a result of ingestion. The ingestion of methanol has resulted in a wide range of responses, probably owing to the concurrent intake of varying amounts of ethanol. Ethanol is selectively metabolized by the body, allowing detoxification by respiration to occur to some extent. By mouth, 25–100 mL of methanol can cause death. The initial symptoms vary: weakness, fatigue, headache, dizziness, nausea, and abdominal pain are typical. A latent period of 6–30 h usually follows the initial symptomatic episode. The same responses occur only in much greater severity; in addition, loss of vision occurs. If death does not result from cardiac or respiratory arrest, permanent blindness may be a residual effect. So far it is not clear whether blindness results from inhalation. Table 4.7 gives estimated exposure limits for some time periods. Some more references on this respect can be found elsewhere [86,144]

Chapter 5

Experimental Aspects

Several different experimental devices were used in this investigation. The experimental part describes the equipment used and its operation, as well as the procedures for preparing the catalysts and analyzing various samples. An experimental apparatus similar to those used by Dosi [42,43], Jain [76], Hahn [83], and Rouleau [137] was built and used in the kinetic study. The other studies were performed using equipment available in the Chemistry, Physics, Geology, and Chemical Engineering departments.

5.1 Chemicals and Equipment

The calibrating gas mixture (9.76% CO₂, 9.89% CO, 80.35% N₂), the compressed helium (High-purity grade 99.995%) and the compressed air (21.04% O₂, 78.96% N₂) cylinders were purchased from Air Products (Brampton, Ont.). Traces of moisture in the air as well as in the gas products were removed by passing them through drying tubes packed with Molecular Sieve 13X from Chromatographic Specialties (Brockville, Ont.). All gas lines were made of either 0.3175 cm OD or 0.635 cm OD stainless steel tubing from AE Auto Clave of Canada Ltd. (Burlington, Ont.). All valves used were made of stainless steel and were acquired from Ottawa Valves & Fittings (Ottawa,

Ont.). Flow rates for each gas stream were measured by rotameters (body) model no. 622 PSV, with flowmeter tube size R-15-2-AA from Matheson of Canada Ltd (Whitby, Ont.).

An infusion Syringe Pump, model 901, from Harvard Apparatus Co. Inc. (Millis, MA) and 10 cm³ gas tight syringes model 1010-LT from Hamilton Co. (Reno, NV) were used to inject methanol in the feed stream. The stainless steel tubing carrying the air-methanol mixture to the reactor, and the products from the reactors to the sampling bottle was continuously heated externally by heating tapes from Canada Wide Scientific Ltd (Ottawa, Ont.). The thermocouples utilized to sense the temperature inside the reactor and the hot inlet chamber were of the J-iron-constantan type, and obtained from TC Wires & Cables (Middlesex, GB).

The temperature controllers used, from Honeywell, were effective for a temperature range of 273 to 1573 K. Variable Autotransformers of the type 3PN 1010 from STACO Inc. (Dayton, OH) were used to boost the reactor assembly heaters and the heating tapes. The two way direct Solenoid Valve was purchased from Ascoelectric Ltd (Brantford, Ont.). Both chromatographic columns 4.57 m $\times$ 0.3175 cm OD 15 wt% Sucrose-octa-acetate on Chromosorb T and 3.05 m $\times$ 0.3175 cm OD Hayesep T- were acquired from Chromatographic Specialties (Brockville, Ont.).

Most chemical products were bought from either BDH Ltd. (Toronto, Ont.) or Fisher Ltd. (Ottawa, Ont.) : Pumice stone, methanol ACS, formaldehyde solution (for calibration), antimony trichloride, ammonium molybdate, antimony pentoxide. Y zeolite rare earth exchanged, was obtained from Strem Chemicals Inc. (Newburyport, MA).

5.1.1 Preparation of Catalyst

Several catalysts were used during this research. Each catalyst, at the proper W/F ratio, was mixed with an inert medium (pumice stone 0.246 to 0.175

mm clear opening size) up to a volume of 7 cm³. This was the standard size for the catalyst bed in the reactor. The steps to prepare the catalysts are described below.

Pure molybdenum trioxide catalyst was obtained by the thermal decomposition of ammonium molybdate. Ammonium molybdate was heated at 423 K for 6 hours and for 2 hours each at 473 K, 573 K and 673 K. Finally, it was calcined at 773 K for 6 hours and activated at 873 K for 2 more hours. Antimony oxide catalyst was prepared by mixing antimony pentoxide with distilled water to form a paste which is slowly dried. It was then calcined at 473 K to 923 K at increments of 100 K every hour and held at 923 K for 18 hours. Antimony-Molybdenum oxide catalysts were prepared by dissolving a known amount of ammonium molybdate completely in water to which a weighed amount of antimony pentoxide was added. The resulting solution was slowly evaporated to dryness, calcined from 473 K to 923 K with 100 K increments every hour and held at 923 K for 18 hours. The catalysts thus formed were ground to a particle size of 0.246 to 0.175 mm.

A catalyst sample prepared to give a 1:1 ratio of MoO₃:Sb₂O₄ was analyzed to test the accuracy of the preparation procedure. 0.1 g of ground catalyst was mixed with 1.0 g of LiBO₄ (Spectrafux 100). This sample was fused at 1273 K for 20 min and the resulting bead dissolved in 100 mL of 0.1 N HNO₃. The solution was analyzed by DCP-AES (ARL nee Beckman Spectra Span V Direct Current Plasma Atomic Emission Spectrophotometer). The analysis gave 47.07 wt.% MoO₃ and 52.93 wt.% Sb₂O₄.

Antimony-Molybdenum oxide catalysts on zeolite support were prepared in a similar way. After dissolving weighed amounts of ammonium molybdate and antimony pentoxide in water, a known amount of type Y zeolite rare earth exchanged, was added to the slurry, and the preparation process continued as before. This type Y zeolite has been used in previous studies (see Díaz [41] and Sambi [139]).

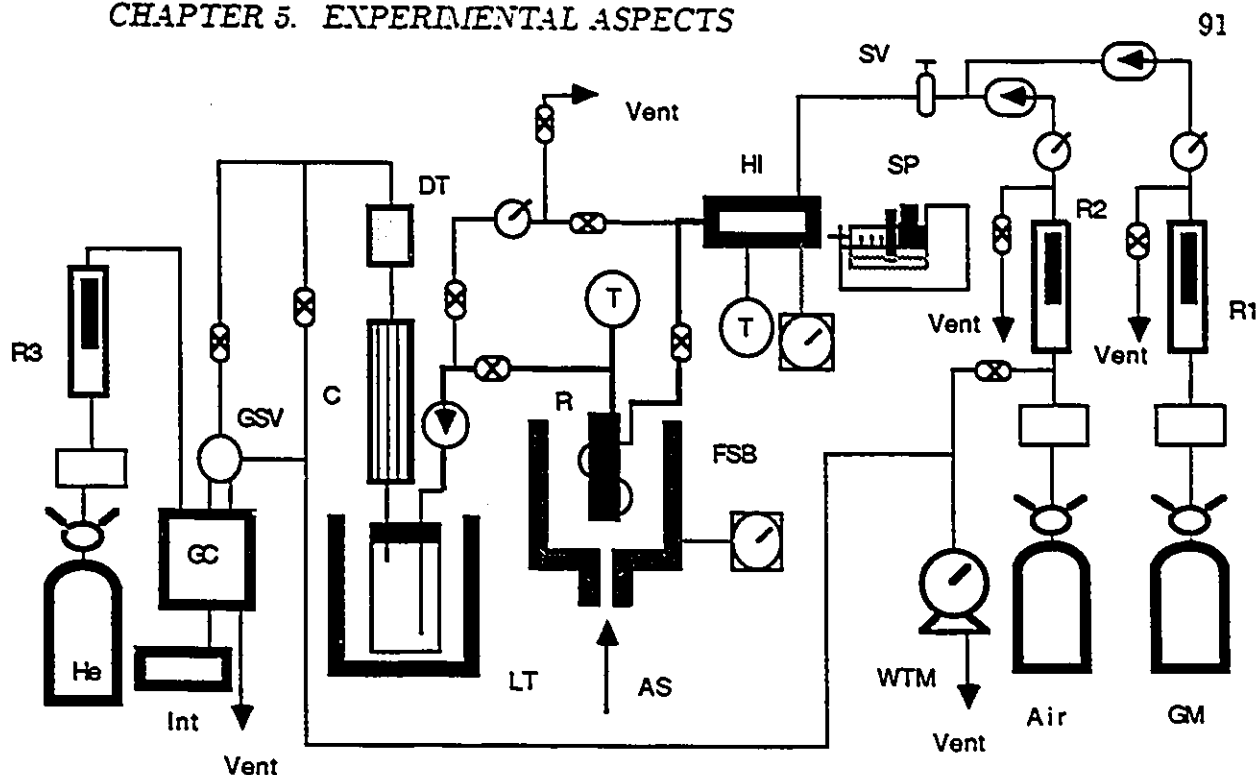
An *AccuSorb 2100E* Physical Adsorption Analyzer from Micromeritics Instruments Corp. of Georgia, U.S.A., was used to determine specific surface area using the Langmuir adsorption equation [4] or the BET method [30]. It was used to determine pore structure which includes pore size distribution, total pore volume and distribution, total pore area and distribution, and relative pore complexity [16,133].

5.2 Experimental Apparatus

A schematic diagram of the apparatus used is shown in Figure 5.1. A helium gas stream was supplied as carrier gas to the gas chromatograph. A second stream carrying a mixture of gases (CO_2 , CO , N_2) and a third stream carrying air were used to prepare gaseous mixtures for calibration. This air stream was also connected to the hot inlet chamber. Another air stream was used for fluidizing the sand bed in the reactor assembly. Dry air was passed at high velocity through a temperature controlled *hot inlet chamber* (temperature ~ 473 K). In this chamber methanol was infused into the feed streams by means of a syringe pump. Methanol was continuously vaporized and carried away in the air stream. The reactant stream coming out of the hot inlet chamber could either be sent directly to the liquid trap for calibration or to the preheater and reactor for an experimental run. Stainless steel tubing carrying the air and methanol mixture to the reactor was heated externally by heating tape. The feed stream going to the reactor was preheated in stainless steel tubing wound around the reactor. The reactor was 19.05 cm $\times$ 1 cm ID stainless steel tube. A schematic of the reactor assembly is shown in Figure 5.2. A porous stainless steel plate was fixed at the bottom of the reactor. At the top of the reactor an iron-constantan thermocouple was connected to a temperature controller. The reactor and preheater were kept immersed in a constant temperature fluidized bed furnace.

The container for the fluidized sand bed was a 9 cm OD steel cylinder. Sand

CHAPTER 5. EXPERIMENTAL ASPECTS



Key

Regulator
Bellow valve

Check valve

Purification

Thermocouple

Temperature Controller

Pressure gauge

AS Air Supply

C Condenser

DT Drying Tube

FSB Fluidized Sand Bed

GC Gas Chromatograph

GM Gas Mixture (N_2 , CO_2 , CO)

GSV Gas Sampling Valve

HI Hot Inlet

Int Integrator

LT Liquid Trap

R1,R2,R3 Rotameters

SP Syringe Pump

SV Solenoid Valve

WTM Wet Test Meter

Figure 5.1: Experimental Apparatus

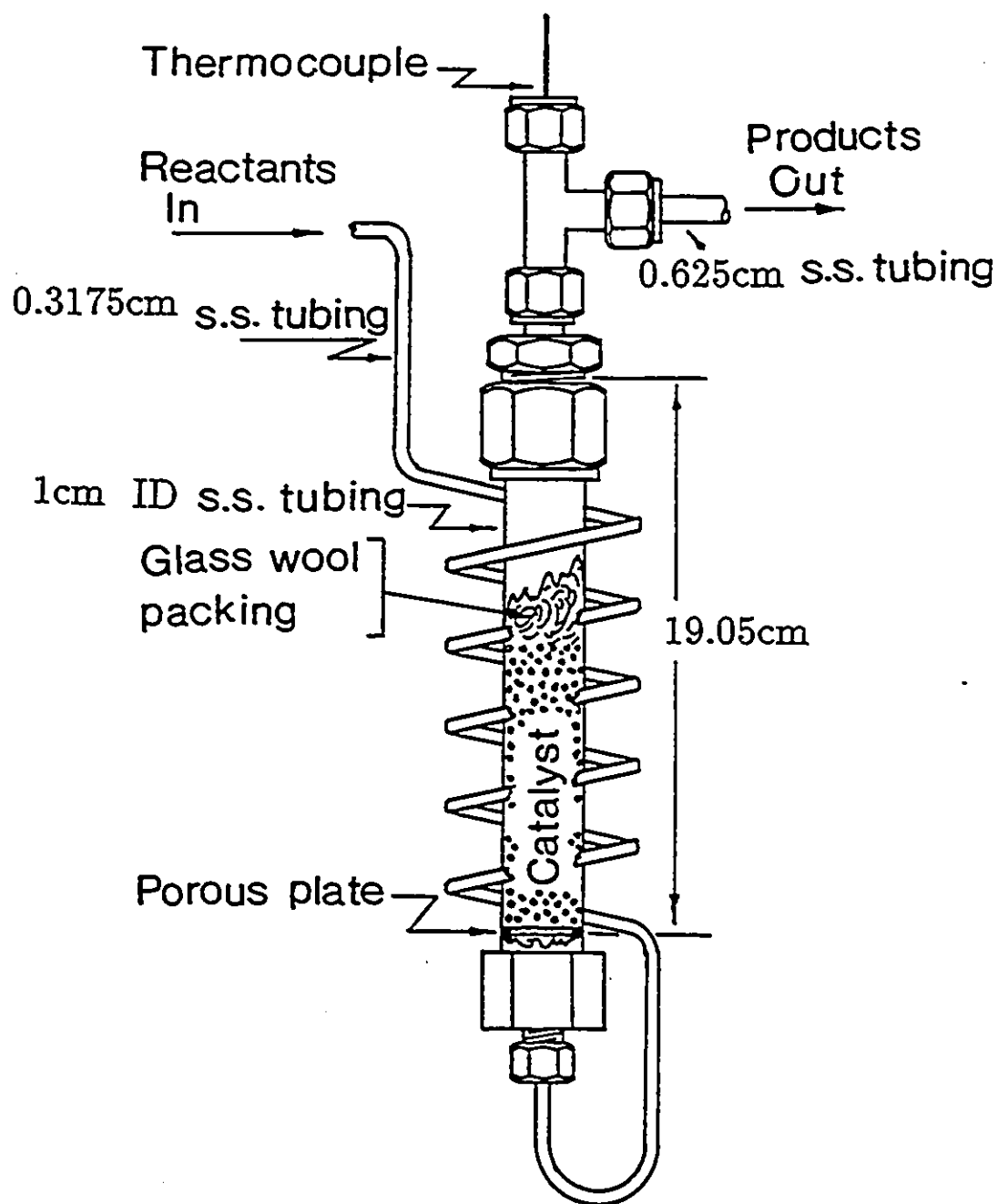


Figure 5.2: Reactor and Pre-heater

size was between 0.37 and 0.25 mm (40/60 mesh). A porous stainless steel plate was welded at the bottom. This cylinder was connected to the building air supply. By using a metering valve the air passing through the sand bed could be regulated. Sufficient air was passed at all times in order to keep the sand fluidized which would result in a uniform temperature around the reactor. Ceram-A-Flex beaded heating wires were wrapped around the cylinder and connected to one of the autotransformers and in series with a temperature controller. This would control the reactor heating system (with the thermocouple) as to provide an efficient way to keep the operation isothermal. The temperature in the sand bed was adjusted by changing either the input voltage in the autotransformer or more easily, by changing the temperature set in the temperature controller. The temperature inside the sand bed was checked several times at steady state with a digital thermometer, and it was always found to be within ± 3 K of the specified temperature.

Products coming out of the reactor were passed through stainless steel tubing which was heated externally. They were then passed through a liquid trap, from which samples were taken for further analyses. Within the liquid trap, connected on line, there was a sampling bottle where heavier products such as HCHO , CH_3OH , and H_2O were continuously condensed. This bottle was a 24 cm $\times$ 4.5 cm OD pyrex bottle with a 29/42 ground joint at the top where a two-hole rubber stopper was fitted. A properly isolated 4 L Dewar flask contained the ice that surrounded the sampling bottle. Gases and uncondensed vapors passed through a 0.635 cm OD stainless steel tubing placed in a 32 cm $\times$ 6.3 cm OD condenser cylinder. Fresh cold water passed through this cylinder to cool the gas products going through the tubing. Any products condensing in the inside tube dropped back into the liquid trap. Products coming out of the condenser were passed through a moisture trap, a 13 cm $\times$ 5.8 cm OD acrylic tube filled with molecular sieve 13X. All traces of moisture from the gas products were removed in the drying tube and in the condenser.

Gaseous products were then passed through an HP 5700 gas chromatograph using a sampling valve with a 0.5 cm³ sampling loop. A 304.8 cm $\times$ 0.3175

cm OD (10' $\times$ 0.125") Hayesep T stainless steel column was used to analyze the gas stream. This column was capable of separating N₂, CO, CO₂, O₂ and CH₄¹. Liquid samples were analyzed by injecting them through a 1 μ L syringe into the same gas chromatograph. A 457.2 cm $\times$ 0.3175 cm OD (15' $\times$ 0.125") stainless steel column containing 15 wt% Sucrose-octa-acetate coated on Chromosorb T was used to analyze the liquid products. The gas chromatograph was connected to an HP 7127A strip chart recorder and/or to an HP 3380A integrator according to the needs. A Precision Scientific wet test meter was used to monitor the gas flow.

5.2.1 Analysis Procedure

A 304.9 cm $\times$ 0.3175 cm OD Hayesep T stainless steel column was utilized to analyze the gas products containing CO, CO₂, N₂ and O₂. A HP gas chromatograph (model No. 5700A) attached to a HP integrator (model 3380A) performed the analysis of the exit gases. A 0.5 cm³ sampling loop was used to inject the gas sample into the column. The auxiliary temperature control as well as the injection port temperature control were shut off during the analysis. The detector was kept at 423 K with a DC current of 250 mA. The carrier gas flow (Helium) was maintained at 30 cm³/min. Attenuation was set at 512 for N₂, then increased to 16 for better peak resolution. The oven temperature programming was set for 273 K (4 min)-8 K/min-343 K (2 min). The 273 K temperature was attained by injecting liquid nitrogen through a solenoid valve attached to the temperature control. This on-line analysis was tested using mixtures of the calibration gas mixture and air, giving reliable results. A typical analysis of the gas mixtures is given in Figure 5.3.

A 457.2 cm $\times$ 0.3175 cm OD stainless steel column containing 15 wt% Sucrose-octa-acetate coated on Chromosorb T was used for analyzing liquid products.

¹An Orsat apparatus was kept as an alternative device in case of break down of the gas chromatograph due to the large amount of oxygen in the gas stream. The reliability of the Orsat apparatus was properly tested and verified. For utilization of the Orsat apparatus see reference [52]

The temperature for the injection port and the detector were 423 K and 473 K respectively. The oven temperature was kept isothermal at 373 K, as this is the maximum advisable operating temperature for this column. The sensitivity was set at 250 mA and the attenuation varied between 64 and 128 depending on the results. A liquid sample of 1 μ L was used for all analyses. A certified formaldehyde solution from Fisher Ltd. was used for obtaining the retention times for the different expected products (formaldehyde, methanol and water). Further to this, known amounts of other possible by-products such as ethyl-ether, methyl formate, dimethoxymethane, and formic acid were added to create some new standards and would have accounted for these products had they been formed during the reaction. A typical analysis of liquid products is shown in Figure 5.4.

5.2.2 Operating Procedure

The following operating procedure was followed in the collection of data:

- i) The system was checked for possible leaks. In order to do that an air pressure of about 207 kPa was maintained in the system. The connections were tested with 'snoop'. If after 30 min there was no indication of pressure drop the procedure continued, otherwise the leak was located and fixed.
- ii) Some glass wool was placed in the reactor on top of the porous plate. A weighed amount of catalyst was mixed with pumice stone to a volume of 7 cm³ and was placed in the reactor. The bed was covered with glass wool. The thermocouple assembly was placed on top of the reactor.
- iii) The reactor was placed upright in the fluidized bed and clamped. The top of the furnace was covered with asbestos sheets in order to prevent out-flow of sand. By using quick-connects the reactor is connected to the incoming reactants line and the outgoing products

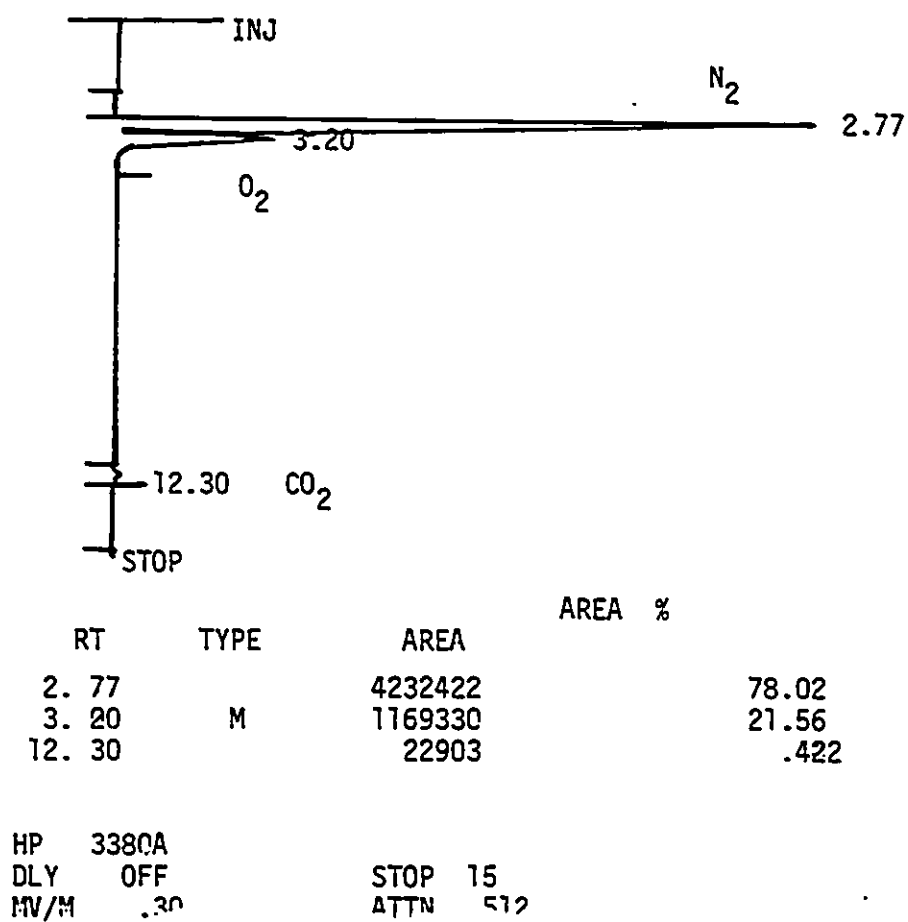


Figure 5.3: Typical Analysis of Gas Products

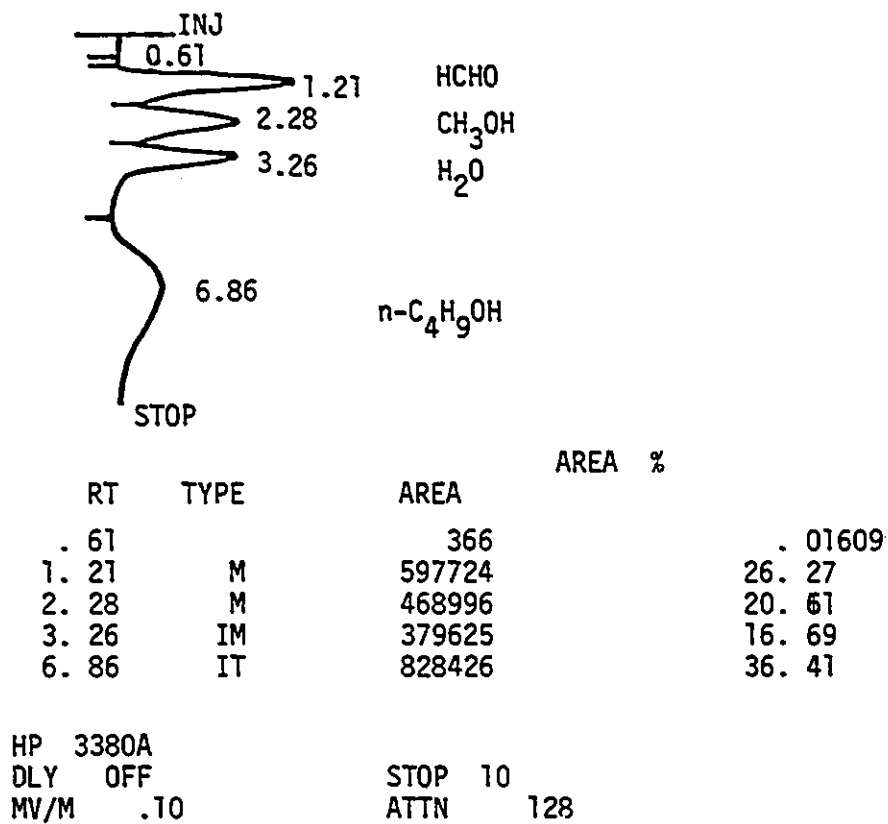


Figure 5.4: Typical Analysis of Liquid Products

line.

- iv) The liquid trap was placed in position and the Dewar flask was filled with ice. Next the water source for the condenser was turned on.
- v) The air feed was turned on and the system checked for possible leaks.
- vi) The power to the hot inlet chamber and heating tapes was switched on.
- vii) The infusion pump was switched on, which in turn started feeding methanol.
- viii) The power to the reactor heating system and autotransformer voltage were adjusted and air flow rate to the fluidized bed controlled so that the desired temperature was attained.
- ix) The gas chromatograph was turned on and the required operating conditions set. After start-up, the gas chromatograph stayed on till all analyses for that run were carried out.
- x) The integrator-recorder was turned on and its baseline checked.
- xi) The gas flow rate in the rotameters was adjusted to give constant molar flow as was required for the experiment. Air is always fed at a rate larger than that stoichiometrically required (i.e. in excess).
- xii) Methanol and air were fed to the system for about one hour. After this period of time steady state conditions are verified by analyzing gas products and checking reactor temperature and air flow rate.
- xiii) For sampling, the bottle in the Dewar flask was replaced with one that contained some *n*-butanol that served as a solvent as explained earlier in Section 4.1.3. Samples were collected for about one hour. During this time gas products were repeatedly analyzed.
- xiv) Liquid sample was removed from the sampling tube and poured into a small vial ready to be analyzed.

- xv) After all analyses were done, the infusion pump was shut off and the syringe removed. Air was allowed to flow through the system to cleanse for one to two hours.
- xvi) Next new operating conditions were set and the process restarted.
- xvii) If the reactor was going to be removed the system was left to cool down, letting air flowing through at all times.
- xviii) Columns were checked periodically (at the start of every analysis) to verify their proper performance.

5.3 Surface Characterization Studies

Techniques for characterization of solid surfaces, especially those related to spectroscopic analysis, have increased greatly in the past decade. These techniques have deepened our knowledge and understanding of surface phenomena. Those used in this investigation are now briefly described.

5.3.1 ESR

With Electron Spin Resonance (ESR), also called Electron Paramagnetic Resonance (EPR), one can identify modified crystal structures, free radicals which are naturally or artificially produced, conduction electrons in metals and acceptors or donors in semiconductors. One of the principal applications is in the investigation of oxidation and reduction processes and in surface catalysts studies. A *B-ER 414/418 s* spectrometer from Bruker-Physik AG was used to investigate the characteristics of the catalyst surface that would endow it with such high activity. This equipment is operated by a technician from the physics department. All catalysts' analyses were performed at room temperature. The operating conditions for the equipment were as follows: the microwave frequency was maintained at 9.59 GHz, the modulator/receiver frequency was 100 kHz, the field modulation intensity was 5 Gpp, the gain

was set at 3.2×10^5 in most cases but varied if some adjustment was needed, scan range was 6000 G with a mid range of 3500 G and a scan time of 500 s. Further information can also be found elsewhere [8,21,90].

5.3.2 SEM

There are a variety of problems in catalytic research, such as the relationship between activity and particle size, the morphological changes brought about by promoters, the formation of high-surface-area metal dispersions due to thermal decomposition of salts, sintering, fouling, and the dispersion of supported particle catalysts among others, which demand the use of high-resolution surface observations. Most of this valuable work has been done using the Scanning Electron Microscope (SEM). The equipment available is a *Bausch & Lomb Nanolab 7* SEM coupled with a *Keveex* energy disperser x-ray analyzer. Further details on the principles of SEM are given by Sageant and Embury [142] and Sanders [140].

5.3.3 XRD

X-Ray Diffraction (XRD) was developed during the first half of the century and was soon applied to identify solid phases involved with heterogeneous catalysts. Thanks to x-ray methods we can have a detailed picture of the dispersion of small metal particles on supports including particle size distribution. Measurements can be performed in the broadest range of temperatures and pressures used in catalytic reactions. In studying zeolites it is possible to determine the positions of the active sites even during the course of catalytic reactions. More detailed information is given by Gallezot [54]. The equipment used is a *Philips PW 1009* x-ray diffractometer that uses the *Debye Scherrer* photographic technique. The facilities for this analysis are at the Physics department.

5.4 Adsorption Studies

For this investigation only studies on physical adsorption are considered. For these studies the *AccuSorb 2100E* Physical Adsorption Analyzer is used.

Chapter 6

Results and Discussion

Experimental data were obtained by using an integral fixed bed reactor, which was operated at steady state isothermal conditions at nearly atmospheric pressure and between 623–723 K. The effects of several variables, namely $\text{Sb}_2\text{O}_4/\text{MoO}_3$ ratio, reaction temperature, partial pressure of methanol, and the reciprocal of the space velocity or space time (W/F), on the conversion, selectivity and yield of the oxidation of methanol to formaldehyde were studied. The feed rate was kept constant ¹ and the methanol concentration in the feed was changed by altering the flow rate of air. The reciprocal of space velocity (W/F) was varied by changing the weight of the catalyst charged in the reactor. The conversion of methanol ($\bar{C}$) and the yield of formaldehyde (Y) were computed as the moles of methanol reacted and moles of formaldehyde formed per mole of methanol fed. The selectivity of the catalyst (S) was defined as the ratio of the number of moles of formaldehyde formed to that of the total carbon containing products (formaldehyde, carbon dioxide and carbon monoxide, etc.) formed per unit time. The ratio of moles of methanol to moles of air in feed multiplied by one hundred was defined as $\bar{R}$.

¹except set T, which shows the effect of feed velocity on conversion

6.1 Preliminary Study

Preliminary experimental data were gathered (a) to verify the proper operation of the experimental apparatus, (b) to test the performance of the whole system by running it under similar operating conditions as previous researchers have with a known catalyst and, (c) to verify the effect of the inert medium used in the experiments.

After analyzing the results of these preliminary runs, one can conclude that the results were reproducible, thereby the system was reliable, and one can safely use pumice stone as inert medium knowing that its effect in the reaction studied is negligible.

6.1.1 Results with Molybdenum Trioxide

MoO_3 has been largely studied as an oxidation catalyst in the production of formaldehyde from methanol [7,42,79,128]. Under the most favorable conditions its selectivity is $\sim 100\%$. However, its conversion reaches a plateau at about 55% which makes this catalyst alone of very little use for a chemical industrial process.

To test the performance of the experimental apparatus a set of runs, termed set A, was carried out using MoO_3 as catalyst. For this set of runs the intent was to verify the proper behaviour of a known catalytic system, in this case by increasing temperature while keeping the remaining operating conditions constant.

For set A the temperature was varied from 623 to 723 K and samples were taken every 25 K (samples A01 to A05). Other operating conditions were set at the centre point of the fractional factorial design, i.e. methanol feed rate of 0.0206 mL/min, W/F of 27.5 and $\bar{R}$ of 6. Results for these runs are shown in Table 6.1 and in Figure 6.1. The reaction followed the expected behaviour. At lower temperatures, lower conversion and higher selectivity were measured.

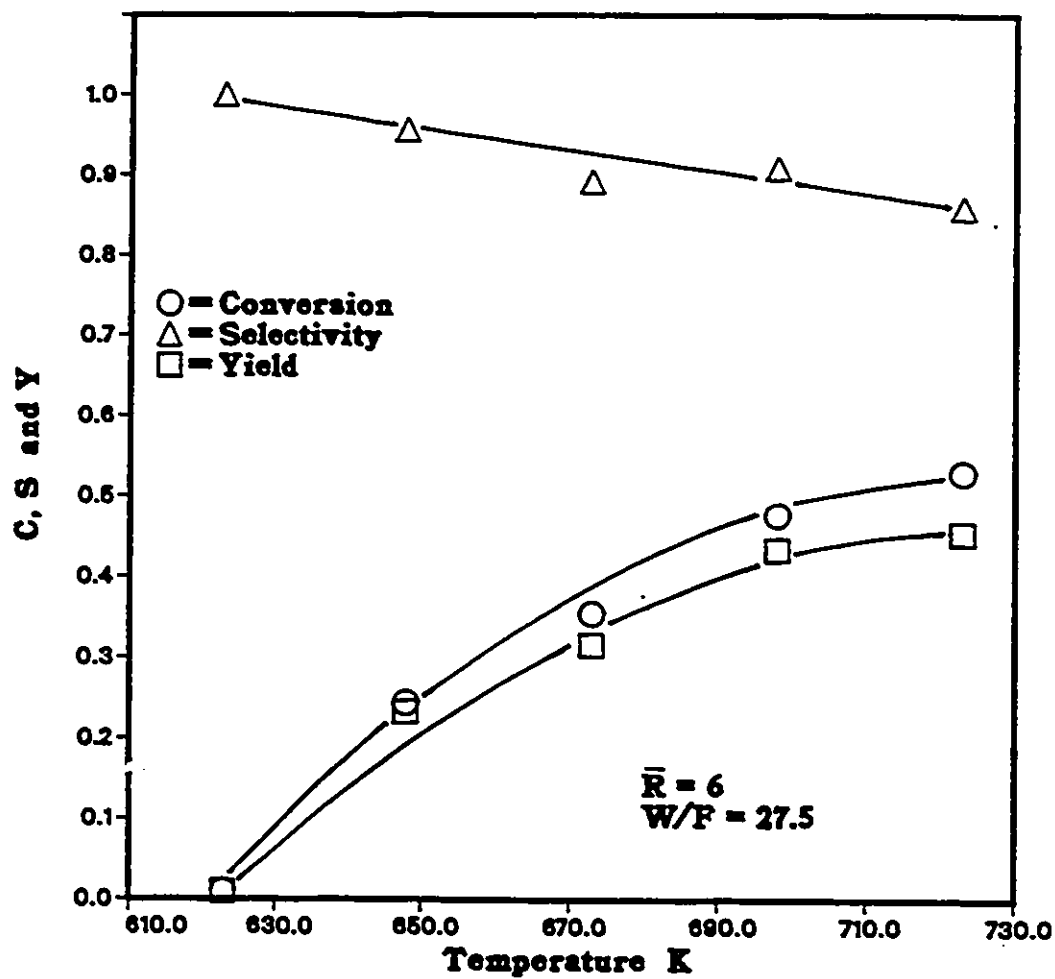


Figure 6.1: Effect of Temperature on Conversion, Selectivity and Yield with MoO_3 as Catalyst

Table 6.1: Effect of Temperature on Conversion, Selectivity and Yield with MoO_3 as Catalyst

Run	Temperature (K)	W/F	R	Conversion (%)	Selectivity (%)	Yield (%)
A01	623	27.5	6	0.5	100.0	0.5
A02	648	27.5	6	24.4	95.6	23.3
A03	673	27.5	6	35.5	89.2	31.6
A04	698	27.5	6	47.7	90.9	43.4
A05	723	27.5	6	52.8	85.9	45.4

As the temperature increased, conversion reached a maximum, but selectivity decreased due to oxidation of some methanol molecules to CO and CO_2 as observed in Figure 6.2. These results agree with data found in literature [7,78,79,128,170].

6.1.2 Results with Inert Medium

Pumice stone is used as an inert medium to standardize the reactor bed size to 7 cm^3 . The advantages of diluting the catalyst with an inert medium in a catalyst bed have been outlined by van Klinken and van Gougen [161]. Pumice stone is composed of amorphous fused silica (67–75 wt%), aluminum oxide (10–20 wt%), and silicates of potassium, sodium and calcium. Silica-aluminas are not completely inert supports, as a matter of fact they are classified by Fogar [50] as catalytically active supports. It is clear that their activity is far less than that of those supports that strongly interact with the active component of the catalyst, like TiO_2 or V_2O_5 , which are also catalysts. In order to verify how the inert medium affects the reaction, a set of experimental runs, termed set B, was carried out.

Set B keeps the operating conditions of the centre point, i.e. air flow of 0.509 mol/h and methanol feed rate of 0.0305 mol/h (0.0206 mL/min). Temperature was varied from 648 to 723 K at intervals of 25 K. Results for these runs

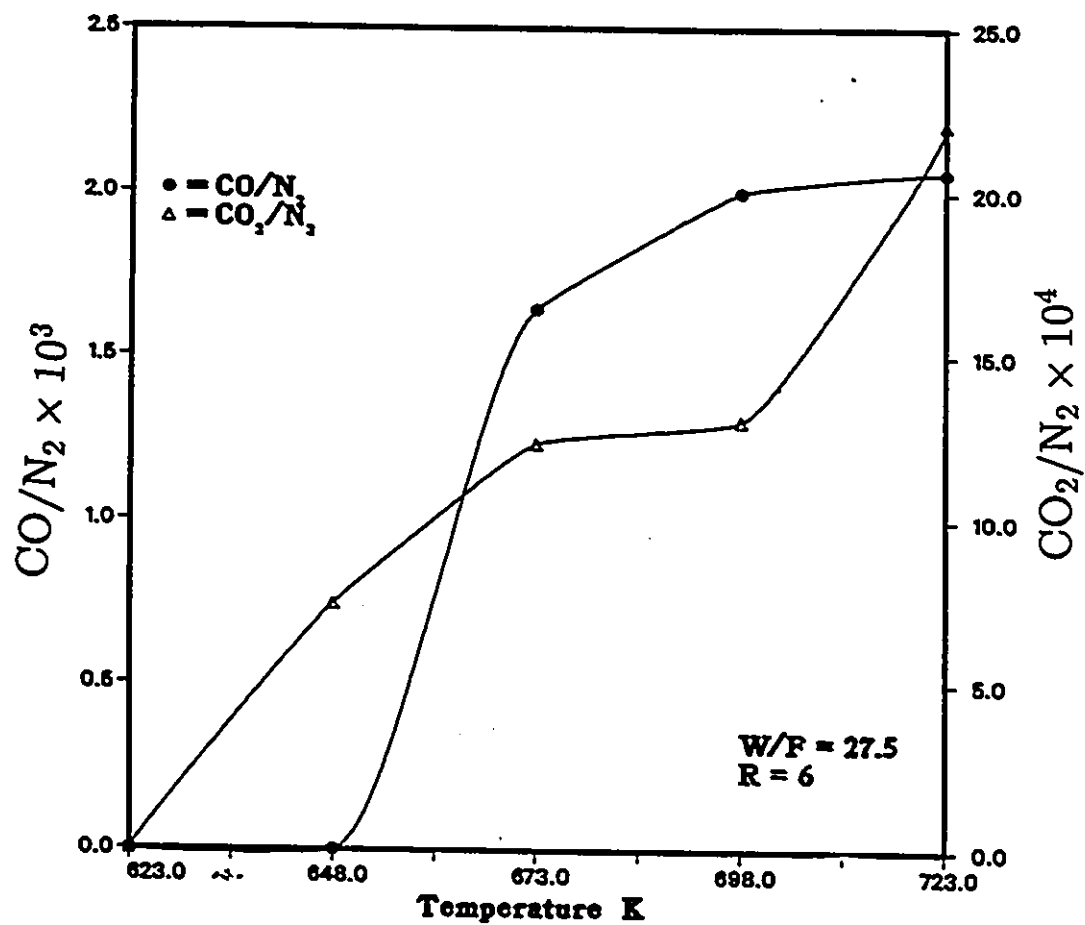
Figure 6.2: Formation of Carbon Oxides with Temperature with MoO_3

Table 6.2: Effect of Temperature on Inert Medium

Run	Temperature (K)	W/F	R	Conversion (%)	Selectivity (%)	Yield (%)
B01	648	27.5	6	0.9	17.4	0.2
B02	673	27.5	6	2.2	15.9	0.4
B03	698	27.5	6	3.5	21.1	0.7
B04	723	27.5	6	15.1	13.9	2.1

are shown in Table 6.2 and Figure 6.3. It can be seen that production of formaldehyde due to thermal or support effects is in fact negligible, less than 1.5% in all operating temperatures used in the kinetic study. Production of CO_2 increased with temperature as expected, but it still can be considered negligible. Some traces of CO were detected at higher temperatures but they are not considered significant either.

As these values for CO and CO_2 are low and produced only by reaction on the surface of the pumice stone, they were considered as 'threshold' values. For any practical purposes any value below these figures was dismissed as 'traces' and considered negligible.

6.1.3 Results with Antimony Oxide

Contrary to molybdenum trioxide, antimony oxide has not been extensively investigated and information in the literature about its use in oxidation of methanol is scarce. One of the few studies on this catalysts was made by Abadzhieva and Klissurski [6]. Some other studies on this catalyst have been carried out, e.g. Godin *et al.*[60], but aimed at different reaction systems.

To test the effect of antimony oxide on the conversion of methanol to formaldehyde, a set of runs similar to set A for molybdenum trioxide was carried out. This set is termed set D. Results for these runs are shown in Table 6.3 and Figure 6.4. From these it is obvious that the activity of Sb_2O_4 is almost an

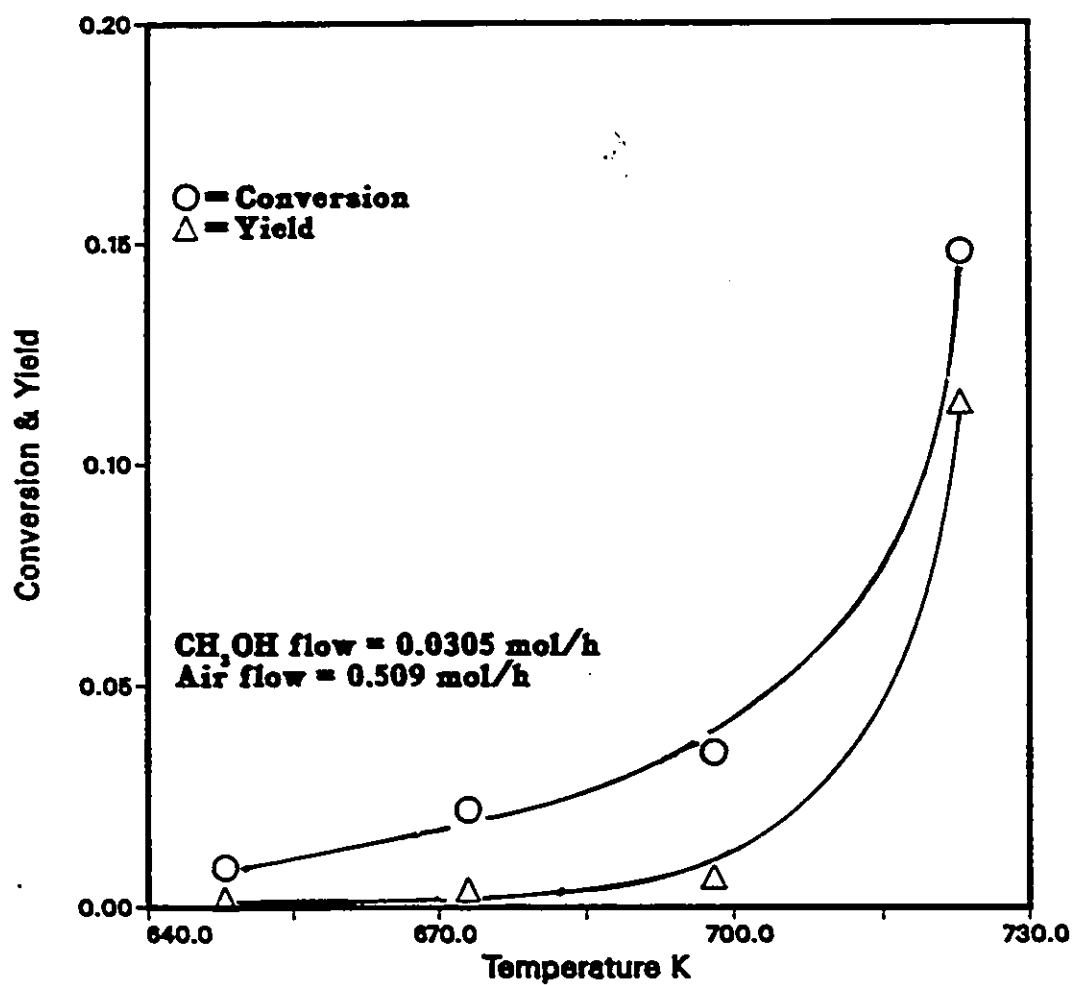


Figure 6.3: Effect of Temperature on the Conversion of Methanol on Pumice Stone

Table 6.3: Effect of Temperature on Conversion, Selectivity and Yield with Sb_2O_3 as Catalyst

Run	Temperature (K)	W/F	R	Conversion (%)	Selectivity (%)	Yield (%)
D01	623	27.5	6	2.9	3.8	0.1
D02	648	27.5	6	4.5	15.8	0.7
D03	673	27.5	6	5.1	20.0	1.0
D04	698	27.5	6	12.6	65.6	8.3
D05	723	27.5	6	30.6	71.7	22.2

order of magnitude lower than that of MoO_3 [6]. And although its selectivity seems low at lower temperatures, it is masked by the amount of carbon oxides produced by the pumice stone. A large change in conversion, selectivity and yield is observed from 673 to 723 K.

6.2 Screening Study

The results obtained from the screening study show the effectiveness of the experimental design in helping sort out the sought catalyst composition.

6.2.1 Model Building with MoO_3

The third set of runs, set C, was designed using a fractional factorial design and also with modifications suggested by Hunt and Jaworsky [72] and McLean [114]. For this design it was considered that yield is some times computed by multiplying the recorded values of conversion and selectivity. A 2^{3-1}_{III} fractional factorial design is defined for the experimental runs. That means four runs at different operating conditions and at least two centre point runs. A *defining relation* is given by $I = X_1X_2X_3$ as explained in Section 3.1.1. Such design is better illustrated in Table 3.2.

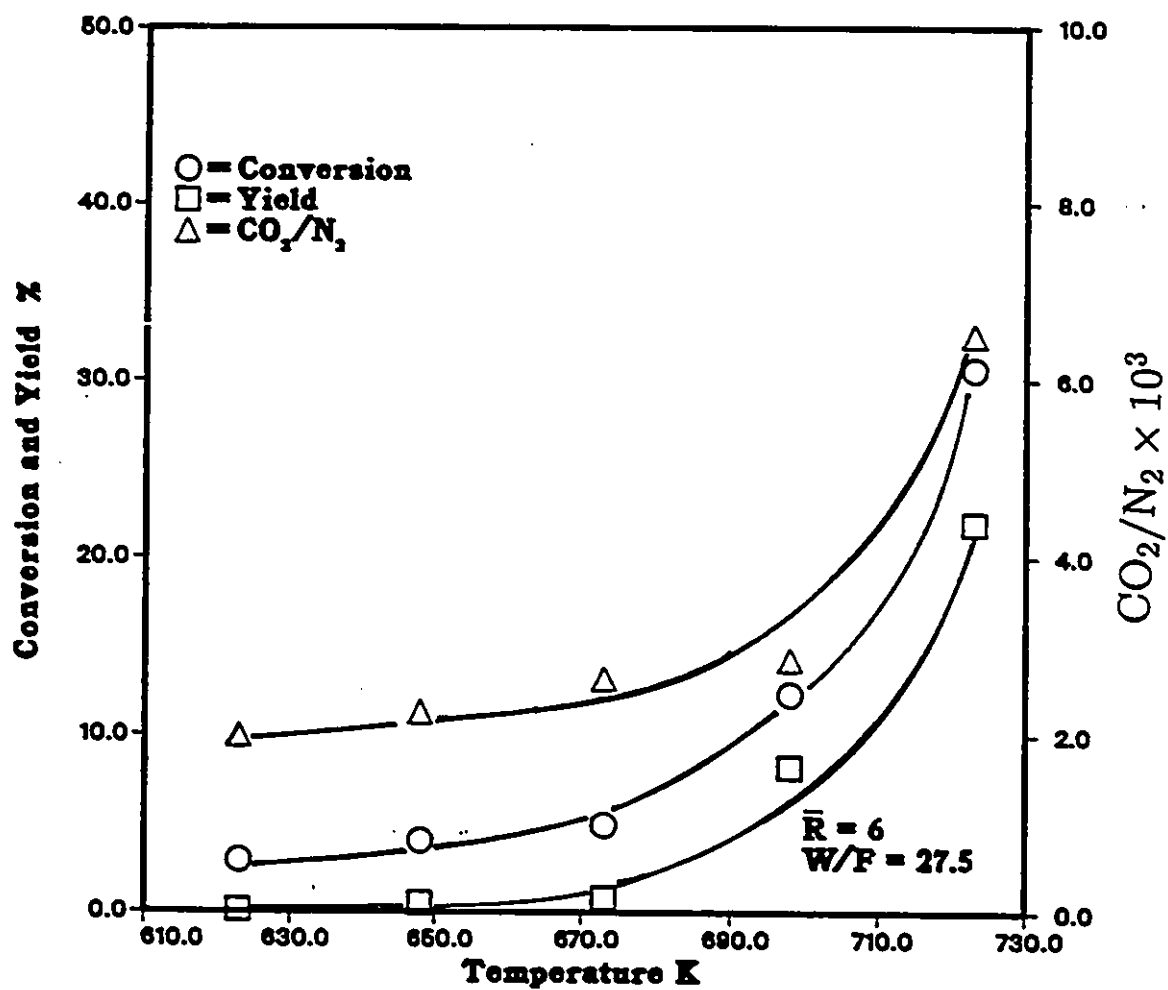


Figure 6.4: Effect of Temperature on the Conversion of Methanol on Antimony Oxide

Table 6.4: Fractional Factorial Design Runs with MoO_3

Run	Temperature (K)	W/F	R	Conversion (%)	Selectivity (%)	Yield (%)
C01	673	27.5	6	45.5	93.3	42.5
C02	648	16.25	8	30.1	91.9	27.6
C03	698	16.25	4	44.0	95.1	41.8
C04	648	38.75	4	58.9	72.5	42.7
C05	698	38.75	8	53.0	97.6	51.7
C06	673	27.5	6	30.7	95.5	29.3

Table 6.5: Runs at Centre Point with MoO_3

Run	Temperature (K)	W/F	R	Conversion (%)	Selectivity (%)	Yield (%)
A03	673	27.5	6	35.5	89.2	31.6
C01	673	27.5	6	45.5	93.3	42.5
C06	673	27.5	6	30.7	95.5	29.3

Results for these fractional factorial design runs are given in Table 6.4. Results for the runs at the centre point are summarized in Table 6.5.

As can be seen run C01 gave significantly higher conversion than the other two runs at the same conditions. This is explained by Adkins and Peterson [7] and by Hahn [83] on the basis that a catalyst that has been less than twelve hours on stream is more active, and this gives higher conversion. Between twelve and twenty four hours are required for MoO_3 to attain a steady state conversion. All runs in set C, except C06, were carried out when the catalysts had higher activity.

As mentioned above in Section 3.1.1 yield can be expressed as the product of conversion and selectivity. Let us recall the definitions on Section 3.1.1: y_1 as conversion, y_2 as selectivity, and Y as yield. Also we recall the variables for

temperature, space time and methanol to air ratio:

$$X_1 = \frac{T - 673}{25} \quad (6.1)$$

$$X_2 = \frac{W/F - 27.5}{11.25} \quad (6.2)$$

$$X_3 = \frac{\bar{R} - 6}{2} \quad (6.3)$$

Taking data from Table 6.4 our models result are as follows:

$$y_1 = 0.465 + 0.02X_1 + 0.0945X_2 - 0.0495X_3 \quad (6.4)$$

$$y_2 = 0.89275 + 0.07075X_1 - 0.04225X_2 + 0.05475X_3 \quad (6.5)$$

$$\begin{aligned} Y_{\text{MeO}_3} = & 0.4151 + 0.0508X_1 + 0.0647X_2 - 0.0187X_3 \\ & + 0.001415X_1^2 + 0.005841X_1X_2 - 0.002401X_1X_3 \\ & - 0.003993X_2^2 + 0.007265X_2X_3 - 0.00271X_3^2 \end{aligned} \quad (6.6)$$

This preliminary result seems to indicate what is generally common in this kind of reactions, using an oxide metal catalyst: higher temperatures, larger catalyst to feed flow rate ratio and lower alcohol to oxygen ratio give higher yields.

6.2.2 Model Building with Sb_2O_4

Set E was carried out using the same experimental scheme as set C. By defining yield, conversion and selectivity as before, as well as the normalized variables X_1 , X_2 , and X_3 we could obtain our statistical model. Results from these runs are shown in Table 6.6. From there our model results as follows:

$$y_1 = 0.162 + 0.078X_1 - 0.068X_2 - 0.055X_3 \quad (6.7)$$

$$y_2 = 0.38625 + 0.31225X_1 - 0.00425X_2 - 0.00425X_3 \quad (6.8)$$

Table 6.6: Fractional Factorial Design Runs with Sb_2O_4

Run	Temperature (K)	W/F	R	Conversion (%)	Selectivity (%)	Yield (%)
E01	673	27.5	6	51.3	87.7	45.0
E02	648	16.25	8	9.7	7.4	0.7
E03	698	16.25	4	36.3	70.7	25.6
E04	648	38.75	4	7.1	7.4	0.5
E05	698	38.75	8	11.7	68.9	8.0
E06	673	27.5	6	52.3	77.9	40.8

$$\begin{aligned}
Y_{\text{Sb}_2\text{O}_4} = & 0.0626 + 0.0807X_1 - 0.027X_2 - 0.0219X_3 \\
& + 0.0244X_1^2 - 0.0216X_1X_2 - 0.0175X_1X_3 \\
& + 0.0003X_2^2 + 0.0005X_2X_3 + 0.0002X_3^2 \quad (6.9)
\end{aligned}$$

These results indicate almost similar behaviour as the MoO_3 catalyst. An exception can be noticed in the effect of the space time (W/F). However, the effect of the catalyst to methanol flow rate may be camouflaged due to the low conversion and the highly dominant effect of temperature on conversion.

The results obtained with Sb_2O_4 did not agree completely with those given in the literature [6,60,165], probably because those results in the literature were obtained by carrying out the experiments with pure Sb_2O_4 . Here the effect of the dilution with pumice stone may account for such differences, as the effect of the inert medium on the final product is not negligible when conversions are very low and the catalyst used has low activity.

6.2.3 Results with Mo-Sb Oxide Mixtures

As shown in Table 3.1 five new catalysts were made mixing different amounts of ammonium molybdate and antimony pentoxide in order to give the desired composition ratio. The objective was to find an optimum composition, one that gave the highest yield. This high-yield catalyst would be characterized

Table 6.7: Catalysts' Composition

Catalyst	Tag (set #)	Sb ₂ O ₄ (wt%)	MoO ₃ (wt%)	Colour
I	B	0.0	100.0	cream-blue
II	E	100.0	0.0	light yellow
III	J	83.33	16.66	green-yellow
IV	H	66.66	33.33	yellow-green
V	F	50.0	50.0	yellow-cream
VI	G	33.33	66.66	cream-yellow
VII	I	16.66	83.33	cream

later in a kinetic study, as well as analyzed with several spectroscopic techniques. These analyses would help explain the extremely high yields obtained in such a catalyst by linking them with the high activity on the catalyst surface.

Table 6.7 shows the catalysts used, their compositions and their tag for proper identification.

It is to be noticed that there is a change in the colour with a change in the composition of the catalyst. As the amount of MoO₃ increased the catalyst's colour became lighter.

The results of the fractional factorial design model building scheme are shown in Tables 6.8 to 6.10.

Even at first glance one notices the higher efficiency of the oxide mixtures compared with the single oxides. This is noted in the high values of parameter a_0 which is an estimate of $E(Y)$ at the centre point of the experimental design. The results obtained with catalyst IV (Sb₂O₄ – MoO₃ (2:1)) were the most interesting and striking ones. In all fractional factorial design runs its selectivity was 100%. This may not be true for all operating conditions; as proven later in the kinetic study; but indicates that this catalyst may give the best results we were looking for.

Table 6.8: Statistical Models for Conversion

Catalyst	b_0	b_1X_1	b_2X_2	b_3X_3
I	0.465	0.02	0.0945	-0.0495
II	0.162	0.078	-0.068	-0.055
III	0.7092	0.0657	0.0792	-0.0512
IV	0.7072	0.1377	0.1247	0.0302
V	0.6287	0.0492	0.1202	-0.0382
VI	0.533	0.077	0.154	-0.076
VII	0.7082	0.1622	-0.0017	0.0882

Table 6.9: Statistical Models for Selectivity

Catalyst	c_0	c_1X_1	c_2X_2	c_3X_3
I	0.8927	0.0707	-0.0422	0.0547
II	0.3862	0.3122	-0.0042	-0.0042
III	0.6567	-0.0652	-0.3432	-0.0652
IV	1.0	0.0	0.0	0.0
V	0.6767	-0.0447	-0.2772	-0.0597
VI	0.7407	-0.0342	-0.2592	-0.0342
VII	0.7055	0.0045	0.2945	-0.0045

Table 6.10: Statistical Models for Yield

Catalyst	a_0	a_1X_1	a_2X_2	a_3X_3	$a_{11}X_1^2$
I	0.4151	0.0508	0.0647	-0.0187	0.0014
II	0.0626	0.0807	-0.027	-0.0219	0.0244
III	0.4658	-0.0031	-0.1941	-0.0799	-0.0043
IV	0.7072	0.1377	0.1247	0.0303	0.0
V	0.4255	0.0052	-0.0929	-0.0635	-0.0022
VI	0.3948	0.0388	-0.0241	-0.0746	-0.0026
VII	0.4997	0.1177	0.2073	0.0591	0.0007
	$a_{12}X_1X_2$	$a_{13}X_1X_3$	$a_{22}X_2^2$	$a_{23}X_2X_3$	$a_{33}X_3^2$
I	0.0058	-0.0024	-0.004	0.0073	-0.0027
II	-0.0216	-0.0175	0.0003	0.0005	0.0002
III	-0.0277	-0.0009	-0.0272	0.0124	0.0033
IV	0.0	0.0	0.0	0.0	0.0
V	-0.019	-0.0012	-0.0333	0.0034	0.0023
VI	-0.0252	0.0	-0.0399	0.0144	0.0026
VII	0.0478	-0.0003	-0.0005	0.026	-0.0004

Furthermore, the resulting model is a lot simpler as from a potential second-order model, it reduces to a first-order model where interactions are technically non-existent. As well it indicates that increments in the three operating conditions, temperature, space time, and methanol-air flow rate would likely increase yield.

As the number of replicate data at the centre point is not large enough, any calculation on their adequacy might not be considered statistically valid. Nonetheless, the values obtained were close to one another, and were used to draw Figure 6.5. This figure shows the effect of MoO_3 content in the catalyst on conversion ($\circ$) and selectivity (Δ) at the centre point operating conditions. Pure Sb_2O_4 (0% MoO_3) and MoO_3 (0% Sb_2O_4) were moderately active and could convert a maximum of about 33% methanol. As the MoO_3 was increased to about 33 wt% of catalyst content, conversion and selectivity of formaldehyde increased. With further increase in the amount of MoO_3 , conversion dropped. However the selectivity stayed fairly constant at about 100%.

Coupling the results obtained at the centre point operating conditions with those obtained from the fractional factorial design and model building scheme a composition of 33 wt% MoO_3 and 67 wt% Sb_2O_4 was chosen to be an optimum composition of the catalyst which was used for further detailed kinetic study of the reaction. ESR studies of these oxide catalysts seem to confirm our choice, and may explain the high performance of the catalyst chosen.

As the goal of this screening study, to sort out the 'best' catalyst for the oxidation of methanol to formaldehyde, was accomplished, detailed analysis of the models was not considered relevant to the scope of this research.

A 0.246 to 0.175 mm particle size catalyst with a $\text{Sb}_2\text{O}_4/\text{MoO}_3$ ratio of 2:1, had a surface area of 6.1 m^2/g and a bulk density of 1.678 g/cm^3 . The colour of the catalyst before being used for methanol oxidation was yellow-green and turned black after use.

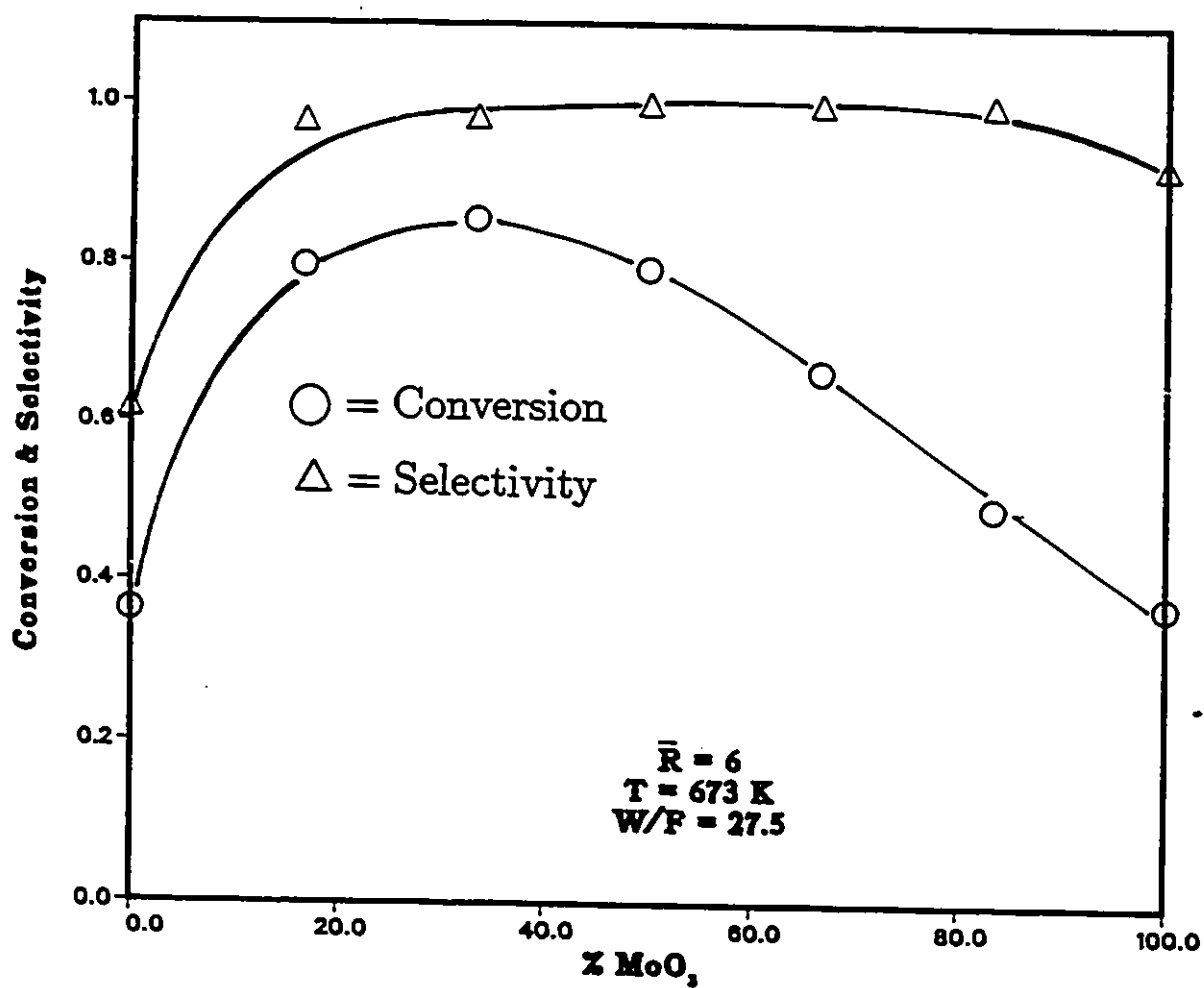


Figure 6.5: Effect of Catalyst Composition on Conversion

Table 6.11: ESR Catalysts' Activity

Catalyst	MoO ₃ (wt%)	Sb ₂ O ₄ (wt%)	Relative Intensity	Spins/g $\times 10^{16}$	<i>g</i>
I	100	0	0.82	$< 10^{-3}$	1.93CS
II	0	100	-	0	-
III	16.66	83.33	20.14	4.47	1.9227
IV	33.33	66.66	26.02	4.98	1.9205
V	50.0	50.0	19.16	4.23	1.9259
VI	66.66	33.33	14.17	2.90	1.9259
VII	83.33	16.66	6.25	1.52	1.9317

6.2.4 ESR Spectra

Several spectra were taken at ambient temperature of the different metal oxide mixtures. These spectra compare the level of activity of each catalyst as per the changes of electronic state in the compound.

Figure 6.6 shows the ESR signal intensity versus composition of MoO₃ in the Sb-Mo oxide mixture. Figure 6.7 shows the number of ESR paramagnetic spins per gram versus composition of MoO₃ in the Sb-Mo oxide mixture. Other results, including the splitting factors are also summarized in Table 6.11. The spectra obtained from MoO₃, Sb₂O₄ and Sb₂O₄-MoO₃ (2:1) are shown in Figures J.1, J.2 and J.3 respectively.

The ESR spectra showed some variation with change in the composition of the catalyst. The similarities in the shape of the curves between Figures 6.6, 6.7 and 6.5 suggest that there is some relation between the high performance of this catalyst and the changes on its surface. In the case of molybdenum mixtures it has been already found [149] that the yield of certain products correlates with the ESR signal intensity. In all cases the catalyst found at the uppermost point of the crest of the curve was that containing 67 wt% Sb₂O₄-33 wt% MoO₃.

The splitting factors were calculated for every case using equations 2.54 and 2.55.

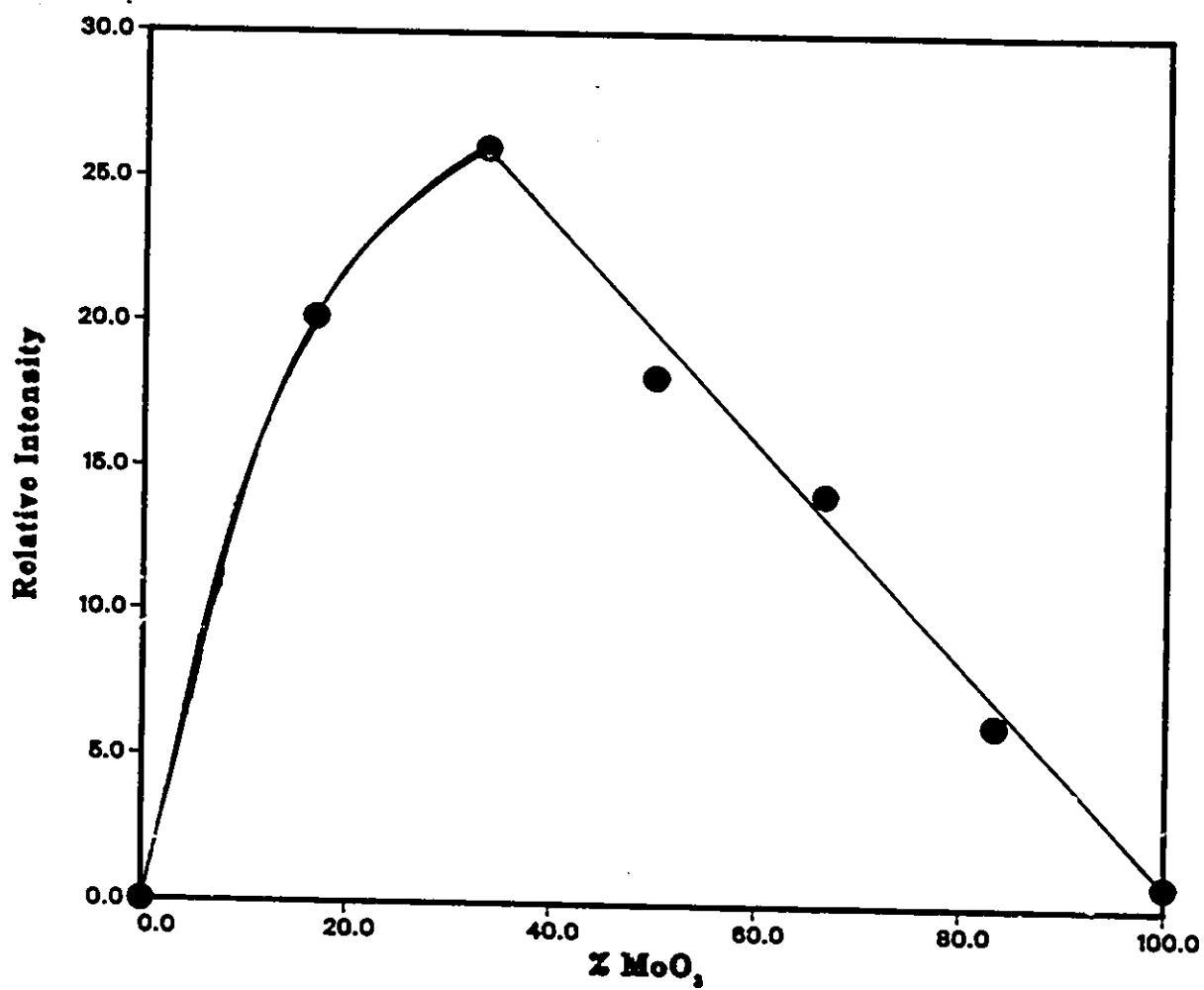


Figure 6.6: ESR Signal Intensity vs Composition of MoO₃ in Catalyst

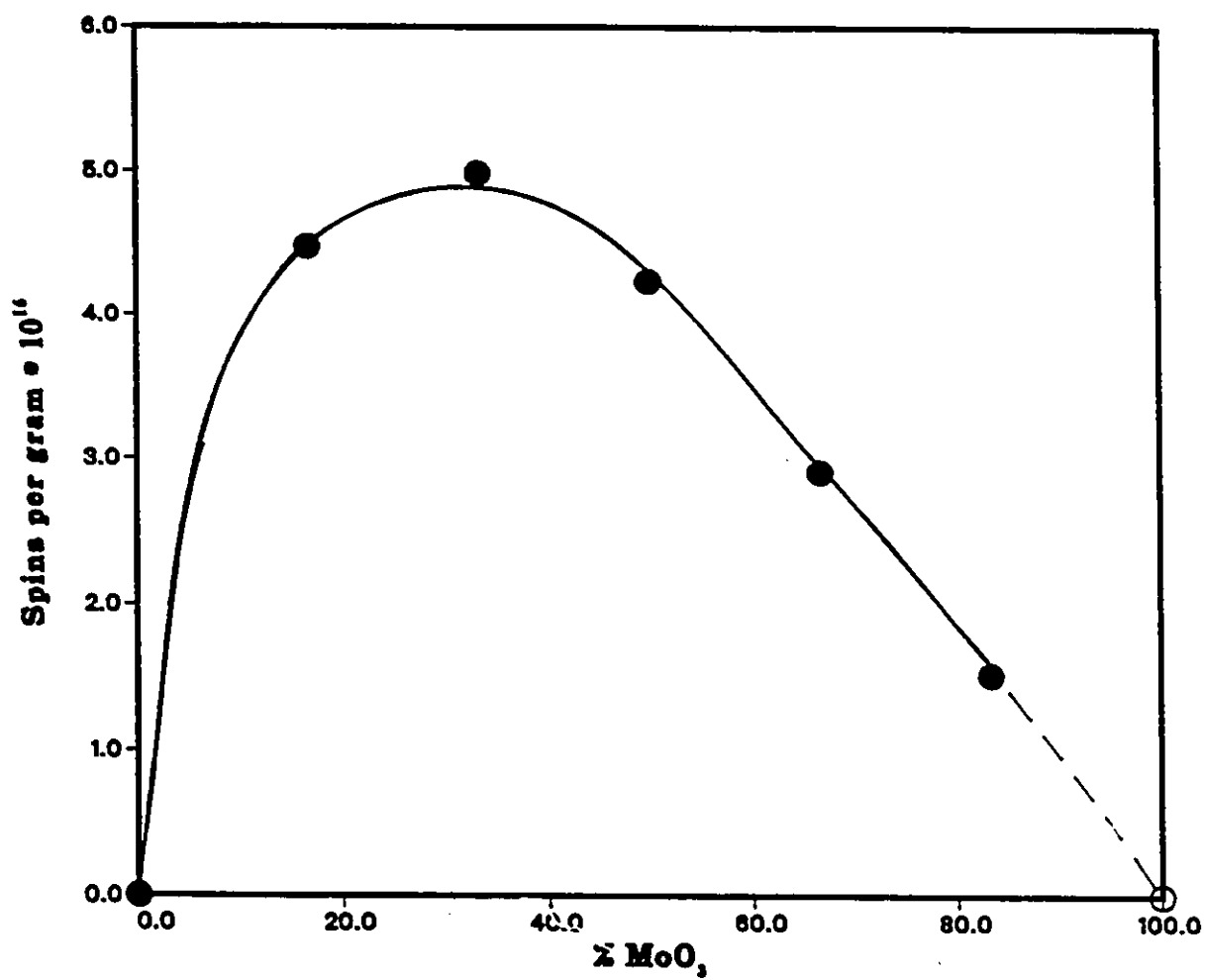


Figure 6.7: ESR Paramagnetic Spins per gram vs. Composition of MoO₃ in Catalyst

The g values varied between 1.92 and 1.93 and the one for MoO_3 alone was 1.9368. This is approximately the same as observed by others [104,149]. No appreciable hyperfine structure components due to the odd isotopes of molybdenum were observed in the solid samples.

Molybdenum can exist in any of the four valencies, 6+, 5+, 4+, and 3+ corresponding to d^0 , d^1 , d^2 and d^3 configurations. Hexavalent molybdenum is diamagnetic and, therefore gives no ESR signal. The tetravalent molybdenum, even if it were paramagnetic, would not be observed except at very low temperatures. Also it would be expected that any observed resonance due to d^2 , would have a large zero field splitting and therefore would give a very broad signal. This leaves as the only two possible ions present Mo^{5+} and Mo^{3+} . It has been confirmed [104] that both ions are formed during thermal decomposition of ammonium molybdate. Mo^{3+} is expected to give a g value near 2.00.

Figure J.1 shows a very weak signal for both ions. Mo^{5+} gave a g value of 1.936 and Mo^{3+} a g value of 1.993. However in all the other spectra the hyperfine line for Mo^{3+} was so small that could be confounded with noise or with the large signal produced by Mo^{5+} . In our case the signal is probably due to a change of electronic state in the compound, most likely Mo^{6+} going to Mo^{5+} . These spectra agree with data found in the literature [103,104,153].

It is well known that MoO_3 forms a number of nonstoichiometric oxides on heat treatment in a reducing atmosphere. The departure from stoichiometry is generally associated with the formation of colour centres. The general interpretation had been that the colouration is due to crystal field spectra of electrons in the Mo^{5+} state. The mixtures with Sb_2O_4 , a yellow compound, shown in Table 6.7 suggests an intimate interaction at levels of the basic crystalline structure.

In Sb_2O_4 , the Sb^{5+} and Sb^{3+} ions are present in equal proportions. The β - Sb_2O_4 , monoclinic, is obtained from the decomposition of Sb_2O_5 at 1000 K, but in the presence of vanadium, iron or molybdenum ions the transformation

can be achieved at lower temperatures [62]. Although the mechanism is not clear, both molybdenum and vanadium behave as dopants, which become incorporated in the bulk of β - Sb_2O_4 during its formation. The resulting oxides have a distinct defect structures, in which V^{5+} replaces some of the Sb^{3+} ions in the lattice, and Mo occupies interstitial sites [157].

The large signal shown in Figure J.2 was due to Sb^{3+} ions. In the Sb-Mo oxide spectra this signal changed its intensity apparently accordingly to the activity of the catalyst. The presence of Sb^{3+} increases the number of Mo^{5+} ions to a maximum, as seen in Figure J.3. Thereafter the activity decreases. The catalyst with the highest activity for Mo^{5+} also showed the largest intensity for Sb^{3+} . This supports the idea of some interaction between the two types of ions caused probably when Mo occupies interstitial sites. Again the oxides ratio found seems to be the most effective one.

6.2.5 XRD Spectra

Each one of the unsupported metal oxide catalysts was photographed using the *Debye Scherrer* technique. The film taken from MoO_3 suggests that this oxide was in its β -form, orthorhombic. The other possible crystalline state for MoO_3 is cubic and this state was easily dismissed. The film taken from Sb_2O_4 suggests that both states α , orthorhombic, and β , monoclinic, were present in this catalyst, but the ratio could not be determined by this spectroscopic method. It is known [62] that the β -phase is more active and preferred for catalyst preparation. Although the preparation procedure for pure Sb_2O_4 was the same as for the metal oxide mixtures, the effect of the molybdenum ion has been found determinant in the formation of β - Sb_2O_4 [157].

The analysis of the metal oxide mixtures proved to be much more difficult. Several known oxide mixtures were tried, Mo-doped Sb_2O_4 [157], α - Sb_2O_4 [159], Mo_3Sb_7 [77], Mo_4O_{11} [84], MoO_3 [5,11,145], β - Sb_2O_4 [134] and $\text{Sb}_2\text{Mo}_{10}\text{O}_{31}$ [127]. However, none of these phases could be identified conclusively. The best evidence found indicates that part of the specimen is

composed of Mo-doped β - Sb_2O_4 . This would again explain the location of Mo atoms in the interstitial sites.

The lattice parameters, as well as the space groups of the crystalline structures that were compared with the specimens are given in Table I.1.

6.3 Kinetic Analysis of Data

6.3.1 Factors Affecting Rate Mechanism

The rate equation is generally derived in terms of temperature, pressure and composition of the reactants. The other factors which might affect kinetics are considered below:

- I. Activity of Catalyst – Catalyst activity remained fairly constant over all the runs for the kinetic study. This was confirmed by carrying out replicate runs at the centre point operating conditions every four runs. These results are shown in Appendix G.2.
- II. Homogeneous Reactions and Reactions in the Absence of Catalyst – As indicated in Section 6.1.2 the amount of product produced in the absence of catalyst at the operating conditions for the kinetic analysis is negligible.
- III. Side Reactions – Formation of carbon monoxide is believed to be caused by thermal decomposition of formaldehyde [25,80]. Carbon dioxide is formed by the oxidation of carbon monoxide. As observed in most of the experimental data, especially those obtained for the kinetic analysis, the amount of carbon oxides formed was quite small compared to the total products. Experimental runs where carbon oxides formed were more than 5% of total products were not considered for kinetic analysis. As selectivity was very high this was not a matter of concern. Also, no traces of dimethyl ether, formic acid,

dimethoxy methane, or methyl formate were found in the analysis of the products.

- IV. Pressure Drop Through Catalyst Bed – Total pressure inside the reactor measured in the absence of catalyst was 117.25 kPa (879.5 Torr). The pressure drop inside the catalyst bed was calculated following the procedures given by Bird *et al.*[23]. At the maximum air flow rate used (17.03 L/h) the pressure drop was 7.85 kPa and 3.12 kPa at the minimum air flow rate (6.8 L/h). As the maximum pressure drop did not exceed 10 kPa, the measured pressure at the outlet of the reactor, 107.65 kPa (807.5 Torr) was taken for ease of calculation, as the total pressure in the catalyst bed.
- V. Departure from Plug Flow – In the present study, plug flow in the reactor was assumed. The flat pattern in the tube is affected by a number of factors. The two most important ones are axial dispersion and channeling. As stated in Section 2.5.1 the effects of axial dispersion can be considered negligible for $\frac{L}{d_p} > 350$. This value in our case is about 875. Channeling is avoided by having a large $\frac{d_t}{d_p}$ ratio; larger than 20 according to some authors [143]. The present case gives a value of 44. Hence, the assumption of plug flow could not result in any significant error.
- VI. Diffusion – Diffusion can be of two kinds:
- (a) Molecular Diffusion: When the mean free path of diffusing molecules is small with respect to pore radius, collisions between molecules of reactants control the diffusion process. This is known as molecular or bulk diffusion. In such cases, the partial pressures of the different reactants control the diffusion process. In most cases this type of diffusion is insignificant unless pressure is very high or pore radii are very large. Since the present work was conducted at nearly atmospheric pressure, molecular diffusion is expected to be negligible. To check

the effect of molecular diffusion several runs, set T, were taken at the same operating conditions with different feed velocity of methanol. As can be seen in Figure 6.8 changing feed velocity had apparently no effect on conversion. Hence, it can be assumed that molecular diffusion did not control the reaction.

- (b) Knudsen Diffusion: When the pore size of the catalyst (or porous medium) is small, collisions between molecules and walls control the diffusion process. The catalyst particles used in the present study had an average particle diameter of 0.21 mm. For such a catalyst particle Knudsen diffusion does not affect results significantly.

To find out if Knudsen diffusion affected the results, a set of runs, termed set R, was carried out at the centre point operating conditions but changing particle diameter. Conversion was nearly the same. Results are shown in Figure 6.9. If Knudsen diffusion were affecting the results significantly, changing catalyst diameter should have resulted in significant change in the rate of reaction. Hence, for such small particles (0.175 to 0.246 mm) the effectiveness factor can be considered one [31,33,41,51,139,151].

- VII. Resistance to External Heat and Mass Transfer – The values of partial pressure and temperature in the bulk stream and at the gas-solid interface may differ significantly in certain systems. In order to simplify the correlation for experimental data, it is necessary to minimize these resistances so that they become negligible. The effect of heat and mass transfer is explained in detail in Section 2.5, and a sample calculation based on the method of Yoshida *et al.* [172], that estimated the temperature and pressure drops from the bulk phase to the catalyst surface, is shown in Appendix F. The maximum temperature drop of 0.1 K and the maximum pressure drop of substantially less than 10 Pa suggested that the heat and mass

transfer effects were negligible.

6.3.2 Effect of Process Variables

The effect of temperature, weight of catalyst to methanol feed ratio (W/F), and methanol to air feed ratio ($\bar{R}$) on the conversion of methanol (C), yield of formaldehyde (Y), and selectivity (S) of the catalyst were investigated. The results are presented in Appendix C. Figures C.1 to C.20 show the effect of temperature on conversion of methanol and yield of formaldehyde. Figures C.21 to C.36 show the effect of space time on conversion of methanol and yield of formaldehyde. Figures C.37 to C.56 show the effect of $\bar{R}$ on conversion of methanol and yield of formaldehyde.

Effect of Temperature

The effect of temperature on conversion, yield and selectivity was investigated in the temperature range 623–698 K. Conversion of methanol increases with temperature. This increase is more accentuated at higher space times. In some cases conversion reached 100%. Selectivity remained nearly at 100% for the range investigated. However, in some cases after reaching a maximum yield for a fixed $\bar{R}$ and W/F the conversion decreased slightly, usually at high W/F and at temperatures beyond 673 K. Figures 6.10 and 6.11 show clearly these effects. This may have happened due to thermal deactivation of some active centres.

Effect of W/F

The effect of W/F on the conversion, selectivity and yield was studied at temperatures between 623 and 698 K, for methanol-air feed ratios, $\bar{R}$, between 4 and 10. For all methanol concentrations an increase in W/F increased the conversion of methanol. This conforms with the fact that the increase

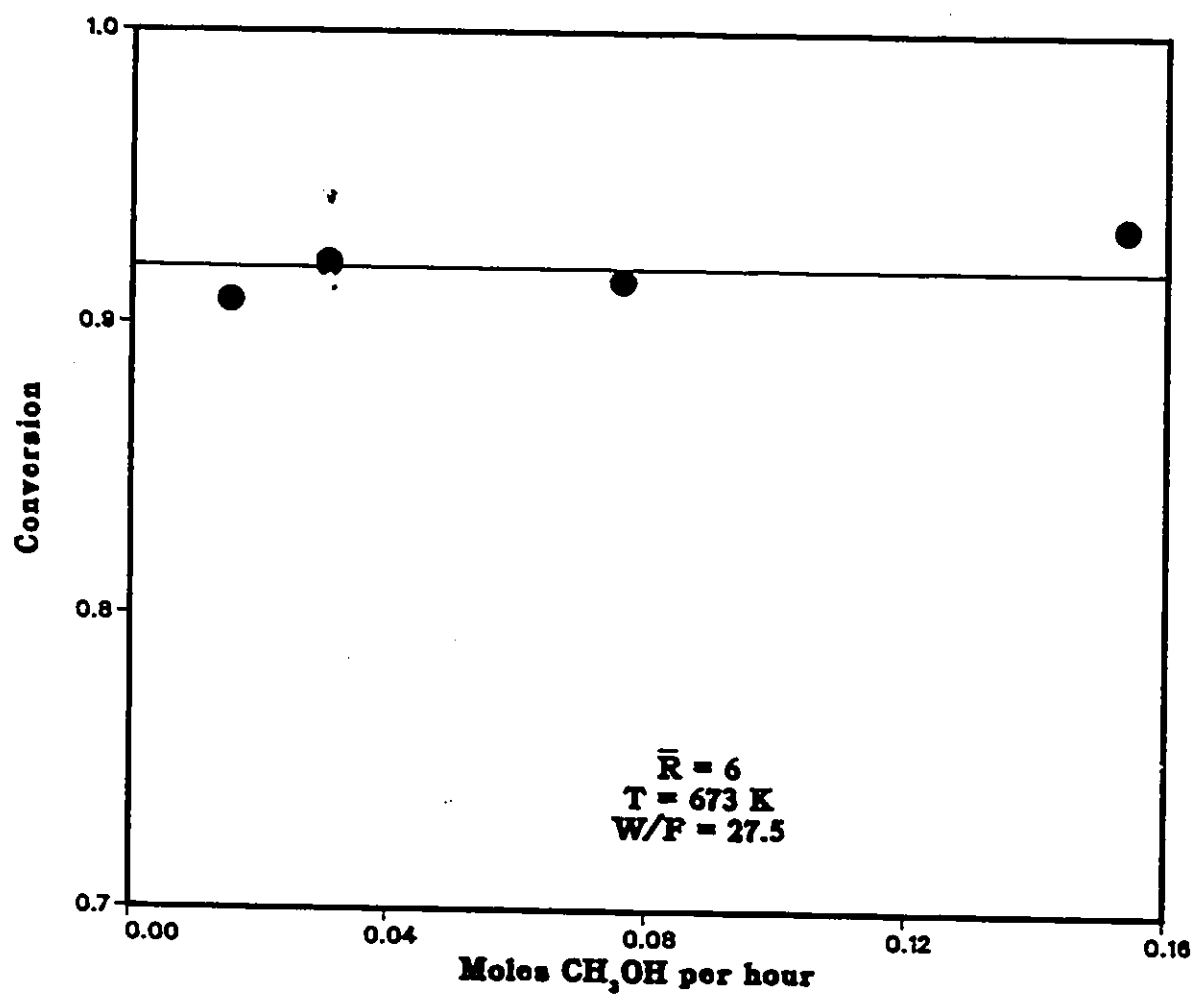


Figure 6.8: Effect of Feed Velocity on Conversion

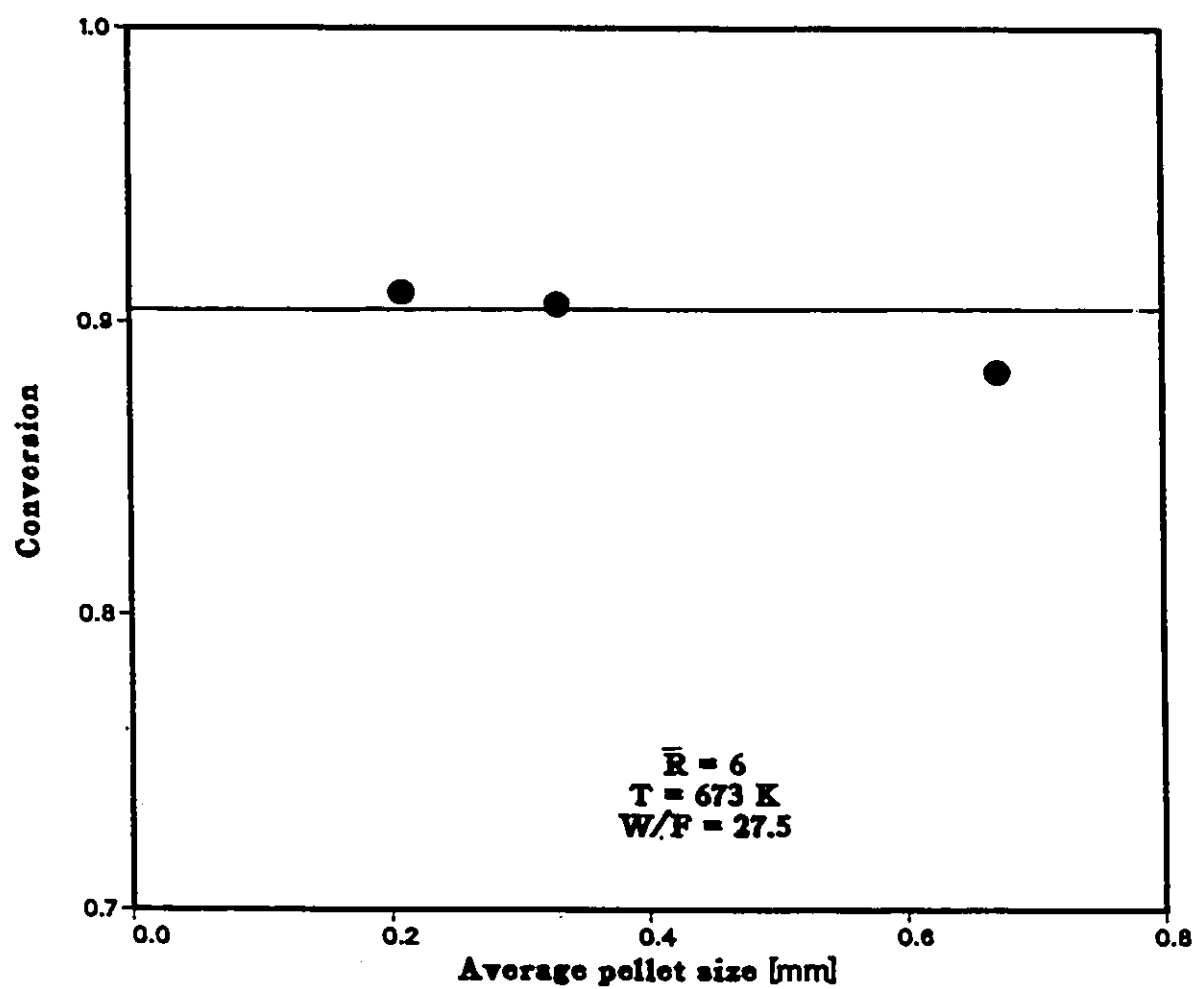


Figure 6.9: Catalyst Size Effect on Conversion

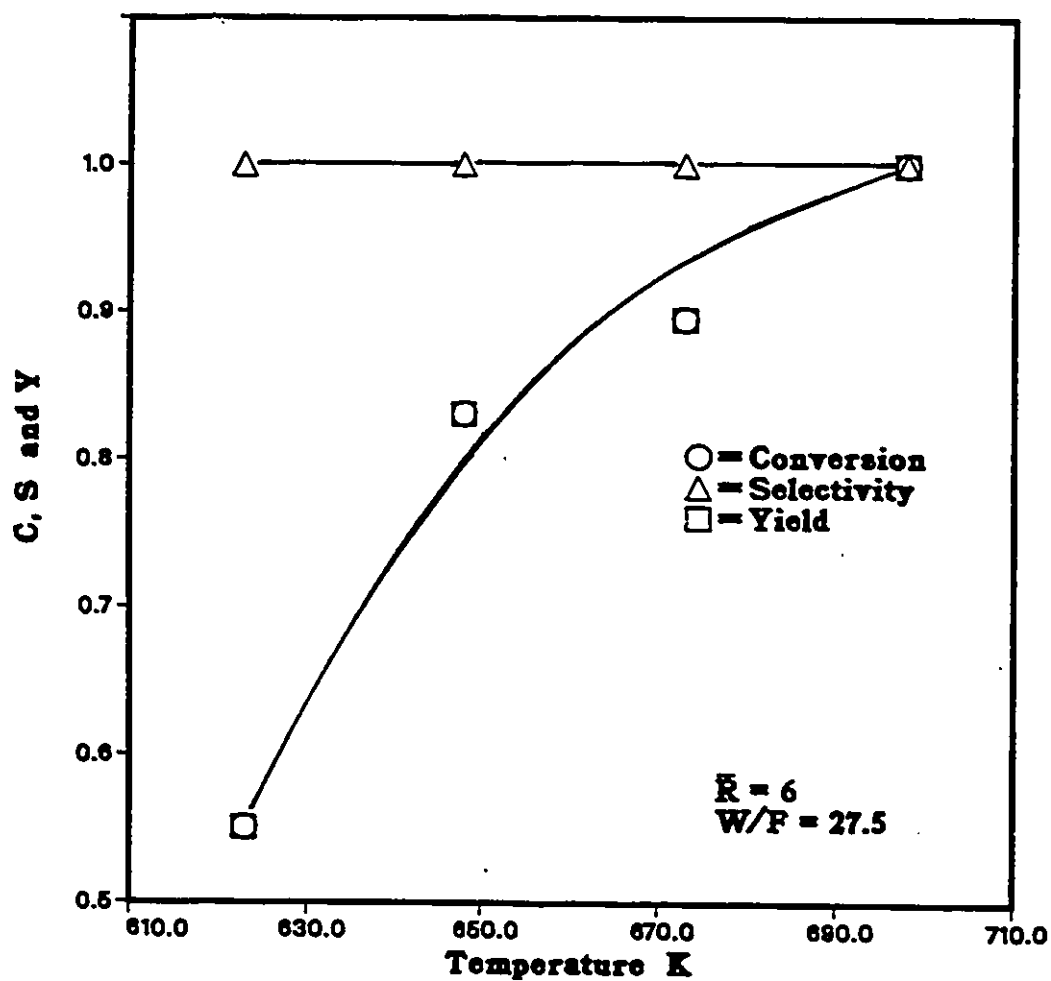


Figure 6.10: Effect of Temperature on Conversion, Selectivity and Yield at W/F of 27.5 and $\bar{R}$ of 6

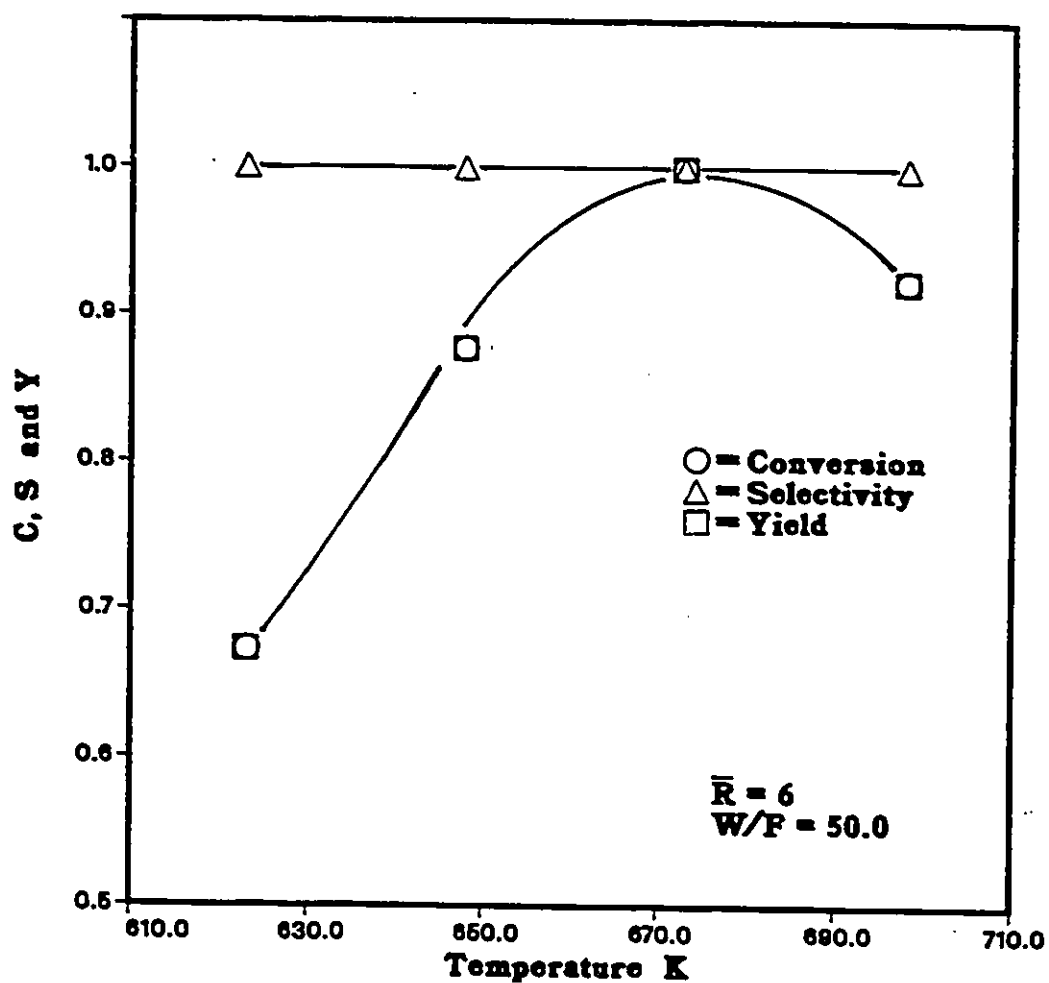


Figure 6.11: Effect of Temperature on Conversion, Selectivity and Yield at W/F of 50.0 and $\bar{R}$ of 6

in W/F ratio with constant feed, gas flow rate and methanol concentration results in increased contact time. However, the rate of increase in conversion dropped progressively, indicating that the decrease in bulk concentration of methanol during the reaction lowers the reaction rate. At a given value of W/F, conversion of methanol increased with higher methanol concentrations in the feed. Figures 6.12 and 6.13 show the importance of an adequate contact time to attain high yields.

Effect of Methanol-Air Flow Ratios

The effect of methanol to air flow ratio, $\bar{R}$, on conversion, selectivity and yield was studied at temperatures between 623 and 698 K, and for space times between 5 and 50. The conversion increased with an increase in methanol concentration. However, at higher values of W/F the conversion and selectivity increased slightly with the increase in concentration of methanol in the feed, especially at large values of $\bar{R}$. This is clearly observed in Figures 6.14 and 6.15. It is also observed that at a given value of $\bar{R}$, conversion of methanol increased with higher space time.

6.3.3 Initial Rates

Yang and Hougen [168] developed a method that is helpful in reducing the numbers of possible rate controlling steps by eliminating some of them. As indicated in Section 3.3.1 it is necessary to obtain the initial rate, also defined as the rate of reaction at zero conversion. This is obtained from a plot of moles of formaldehyde produced per mole of methanol fed versus space time. The initial rate is the slope of the curve as space times approaches zero. Figures 6.16 to 6.19 show this phenomenon.

The plots of moles percentage methanol in feed versus the initial rates, r_o , for all the temperatures studied are given in Figures 6.20 to 6.23.

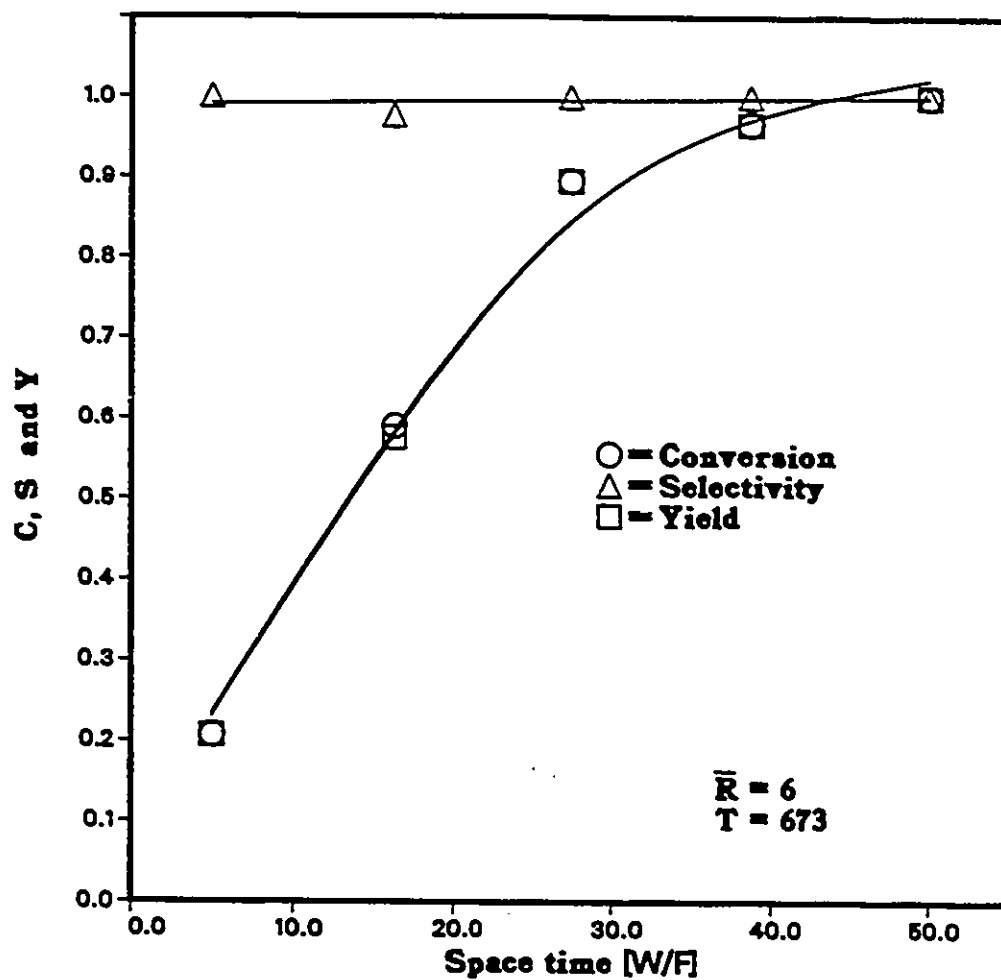


Figure 6.12: Effect of Space Time on Conversion, Selectivity and Yield at T of 673 K and $\bar{R}$ of 6

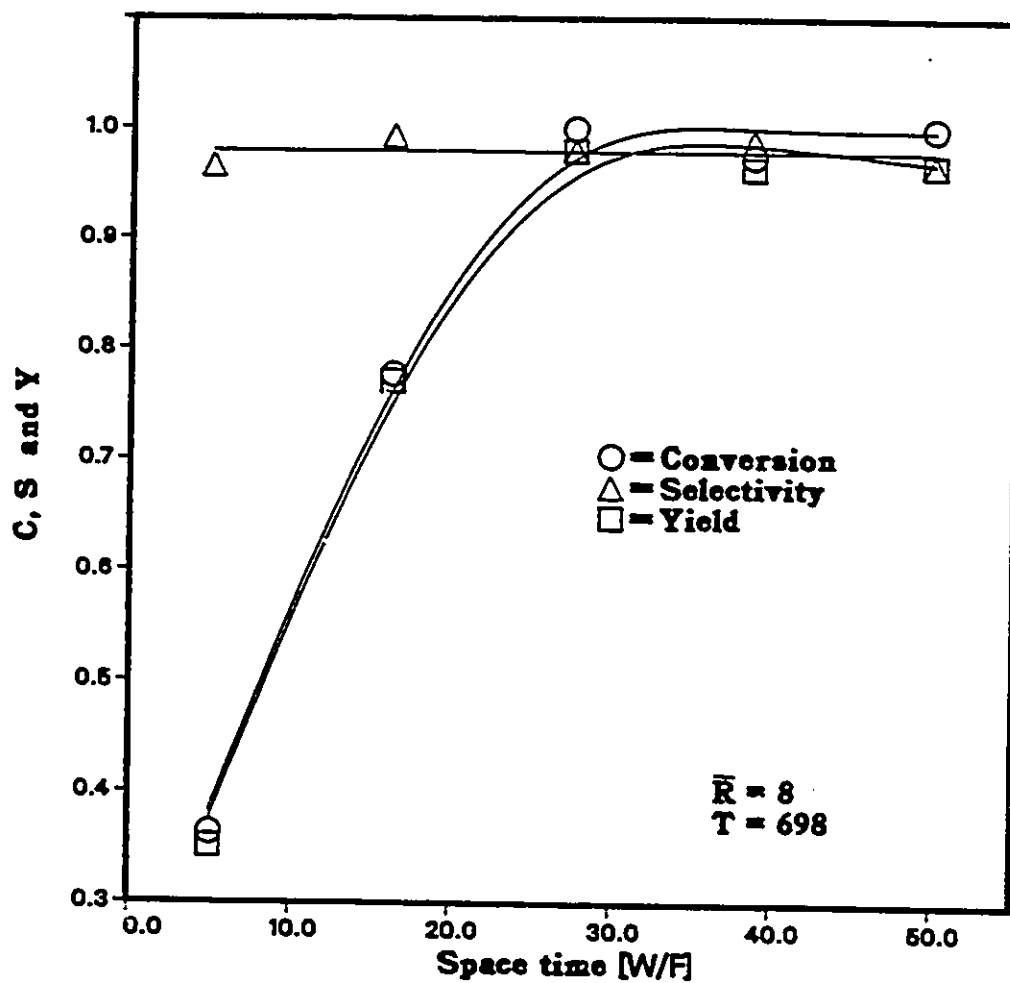


Figure 6.13: Effect of Space Time on Conversion, Selectivity and Yield at T of 698 K and $\bar{R}$ of 8

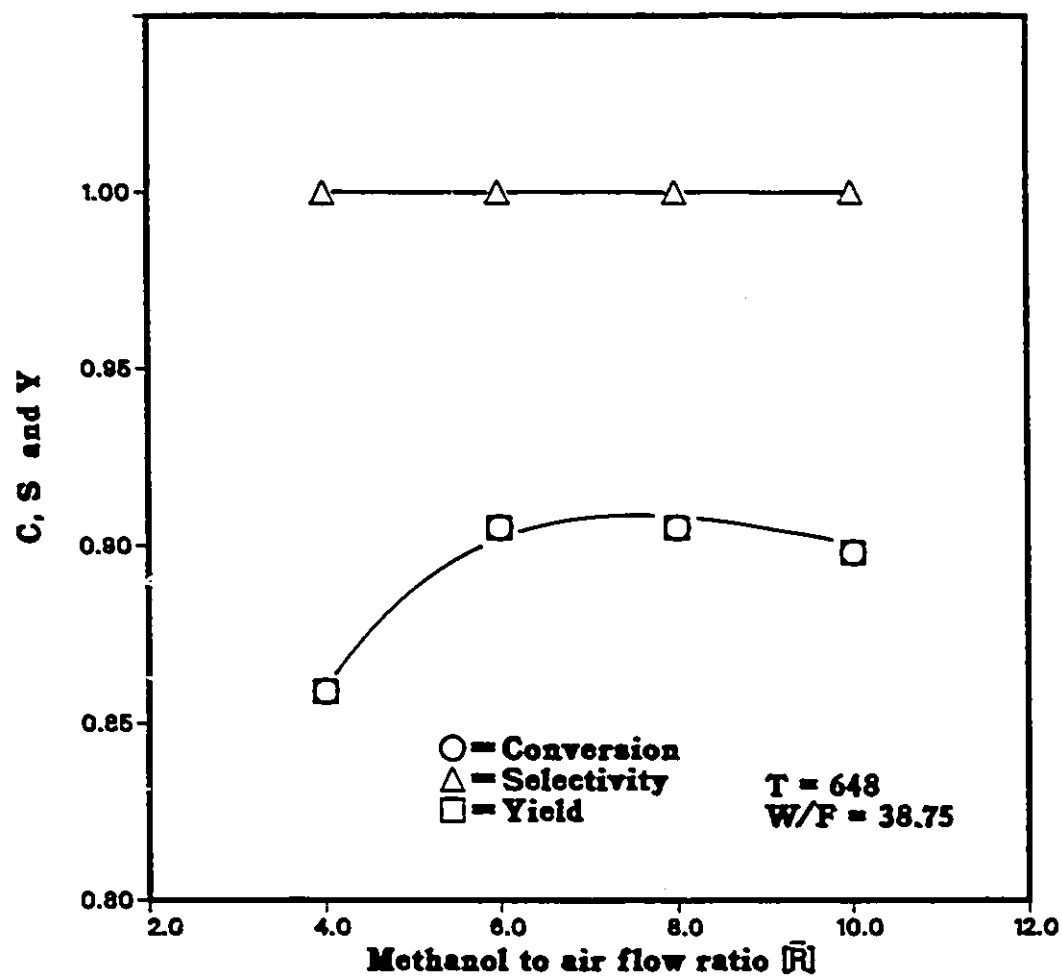


Figure 6.14: Effect of Methanol-Air Flow Rate at T of 648 K and W/F of 38.75

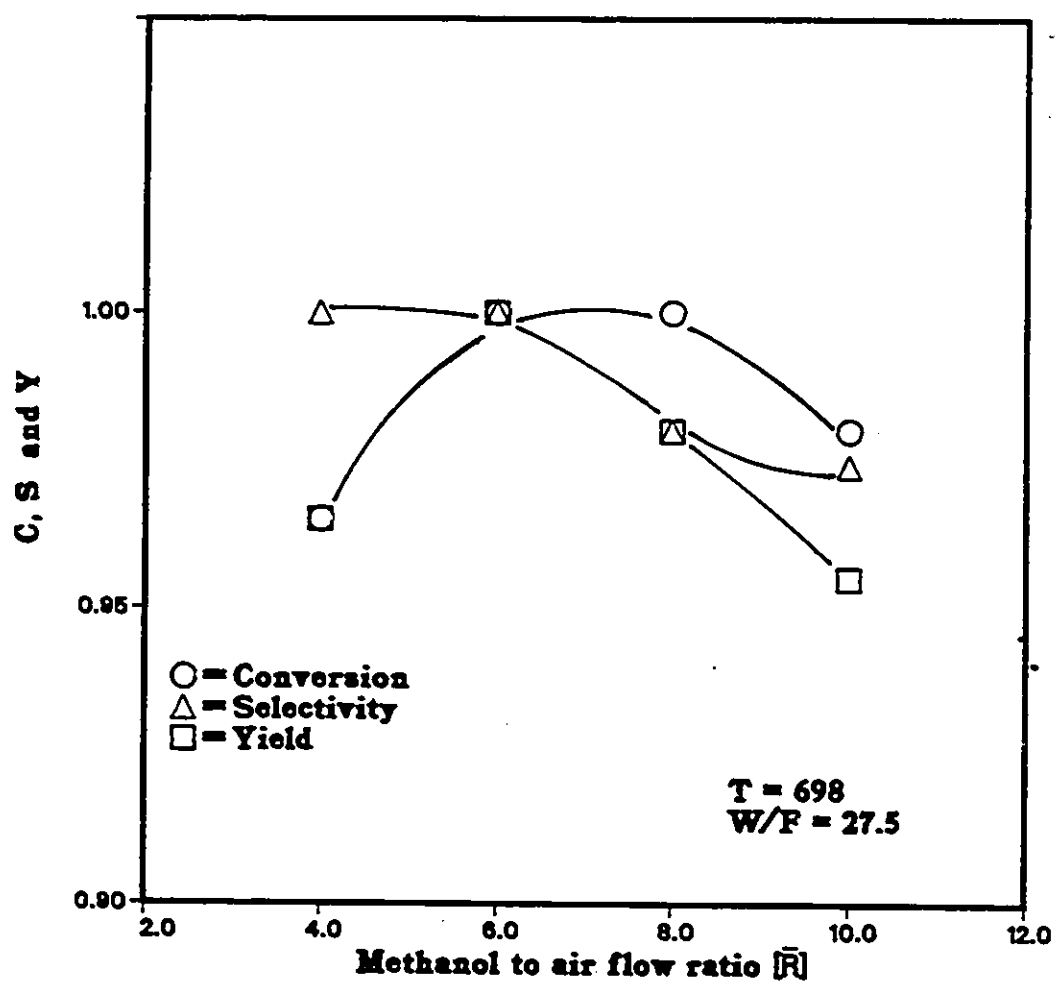


Figure 6.15: Effect of Methanol-Air Flow Rate at T of 698 K and W/F of 27.5

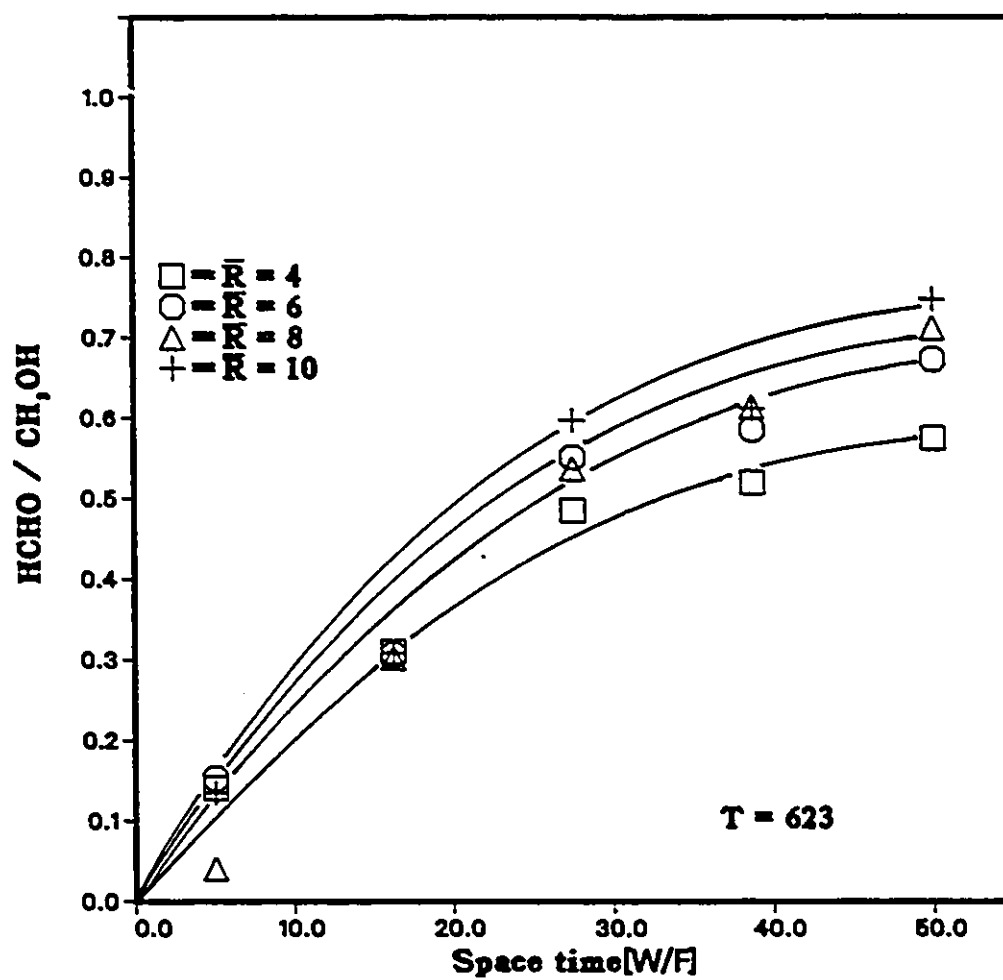


Figure 6.16: W/F Effect on Yield of HCHO at 623 K

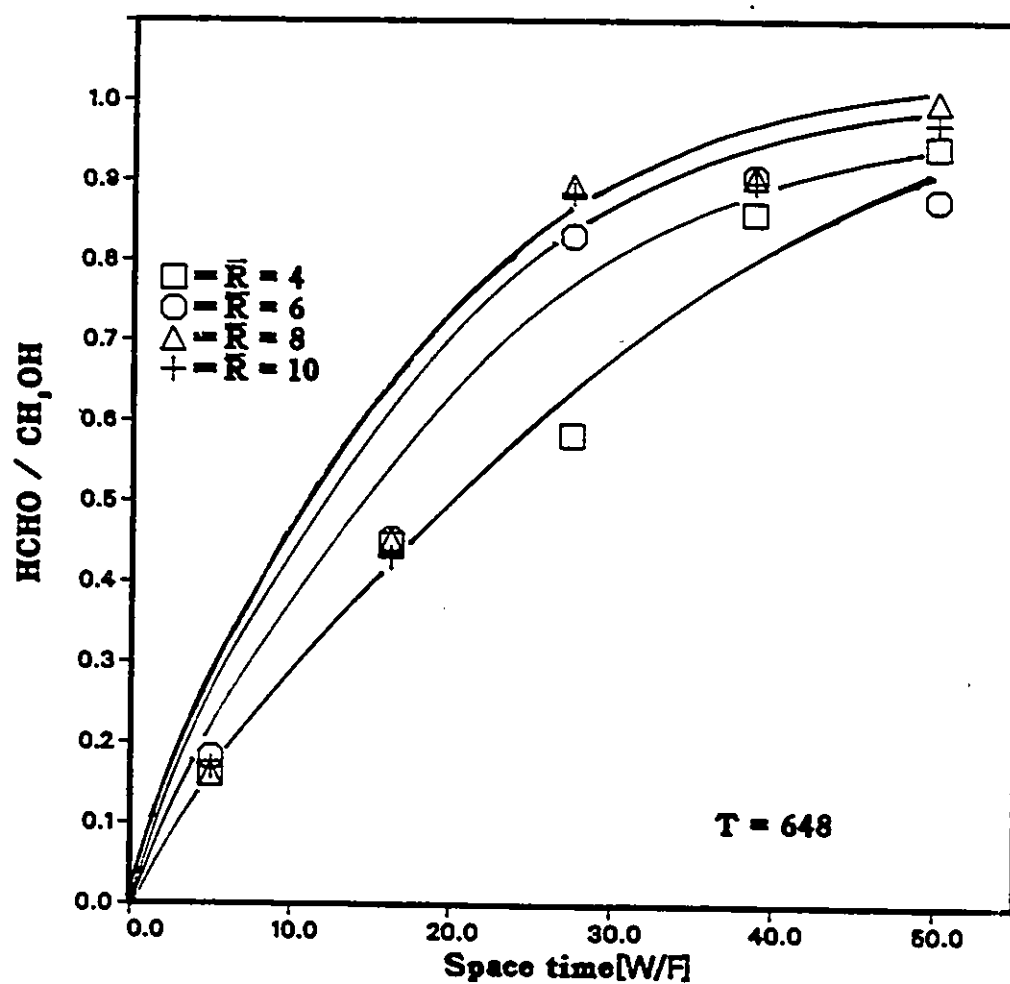


Figure 6.17: W/F Effect on Yield of HCHO at 648 K

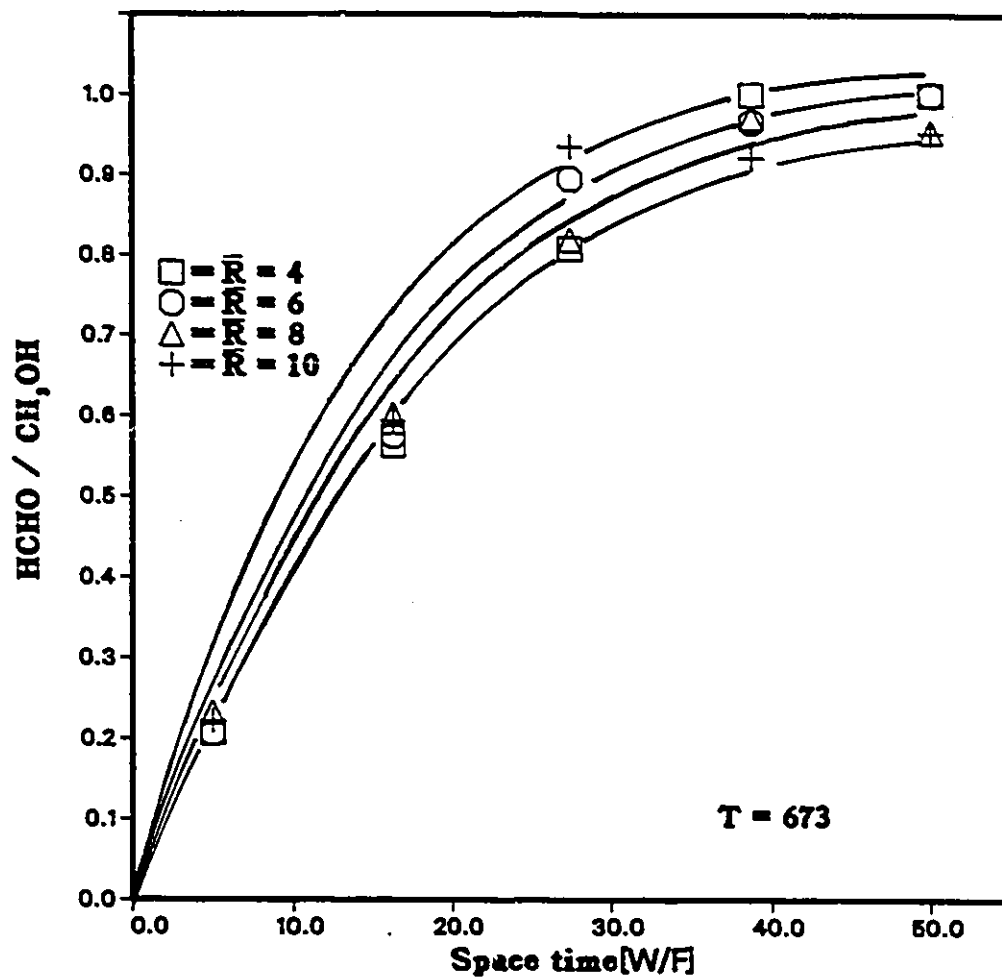


Figure 6.18: W/F Effect on Yield of HCHO at 673 K

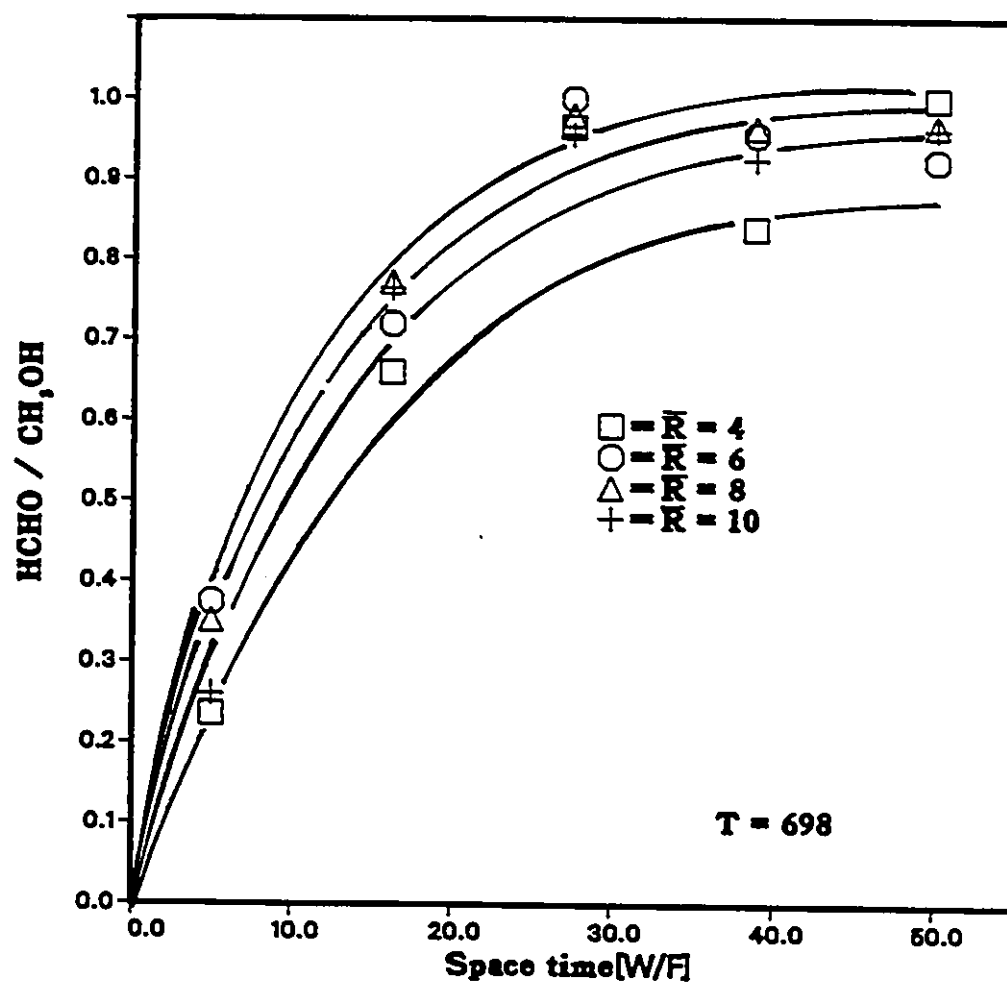
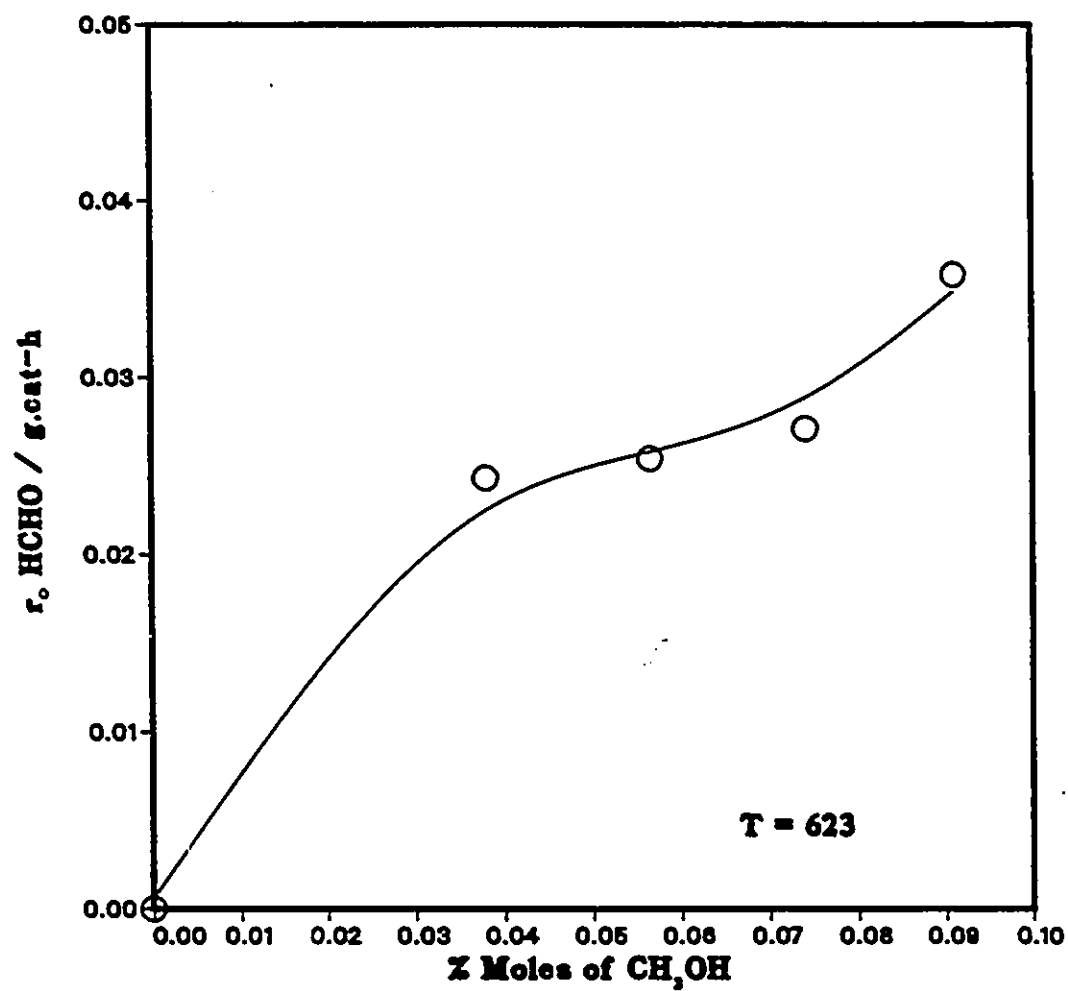
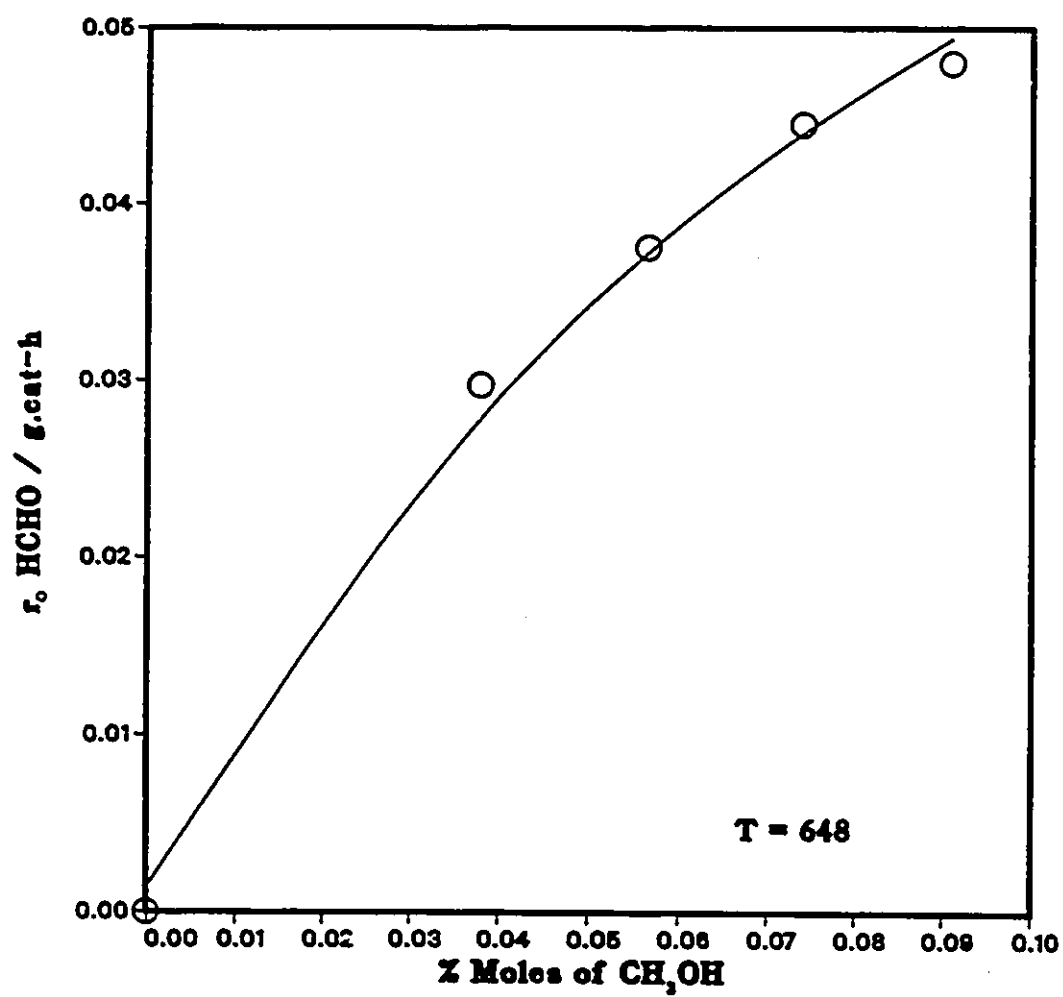
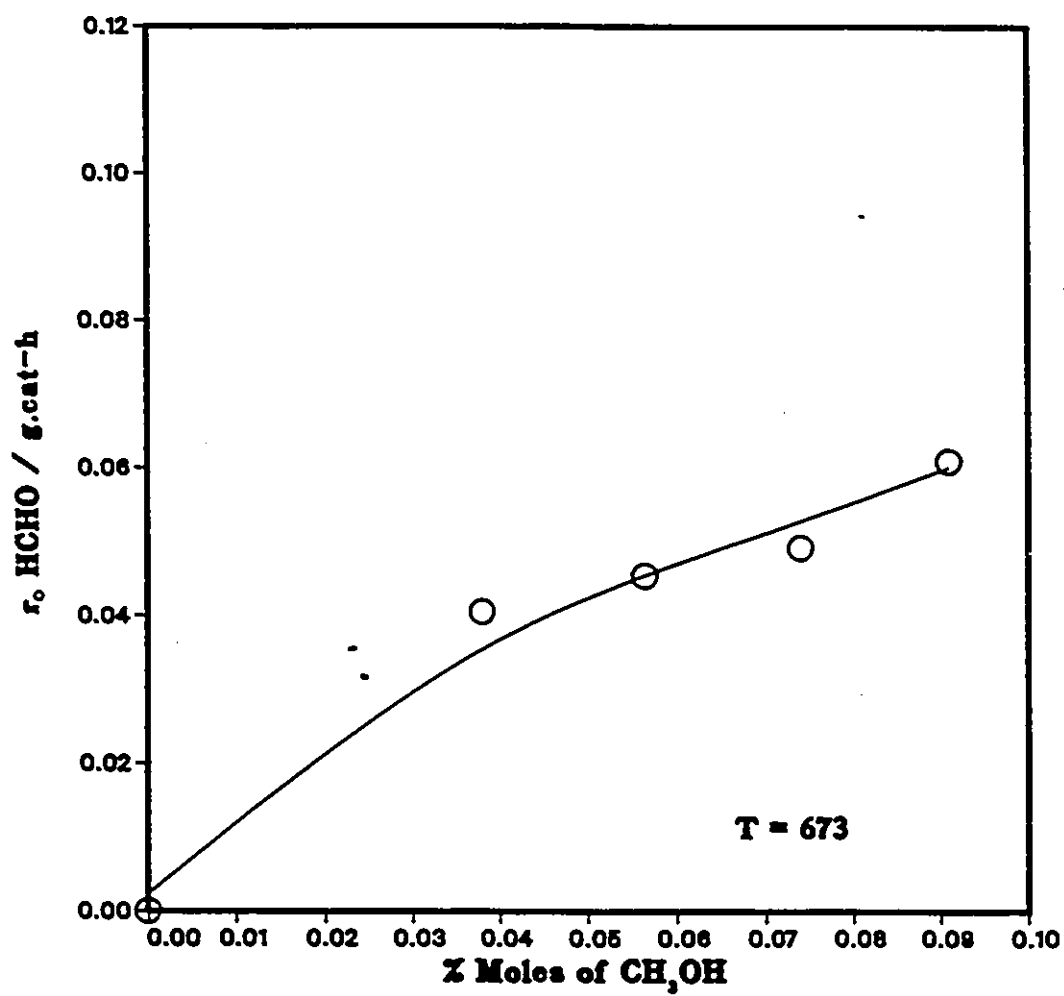
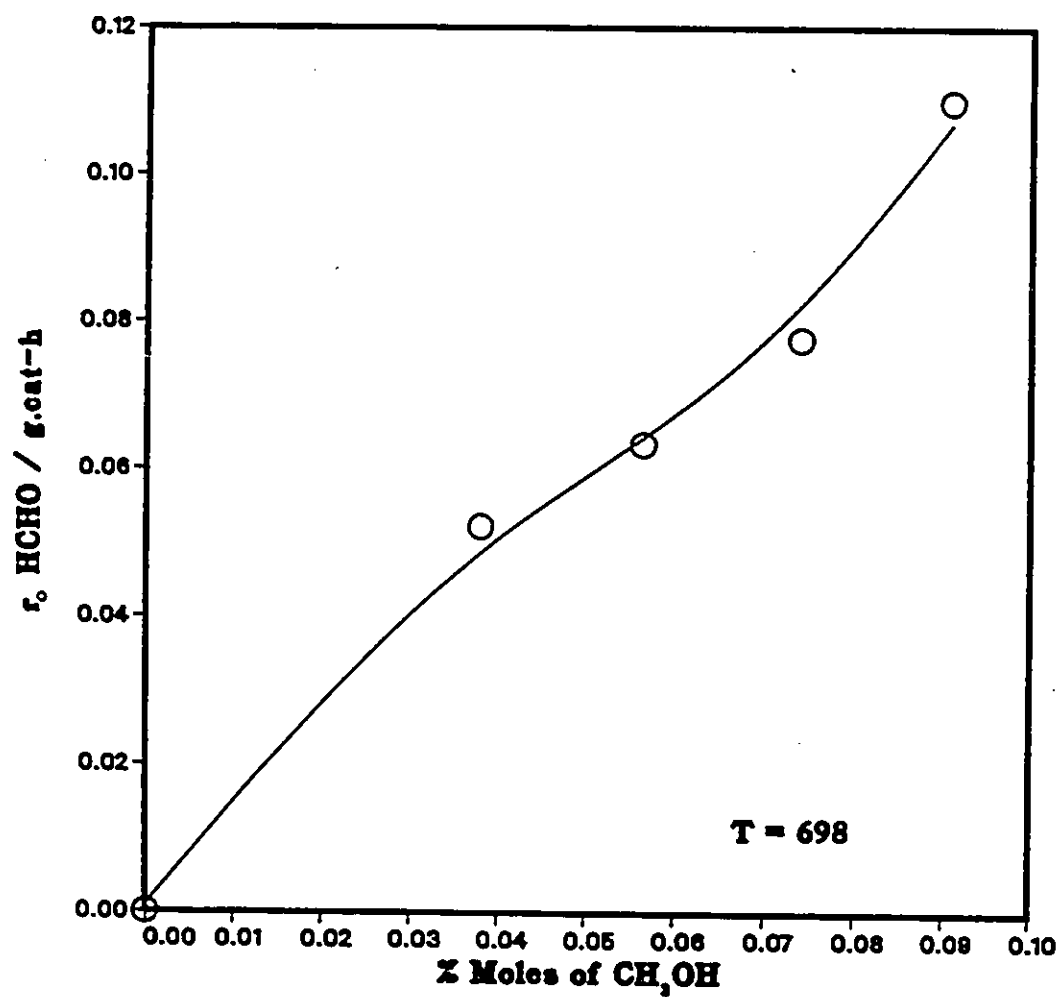


Figure 6.19: W/F Effect on Yield of HCHO at 698 K

Figure 6.20: Initial Rates vs. Moles % CH_3OH at 623 K

Figure 6.21: Initial Rates vs. Moles % CH_3OH at 648 K

Figure 6.22: Initial Rates vs. Moles % CH_3OH at 673 K

Figure 6.23: Initial Rates vs. Moles % CH_3OH at 698 K

Yang and Hougen[168] used the method of initial rates to identify the type of mechanism of reaction that was controlling the reaction. A comparison of the curves in Figures 6.20 to 6.23 with curves suggested by them for the various rate controlling steps, suggested that the desorption of products was not a rate controlling step.

6.3.4 Correlation of Data

For correlation of data, we will utilise the amount of formaldehyde produced per unit mole of methanol fed to the system, i.e. the yield. The integrated form of the rate equation in Table 2.2 can be rearranged into a new form as shown in Table 3.4, where $\alpha = 0.5$ and $y = \beta_0 + \beta_1 x$. The values for y and x in columns six and seven are calculated from the experimental data by substituting the values of W/F and the respective partial pressures. These values of β_0 and β_1 may be determined from the intercept and slope of the line in a y versus x plot, by using the least-squares method as indicated in Section H.1. A computer program, shown in Section B.3, performed the calculations for the eleven different rate equations.

For the two-stage redox mechanism there was no single value of m that would fit over the whole range of temperatures studied. However proper fit was found from 648 to 698 K for $m=1$ and $n=1$. As well, after analyzing the remaining equations a good fit was deemed in the case of $m=2$ and $n=1$ for a temperature of 623 K. This seems to indicate that as temperature increases there is a change in the order of reaction with respect to the consumption of methanol. At low space times the effect of catalyst seems to be stronger than that at very large space times. As a matter of fact, in most cases near complete conversion, i.e. $\sim 100\%$ yield, increasing the amount of catalyst was not only useless but may be counterproductive, as in some cases yield decreased. Bliznakov *et al.*[24] reported that in experiments using a MnO_2 - MoO_3 catalyst the order of reaction with respect to methanol changed from 0.5 to 1 when operating conditions changed.

Table 6.12: Reaction Rate Constant Values

Temperature (K)	m	n	k_1 $\frac{\text{gmol}}{\text{g-torr}^m\text{-h}}$	k_2 $\frac{\text{gmol}}{\text{g-torr-h}}$
623	2	1	1.716×10^{-5}	5.66×10^{-3}
648	1	1	1.13×10^{-3}	5.513×10^{-2}
673	1	1	1.57×10^{-3}	4.834×10^{-2}
698	1	1	2.44×10^{-3}	4.477×10^{-2}

The rate equation found is

$$r = \frac{k_1 P_M}{1 + \frac{k_1 P_M}{2k_2 P_{O_2}}} \quad (6.10)$$

The average value of k_1 and k_2 between 623² and 698 K are listed in Table 6.12.

The activation energies of the individual steps were evaluated from Figure 6.24 using the least-squares method. The respective equations relating k_1 and k_2 with temperature were as follows:

$$\ln k_1 = -6.4039 - \frac{6.9153 \times 10^3}{T} \quad (6.11)$$

$$\ln k_2 = -3.0154 + \frac{1.8809 \times 10^3}{T} \quad (6.12)$$

The values of W/F thus calculated for different conversions were plotted (solid lines in Figures 6.16 to 6.19). The percentage deviation between the experimental and calculated values was 10% or less, except for some values at space times of 38.75 and most values at space time of 50, where it was clearly shown that this 'excess' amount of catalyst was not useful in improving the reaction yield. The value of k_2 seems to slightly increase with increasing temperature. This is possible due to k_2 representing an overall value, rather than a single

²As already explained values for this temperature are taken from a two-stage redox mechanism where $m=2$ and $n=1$

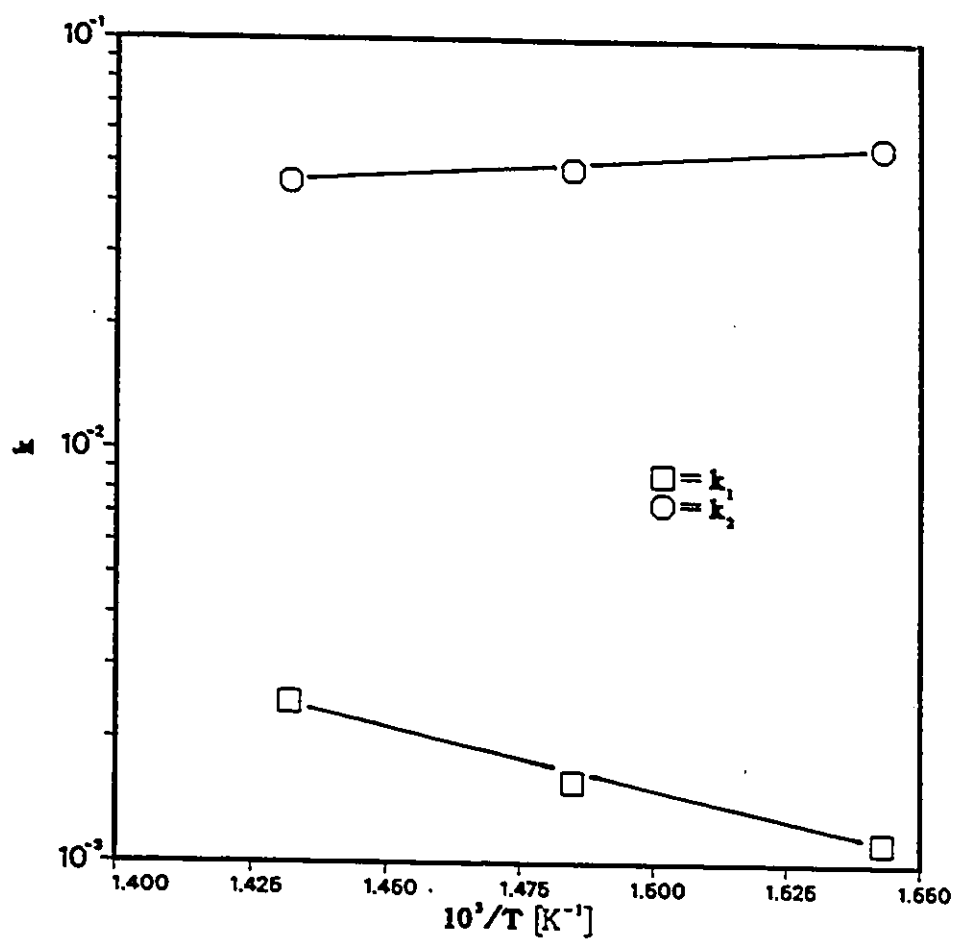
Figure 6.24: Effect of Temperature on the Rate Constants k_1 and k_2

Table 6.13: Results with Sb-Mo Supported on Y zeolite

Run	T (K)	W/F	R	Conversion	Selectivity	Yield
S01	673	27.5	6	0.805	0.622	0.501
S02	648	16.25	4	0.683	0.724	0.494
S03	698	16.25	4	0.830	0.626	0.520
S04	648	16.25	8	0.700	0.616	0.431
S05	698	16.25	8	0.842	0.598	0.504
S06	673	27.5	6	0.800	0.625	0.500
S07	648	38.75	4	0.778	0.787	0.612
S08	698	38.75	4	0.932	0.450	0.420
S09	648	38.75	8	0.784	0.444	0.348
S10	698	38.75	8	0.958	0.403	0.386
S11	673	27.5	6	0.869	0.625	0.543

step rate constant [S3,107]. Such a postulate is quite reasonable in view of the highly exothermic oxidation reaction. For the temperature range 648–698 K the activation energies obtained from Equations 6.11 and 6.12 are 13.742 Kcal/gmol and -3.737 Kcal/gmol respectively. The former value is in close agreement with those obtained in literature [24,25,76,88]. This gives an overall value of 10.05 Kcal/gmol. The general theory says that adsorption is an exothermic process unless dissociation occurs in which case the enthalpy may increase if heat of dissociation is included. No other values of m and n in the two or three-stage redox mechanisms seemed to show proper fitting.

6.4 Results on Supported Catalyst

Using the same Sb:Mo oxide ratio found for the highest yield catalyst, a catalyst supported on rare-earth exchanged Y-zeolite was prepared as described in Section 5.1.1. A complete 2^3_{III} factorial design was carried out with this catalyst. Table 6.13 shows the results of those runs.

Following the steps outlined by Bacon [14] and those of Appendix H.2 a first-order model was fitted to the results obtained in the oxidation of methanol to formaldehyde on Sb-Mo oxide supported on Y zeolite catalyst. The model obtained was based on yield of formaldehyde and uses the same normalized variables X_1 , X_2 , and X_3 , previously defined in Section 3.1.1.

The model obtained was:

$$\begin{aligned} Y = & 0.4644 - 0.0069X_1 - 0.0229X_2 - 0.0471X_3 \\ & - 0.0316X_1X_2 + 0.0346X_1X_3 - 0.0274X_2X_3 \\ & + 0.0229X_1X_2X_3 \end{aligned} \quad (6.13)$$

The fitted model provides an exact fit to the data for this set of experiments since it contains as many parameters as there are tests. Therefore the adequacy of this model cannot be tested. Possible deletion of terms in Equation 6.13 can be investigated however. Because of the absence of correlation among all parameter estimates there are several ways of assessing the significance of each term independently.

In this case we used the available estimate of the pure variance to calculate a confidence interval for each term. If a confidence interval reveals that a zero is a plausible value for a parameter then the term may be deleted from the fitted model. It must be noticed that because all parameter estimates in Equation 6.13 are uncorrelated, setting one or more parameters to zero will not alter the least-squares estimates of the remaining parameters.

Using standard calculations we can estimate the values required from the replicates. The mean, $\bar{Y}$, is 0.5146, the estimated standard deviation, s , is 0.0245, and the estimated variance, s^2 , is 6.023×10^{-4} . Using the estimate of the variance with 6 degrees of freedom, a 90 per cent confidence interval for the true value of each parameter, the estimate of each parameter is given by

$$\hat{\beta} \pm t_{v, \alpha/2} \sqrt{\frac{s^2}{2k}} = \hat{\beta} \pm 0.02123$$

Applying this confidence interval to each of the parameter estimates in equation 6.13 it is seen that only β_1 is plausibly zero. If instead of 90 %, a 95 % confidence interval is used our result is

$$\hat{\beta} \pm t_{v,\alpha/2} \sqrt{\frac{s^2}{2k}} = \hat{\beta} \pm 0.02626$$

This results indicates that β_1 , β_2 and β_{123} are plausibly zero.

These results suggest that temperature and space time by themselves are not significant as operating variable, but their interactions are, indeed, important. As well, it is observed that milder conditions might give better yields.

The use of a support such as Y zeolite increases the difficulty in analyzing a catalyst due to an increment in the number of possible interactions between the catalyst and the active support. As expected there was formation of carbon oxides, but there were no other side reactions. This is encouraging since it envisages the possibility of combining this metal-oxide mixture in small amounts with a large surface area support ³ for the production of formaldehyde. The yields obtained were comparable to the best ones obtained with pure MoO₃. Further studies are needed to improve the preparation of such catalyst. The technique used here did not prove itself of high efficiency in dispersing the metal oxides on the zeolite surface, as can be seen in Figure 6.29.

6.4.1 Adsorption Studies

Physical adsorption studies were carried out on the Sb-Mo (2:1) oxide catalyst supported on Y-zeolite. As indicated in Section 2.8.4 by plotting the volume of nitrogen adsorbed or desorbed at STP versus the relative pressure, i.e. equilibrium pressure over saturation pressure, the adsorption isotherm can be obtained. Such an isotherm is shown in Figure 6.25.

³The Sb-Mo oxide catalyst had a surface area of 6.1 m²/g, whereas the catalyst supported on Y zeolite had a surface area of 367.71 m²/g

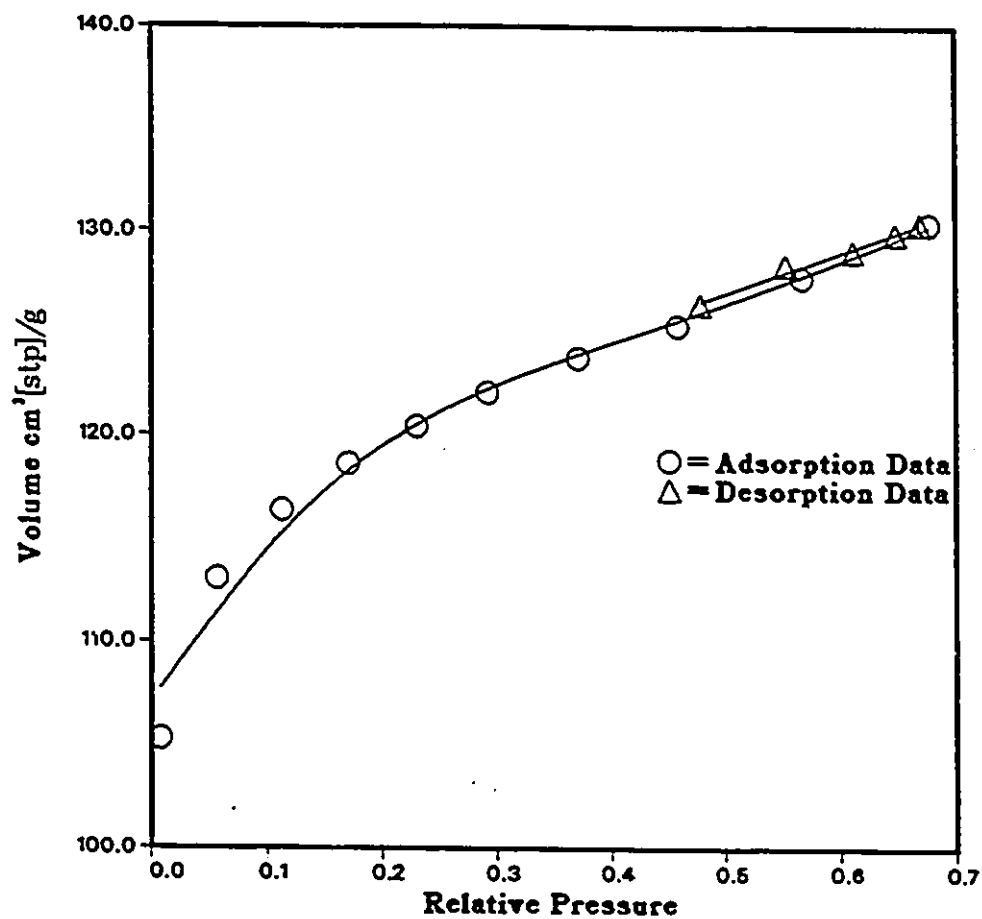


Figure 6.25: Adsorption-Desorption Isotherm for Catalyst: 67% SiO_2 -33% MoO_3 on Y-zeolite

Again, recalling the methodology from Section 2.8.4, the pore volume distribution can be calculated. This is shown in Figure 6.26 where the percent of pore volume associated with radii less than certain pore radius (y-axis) is plotted versus pore radius.

The interesting feature of Figure 6.26 is that it shows that the pore distribution did not change substantially after impregnation with Sb-Mo oxides. It is logical to assume that some of the smaller pores would be blocked by agglomerates of Sb-Mo oxides which is why there is less pore volume associated with less than a certain pore radius in the impregnated zeolite. This also explains why the surface area measured by BET went down from 550 to 367 m^2/g . Although impregnation can not be fully appreciated on the surface, as demonstrated in Figure 6.29, this study indicates that the metal oxide reached the inside of the zeolite pellet, and was later on reached by the reactants and the expected reaction took place.

6.5 Results of SEM

Several photographs were taken of the surface of the catalysts. The most significant ones are presented here to help explain the characteristics of the catalyst surface. In Figure 6.27 one can observe the surface of catalyst IV (67% Sb_2O_4 -33% MoO_3). It seems that any MoO_3 crystal present does not appear in its cubic form but as an orthorhombic structure. Regarding the fact of having monoclinic Sb_2O_4 [62] one can not conclude such fact from the photographs alone, since the other crystalline form of Sb_2O_4 is orthorhombic. Proper characterization of these structures was tried by XRD. The 'shales' shown in the figure are typical of several metal oxide mixtures.

Figures 6.28 and 6.29 show magnifications of pure Y zeolite catalyst and Sb_2O_4 - MoO_3 supported on Y zeolite catalyst. It is observed that the dispersion of metal oxides on the zeolite may not be as good as possible. However some oxide 'shales' can be seen on Figure 6.29. The fact that the surface area

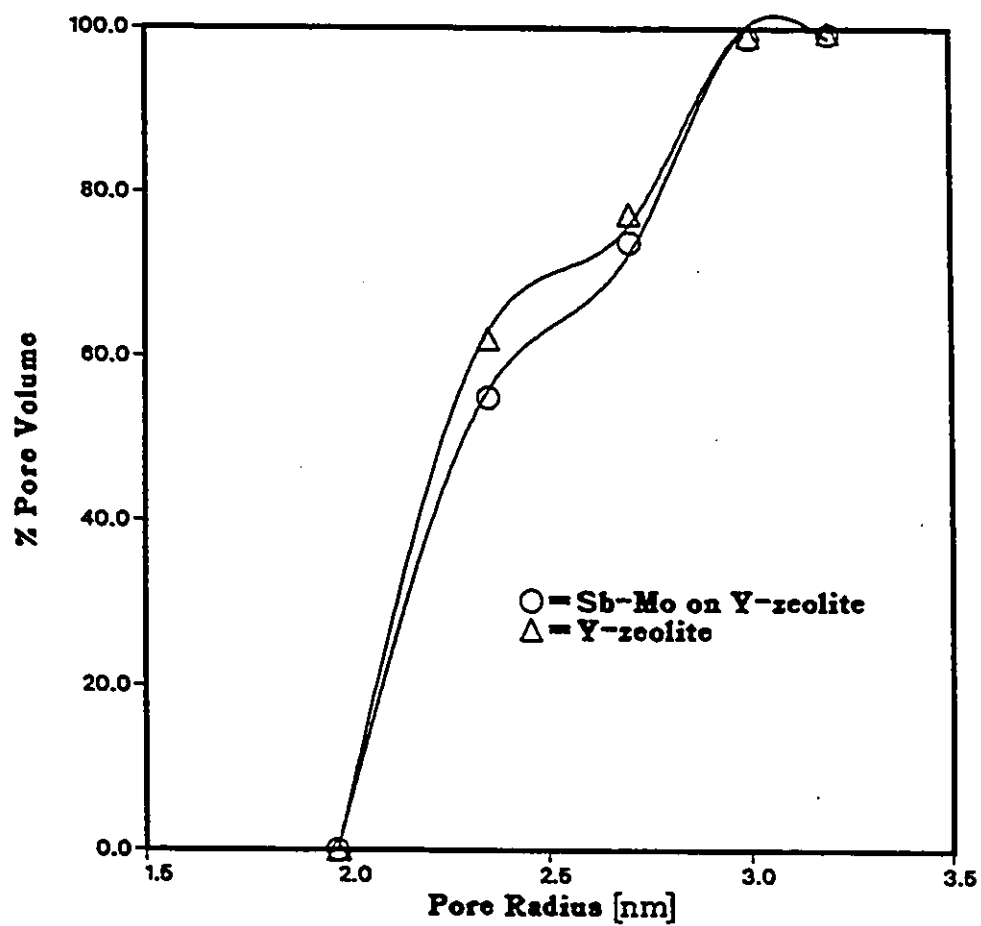


Figure 6.26: Pore Volume Distribution



Figure 6.27: Unsupported $\text{Sb}_2\text{O}_4\text{-MoO}_3$ (2:1)

of the zeolite was reduced from 550 to 367.7 m²/g after the deposition of the oxides, indicates a measure of the dispersion.

6.6 Discussion

The kinetics of the methanol oxidation to formaldehyde has been investigated over the temperature range 623–698 K over an antimony oxide-molybdenum trioxide mixture as catalyst and a possible rate mechanism has been proposed. As previously mentioned there is little work done on the use of mixtures of antimony oxide with molybdenum trioxide as catalyst. Some researchers [47,138,165,174] have used mixtures of these oxides for oxidation and dehydrogenation reactions, but not for the reaction here studied.

It has been verified that the experimental apparatus constructed for this study can produce reliable data: Small variations in the results can be attributed to the diluting inert medium (pumice stone) in the fixed-bed reactor. The reproducibility of the catalysts' preparation scheme did not present any problem. The detection systems for liquid and gas samples have proven reliable as well. Experimental runs with a MoO₃ catalyst have shown expected results accordingly to those in the literature [7,107,169]. From the second-order model obtained from experimental runs with molybdenum trioxide catalysts in Section 6.2.1 we can assume that temperature and space time changes have a higher impact on formaldehyde production than changes in methanol/air feed. This has also been proved by the researchers mentioned above. Results from experimental runs with pumice stone alone (without catalyst) show that its effect is negligible for catalysts of relatively high activity, e.g. MoO₃. Experimental runs with a Sb₂O₄ catalyst show a much lower activity than MoO₃ [6]. This low activity indicates that the real selectivity of the catalyst may be masked by the CO₂ produced by the complete oxidation of methanol on the inert medium, especially at conversions of less than 5%. As expected [6] CO was not produced under these operation conditions.



Figure 6.28: Rare-Earth Exchanged Y Zeolite

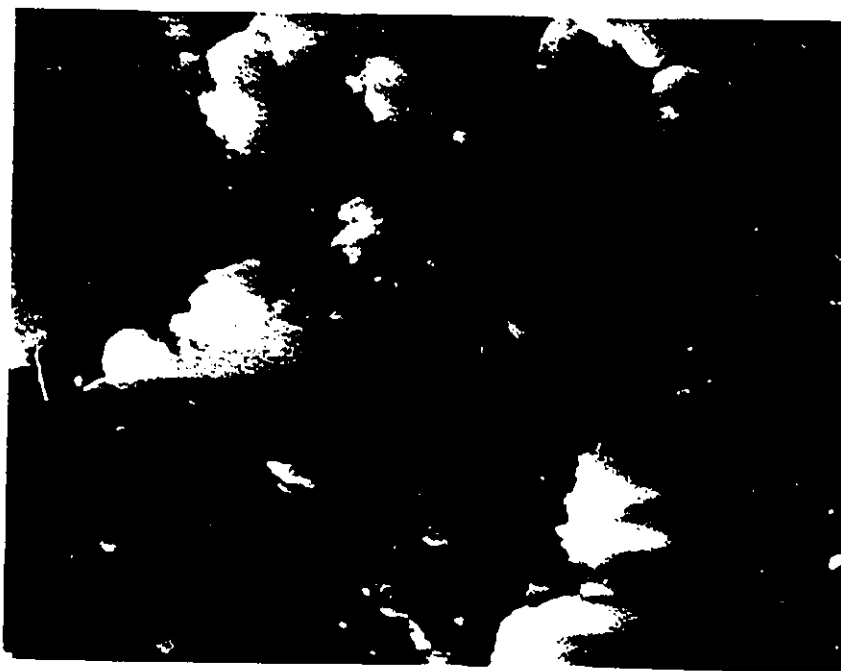


Figure 6.29: Sb_2O_4 - MoO_3 Supported on Y Zeolite

As stated in Section 2.2 there is abundant literature regarding the use of MoO_3 as catalyst for the oxidation of methanol to formaldehyde. Several mixtures of MoO_3 with other oxides have also been investigated [7,22,25,26,78,79,96,107]. However, little information is available regarding antimony oxide as a catalyst for this reaction. Its characteristics as such have been studied by Abadzhieva and Klissurski [6]. Information on the mixtures of antimony oxide with molybdenum trioxide is even more scarce. As part of a broader study on oxidation of alcohols, Fedevich *et al.* [48] used mixtures of Fe-Sb-Mo catalysts. They found that primary alcohols effectively oxidized to the corresponding aldehydes. There is no reference to any possible mechanism, or kinetic study on the effect of Sb-Mo catalyst in such a reaction. Some studies on surface characterization have been carried out in the last few years [115], but with a broader base of molybdenum oxide mixtures, and only a specific study in mind. Neither is there any reference to the effects of any specific support on the behaviour of the above mentioned catalyst.

The primary goal of this study was to produce a high yield Sb-Mo oxide catalyst for the production of formaldehyde under the specified operating conditions. Several catalysts with different Sb:Mo ratios were prepared and tested according to a defined experimental design. Catalysts were prepared unsupported as well as supported—in the case of the best catalyst obtained—on Y zeolite (loaded with $\sim 5\%$ wt. oxides).

A study on the effect of the composition of the catalyst, given in Section 6.2.3, showed that the conversion of methanol increased significantly as molybdenum trioxide content in the catalyst mixture was increased. This behaviour was expected, since a mixture of these two oxides appears to yield a synergistic effect, which has been established by several workers (Sections 1.3 and 2.2). In Figure 6.5, where operating conditions were kept constant, selectivity and conversion increased to a highest point when the oxide mixture was 67% Sb_2O_3 -33% MoO_3 . Thereafter both features declined till the minimum value of $\sim 45\%$, given by pure MoO_3 . The results of the fractional factorial design model building scheme also pointed out in the same direction. Such

a catalyst showed in this study a selectivity of nearly 100%, and a very high conversion. Previous work [110] suggested that a 1:1 oxide ratio would give a catalyst of very high yield, however a 2:1 Sb:Mo oxide ratio seemed more promising. Hence, a mixed catalyst composed of 67% Sb_2O_4 -33% MoO_3 was selected for a detailed kinetic study of methanol oxidation reaction.

As previously mentioned the operating conditions studied were: 623 to 698 K for temperature, 4 to 10 ($100 \times \text{mol}_{\text{CH}_3\text{OH}}/\text{mol}_{\text{air}}\text{h}^{-1}$) for methanol/air feed and 5 to 50 ($\text{g}_{\text{cat}}/\text{mol}_{\text{CH}_3\text{OH}}\text{h}^{-1}$) for space time. The effect of different operating variables has been described in Section 6.3.2. An increase in the temperature resulted generally in an increase in the overall conversion of methanol. However, at 698 K there were some cases where selectivity to formaldehyde decreased due to further oxidation of methanol to carbon oxides. The partial pressure of the reactants was varied by changing the flow rate through the catalyst bed, while keeping the methanol feed rate constant. It was observed that an increase in the partial pressure of methanol resulted in a very little increase in the conversion of methanol. The change in selectivity was negligible when the partial pressure of methanol was changed. The increase in space time caused a dramatic increase in the conversion without affecting the selectivity significantly. Similar results have been reported in the literature for other metal oxide catalysts.

As a result of this study it was found that several operating conditions existed at which the yield was 100%, considering the detecting capabilities of our instruments. The operating conditions at which 100% was attained are given in Table 6.14.

Based on the amount of catalyst used probably the best operating conditions are a reaction temperature of 698 K, a W/F ratio of 27.5 and $\bar{P}$ of 6. However, some other alternatives might be possible. These will depend on the particulars of each case.

The Hougen-Watson method based on the Langmuir-Hinshelwood mechanism, and the initial rate technique were used for the kinetic analysis of the data.

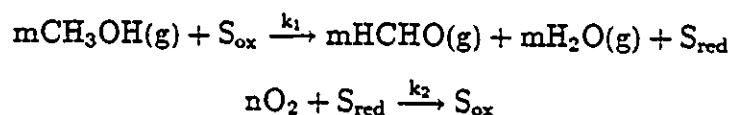
Table 6.14: Best Operating Conditions for Catalyst: 67% Sb₂O₄-33% MoO₃

Run	T (K)	W/F	R
O402	698	27.5	6
P301	673	38.75	4
Q203	648	50.0	8
Q301	673	50.0	4
Q302	673	50.0	6
Q401	698	50.0	4

As seen in Table E.1 the equilibrium constant K_p for methanol oxidation has a very high value at the operating temperatures, as well there is little change in the values of the standard free energy. Hence, this reaction can be considered highly irreversible.

The mechanism and the general kinetics of the oxidation of methanol over antimony-molybdenum oxide have been found to be similar to those obtained by Bliznakov *et al.* [24], Mars and van Krevelen [112], Bhattacharyya *et al.* [22], Hahn [83], Dosi [42] and Yang [169].

Mars and van Krevelen [112] suggested that the oxidation reactions involve a two-stage redox mechanism. According to this mechanism a steady state is assumed between the two steps



Assuming the rate of adsorption to be of the same magnitude as that of the rate of chemical reaction, the following expression was derived by using the method of Hinshelwood [70]

$$r = \frac{k_1 P_M^m}{1 + \frac{\alpha k_1 P_M^m}{k_2 P_{\text{O}_2}^n}} \quad (6.14)$$

Here m and n are the reaction order constants with respect to methanol and oxygen and α is the number of oxygen molecules required to oxidize one

molecule of methanol to formaldehyde. Equation 6.14 was integrated for an integral flow reactor for various values of m and n between 0 and 2. The values that best fitted the experimental data were $m=1$ and $n=1$ for the temperature range 648–698 K, and $\alpha=0.5$.

Jiru *et al.*[79] measured the rate of oxidation of methanol over iron oxide-molybdenum trioxide catalyst using a micro catalytic pulse technique. They first determined the rate of interaction between oxygen and partially reduced catalyst without the participation of methanol in the gaseous phase. The mechanism postulated by Jiru foresees the same type of oxidation-reduction mechanism as the one derived by Mars and van Krevelen, and envisaging that lattice oxygen of the oxide catalyst participated in the oxidation process.

Mars and van Krevelen [112] studied the oxidation mechanism of several hydrocarbons over V_2O_5 . The reaction mechanism obtained was similar to the one postulated in this research. In their case they suggested that since a maximum rate does not occur without changes in the partial pressure of oxygen and an aromatic, a reaction must take place between the aromatic compound and oxygen present on the underlying catalyst surface. They also noted a colour change in the catalyst from yellowish-brown in the oxidized state to greenish-blue in the reduced. This colour change was completely reversible and, on analysis of the reduced catalyst, a high concentration of tetravalent vanadium was found. Vanadium pentoxide contains two kinds of oxygen ions in its lattice: three fifths existing in about the same plane as the vanadium ions and two fifths arranged in planes parallel to and alternating with the first one. It is believed that the alternating lattice oxygen ions are those that interact with aromatic molecules at the surface of the catalyst.

Downie *et al.*[44] studied the kinetics of the oxidation of naphthalene and toluene. They supported a two-stage redox mechanism whereby adsorbed oxygen reacts with the other reactant remaining in the gaseous phase, and the rate of removal of adsorbed oxygen by reaction equals the rate of adsorption by oxygen.

Both mechanisms discussed above, the first in which lattice oxygen atoms react, and the other in which adsorbed oxygen molecules or atoms are removed, lead ultimately to the same rate expression.

It is difficult to prove the participation of lattice oxygen in the catalytic oxidation process in the manner described by Jiru using the pulse technique. The possibility exists that lattice oxygen participates in the reaction. However, in this type of experiments, oxygen could have been adsorbed by the oxide catalyst, and when methanol was injected into the reactor by the pulse technique, it reacted with the adsorbed oxygen.

Machiels and Sleight [102] proposed a mechanism for the oxidation of methanol to formaldehyde over molybdenum-containing catalyst in which the desorption of methanol was reversible and dissociative, forming methoxy groups. The importance of these groups has been pointed out in Section 2.2. The slow step was the breaking of a C-H bond to form adsorbed formaldehyde. The active sites contained terminal Mo=O groups and molybdenum in the reduced form. In a study by Yang [169] on the partial oxidation of methanol to formaldehyde over molybdenum-containing catalyst he found that as the molybdenum content increased, polymolybdate compounds were formed on the surface. His results indicate that the presence of polymolybdates is favorable for the partial oxidation of methanol when O₂ is present as the oxidant. He also indicated that the polymolybdates are terminal Mo=O believed to be the lattice oxygens, and are involved in the breaking of the methyl C-H bonds. In the present investigation it is quite possible that some polymolybdates had been formed on the catalyst. This is an acceptable idea since when polymolybdates are reduced they produce Mo⁵⁺ active centres at the surface of the catalyst, and an anionic vacancy, which in turn would explain the results obtained by ESR and the difficulty in identifying the phases present in the corresponding XRD spectra.

As proposed by Teller *et al.* [157] Mo would be located within the channels of electron density in the Sb₂O₄ structure with concurrent vacancy of two Sb³⁺

atoms. In our case it may be possible that the Mo^{5+} ions would form methoxy groups on terminal oxygen vacant sites, $\text{Mo}=\text{O}$, while bridged oxygen vacancy sites, $\text{Mo}-\text{O}-\text{Mo}$, may be oxidized to form an active site which would react to form a $\text{Mo}-\text{Sb}$ group, thereby being rendered inactive for our reaction, or they may be trapped inside the crystalline structure becoming inaccessible to the reactant molecules. Having only $\text{Mo}=\text{O}$ sites active for the reaction would help explain why a 100% yield was attained.

The colour of a catalyst is one of the characteristic properties of it, and a change in colour may signify a change in the structure. This would help in confirming the validity of the mechanism chosen. Unfortunately the experimental apparatus was not designed for such a verification. In our experiments catalyst samples turned black after several days of operation, and they could not be returned to the original colour on regeneration.

The kinetic study showed how active this $\text{Sb}-\text{Mo}$ oxide catalyst is. According to the proposed mechanism it would not be possible to attain a real 100% yield in any redox reaction. However, within the limits of our detection instruments it is safe to state that this yield, for practical purposes, was in fact reached. This research has opened several other possibilities in the use of this catalyst.

Chapter 7

Conclusions & Recommendations

7.1 Conclusions

Most of the conclusions are given at the end of the discussions on each section of the present study. However, some of the important conclusions are summarized below:

- (a) Sb_2O_4 showed lower activity than MoO_3 .
- (b) Sb-Mo oxide mixtures showed higher oxidation potential than oxides alone.
- (c) A mixture composed of 67% Sb_2O_4 -33% MoO_3 was chosen to be the optimum one.
- (d) The XRD spectra suggest that $\beta\text{-Sb}_2\text{O}_4$ is doped with Mo ions.
- (e) Yields of formaldehyde increased with increase temperature and space time.
- (f) For most cases little increase in conversion was found with an increase in the partial pressure of methanol.

- (g) According to the method of Yang and Hougen [168] it is suggested that the desorption of products was not a rate controlling step.
- (h) A two-stage redox mechanism was found to fit properly with values $m=1$, $n=1$ in the interval 648–698 K.
- (i) The best operating conditions at which a yield of 100% was obtained were a space time of 27.5, a methanol/air ratio of 0.06 and a temperature of 698 K. Several other operating conditions gave a yield of 100%, but they had a higher catalyst load.
- (j) The value of the activation energy for the conversion of methanol to formaldehyde was found to be 13.74 Kcal/gmol.
- (k) A catalyst prepared with the optimum oxide mixture (~ 5 wt%) but supported on Y zeolite gave yields of ~ 60 %.
- (l) A mechanism in which lattice oxygen, probably terminal Mo=O groups in a polymolybdate phase occupying interstitial sites in the β -Sb₂O₄ structure, is involved in the cleavage of methyl C-H bonds may explain the high activity of the catalyst.

7.2 Recommendations

It is advised to pursue research in several aspects that arose from this study.

- (a) Chemisorption studies to analyse the role of lattice oxygen in the Mo-Sb structure.
- (b) Further studies in XRD to properly identify the phases and crystal structures on the surface of the Sb-Mo catalysts. And further analysis of ESR spectra to determine the effect of the amount of certain oxide on the overall activity.
- (c) The use of other supports for this Sb-Mo catalyst, such as SiO₂, other zeolites, V₂O₅, etc. As well as studies about the mechanical strength, deactivation and coke formation of the Sb-Mo catalyst.

- (d) Perform kinetic studies at lower temperature (573–623 K) ranges to re-assess the constants and the order of reaction for the reaction mechanism.

Bibliography

- [1] *Exports by Commodity*. Statistics Canada, April 1990. Catalogue 65-004.
- [2] *Imports by Commodity*. Statistics Canada, April 1990. Catalogue 65-007.
- [3] *The New Lexicon Webster's Encyclopedic Dictionary of the English Language*. Lexicon Pub., Inc., New York, 1988. Canadian Edition.
- [4] *Surface Area and Porosimetry Seminar*. Micromeritics Instrument Corp., Norcross, GA, U.S.A., 1989.
- [5] S. Åsbrink and L. Khilborg. High-pressure single-crystal x-ray diffraction studies of MoO_3 . I. Lattice parameters up to 7.4 GPa. *Journal of Applied Crystallography*, 1988:960-2, 1988.
- [6] N. Abadzhieva and D. Klisurski. Oxidation of methanol to formaldehyde on Sb_2O_4 . *Kinetics & Catalysis*, 28(2):641-2, 1987.
- [7] H. Adkins and W. Peterson. The oxidation of methanol with air over iron, molybdenum, and iron-molybdenum oxides. *Journal of the American Chemical Society*, 53(4):1512-8, April 1931.
- [8] R. Alger. *Electronic Paramagnetic Resonance: Techniques and Applications*. John Wiley & Sons, Inc., New York, 1968.
- [9] J. Allison and W. Goddard III. Oxidative dehydrogenation of methanol to formaldehyde. *Journal of Catalysis*, 92:127-35, 1985.

- [10] J. Anabtawi, R.S. Mann, and K.C. Khulbe. Hydrogenation of pyridine over Ni-W/ Al_2O_3 catalyst. *Journal of Catalysis*, 63:456-62, 1980.
- [11] G. Andersson and A. Magnéli. On the crystal structure of molybdenum trioxide. *Acta Chem. Scand.*, 4:793-4, 1950.
- [12] S. Andrew. Heterogeneous catalyst preparation : The fabrication of microstructures. In B. Delmon, P. A. Jacobs, and G. Poncelet, editors, *Preparation of Catalysts : Scientific Bases for the Preparation of Heterogeneous Catalysts*, pages 429-48, Division de Catalyse, Société Chimique de Belgique, Elsevier Scientific Publishing Co., Amsterdam, 1976.
- [13] L. Aparicio. *Transition Metal-Exchanged Zeolites as Catalysts for Redox Reactions*. PhD thesis, The University of Wisconsin-Madison, 1987.
- [14] D. Bacon. *Collection and Interpretation of Industrial Data*. Technical Report, Department of Chemical Engineering, Queen's University, Kingston, Ontario, 1983.
- [15] M. Baerns, T. Gryzbek, L. Lehmann, G. Maiti, and D. Riepe. Characterization of catalysts for the oxidative coupling of methane. In *The 1989 International Chemical Congress of Pacific Basin Societies: Book of Abstracts*, The Chemical Society of Japan, The Chemical Institute of Canada and The American Chemical Society, 1989. Paper No. 151.
- [16] E. Barrett, L. Joyner, and P. Halenda. The determination of pore volume and area distribution in porous substances. I. Computations for nitrogen isotherms. *Journal of the American Chemical Society*, 73:373-80, 1951.
- [17] D. Barthomeuf. Acidic catalysis with zeolites. In F. Ribeiro, A. Rodrigues, L. Deane, and C. Naccache, editors, *Zeolites : Science and Technology*, pages 317-45, NATO Advanced Study Institute on Zeolite-Science and Technology, Martinus Nijhoff Publishers, The Hague, 1984.

- [18] F. Berry. A Mössbauer investigation of the formation and surface composition of tin-antimony oxide catalysts. *Journal of Catalysis*, 73:349-56, 1982.
- [19] F. Berry and D. Smith. A structural study of tin-antimony oxide catalysts by high-resolution electron microscopy. *Journal of Catalysis*, 88:107-18, 1984.
- [20] F. J. Berry and A. G. Maddock. Tin-119 Mössbauer and ESR investigations of tin-antimony oxide system. *Inorganica Chimica Acta*, 181-2, 1978.
- [21] M. Bersohn and J. Baird. *An Introduction to Electron Paramagnetic Resonance*. W. A. Benjamin Inc., New York, March 1966.
- [22] S. Bhattacharyya, K. Janakiran, and N. Ganguly. Kinetics of the vapor-phase oxidation of methyl alcohol on vanadium pentoxide catalysts. *Journal of Catalysis*, 5(2):128-36, 1967.
- [23] R. Bird, W. Stewart, and E. Lightfoot. *Transport Phenomena*. John Wiley & Sons, Inc., New York, 1960.
- [24] G. Bliznakov, P. Jiru, and D. Klissurski. Beitrag zum studium der oxydationskinetik des methylalkohols am MnO_2 - MoO_3 -katalysator. *Collection of Czechoslovak Chemical Communications*, 31:2995-7, 1966.
- [25] G. Bliznakov, D. Klissurski, and Y. Pesheva. Selective oxidation of methanol to formaldehyde on modified vanadia catalysts. *Revue Roumaine de Chimie*, 32(9-10):985-94, 1987.
- [26] G. Bliznakov, T. Popov, and D. Klissurski. Catalytic activity of bismuth oxide-molybdenum trioxide catalysts in the oxidation of methanol to formaldehyde. *Nauch. Tr. Plovdivski Univ., Mat., Fiz., Khim., Biol.*, 2(11):115-20, 1973. From the Univ. Plovdiv, Plovdiv, Bulg.
- [27] A. P. Bolton. Molecular sieve zeolites. In R. B. Anderson, editor, *Experimental Methods in Catalytic Research*, page 33, Academic Press, New York, 1976.

- [28] G. K. Bores. Scientific basis for catalyst preparation. In B. Delmon, P. A. Jacobs, and G. Poncelet, editors, *Preparation of Catalysts : Scientific Bases for the Preparation of Heterogeneous Catalysts*, pages 223-50. Division de Catalyse, Société Chimique de Belgique, Elsevier Scientific Publishing Co., Amsterdam, 1976.
- [29] P. Brown and J. Forsyth. Experimental study of diffraction by crystal. In B. Coles, editor, *The Crystal Structure of Solids*, chapter 5, pages 65-89, Edward Arnold Pub. Ltd., London, GB, 1973. Series: The Structures and Properties of Solids 2.
- [30] S. Brunauer, P. Emmet, and E. Teller. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60:309, 1938.
- [31] J. Carberry. *Chemical & Catalytic Reaction Engineering*. McGraw Hill Book Co., New York, 1976.
- [32] P. Carcia and E. McCarron. Metal oxides of molybdenum or molybdenum and tungsten. U.S. US 4,753,916, 1988.
- [33] N. Chen. *Process Reactor Design*. Allyn and Bacon Inc., Newton MA, U.S., 1983.
- [34] T. Chilton and A. Colburn. Mass transfer (absorption) coefficients. *Industrial & Engineering Chemistry*, 26(11):1183-7, December 1934.
- [35] J. Chung, R. Miranda, and C. Bennett. Mechanism of partial oxidation of methanol over MoO_3 . *Journal of Catalysis*, 114(2):398-410, 1988.
- [36] D. B. Dadyburjor. Selectivity over unifunctional multicomponent catalyst with nonuniform distribution of components. *Industrial & Engineering Chemistry. Fundamentals*, 24(1):16-27, 1985.
- [37] T. R. Davis and H. F. Rase. Characteristics of a nickel-contaminated cracking catalyst: Differences in the reaction and sintering characteristics of each catalyst component. *Industrial & Engineering Chemistry. Fundamentals*, 25(4):581-8, 1986.

- [38] V. de Beer and G. Schuit. CoO-MoO₃- γ -Al₂O₃ catalyst. Influence of the support. A review. In B. Delmons, P. A. Jacobs, and G. Poncelet, editors, *Preparation of Catalysts : Scientific Bases for the Preparation of Heterogeneous Catalysts*, pages 343-70, Division de Catalyse, Société Chimique de Belgique, Elsevier Scientific Publishing Co., Amsterdam, 1976.
- [39] H. de Lasa. Engineering aspects of catalytic cracking. In F. Ribeiro, A. Rodrigues, L. Deane, and C. Naccache, editors, *Zeolites : Science and Technology*, pages 491-513, NATO Advanced Study Institute on Zeolite-Science and Technology, Martinus Nijhoff Publishers, The Hague, 1984.
- [40] D. Decroocq, R. Bulle, S. Chatila, J. P. Franck, and Y. Jacquin. *Le Craquage Catalytique de Coupes Lourdes. Publications de L'Institut Français du Pétrole*, Société des Éditions Technip, Paris, 1978.
- [41] R. Díaz Real. *Hydrotreatment of Athabasca Bitumen Derived Heavy Gas Oil over Ni-W and Co-Mo Catalysts*. Master's thesis, University of Ottawa, December 1987.
- [42] M. Dosi. *Oxidation of Methanol over Molybdenum-Vanadium Oxide Catalysts*. Master's thesis, University of Ottawa, 1971.
- [43] M. Dosi. *Partial Oxidation of Methane over Halogen Modified Palladium Catalyst*. PhD thesis, University of Ottawa, 1978.
- [44] J. Downie, K. Shelstad, and W. Graydon. Kinetics of the vapour-phase oxidation of toluene over vanadium catalyst. *Canadian Journal of Chemical Engineering*, 39:201-4, October 1961.
- [45] S. Ergun. Fluid flow through packed columns. *Chemical Engineering Progress*, 48(2):89-93, February 1952.
- [46] A. Estévez, A. Fernández, and M. Márquez. Oxidation of methanol to formaldehyde on iron-molybdenum oxide catalyst, with and without chromium as a promoter. *React. Kinet. Catal. Lett.*, 38(1):193-8, 1989.
- [47] E. Fedevich, V. Zhiznevskii, and E. Mokrii. Oxidation of some alcohols on iron-tellurium-molybdenum oxide catalysts. *Khim. Teknol. Resp.*

- Mezhved. Nauk.-Tekh. Sb.*, 15:70-5, 1969. From Ref. Zh. Khim. 1970. Abstr. No. 15B934.
- [48] E. Fedevich, V. Zhiznevskii, and E. Morkii. Oxidations of some alcohols on iron-antimony-molybdenum catalysts. *Visn. L'viv. Politekh. Inst.*, 36:32-40, 1969. From Ref. Zh. Khim. 1970. Abstr. No. 3B1189.
- [49] E. Field. U. S. Patent 2,519,751. 1950.
- [50] K. Fogar. Dispersed metal catalysts. In J. Anderson and M. Boudart, editors, *CATALYSIS. Science and Technology*, chapter 4, pages 227-306, Springer-Verlag, Berlin, Heidelberg, 1984. Vol. 6.
- [51] H. Fogler. *Elements of Chemical Reaction Engineering*. Prentice-Hall, Inc., New Jersey, 1986.
- [52] N. H. Furman, editor. *Scott's Standard Methods of Chemical Analysis*. D. Van Nostrand Co. Inc., 1947. 5th edition.
- [53] I. Fux and I. Ioffe. On model-building methods and complex catalytic reaction kinetic constants estimation from experimental data. In J. Hightower, editor, *Fourth International Congress on Catalysis*, pages 1710-32, The Catalysis Society, Rice University Printing & Reproduction Department, Houston, U.S.A., July 1969.
- [54] P. Gallezot. X-ray techniques in catalysis. In J. Anderson and M. Boudart, editors, *CATALYSIS. Science and Technology*, chapter 4, pages 221-74, Springer-Verlag, Berlin, Heidelberg, 1984. Vol. 5.
- [55] B. Gamson, G. Thodos, and O. Hougen. Heat, mass and momentum transfer in the flow of gases through granular solids. *Transactions of the American Institute of Chemical Engineers*, 39:1-35, 1943.
- [56] D. Gasser and A. Baiker. Methanol oxidation on vanadium oxide catalyst prepared by *in Situ* activation of amorphous vanadium pentoxide precursor. *Journal of Catalysis*, 113(2):325-33, 1988.

- [57] H. Gesser, N. Hunter, and L. Morton. The partial oxidation of methane to methanol at high pressures: A status report. In *The 1989 International Chemical Congress of Pacific Basin Societies: Book of Abstracts*, The Chemical Society of Japan, The Chemical Institute of Canada and The American Chemical Society, 1989. Paper No. 132.
- [58] M. Glashan and A. Williamson. Isothermal liquid-vapor equilibria for system methanol-water. *Journal of Chemical & Engineering Data*, 21(2):196-9, 1976.
- [59] M. Goddard and D. M. Ruthven. Adsorption of C₈ aromatics on NaY zeolite. In D. Olson and A. Bisio, editors, *Proceedings of The Sixth International Zeolite Conference*, pages 268-75, Butterworths & Co. Ltd., Surrey, 1984.
- [60] G. Godin, C. McCain, and E. Porter. The mechanism and kinetics of the oxidation of propylene over tin oxide-antimony oxide catalyst. In J. Hightower, editor, *Fourth International Congress on Catalysis*, pages 347-65, The Catalysis Society, Rice University Printing & Reproduction Department, Houston, U.S.A., July 1969.
- [61] G. Golodets. *Heterogeneous Catalytic Reactions Involving Molecular Oxygen*. Volume 15 of *Studies in Surface Science and Catalysis*, Elsevier Scientific Publishing Co., 1983.
- [62] S. Golunski and D. Jackson. Antimony oxides: a guide to phase changes during catalyst preparation. *Applied Catalysis*, 48:123-35, 1989.
- [63] O. Goncharova and T. Yuréva. Catalytic properties of supported 12-series heteropoly compounds of molybdenum in methanol oxidation. *Kinetics & Catalysis*, 28(2):333-338, 1987. Translated from *Kinetika i Kataliz*.
- [64] G. Gottardi and E. Galli. *Natural Zeolites*. Volume 18 of *Minerals and Rocks*, Springer-Verlag, Berlin, 1985.
- [65] F. Hartley. *Supported Metal Complexes. Catalysis by Metal Complexes*, D. Reidel Publishing Co., Dordrecht, The Netherlands, 1985.

- [66] H. W. Haynes, Jr. , J. F. Parcher, and N. E. Helmer. Hydrocracking polycyclic hydrocarbons over dual-functional zeolite (faujasite)-based catalyst. *Ind. Eng. Chem. Process Des. Dev.*, 22(3):401-9, 1983.
- [67] M. Herskowitz and S. Mosseri. Global rates of reactions in trickle-bed reactors : Effects of gas and liquid flow rates. *Industrial & Engineering Chemistry. Fundamentals*, 22(1), 1983.
- [68] M. Herskowitz and J. M. Smith. Liquid distribution in trickle-bed reactors. Part I : Flow measurements. *AIChE Journal*, 24(3):439-50, 1978.
- [69] M. Herskowitz and J. M. Smith. Liquid distribution in trickle-bed reactors. Part II : Tracer studies. *AIChE Journal*, 24(3):450-4, 1978.
- [70] C. N. Hinshelwood. *The Kinetics of Chemical Change*. Oxford University Press, London, 1940.
- [71] L. Horsley. *Azeotropic Data-III*. Volume 116 of *Advances in Chemistry*, American Chemical Society, Washington, D.C., 1973.
- [72] W. Hunter and A. Jaworski. A useful method for model-building II: Synthesizing response functions from individual components. *Technometrics*, 28(4):321-7, November 1986.
- [73] T. Inui, M. Takari, T. Hagiwara, and M. Yoshikawa. Control of catalyst deactivation caused by coking in metahnol to aromatics conversion on Ga- and Zn-ion-exchanged H-ZSM-5 by addition of other alcohols. In B. Delmon and G. Froment, editors, *Catalyst Deactivation*, Vol. 34, pages 639-50, Elsevier Scientific Publishing Co., Amsterdam, The Netherlands, October 1987. Series: Studies in Surface Science and Catalysis.
- [74] I. Ioffe, V. Fyodorov, B. Gurevitch, M. Ustrayh, I. Fux, and K. Muhenberg. Applications of statistical recognition theory to the prediciton of catalytic action. In J. Hightower, editor, *Fourth International Congress on Catalysis*, pages 1142-65, The Catalysis Society, Rice University Printing & Reproduction Department, Houston, U.S.A., July 1969.

- [75] P. A. Jacobs. *Carbonogenic Activity of Zeolites*. Elsevier Scientific Publishing Co., Amsterdam, 1977.
- [76] S. Jain. *Oxidation of Methanol over Molybdenum Oxide-Tungsten Oxide Catalysts*. Master's thesis, University of Ottawa, 1976.
- [77] P. Jensen and A. Kjekshus. The crystal structure of Mo_3Sb_7 . *Acta Chem. Scand.*, 20:417-22, 1966.
- [78] P. Jiru, J. Tichy, and B. Wichterlova. Kinetik der oxidation des methylalkohols zu formaldehyd an einem oxidkatalysator. *Collection of Czechoslovak Chemical Communications*, 31:674-87, 1966.
- [79] P. Jiru, B. Wichterlova, and J. Tichy. Mechanism of oxidation of methyl alcohol to formaldehyde on oxide catalysts. In *Proceedings of the 3rd International Congress of Catalysis*, page 199, North-Holland Pub. Co., Amsterdam, 1964.
- [80] E. Jones and G. G. Fowlie. Thermodynamics of formaldehyde manufacture from methanol. *Journal of Applied Chemistry*, 3:206-13, May 1953.
- [81] S. Juhas, V. Olejnik, and M. Lichvar. Preparation of gas mixture for formaldehyde production with reduced energy. Czech. CS 242,270, 1988.
- [82] D. Kallo, G. Onyestyak, and J. Paap Jr. Hydrosulfurization of $\text{C}=\text{C}$ bond and Me^{2+} zeolite. In D. Olson and A. Bisio, editors, *Proceedings of The Sixth International Zeolite Conference*, pages 444-53, Butterworths & Co. Ltd., Surrey, 1984.
- [83] K. Hahn. *Catalytic Oxidation of Methanol*. PhD thesis, University of Ottawa, 1968.
- [84] L. Khilborg. Crystal structure studies on monoclinic and orthorhombic Mo_4O_{11} . *Ark. Kemi.*, 21:365-77, 1963.
- [85] K. Khulbe, R. S. Mann, and A. Manoogian. Electron spin resonance of vanadium pentoxide-molybdenum trioxide catalysts. *The Journal of Chemical Physics*, 60(12):4810-3, June 1974.

- [S6] Kirk-Othmer, editor. *Encyclopedia of Chemical Technology*. Volume 11. John Wiley & Sons, Inc., New York, 3rd edition, 1980.
- [S7] K. J. Klingman and H. H. Lee. Catalyst deactivation by multilayer coking: A kinetic model. *AIChE Journal*, 32(2):309-12, February 1986.
- [SS] D. Klissurski. Regularities in the selection of oxide catalysts for reaction of the type: methanol oxidation to formaldehyde. In J. Hightower, editor, *Fourth International Congress on Catalysis*, pages 649-60, The Catalysis Society, Rice University Printing & Reproduction Department, Houston, U.S.A., July 1969.
- [S9] D. Klissurski and G. Bliznakov. On catalytic oxidation of methanol to formaldehyde on MnO_2 - MoO_3 catalysts. *Comptes Rendu de l'Academie Bulgare des Sciences*, 18:549-552, 1965.
- [90] R. Kokes. Electron spin resonance spectroscopy. In R. Anderson and P. Dawson, editors, *Experimental Methods in Catalytic Research*, chapter 11, Academic Press, New York, 1976. Vol. 1, Physical Chemistry Series.
- [91] K. Konuma and Y. Tsurita. Manufacture of iron molybdate oxidation catalysts. Jpn. Kokai Tokkyo Koho JP 63 20,037 [SS 20,037], 1988.
- [92] K. Konuma and Y. Tsurita. Production of formaldehyde by methanol oxidation over iron-molybdenum catalyst. Jpn. Kokai Tokkyo Koho JP 63 22,536 [SS 22,536], 1988.
- [93] A. Kooh, J. Dubois, H. Mimoun, and C. Cameron. Maximizing the yield of methane coupling products with P-type semiconducting solids. In *The 1989 International Chemical Congress of Pacific Basin Societies: Book of Abstracts*, The Chemical Society of Japan, The Chemical Institute of Canada and The American Chemical Society, 1989. Paper No. 86.

- [94] Y. Kotera, K. Ogawa, M. Oba, K. Shimonura, M. Yonemura, A. Veno, and N. Todo. Preparation of $\text{MoO}_3\text{-CoMo-Al}_2\text{O}_3$ catalyst and its characteristics. In B. Delmon, P. A. Jacobs, and G. Poncelet, editors, *Preparation of Catalysts : Scientific Bases for the Preparation of Heterogeneous Catalysts*, pages 371-80, Division de Catalyse, Société Chimique de Belgique, Elsevier Scientific Publishing Co., Amsterdam, 1976.
- [95] L. Kouselka, P. Kupec, J. Kovac, and L. Butkovsky. Reaction mixture for formaldehyde production from methanol. Czech. CS 250,590, 1988.
- [96] L. Koval, V. Muzykantov, L. Kurina, and G. Boreskov. Reactivity of oxygen on the surface of complex oxides. IV. Isotope exchange of oxygen and selectivity in the oxidation of methanol on vanadium-chromium oxide catalyst. *Kinetika i Kataliz*, 15(5):1193-7, 1974. [English translation: Kinetics and Catalysis].
- [97] K. Laidler. *Chemical Kinetics*. McGraw Hill Book Co., New York, 2nd edition, 1965.
- [98] L. Lapidus and N. Amundson, editors. *Chemical Reactor Theory: A Review*. Prentice-Hall, Inc., New Jersey, 1977.
- [99] D. Lazarov, St. Manev, and K. Ivanov. Oxidation of methanol on the surfaces of copper-silver alloys. *Material Chemistry*, 7:331-46, 1982.
- [100] M. Lo Jacono and M. Schiavello. The influence of preparation methods on structural and catalytical properties of transition metal ions supported on alumina. In B. Delmon, P. A. Jacobs, and G. Poncelet, editors, *Preparation of Catalysts : Scientific Bases for the Preparation of Heterogeneous Catalysts*, pages 473-88, Division de Catalyse, Société Chimique de Belgique, Elsevier Scientific Publishing Co., Amsterdam, 1976.
- [101] C. Louis, J. Tatibuët, and M. Che. Catalytic properties of silica-supported molybdenum catalysts in methanol oxidation: The influence of molybdenum dispersion. *Journal of Catalysis*, 109(2):354-66, 1988.

- [102] C. Machiels and A. Sleight. Proc. Int. Conf. Uses of Molybdenum 4th, August 1982. Climax Molybdenum Co., Golden CO.
- [103] R. Maksimovskaya, V. Anufrienko, and G. Kolovertnov. Electron paramagnetic spectra of molybdate catalysts. *Kinetika i Kataliz*, 9(5):1186-7, Sept.-Oct. 1968.
- [104] R. Mann and K. Khulbe. ESR study of MoO_3 obtained from thermal decomposition of ammonium molybdate. *Bulletin of the Chemical Society of Japan*, 48(3):1021-3, March 1975.
- [105] R. S. Mann. February 1989. Personal Communication.
- [106] R. S. Mann and M. Dosi. Kinetics of vapor-phase oxidation of methyl alcohol on vanadium pentoxide-molybdenum trioxide catalyst. *Journal of Catalysis*, 28(3):282-8, 1973.
- [107] R. S. Mann and K. Hahn. Kinetics of vapor-phase oxidation of methyl alcohol over manganese dioxide-molybdenum trioxide catalyst. *Journal of Catalysis*, 15(4):329-41, December 1969.
- [108] R. S. Mann and K. W. Hahn. Oxidation of methanol over manganese dioxide-molybdenum trioxide catalyst. *Ind. Eng. Chem. Process Des. Dev.*, 9(1):43-6, January 1970.
- [109] R. S. Mann, S. Jain, and M. Dosi. Catalytic oxidation of methanol over molybdenum oxide-tungsten oxide. *Journal of Applied Chemistry and Biotechnology*, 27(2), 1977.
- [110] R. S. Mann, N. Tan, K. C. Khulbe, and R. Díaz Real. Catalytic oxidation of methanol over molybdenum oxide-antimony oxide. In *The 17th Australasian Chemical Engineering Conference*, CHEMECA 85, Broadbeach, Qsl., August 1989. Paper 17d.
- [111] M. P. Manning, J. G. Garmirian, and R. C. Reid. Carbon deposition studies using nickel and cobalt catalysts. *Ind. Eng. Chem. Process Des. Dev.*, 21(3):404-9, 1982.

- [112] P. Mars and D. van Krevelen. Oxidations carried out by means of vanadium oxide catalyst. *Special Supplement to Chemical Engineering Science*, 3:41-57, 1954.
- [113] F. Matsuda and K. Kato. Manufacture of formaldehyde. Jpn Kokai Tokkyo Koho JP 62 142,133 [SS 142,133], 1988.
- [114] D. Mclean. May 1989. Personal Communication.
- [115] D. Mesaros. *ESR investigation of methanol oxidation catalysis*. PhD thesis, University of Wisconsin, 1986.
- [116] D. Mesaros and C. Dybowski. Reduction of single-crystal molybdenum trioxide: An Electron Spin Resonance investigation after reaction with methanol. *Langmuir*, 4(4):9S3-S, 1988.
- [117] H. Midorikawa and J. Masamoto. Catalyst regeneration in manufacture of formaldehyde by methylal or methanol oxidation. Jpn. Kokai Tokkyo Koho JP 63 240,948 [SS 240,948], 1988.
- [118] S. Mikhail and W. Kimel. Densities and viscosities of methanol-water mixtures. *Journal of Chemical & Engineering Data*, 6(4):533-7, October 1961.
- [119] F. Ng and G. Barker. Activation of methane by supported superacids. In *The 1989 International Chemical Congress of Pacific Basin Societies: Book of Abstracts*, The Chemical Society of Japan, The Chemical Institute of Canada and The American Chemical Society, 1989. Paper No. 77.
- [120] T. Nishizawa, H. Hattori, T. Uematsu, and T. Shiba. Catalytic activities of cation-exchanged zeolites. In J. Hightower, editor, *Fourth International Congress on Catalysis*, pages 994-1005, The Catalysis Society, Rice University Printing & Reproduction Department, Houston, U.S.A., July 1969.
- [121] J. Nováková, L. Kubelková, and Z. Dolejšek. Primary reaction steps in the methanol-to-olefine transformation on zeolites. *Journal of Catalysis*, 108(1):208-13, 1987.

- [122] M. Olearnik, A. Miskoc, L. Butkovsky, V. Olejnik, and S. Juhas. Method for separation of formaldehyde from reaction gas. Czech. CS 245,087, 1987.
- [123] T. Ono, T. Yamanaka, Y. Kubokawa, and M. Komiyama. Structure and catalytic activity of Sb oxide highly dispersed on SnO_2 for propene oxidation. *Journal of Catalysis*, 109(2):423-32, 1988.
- [124] K. Otsuka. Partial oxidation of methane over solid catalysts. In *The 1989 International Chemical Congress of Pacific Basin Societies: Book of Abstracts*, The Chemical Society of Japan, The Chemical Institute of Canada and The American Chemical Society, 1989. Paper No. 2S.
- [125] K. Otsuka, Y. Wada, T. Komatsu, M. Inaida, and A. Morikawa. Isotopic studies on the mechanism of oxidative methane coupling over metal oxides. In *The 1989 International Chemical Congress of Pacific Basin Societies: Book of Abstracts*, The Chemical Society of Japan, The Chemical Institute of Canada and The American Chemical Society, 1989. Paper No. 13S.
- [126] R. Park. Introduction of surface spectroscopies. In R. Anderson and P. Dawson, editors, *Experimental Methods in Catalytic Research*, chapter 1, pages 1-41, Academic Press, New York, 1976. Vol. 3, Physical Chemistry Series.
- [127] P. Parmentier and C. Gleitzer. Structure cristalline de $\text{Sb}_2\text{Mo}_{10}\text{O}_{31}$. *Acta Crystallographica*, B35:1963-7, 1979.
- [128] N. Pernicone, G. Liberti, and L. Ersini. Catalytic activity of MoO_3 and the mixtures of MoO_3 with trivalent metal molybdates in the oxidation of CH_3OH to CH_2O . In J. Hightower, editor, *Fourth International Congress on Catalysis*, pages 366-84, The Catalysis Society, Rice University Printing & Reproduction Department, Houston, U.S.A., July 1969.
- [129] R. Perry and C. Chilton, editors. *Chemical Engineer's Handbook*. McGraw Hill Book Co., 5th edition, 1975.

- [130] B. Popov, N. Skomorokhva, V. Karonik, and V. Kolesnichenko. Catalytic properties of some copper intermetallides in the oxidative dehydrogenation of methanol. *React. Kinet. Catal. Lett.*, 27(2):419-423, 1985.
- [131] T. Popov, D. Klissurski, K. Ivanov, and J. Pesheva. Effect of ultrasonic treatment of the physicochemical properties of Cr-Mo-O catalysts for methanol oxidation. In B. Delmond, P. Jacobs, and G. Poncelet, editors, *Preparation of Catalysts IV. Vol. 31*, pages 191-7, Elsevier Scientific Publishing Co., Amsterdam, The Netherlands, 1987. Series: Studies in Surface Science and Catalysis.
- [132] M. Reisch. *Business*: top 50 chemicals production reaches record high. *Chemical & Engineering News*, 67(15):11-14, April 1989.
- [133] B. Robert. A procedure for estimating pore volume and area distribution from sorption isotherms. *Journal of Colloid and Interface Science*, 23:266-73, 1967.
- [134] D. Rogers and A. Skapski. The crystal structure of β -Sb₂O₄: A new polymorph. *Proceedings of the Royal Society*, 400-1, 1964.
- [135] J. Rost, H. Kretzschmar, K. Linke, and K. Wuerkert. Apparatus for cooling formaldehyde containing reaction gases from methanol oxidation. Ger. [East] DD 249,474, 1988.
- [136] J. Rost, E. Reichel, I. Bartosch, H. Frydrych, P. John, H. Kretzschmar, and W. Ost. Formaldehyde manufacture by air oxidation. Ger. (East) DD 249,473, 1987.
- [137] D. Rouleau. *Catalytic Oxidation of Isobutylene*. PhD thesis, University of Ottawa, April 1964.
- [138] P. Ruiz, B. Zhou, M. Remy, T. Machej, F. Aoun, B. Doumain, and B. Delmon. Two-phase catalysts in selected oxidation and related reactions. *Catalysis Today*, 1:181-95, 1987.
- [139] I. Sambi. *Hydrotreatment of Athabasca Bitumen Derived Heavy Gas Oil over Modified Zeolite Supported Catalyst*. PhD thesis, University of

Ottawa, 1985.

- [140] J. Sanders. The electron microscopy of catalysts. In J. Anderson and M. Boudart, editors, *CATALYSIS. Science and Technology*, chapter 2, pages 51-158, Springer-Verlag, Berlin, Heidelberg, 1985. Vol. 7.
- [141] A. Sanger. Oxidative coupling of methane on mixed oxide catalysts. In *The 1989 International Chemical Congress of Pacific Basin Societies: Book of Abstracts*, The Chemical Society of Japan, The Chemical Institute of Canada and The American Chemical Society, 1989. Paper No. 143.
- [142] C. Sargeant and J. Embury. Transmission and scanning electron microscopy. In R. Anderson and P. Dawson, editors, *Experimental Methods in Catalytic Research*, chapter 4, pages 140-86, Academic Press, New York, 1976. Vol. 2, Physical Chemistry Series.
- [143] C. N. Satterfield. *Heterogeneous Catalysis in Practice*. McGraw Hill Book Co., New York, 1980.
- [144] I. Sax. *Dangerous Properties of Industrial Materials*. Reinhold Book Corp., Albany, N.Y., 3rd edition, 1968.
- [145] N. Schönberg. I. On the existence of a metallic molybdenum oxide. *Acta Chem. Scand.*, 8:617-9, 1954.
- [146] J. Schroeder, J. Halawa, M. Mieczyslaw, T. Kelm, I. Cieslik, A. Jakubowicz, E. Kauf, and B. Zarychta. Method and apparatus for temperature stabilization in formaldehyde production. Pol. PL 130,292, 1988.
- [147] H. Schultz, Z. Siwei, and W. Baumgartner. Coke forming reactions during methanol conversion on zeolite catalysts. In B. Delmon and G. Froment, editors, *Catalyst Deactivation, Vol. 34*, pages 479-92, Elsevier Scientific Publishing Co., Amsterdam, The Netherlands, October 1987. Series: Studies in Surface Science and Catalysis.
- [148] J. Scott, editor. *Zeolite Technology and Applications : Recent Advances*. Noyes Data Corp., New Jersey, 1980.

- [149] K. S. Seshadri and L. Petrakis. Electron spin resonance spectra and catalytic activity of molybdenum oxide on various supports. *The Journal of Physical Chemistry*, 74(23):4102-S, 1970.
- [150] J. H. Sinfelt. Influence of technology on catalytic science. *Industrial & Engineering Chemistry. Fundamentals*, 25(1):2-9, 1986.
- [151] J. Smith. *Chemical Engineering Kinetics*. McGraw Hill Book Co., New York, 3rd edition, 1981.
- [152] C. Strouts, H. Wilson, and R. Parry-Jones, editors. *Chemical Analysis*, chapter 28. Volume II, Clarendon Press, Oxford, 1962.
- [153] A. Sultanov, G. Talipov, N. Inoyatov, V. Tatarskii, and K. Samigov. EPR study of aluminum-nickel-molybdenum oxide catalysts. *Kinetika i Kataliz*, 12(5):1259-63, Sept.-Oct. 1971.
- [154] E. A. Swabb and B. C. Gates. Diffusion, reaction, and fouling in H-Mordenite crystallites. The catalytic dehydration of methanol. *Industrial & Engineering Chemistry. Fundamentals*, 11(4):540-5, 1972.
- [155] M. Szustakowki, J. Schroeder, E. Francman, I. Cieslik, B. Zarychta, T. Kelm, and A. Jakubowicz. Process and catalysts for formaldehyde manufacture from methanol. Pol. PL 140,697, 1987.
- [156] L. Tataryn. *Formaldehyde on trial (the politics of health in a chemical society)*. James Lorimer & Co., Toronto, 1983.
- [157] R. Teller, M. Antonio, J. Brazdil, M. Mehicic, and R. Grasselli. Stabilization of high-temperature antimony oxide with molybdenum incorporation. Structure of Mo-doped Sb_2O_4 by powder neutron diffraction and extended x-ray absorption fine structure spectroscopy. *Inorganic Chemistry*, 24(21):3370-5, 1985.
- [158] C. L. Thomas. Chemistry of cracking catalysts. *Industrial & Engineering Chemistry*, 41(11):2564-73, November 1949.
- [159] G. Thornton. A neutron diffraction study of $\alpha\text{-Sb}_2\text{O}_4$. *Acta Crystallographica*, B33:1271-3, 1977.

- [160] H. Topsøe, B. Clausen, N. Topsøe, and E. Pedersen. Recent basic research in hydrodesulfurization catalysts. *Industrial & Engineering Chemistry, Fundamental*, 25(1):25-36, 1986.
- [161] J. van Klinken and R. H. van Dongen. Catalyst dilution for improved performance of laboratory trickle-flow reactors. *The Chemical Engineering Journal*, 35:59-66, 1980.
- [162] P. B. Venuto and E. T. Habib, Jr. *Fluid Catalytic Cracking with Zeolite Catalysts*. Volume 1 of *Chemical Industries*, Marcel Dekker, Inc., New York, 1979.
- [163] P. Vollhardt. *Organic Chemistry*. W. H. Freeman and Co., New York, 1987.
- [164] J. Walker. *Formaldehyde*. Volume 159 of *American Chemical Society Monographs*, Robert E. Krieger Pub. Co., New York, 3rd edition, 1975.
- [165] L. Wang, M. Tsuda, K. Eguchi, and H. Arai. The active species of Sb-Mo-O catalyst for the oxidative esterification of ethanol. *Chemistry Letters*, 1889-92, 1987.
- [166] R. Weast, editor. *Handbook of Chemistry & Physics*. CRC Press Inc., Boca Raton, FL, 1985-1986. 66th edition.
- [167] C. Wilke and O. Hougen. Mass transfer in the flow of gases through granular solids extended to low modified Re numbers. *Transactions of the American Institute of Chemical Engineers*, 41:445-51, 1945.
- [168] K. Yang and O. Hougen. Determination of mechanism of catalyzed gaseous reactions. *Chemical Engineering Progress*, 46(3):146-58, March 1950.
- [169] T. Yang. *The Partial Oxidation of Methanol to Formaldehyde over Molybdenum-Containing Catalysts*. PhD thesis, Texas A&M University, 1982.
- [170] T. Yang and J. Lunsford. Partial oxidation of methanol to formaldehyde over molybdenum oxide on silica. *Journal of Catalysis*, 103(1):55-64,

1987.

- [171] T. Yegovich, F. Kurata, and G. Swift. Density and viscosity of aqueous solutions of methanol and acetone from freezing point to 10 °C. *Journal of Chemical & Engineering Data*, 16(2):222-6, 1971.
- [172] F. Yoshida, D. Ramaswami, and O. Hougen. Temperatures and partial pressures at the surfaces of catalyst particles. *AIChE Journal*, 8(1):5-11, 1962.
- [173] C. Yu, W. Hatcher, and W Bertsch. Hydrodenitrogenation of quinoline with Y-type zeolite. *Industrial Engineering Chemistry Research*, 28:13-20, 1989.
- [174] B. Zhou, S. Ceckiewicz, and B. Delmon. Synergy in N-Ethylformamide dehydration by mixtures of MoO_3 and $\alpha - \text{Sb}_2\text{O}_4$. *The Journal of Physical Chemistry*, 91(19):5061-7, 1987.

Appendix A

Calibration Curves

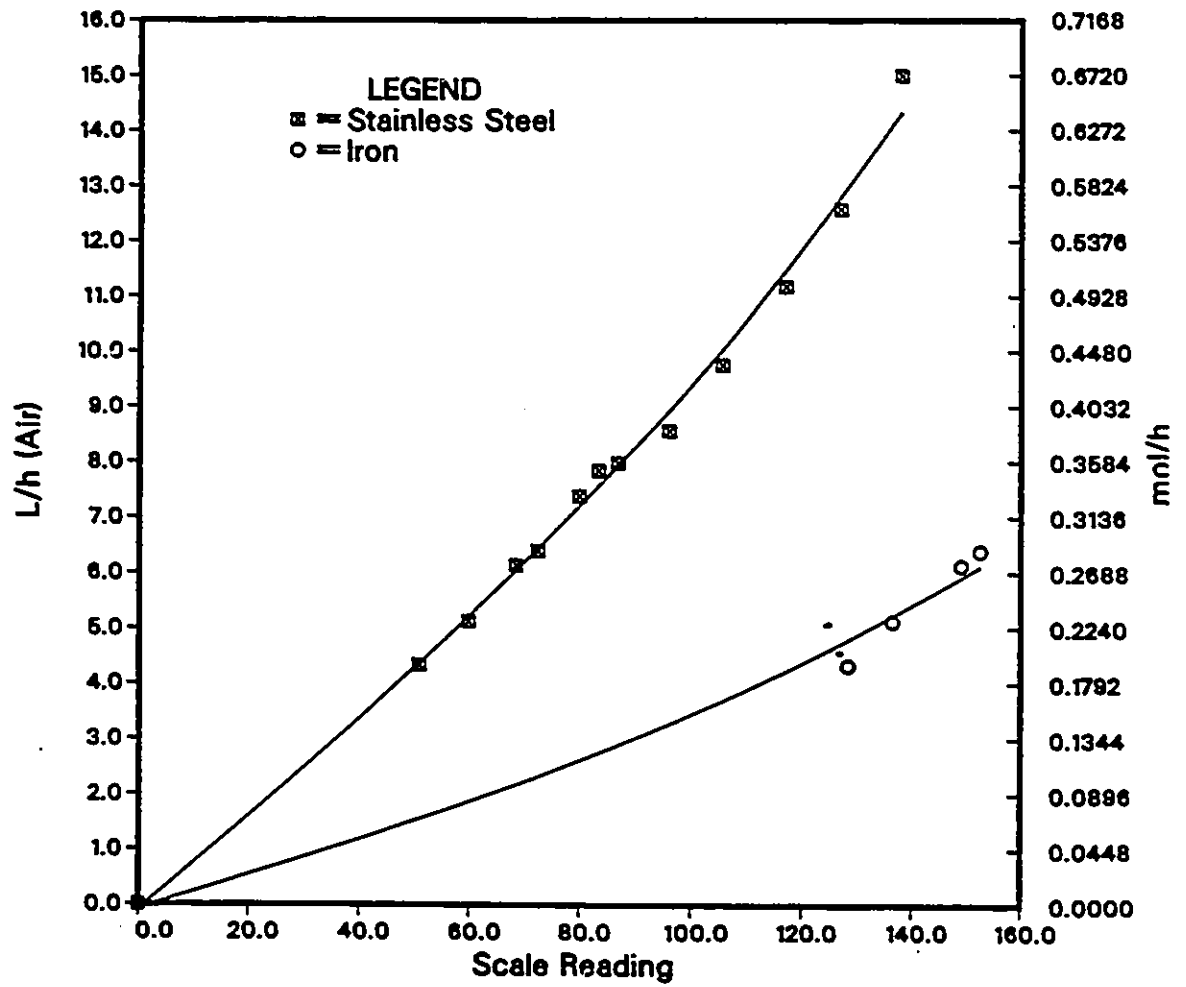
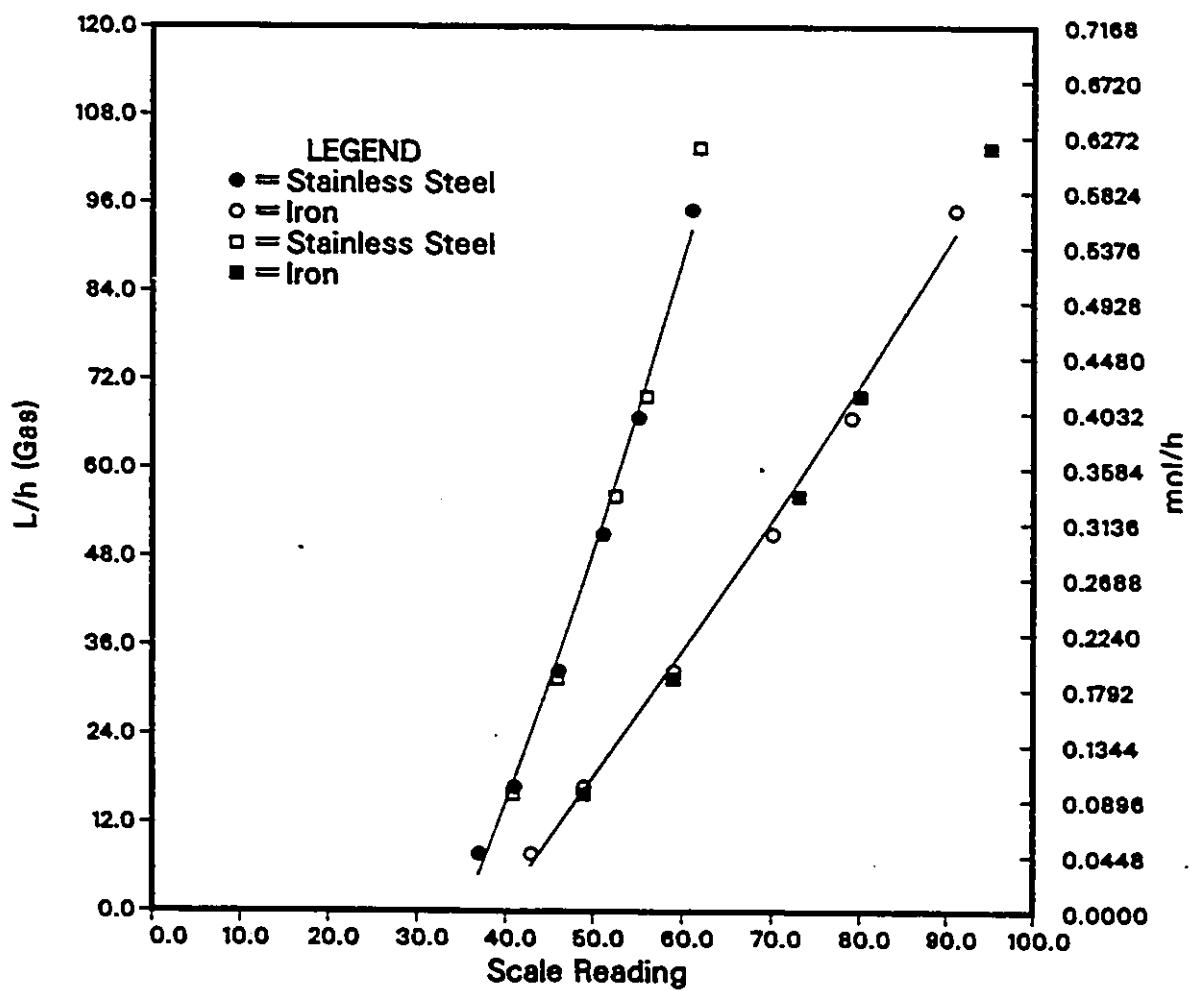


Figure A.1: Calibration Curve for Air

Figure A.2: Calibration Curve for Gas Mixture (CO,CO₂,N₂)

Appendix B

Computer Programs

B.1 Programs for Mass Balance

B.1.1 Main Program: MBAL FORTRAN

```
C
C
C
C
      INTEGER N,I
      REAL RUN(300),REP(300),MO(300),GFR(300),C2N(300),
      *CN(300),FW(300),MW(300),
      *N2(300),FC2(300),FC(300),WT(300),FT(300),
      *MT(300),FF(300),T(300),FM(300),
      *MOL(300),ERR(300),CON(300),SEL(300),
      *YIE(300),TT(300),WF(300),R(300)
C
      READ(8,10) N
10  FORMAT(I3)
      DO 30 I=1,N
      READ(8,11) RUN(I),TT(I),WF(I),R(I),GFR(I),C2N(I),
      1CN(I),FW(I),MW(I),MO(I)
11  FORMAT(A4,1X,F4.0,1X,F5.2,1X,F4.1,3(1X,E8.3),1X,F6.4,
```

```

11X,F7.4,1X,E9.4)
30 CONTINUE
DO 31 I=1,N
  N2(I)=GFR(I)*0.79
  FC2(I)=N2(I)*C2N(I)
  FC(I)=N2(I)*CN(I)
  WT(I)=1/(1+FW(I)+MW(I))
  FT(I)=FW(I)*WT(I)
  MT(I)=MW(I)*WT(I)
  FF(I)=FT(I)*(MO(I)+FC2(I)+FC(I))/(1-FT(I))
  T(I)=MO(I)+FF(I)+FC(I)+FC2(I)
  FM(I)=MT(I)*T(I)
  MOL(I)=FF(I)+FM(I)+FC(I)+FC2(I)
  ERR(I)=(MO(I)-MOL(I))/MO(I)*100
  CON(I)=1-FM(I)/MOL(I)
  SEL(I)=FF(I)/(FF(I)+FC(I)+FC2(I))
  YIE(I)=CON(I)*SEL(I)
31 CONTINUE
20 FORMAT(1X,////////)
  WRITE(9,21)
21 FORMAT(1X,///,15X,'MATERIAL BALANCE',////)
  WRITE(9,22)
22 FORMAT(1X,'RUN ',2X,'ME (MOL/H)',2X,'GFR (MOL/H)',
*2X,'CO2/N2',3X,'CO/N2',4X,'F/W',5X,'M/W',//)
DO 12 I=1,N
  WRITE(9,23) RUN(I),MO(I),GFR(I),C2N(I),CN(I),FW(I),MW(I)
23 FORMAT(1X,A4,2X,E10.5,1X,E8.3,3X,E8.3,2X,E8.3,2X,F6.4,1X,F7.4)
12 CONTINUE
  WRITE(9,20)
  WRITE(9,26)
26 FORMAT(1X,'RUN ',4X,'N2 (MOL/H)',1X,'W/T',8X,'F/T',
*8X,'M/T',4X,'T (MOL/H)',3X,'FF (MOL/H)',1X,'FM (MOL/H)',1X,
*'TMOL(OUT)/H',//)
DO 13 I=1,N
  WRITE(9,24) RUN(I),N2(I),WT(I),FT(I),MT(I),T(I),FF(I),
*FM(I),MOL(I)
24 FORMAT(1X,A4,2X,E8.3,2X,7(E9.4,2X))

```

```

13  CONTINUE
    WRITE(9,20)
    WRITE(9,27)
27  FORMAT(1X,'RUN ',4X,'T (K) ',2X,'W/F',5X,'R',7X,
    *'ERROR',5X,'CONV ',3X,'SELECT',
    *3X,'YIELD',//)
    DO 14 I=1,N
    WRITE(9,25) RUN(I),TT(I),WF(I),R(I),ERR(I),CON(I),SEL(I),YIE(I)
25  FORMAT(1X,A4,4X,F6.1,3X,F5.2,3X,F4.1,4(3X,F7.3))
14  CONTINUE
    STOP
    END

```

B.1.2 Exec (Main program): MB EXEC

To execute type 'MB'. It automatically executes MBAL FORTRAN. Data will be taken from a file called MB DATA, and results will be written in a file called MB RESULT, from where they can be printed (as in Section D.2).

```

GLOBAL TXTLIB VLKMLIB VFORTLIB CMSLIB IMSLDLIB PLOTLIB
FORTVS MBAL
FILE 8 DISK MB DATA(LRECL 80 BLKSIZE 80 RECFM F PERM
FILE 9 DISK MB RESULT A (PERM RECFM F LRECL 132
LOAD MBAL(CLEAR START

```

B.2 Programs for Experimental Modelling

B.2.1 Main Program: MODEL FORTRAN

```

C
C
C
REAL S,C,X1,X2,X3,X,T,WF,R,SUM,XTX,XT,XTS,XTC,XTXI,A,D,CON,SEL,Y
INTEGER I,J,K,INDX
DIMENSION S(4),C(4),X1(4),X2(4),X3(4),X(4,4),X0(4),T(4),WF(4),

```

```

      *R(4),XT(4,4),XTX(4,4),XTS(4),XTC(4),XTXI(4,4),INDX(4),A(4,4),
      *CON(4),SEL(4),Y(10)
      DO 10 I=1,4
      READ(5,20) C(I),S(I),X1(I),X2(I),X3(I),T(I),WF(I),R(I)
20  FORMAT(1X,F5.3,1X,F5.3,3(1X,F4.1),1X,F5.1,1X,F5.2,1X,F3.0)
      X0(I)=1
      X(I,1)=X0(I)
      X(I,2)=X1(I)
      X(I,3)=X2(I)
      X(I,4)=X3(I)
10  CONTINUE
      WRITE(6,70)
70  FORMAT(//,1X,'CON    SEL    X1  X2  X3  TEMP  W/F    R',//)
      DO 71 I=1,4
      WRITE(6,20) C(I),S(I),X1(I),X2(I),X3(I),T(I),WF(I),R(I)
71  CONTINUE
      WRITE(6,21)
      DO 11 I=1,4
      WRITE(6,22) (X(I,J),J=1,4)
11  CONTINUE
21  FORMAT(////////,5X,'MATRIX: X',//)
22  FORMAT(/,3X,4(F3.0,2X))

C
C----- X TRANSPOSE
C
      DO 12 I=1,4
      DO 12 J=1,4
      XT(I,J)=X(J,I)
12  CONTINUE
      WRITE(6,23)
23  FORMAT(//,5X,'MATRIX: X TRANSPOSE',//)
      DO 13 I=1,4
      WRITE(6,22) (XT(I,J),J=1,4)
13  CONTINUE

C
C----- X TRANSPOSE X

```

```

C
    SUM=0
    DO 14 I=1,4
    DO 55 J=1,4
    DO 15 K=1,4
    SUM=SUM+XT(J,K)*X(K,I)
15  CONTINUE
    XTX(I,J)=SUM
    SUM=0
55  CONTINUE
14  CONTINUE
    WRITE(6,24)
24  FORMAT(//,5X,'MATRIX: X TRANSPOSE X',//)
    DO 16 I=1,4
    WRITE(6,22) (XTX(I,J),J=1,4)
16  CONTINUE
C
C-----X TRANSPOSE S
C
    SUM=0
    DO 17 J=1,4
    DO 18 K=1,4
    SUM=SUM+XT(J,K)*S(K)
18  CONTINUE
    XTS(J)=SUM
    SUM=0
17  CONTINUE
    WRITE(6,25)
25  FORMAT(//,5X,'MATRIX: X TRANSPOSE S',//)
    DO 19 I=1,4
    WRITE(6,26) I,XTS(I)
19  CONTINUE
26  FORMAT(2X,'XTS(',I1,') = ',F6.3)
C
C-----X TRANSPOSE C
C
    SUM=0

```

```

        DO 50 J=1,4
        DO 51 K=1,4
        SUM=SUM+XT(J,K)*C(K)
51  CONTINUE
        XTC(J)=SUM
        SUM=0
50  CONTINUE
        WRITE(6,27)
27  FORMAT(//,5X,'MATRIX: X TRANSPOSE C',//)
        DO 52 I=1,4
        WRITE(6,28) I,XTC(I)
52  CONTINUE
28  FORMAT(2X,'XTC(',I1,') = ',F6.3)
        SUM=0.
C
C------(X TRANSPOSE X) INVERSE
C
        DO 32 I=1,4
        DO 31 J=1,4
        A(I,J)=XTX(I,J)
        XTXI(I,J)=0.
31  CONTINUE
        XTXI(I,I)=1.
32  CONTINUE
        CALL LUDCMP(A,4,4,INDX,D)
        DO 33 J=1,4
        CALL LUBKSB(A,4,4,INDX,XTXI(1,J))
33  CONTINUE
        WRITE(6,34)
34  FORMAT(//,5X,'MATRIX: (X TRANSPOSE X) INVERSE',//)
        DO 35 I=1,4
        WRITE(6,36) (XTXI(I,J),J=1,4)
35  CONTINUE
36  FORMAT(/,3X,4(F5.2,2X))
C
C------(X TRANSPOSE X) INVERSE X TRANSPOSE C
C

```

```

      SUM=0
      DO 40 J=1,4
        DO 41 K=1,4
          SUM=SUM+XTXI(J,K)*XTC(K)
41      CONTINUE
        CON(J)=SUM
        SUM=0
40      CONTINUE
        WRITE(6,42)
42      FORMAT(//,5X,'MATRIX: (X TRANSPOSE X) INVERSE X TRANSPOSE C',//)
      DO 43 I=1,4
        K=I-1
        WRITE(6,44) K,CON(I)
44      FORMAT(2X,'C',I1,' = ',F8.5)
43      CONTINUE
C
C------(X TRANSPOSE X) INVERSE X TRANSPOSE S
C
      SUM=0
      DO 45 J=1,4
        DO 46 K=1,4
          SUM=SUM+XTXI(J,K)*XTS(K)
46      CONTINUE
        SEL(J)=SUM
        SUM=0
45      CONTINUE
        WRITE(6,47)
47      FORMAT(//,5X,'MATRIX: (X TRANSPOSE X) INVERSE X TRANSPOSE S',//)
      DO 48 I=1,4
        K=I-1
        WRITE(6,49) K,SEL(I)
49      FORMAT(2X,'S',I1,' = ',F8.5)
48      CONTINUE
C
C-----YIELD EQ. PARAMETERS (2ND ORDER)
C
      Y(1)=CON(1)*SEL(1)

```

```

Y(2)=CON(1)*SEL(2)+CON(2)*SEL(1)
Y(3)=CON(3)*SEL(1)+CON(1)*SEL(3)
Y(4)=CON(4)*SEL(1)+CON(1)*SEL(4)
Y(5)=CON(2)*SEL(2)
Y(6)=CON(3)*SEL(2)+CON(2)*SEL(3)
Y(7)=CON(4)*SEL(2)+CON(2)*SEL(4)
Y(8)=CON(3)*SEL(3)
Y(9)=CON(4)*SEL(3)+CON(3)*SEL(4)
Y(10)= CON(4)*SEL(4)
C
C
C
WRITE(6,61)
61 FORMAT(///,5X,'YIELD 2ND ORDER EQUATION PARAMETERS',///)
DO 60 I=1,10
WRITE(6,62) I,Y(I)
62 FORMAT(/,3X,'Y(',I2,') = ',F9.4)
60 CONTINUE
C
C
C
STOP
END

SUBROUTINE LUDCMP(A,N,NP,INDX,D)
REAL AAMAX,DUM,D,SUM
INTEGER IMAX,I,J,K,N,NP
PARAMETER (NMAX=100,TINY=1.0E-20)
DIMENSION A(NP,NP),INDX(N),VV(NMAX)
D=1
DO 112 I=1,N
AAMAX=0
DO 111 J=1,N
IF (ABS(A(I,J)).GT.AAMAX) AAMAX=ABS(A(I,J))
111 CONTINUE
IF (AAMAX.EQ.0) PAUSE 'SINGULAR MATRIX'
VV(I)=1./AAMAX

```

```
112 CONTINUE
    DO 119 J=1,N
    DO 114 I=1,J-1
        SUM=A(I,J)
        DO 113 K=1,I-1
            SUM=SUM-A(I,K)*A(K,J)
113     CONTINUE
        A(I,J)=SUM
114     CONTINUE
        AAMAX=0
        DO 116 I=J,N
            SUM=A(I,J)
            DO 115 K=1,J-1
                SUM=SUM-A(I,K)*A(K,J)
115     CONTINUE
            A(I,J)=SUM
            DUM=VV(I)*ABS(SUM)
            IF (DUM.GE.AAMAX) THEN
                IMAX=I
                AAMAX=DUM
            ENDIF
116     CONTINUE
            IF(J.NE.IMAX) THEN
                DO 117 K=1,N
                    DUM=A(IMAX,K)
                    A(IMAX,K)=A(J,K)
                    A(J,K)=DUM
117     CONTINUE
                D=-D
                VV(IMAX)=VV(J)
            ENDIF
            INDX(J)=IMAX
            IF (A(J,J).EQ.0)A(J,J)=TINY
            IF(J.NE.N)THEN
                DUM=1./A(J,J)
                DO 118 I=J+1,N
                    A(I,J)=A(I,J)*DUM
```

```
118  CONTINUE
      ENDIF
119  CONTINUE
      RETURN
      END

SUBROUTINE LUBKSB(A,N,NP,INDX,B)
REAL SUM
INTEGER LL,II,I,J,NP,N
DIMENSION A(NP,NP),INDX(N),B(N)
II=0
DO 212 I=1,N
  LL=INDX(I)
  SUM=B(LL)
  B(LL)=B(I)
  IF(II.NE.0)THEN
    DO 211 J=II,I-1
      SUM=SUM-A(I,J)*B(J)
211    CONTINUE
    ELSE IF (SUM.NE.0) THEN
      II=I
    ENDIF
  B(I)=SUM
212 CONTINUE
  DO 214 I=N,1,-1
    SUM=B(I)
    IF(I.LT.N) THEN
      DO 213 J=I+1,N
        SUM=SUM-A(I,J)*B(J)
213    CONTINUE
    ENDIF
    B(I)=SUM/A(I,I)
214 CONTINUE
  RETURN
  END
```

B.2.2 Exec (Main Program) : MD EXEC

To execute type 'MD'. It automatically executes MODEL FORTRAN. Data will be taken from a file called MD DATA, and results will be written in a file called MD RESULT, from where they can be printed.

```
GLOBAL TXTLIB VLKMLIB VFORTLIB CMSLIB INSLDLIB PLOTLIB
FORTVS MODEL
FILE 5 DISK MD DATA(LRECL 80 BLKSIZE 80 RECFM F PERM
FILE 6 DISK MD RESULT A (PERM RECFM F LRECL 132
LOAD MODEL(CLEAR START
```

B.3 Program for Kinetic Constants

B.3.1 Main Program: REAC FORTRAN

```
C
C
C
      REAL TP,MM,NN,T,R,AL,PM,PN,PO,WF,XC,X,Y,B1,B0,RATIO,K1,K2,K11,K22,
      *RR
      INTEGER NM,IX,III,II,I,NR,N,NT,L
      DIMENSION WF(15),XC(15),X(15),Y(15),K1(15),K2(15)
      WRITE(6,20)
      READ(5,10) TP,NM
      DO 30 IX=1,NM
      READ(5,11) NT,MM,NN
      WRITE(6,21) IX,MM,NN
      WRITE(6,22)
      WRITE(6,23)
      WRITE(6,22)
      DO 31 III=1,NT
      READ(5,12) T,NR
      WRITE(6,24) T
```

```

DO 32 II=1,NR
READ(5,13) R,AL,N
PM=TP*R
PM=TP*(1-R)*0.79
PO=TP*(1-R)*0.21
DO 33 I=1,N
READ(5,14) WF(I),XC(I)
IF(IX.EQ.1) THEN
  Y(I)=-WF(I)*(PM/(ALOG(1-XC(I))))
  X(I)=4*AL*(PO-0.5*XC(I)*PM)**0.5/(ALOG(1-XC(I)))
ENDIF
IF(IX.EQ.2) THEN
  Y(I)=WF(I)/(XC(I)*AL)
  X(I)=-ALOG(1-XC(I))/(PM*XC(I)*AL)
ENDIF
IF(IX.EQ.3) THEN
  Y(I)=WF(I)/(XC(I)*AL)
  X(I)=2*(1-XC(I))**0.5/(PM**0.5*XC(I)*AL)
ENDIF
IF(IX.EQ.4) THEN
  Y(I)=-WF(I)*PM/(ALOG(1-XC(I)))
  X(I)=-2*AL*ALOG(PO-0.5*XC(I)*PM)/(ALOG(1-XC(I)))
ENDIF
IF(IX.EQ.5) THEN
  Y(I)=-WF(I)*PM**0.5/(2*(1-XC(I))**0.5)
  X(I)=2*AL*(PO-0.5*XC(I)*PM)**0.5/
1 (PM**0.5*(1-XC(I))**0.5)
ENDIF
IF(IX.EQ.6) THEN
  Y(I)=WF(I)*(1-XC(I))*PM**2
  X(I)=-4*AL*PM*(1-XC(I))*(PO-0.5*PM*XC(I))**0.5
ENDIF
IF(IX.EQ.7) THEN
  Y(I)=WF(I)*PM**2*(1-XC(I))
  X(I)=-2*AL*PM*(1-XC(I))*ALOG(PO-0.5*PM*XC(I))
ENDIF
IF(IX.EQ.8) THEN

```

```

      Y(I)=WF(I)/(AL*XC(I))
      X(I)=1/(PM**2*(1-XC(I))*XC(I)*AL)
    ENDIF
    IF(IX.EQ.9) THEN
      Y(I)=WF(I)/(AL*XC(I))
      X(I)=1/(PM**1.5*AL*XC(I)*(1-XC(I))**0.5)
    ENDIF
    IF(IX.EQ.10) THEN
      Y(I)=WF(I)*PM**1.5*(1-XC(I))**0.5
      X(I)=-4*AL*PM**0.5*(1-XC(I))**0.5*(PO-0.5*PM*XC(I))**0.5
    ENDIF
    IF(IX.EQ.11) THEN
      Y(I)=WF(I)*PM**1.5*(1-XC(I))**0.5
      X(I)=-2*AL*(1-XC(I))**0.5*PM**0.5*ALOG(PO-0.5*PM*XC(I))
    ENDIF
33  CONTINUE
C    DO 35 I=1,N
C    WRITE(6,27) I,X(I),I,Y(I)
C35  CONTINUE
      CALL LS(X,Y,N,B1,B0,RATIO)
      IF(IX.EQ.1) THEN
        K1(II)=1/B0
        K2(II)=1/B1
      ENDIF
      IF(IX.EQ.2) THEN
        K1(II)=1/B1
        K2(II)=1/B0
      ENDIF
      IF(IX.EQ.3) THEN
        K1(II)=1/B1
        K2(II)=1/B0
      ENDIF
      IF(IX.EQ.4) THEN
        K1(II)=1/B0
        K2(II)=1/B1
      ENDIF
      IF(IX.EQ.5) THEN

```

```
        K1(II)=1/B0
        K2(II)=1/B1
    ENDIF
    IF(IX.EQ.6) THEN
        K1(II)=1/B0
        K2(II)=1/B1
    ENDIF
    IF(IX.EQ.7) THEN
        K1(II)=1/B0
        K2(II)=1/B1
    ENDIF
    IF(IX.EQ.8) THEN
        K1(II)=1/B1
        K2(II)=1/B0
    ENDIF
    IF(IX.EQ.9) THEN
        K1(II)=1/B1
        K2(II)=1/B0
    ENDIF
    IF(IX.EQ.10) THEN
        K1(II)=1/B0
        K2(II)=1/B1
    ENDIF
    IF(IX.EQ.11) THEN
        K1(II)=1/B0
        K2(II)=1/B1
    ENDIF
    RR=R*100
    WRITE(6,25) RR,K1(II),K2(II)
32  CONTINUE
    K11=0
    K22=0
    DO 34 L=1,NR
        K11=K11+K1(L)
        K22=K22+K2(L)
34  CONTINUE
    K11=K11/NR
```

```

      K22=K22/NR
      WRITE(6,26) K11,K22
31  CONTINUE
30  CONTINUE
10  FORMAT(F6.1,1X,I2)
11  FORMAT(I2,1X,F3.1,1X,F3.1)
12  FORMAT(F6.1,1X,I2)
13  FORMAT(F4.2,1X,F4.2,1X,I2)
14  FORMAT(F6.2,1X,F5.3)
20  FORMAT(//,'RATE CONSTANTS FOR VARIOUS MECHANISMS',//)
21  FORMAT(10X,'RATE CONSTANTS FOR MECHANISM # ',I2,5X,'FOR M = ',
    *F3.1,3X,'N = ',F3.1,//)
22  FORMAT(/,'*****
*****',/)
23  FORMAT(' ',1X,'TEMPERATURE      R      K1      K2',//,
    *1X,'(K)      (%)      ',//)
24  FORMAT(/,3X,F6.2,/)
25  FORMAT(15X,F4.1,10X,G10.4,08X,G10.4,/)
26  FORMAT(20X,'AVERAGE',2X,G10.4,10X,G10.4,//)
27  FORMAT(3X,'X(',I2,') = ',G10.3,2X,'Y(',I2,') = ',G10.3)
      STOP
      END

      SUBROUTINE LS(X,Y,I,SLOPE,AINTER,RATIO)
      REAL SX,SY,SXY,SXS,SY,SLOPE,AINTER,RATIO
      INTEGER J
      DIMENSION X(I),Y(I)
      SX=0
      SY=0
      SXY=0
      SXS=0
      SYS=0
      DO 52 J=1,I
      SX=SX+X(J)
      SY=SY+Y(J)
      SXY=SXY+X(J)*Y(J)
      SXS=SXS+X(J)**2

```

```
      SYS=SYS+Y(J)**2
S2    CONTINUE
      SLOPE=(SXY-SX*SY/I)/(SXS-SX**2/I)
      AINTER=SY/I-SLOPE*SX/I
      RATIO=(SXY-SX*SY/I)**2/(SXS-SX**2/I)/(SYS-SY**2/I)
      RETURN
      END
```

B.3.2 Exec (Main Program): REAC EXEC

To execute type 'REAC'. It automatically executes REAC FORTRAN. Data will be take from a file called REAC DATA, and results will be written in a file called REAC RESULT, from where they can be printed (as in Section D.3).

```
GLOBAL TXTLIB VLNMKLIB VFORTLIB CMSLIB INSLDLIB PLOTLIB
FORTVS REAC
FILE 5 DISK REAC DATA(LRECL 80 BLKSIZE 80 RECFM F PERM
FILE 6 DISK REAC RESULT A (PERM RECFM F LRECL 132
LOAD REAC(CLEAR START
```

Appendix C

Kinetic Analysis Graphs

C.1 Temperature Effect of Conversion and Yield of HCHO

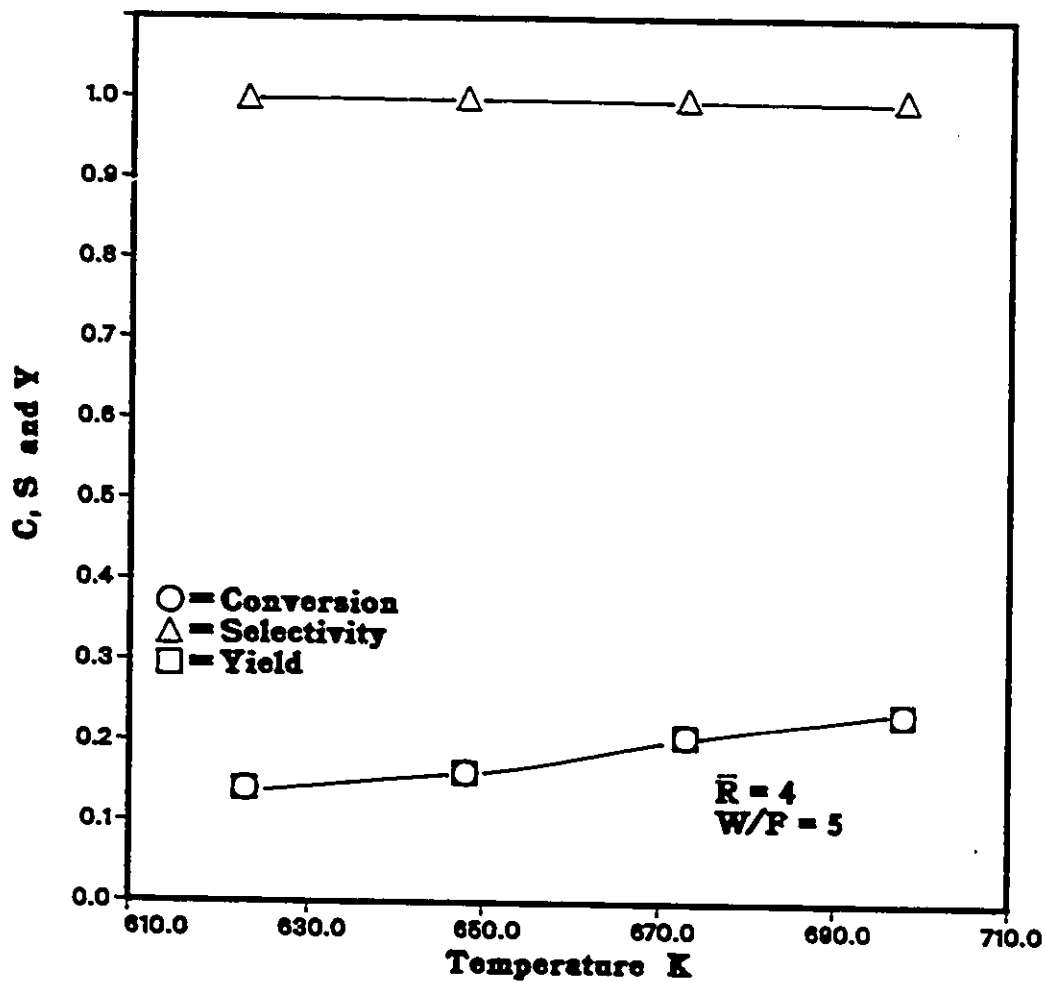


Figure C.1: Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 4

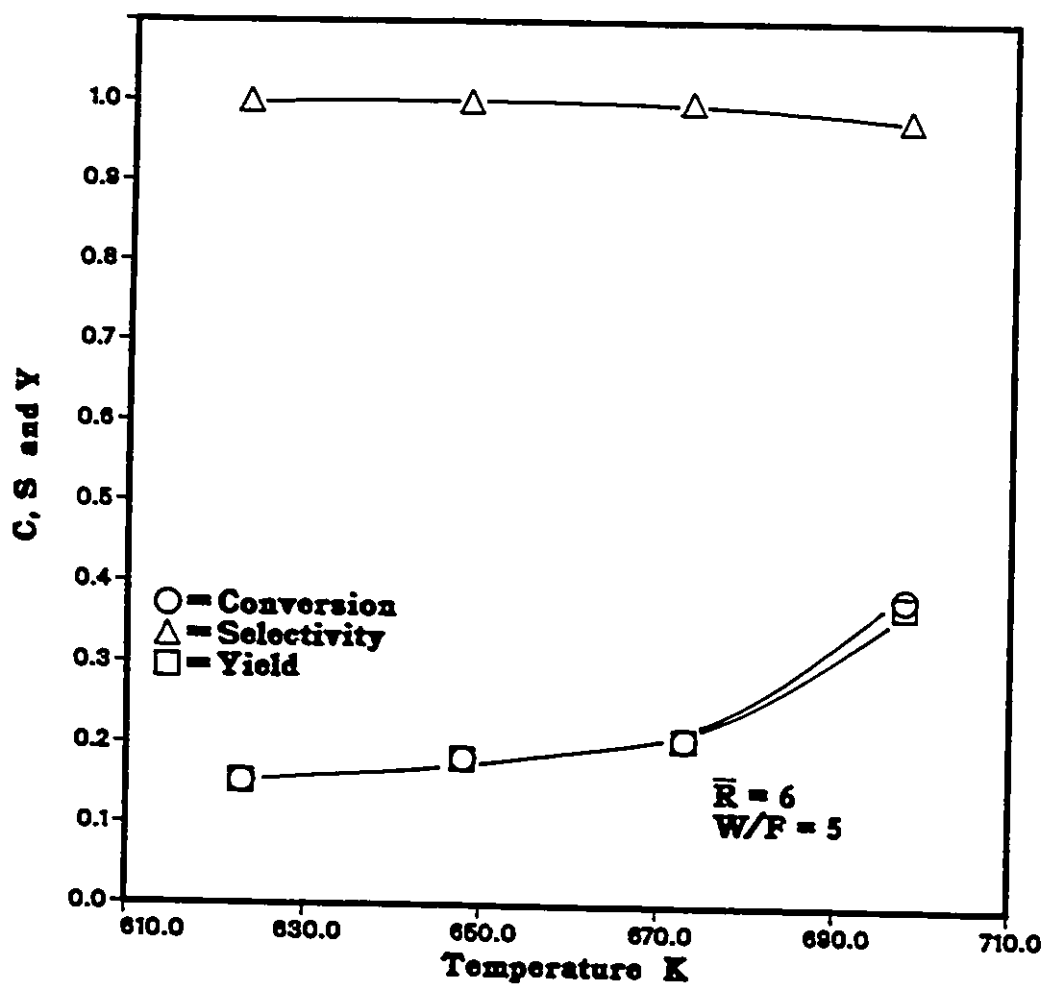


Figure C.2: Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 6

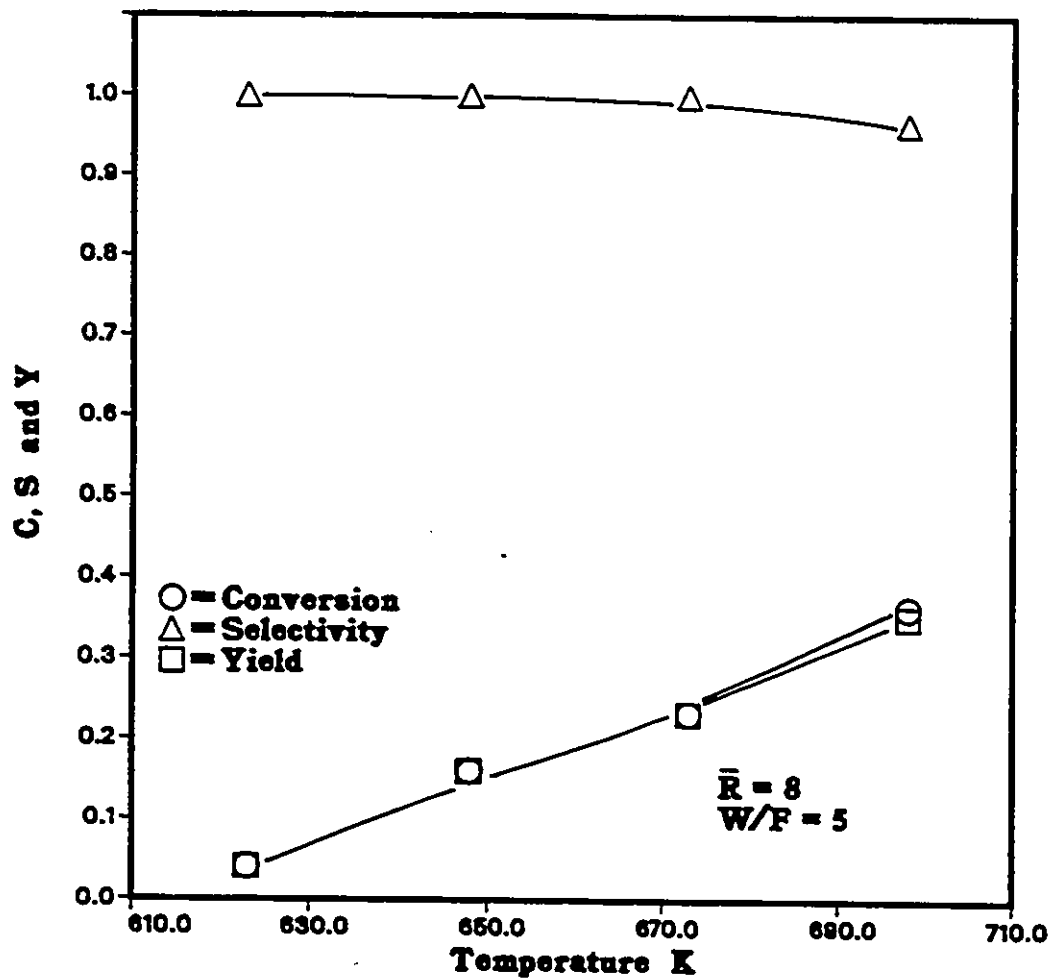


Figure C.3: Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 8

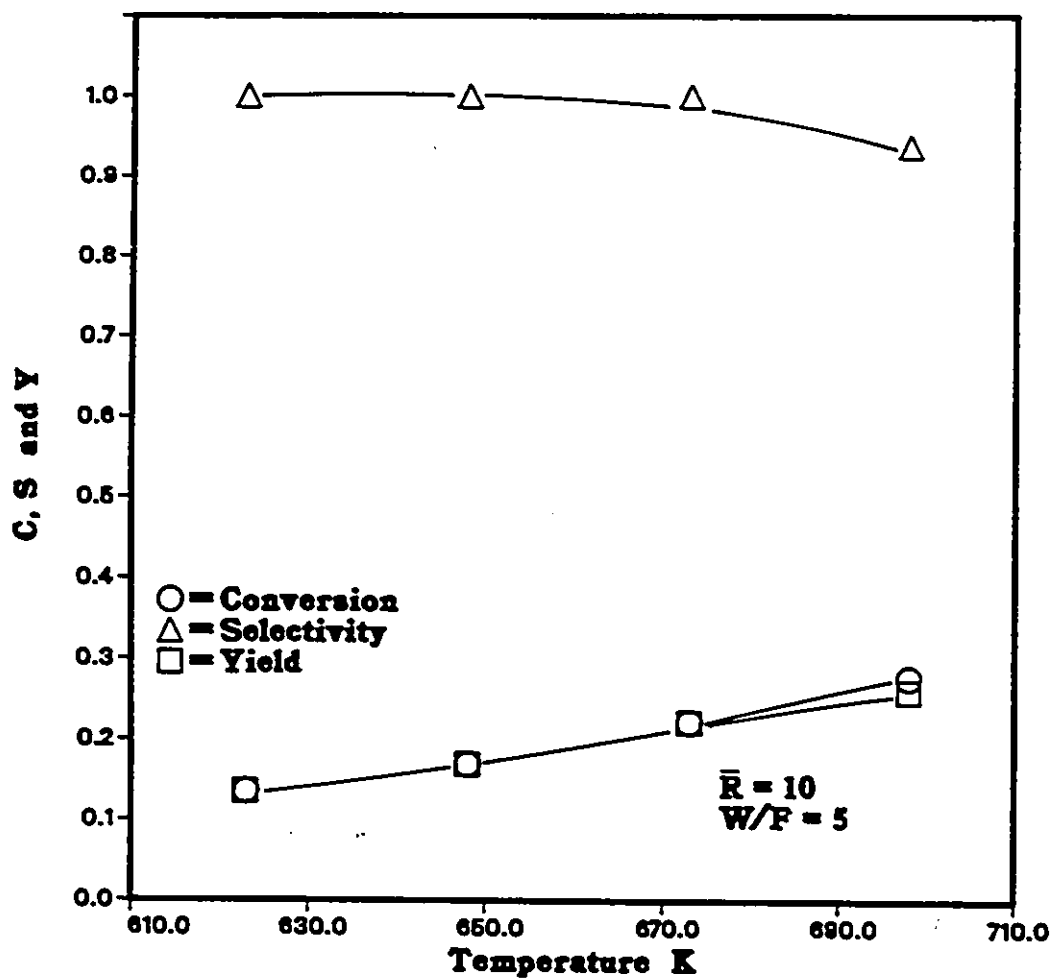


Figure C.4: Temperature Effect on Conversion and Yield of HCHO at W/F of 5 and $\bar{R}$ of 10

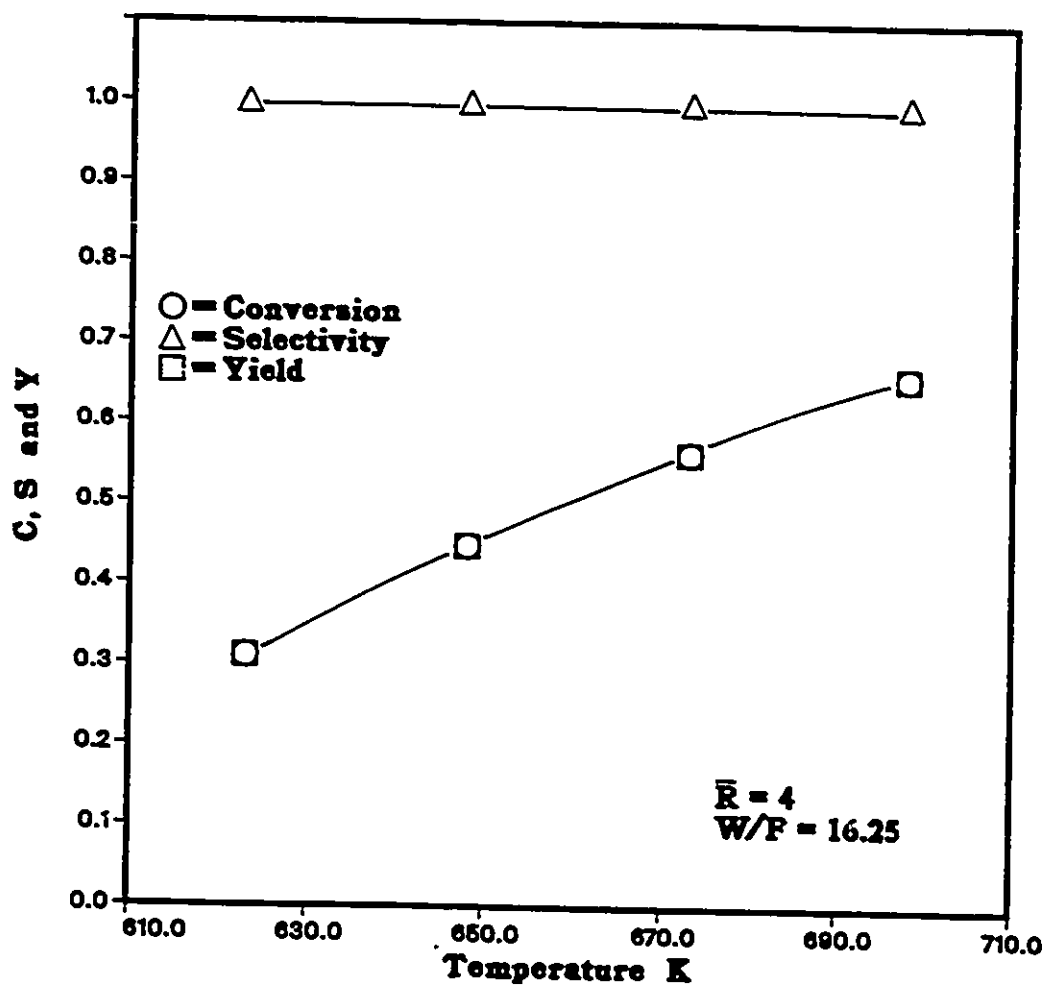


Figure C.5: Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 4

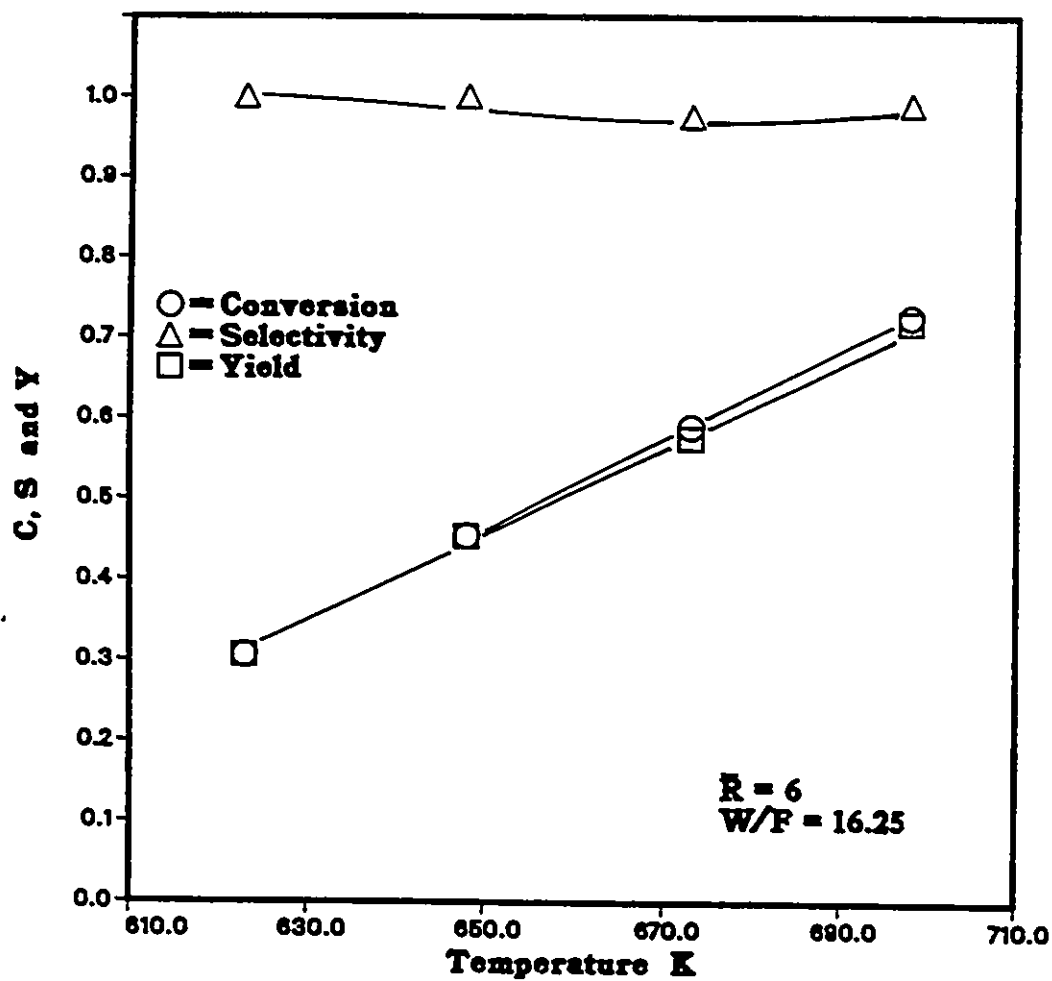


Figure C.6: Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 6

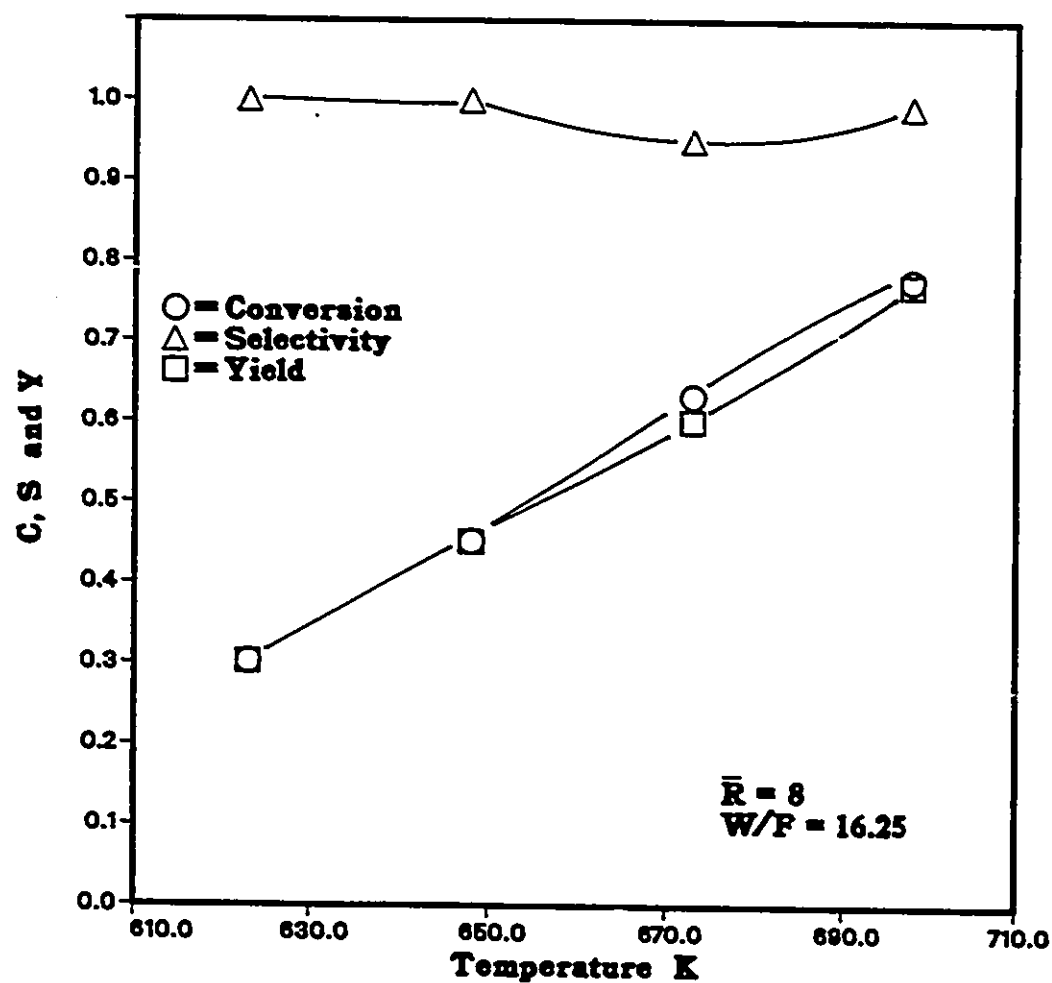


Figure C.7: Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 8

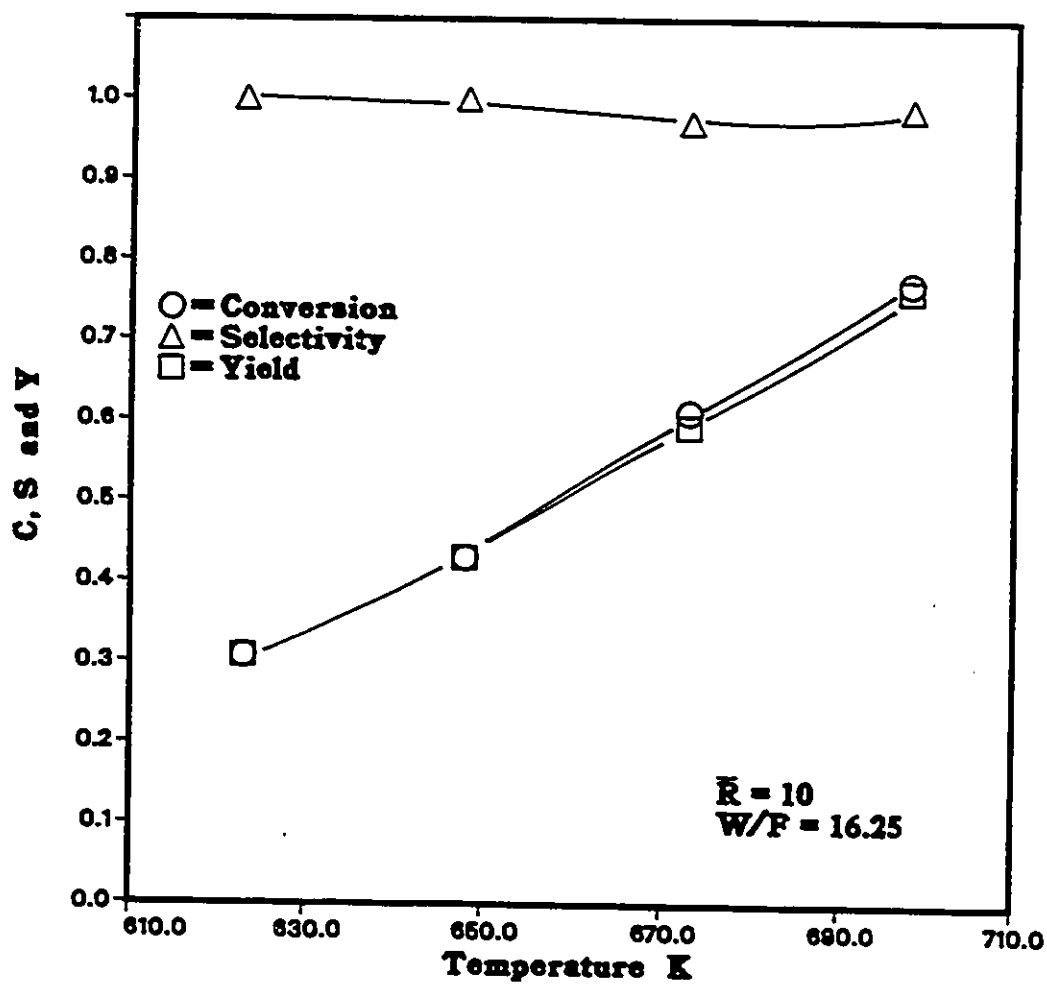


Figure C.S: Temperature Effect on Conversion and Yield of HCHO at W/F of 16.25 and $\bar{R}$ of 10

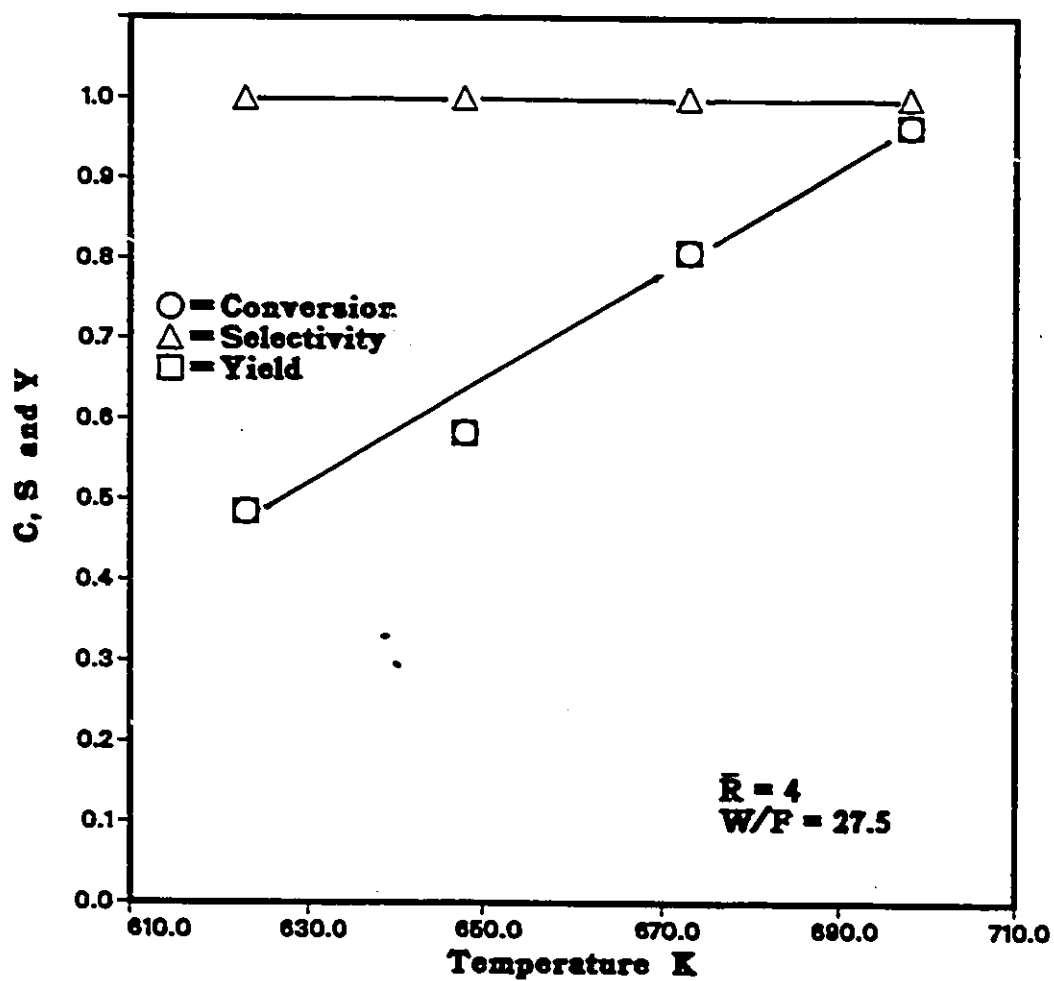


Figure C.9: Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 4

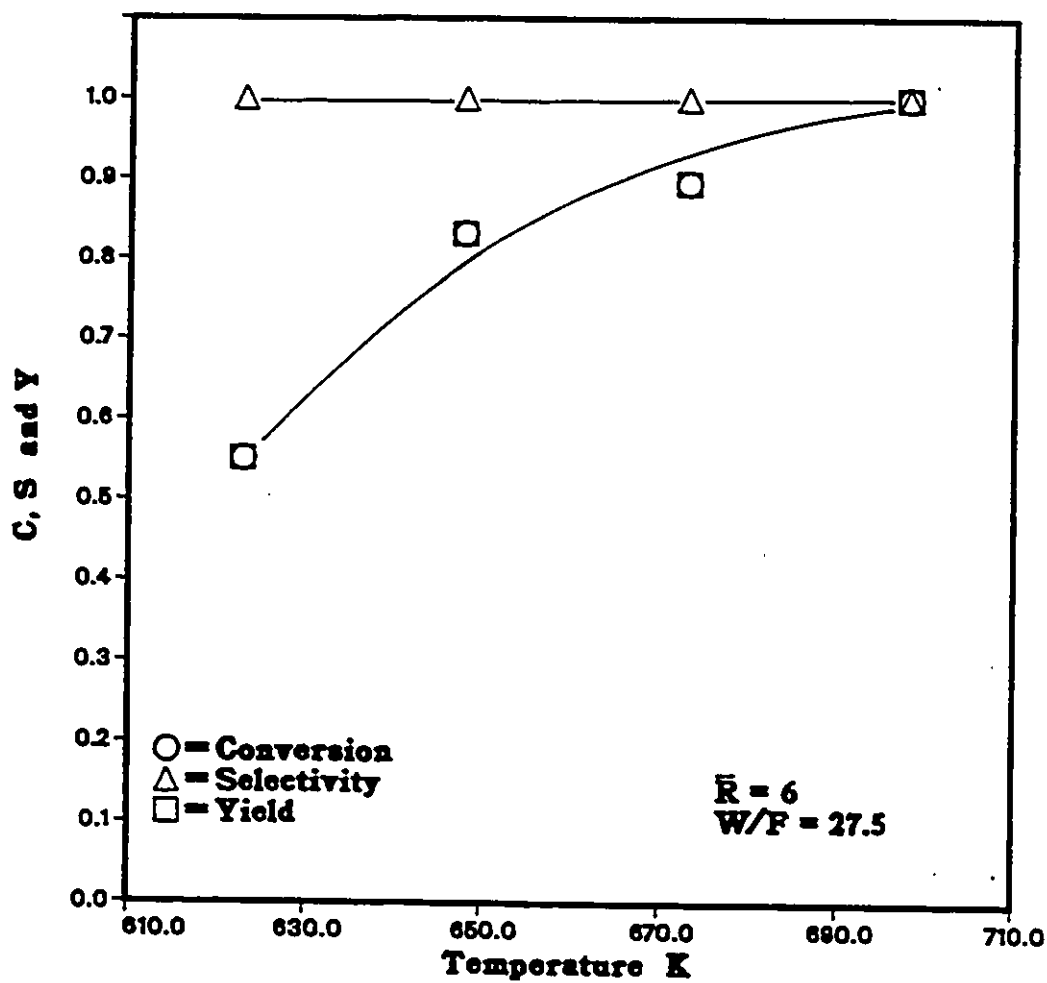


Figure C.10: Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 6

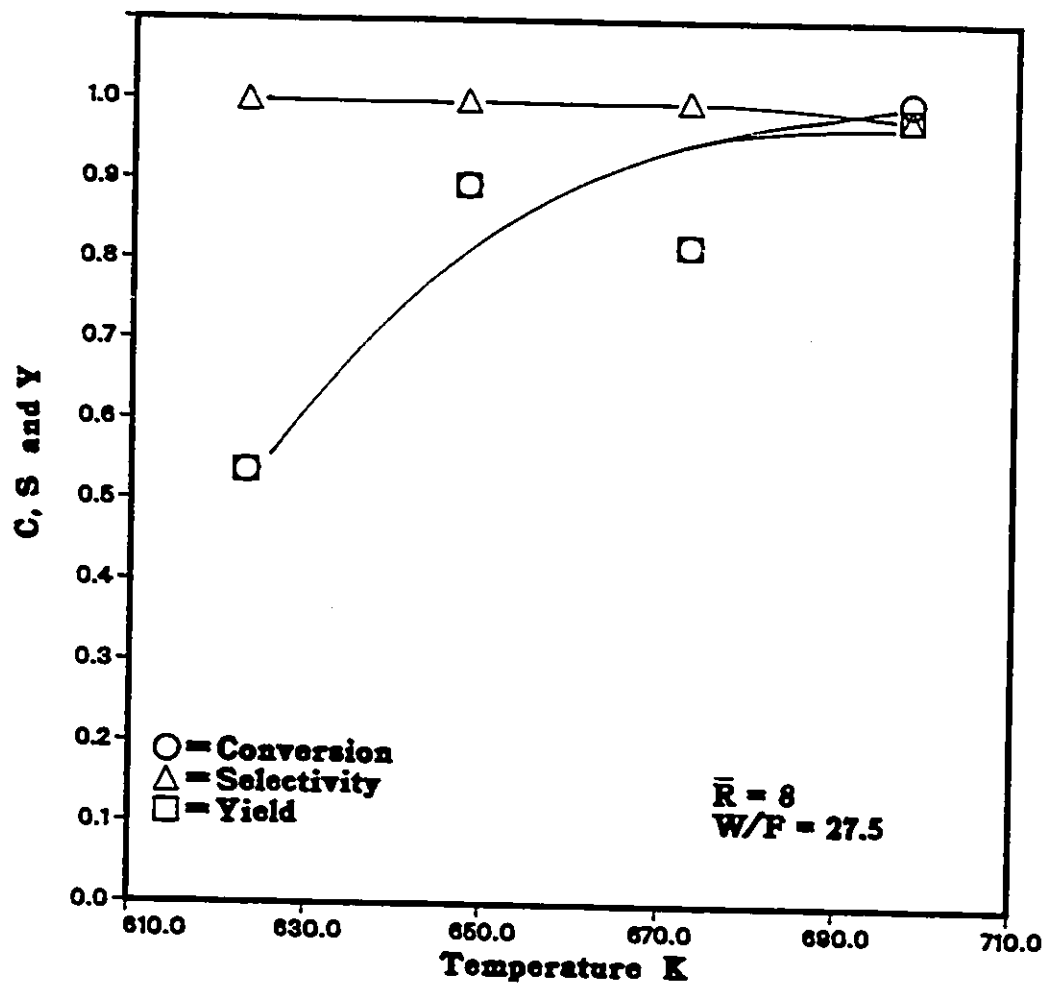


Figure C.11: Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 8

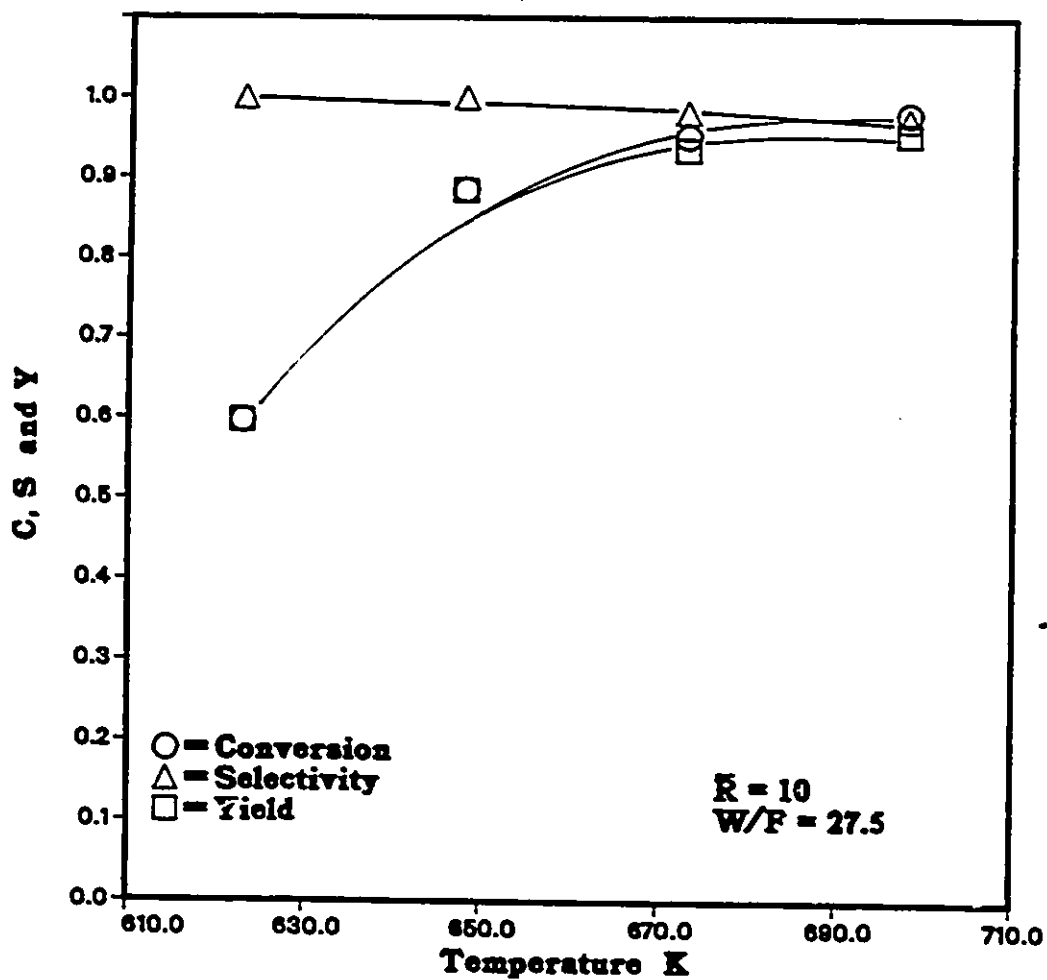


Figure C.12: Temperature Effect on Conversion and Yield of HCHO at W/F of 27.5 and $\bar{R}$ of 10

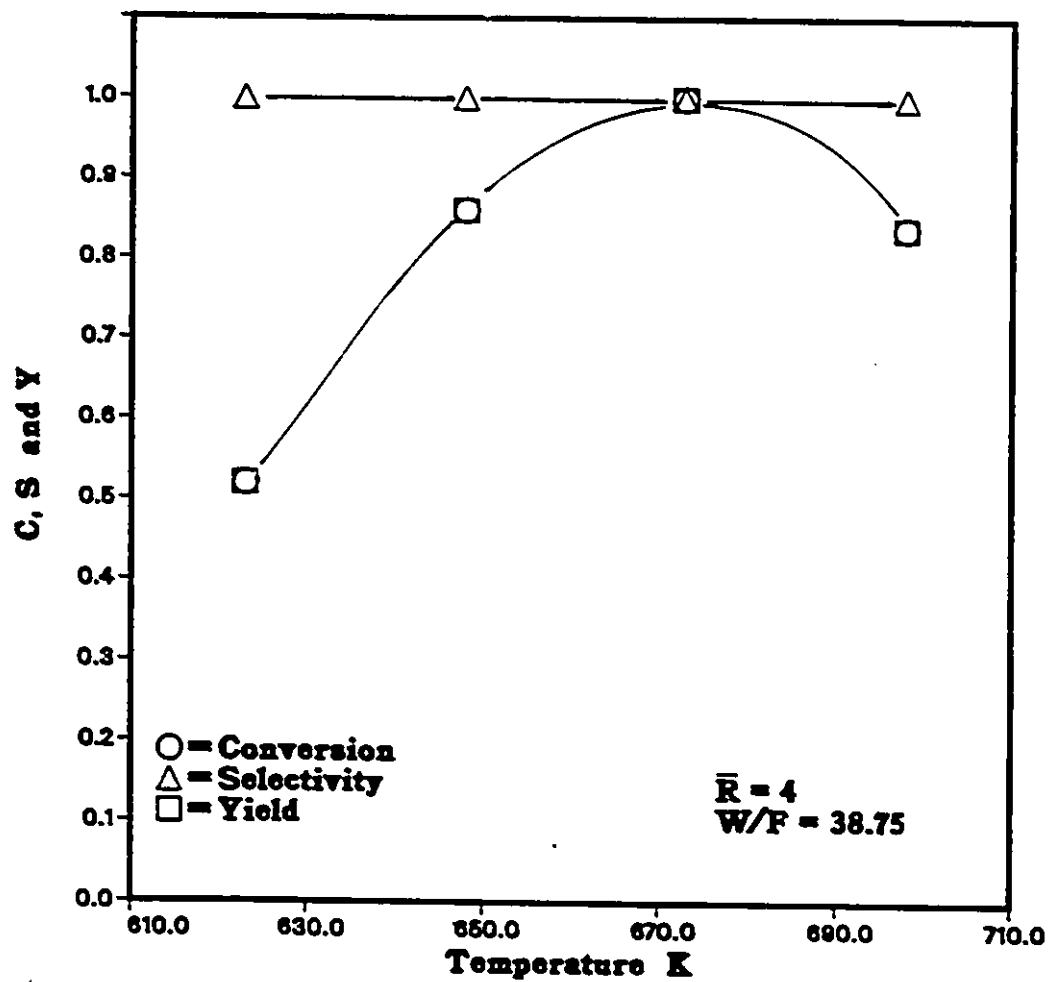


Figure C.13: Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 4

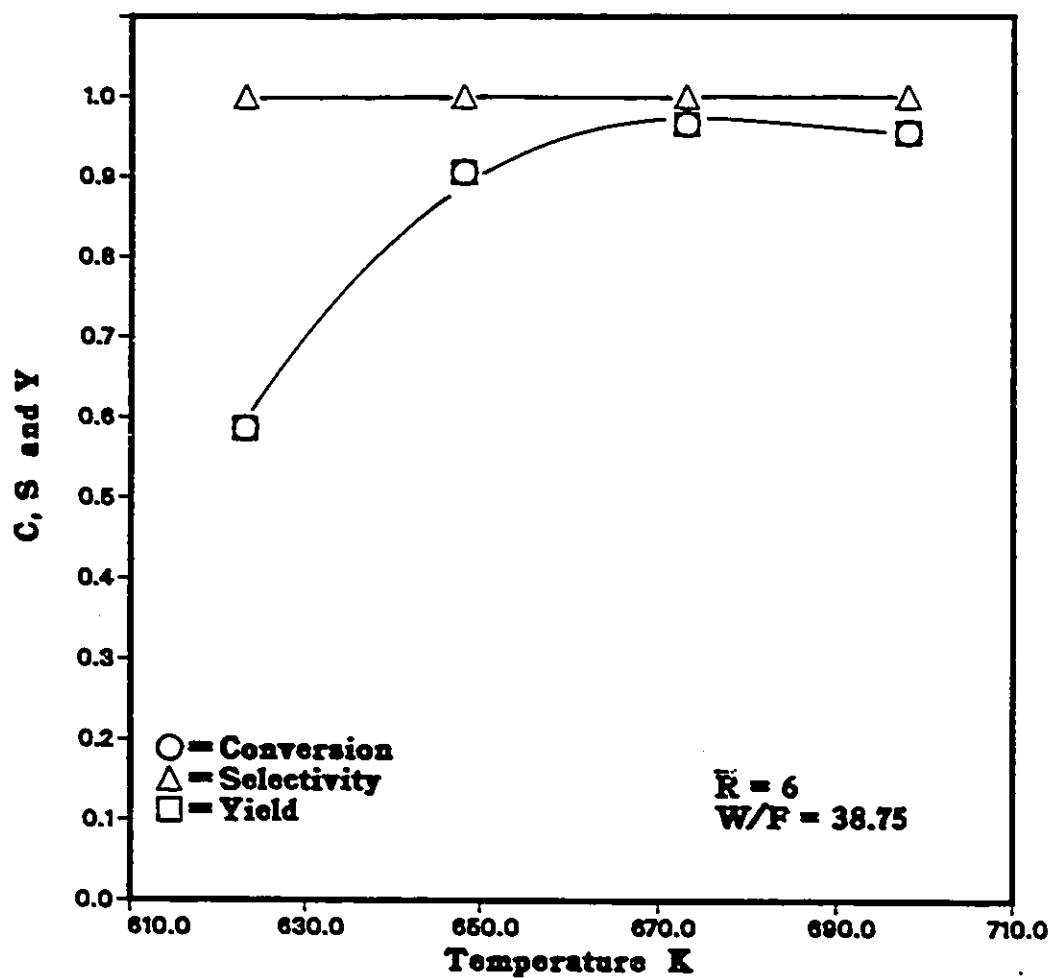


Figure C.14: Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 6

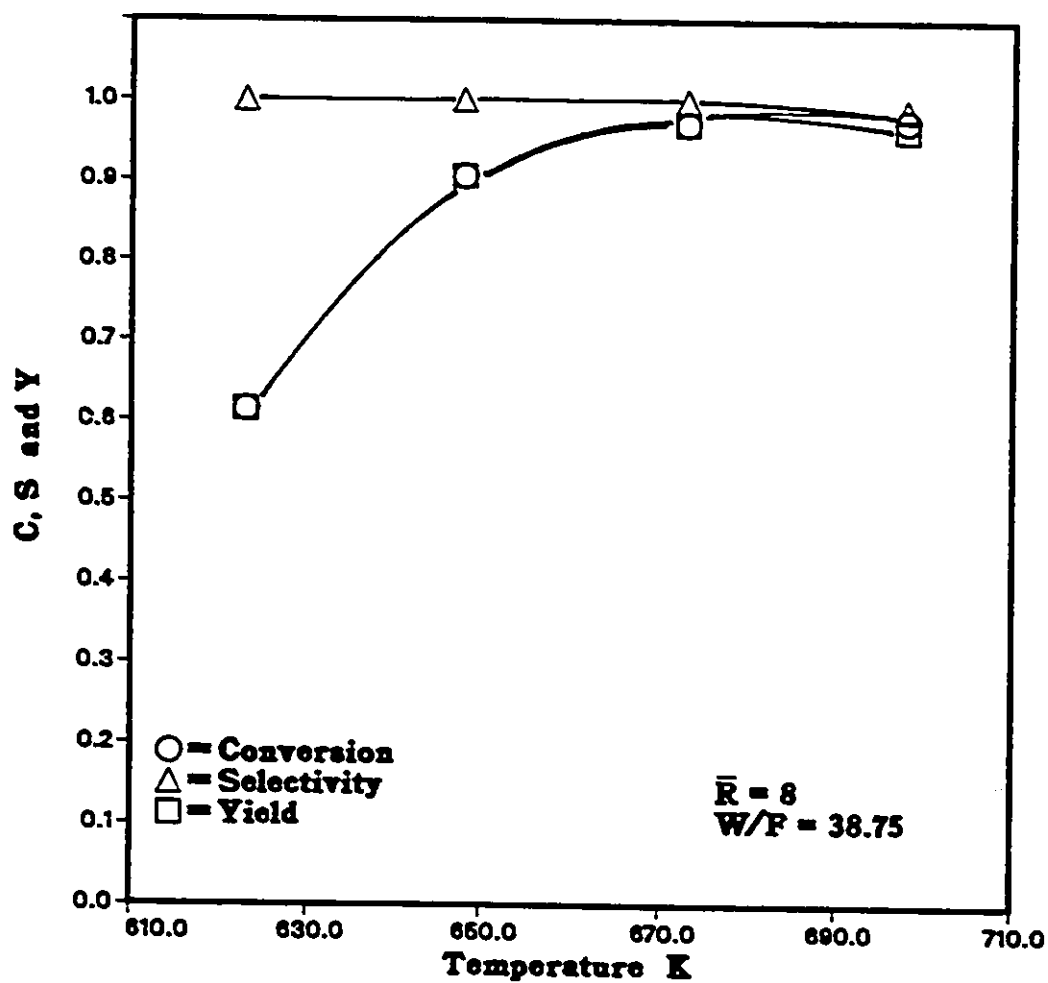


Figure C.15: Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 8

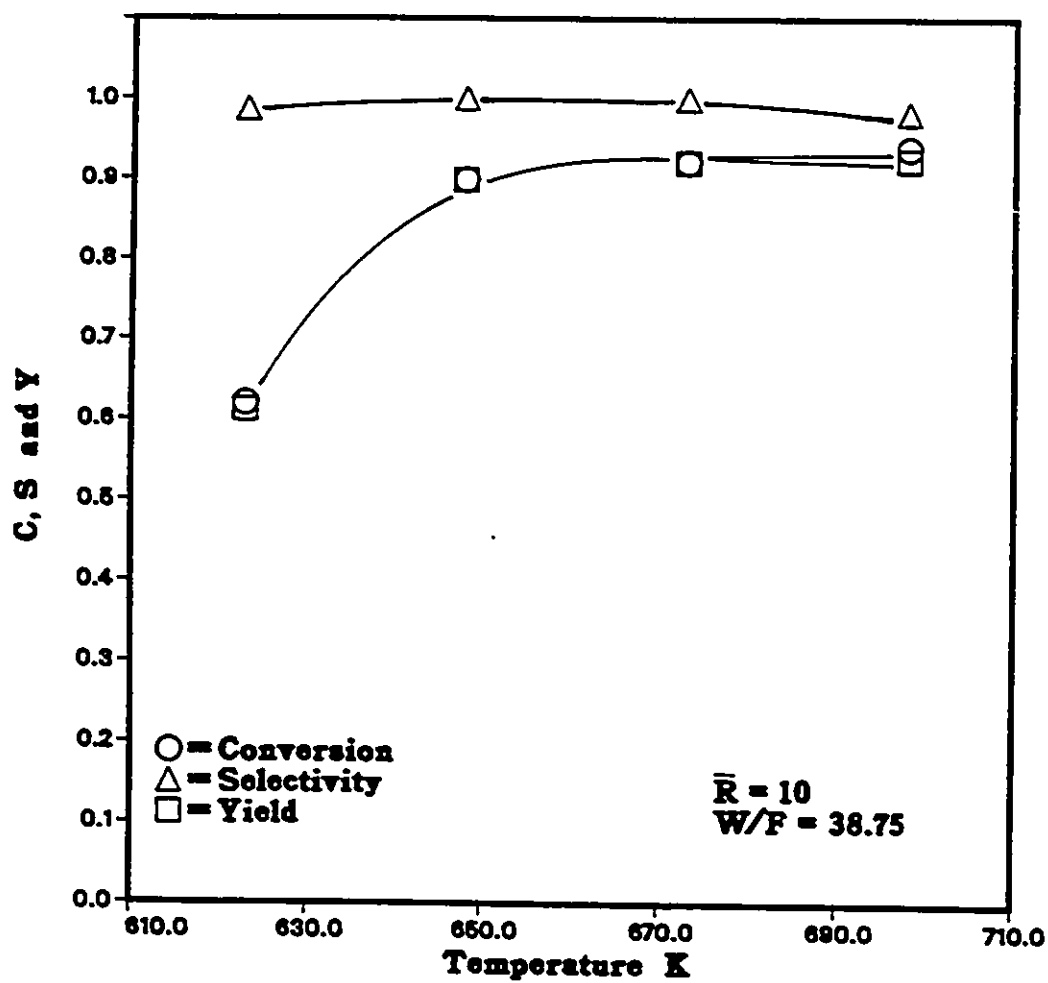


Figure C.16: Temperature Effect on Conversion and Yield of HCHO at W/F of 38.75 and $\bar{R}$ of 10

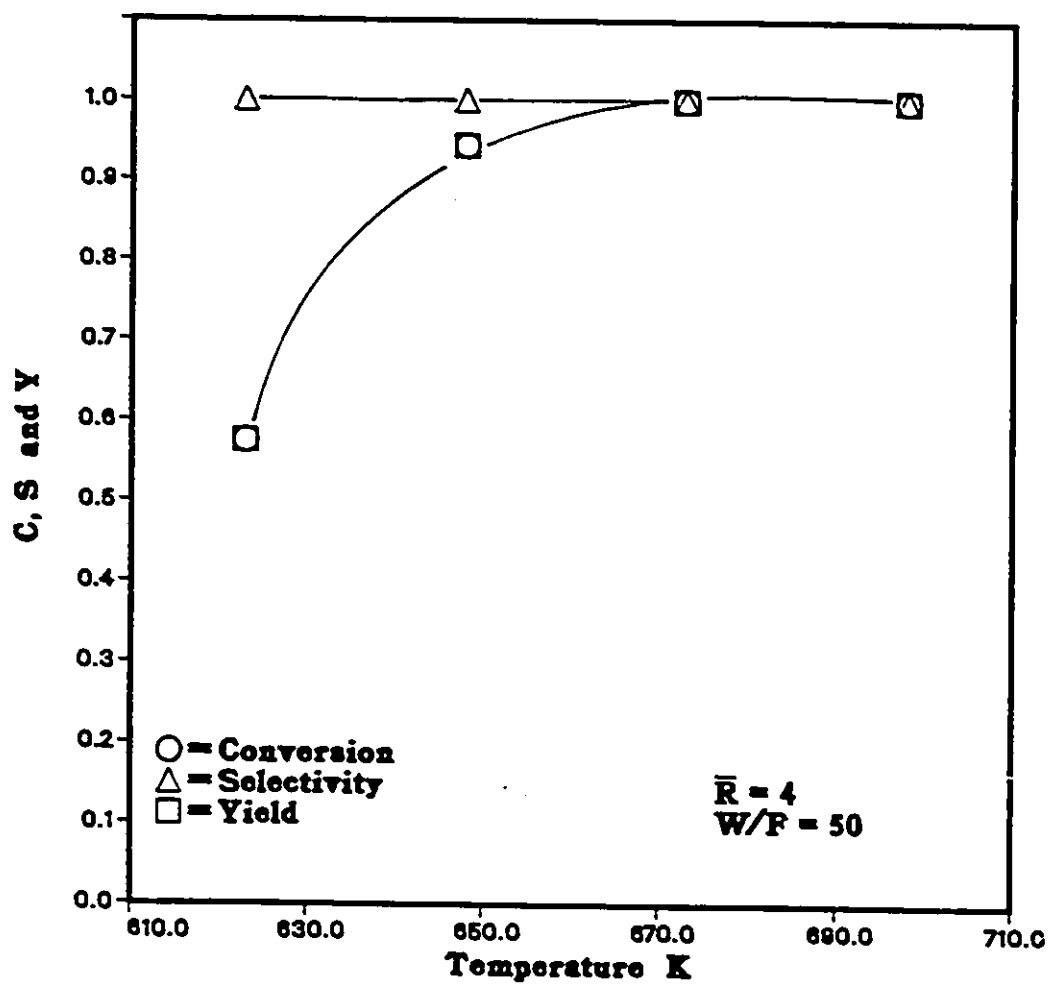


Figure C.17: Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 4

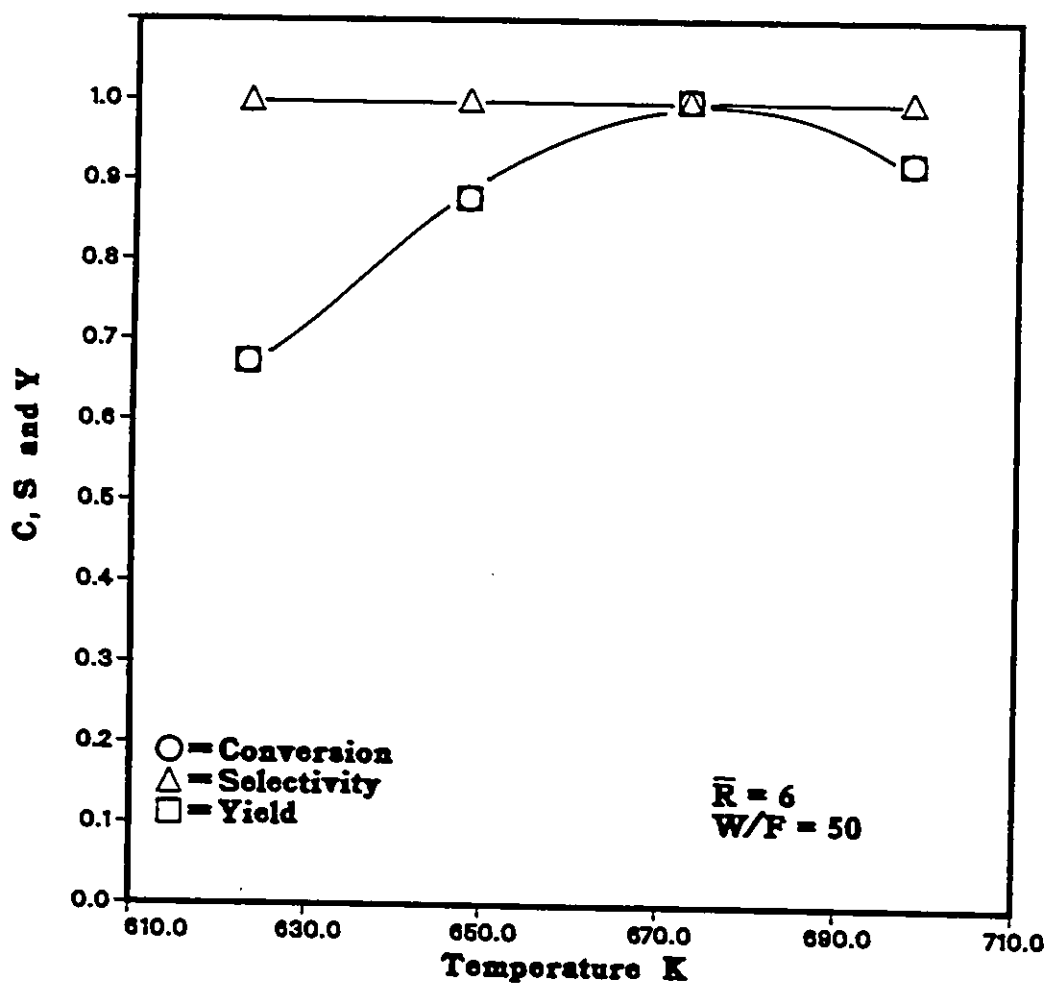


Figure C.18: Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 6

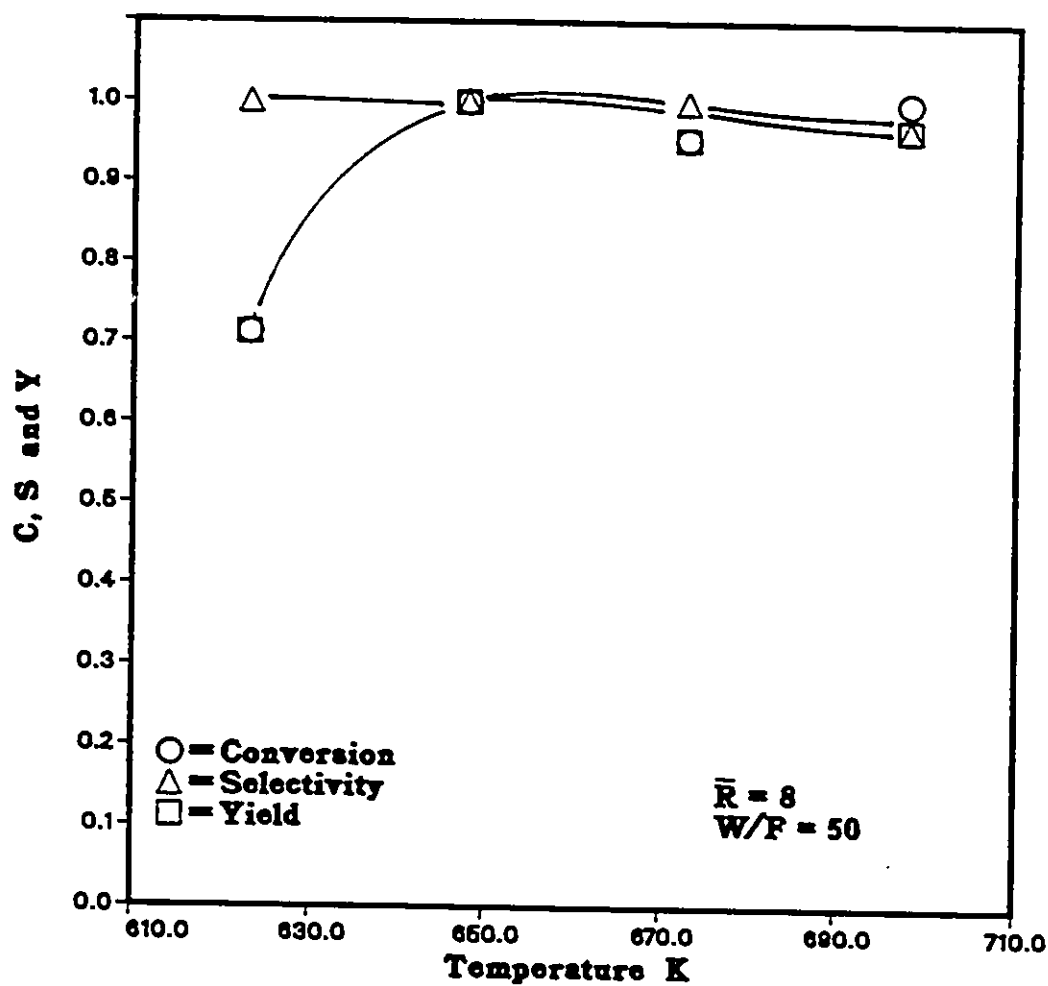


Figure C.19: Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 8

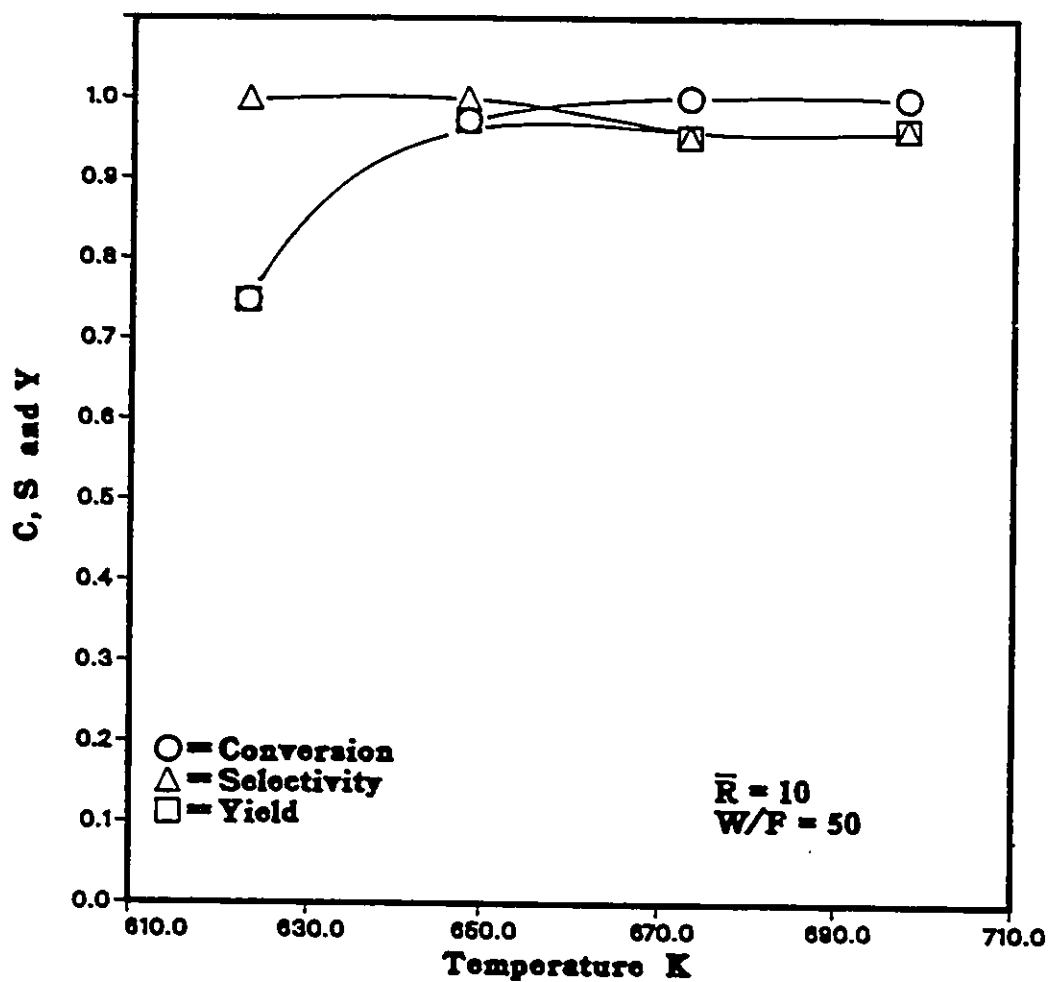


Figure C.20: Temperature Effect on Conversion and Yield of HCHO at W/F of 50 and $\bar{R}$ of 10

C.2 W/F Effect on Conversion and Yield of HCHO

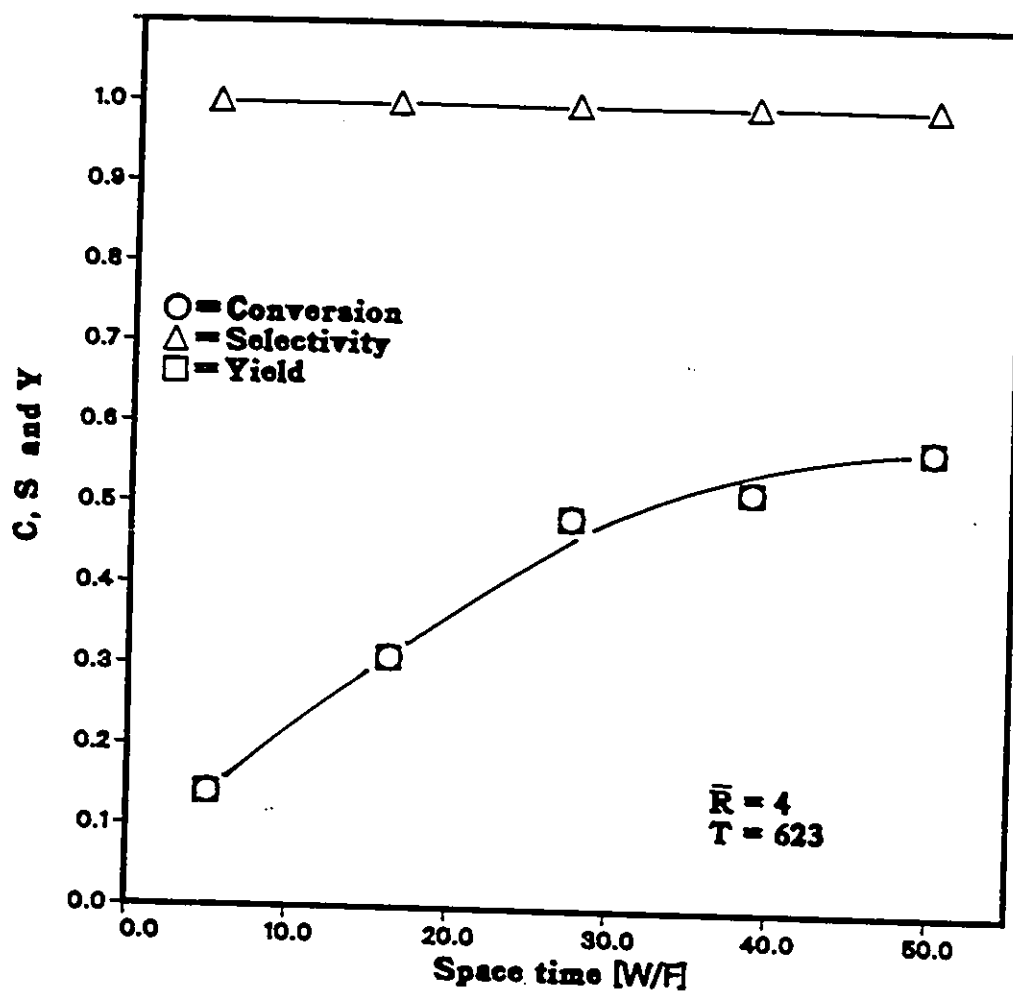


Figure C.21: W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 4

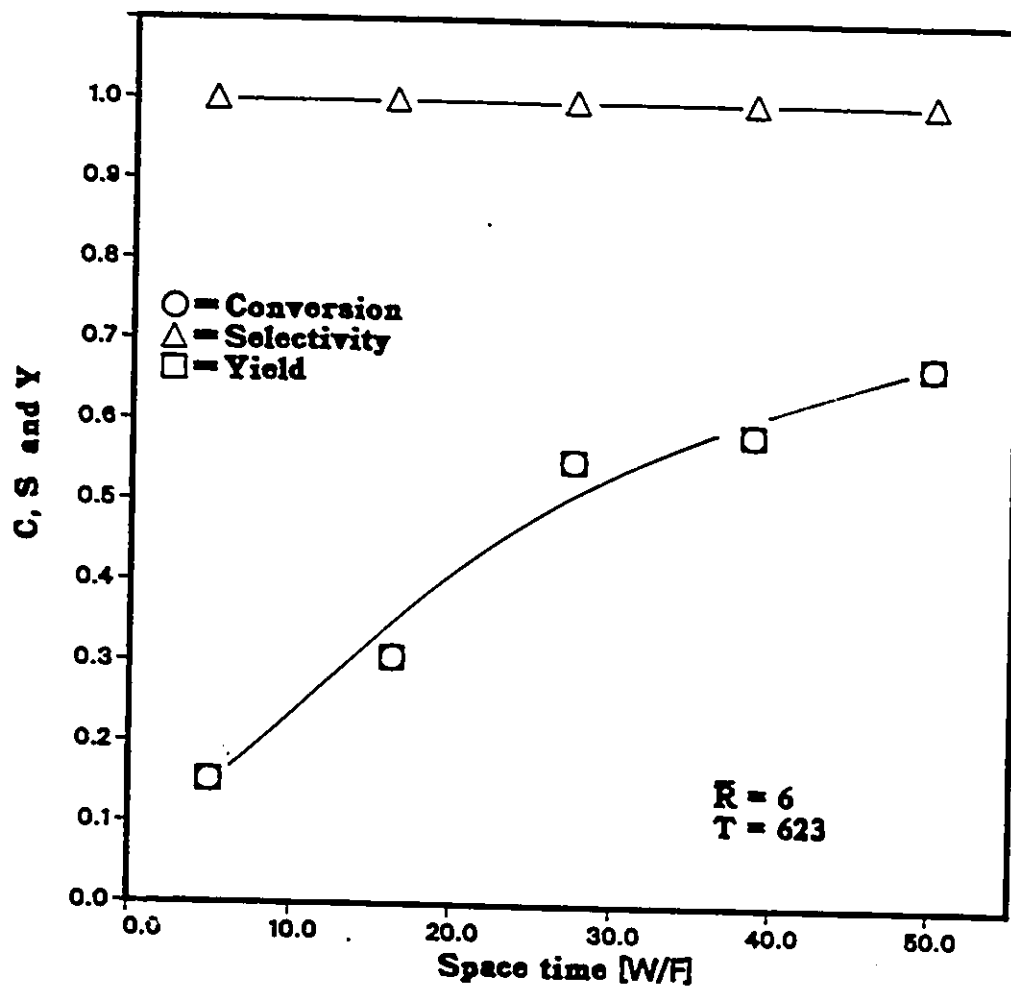


Figure C.22: W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 6

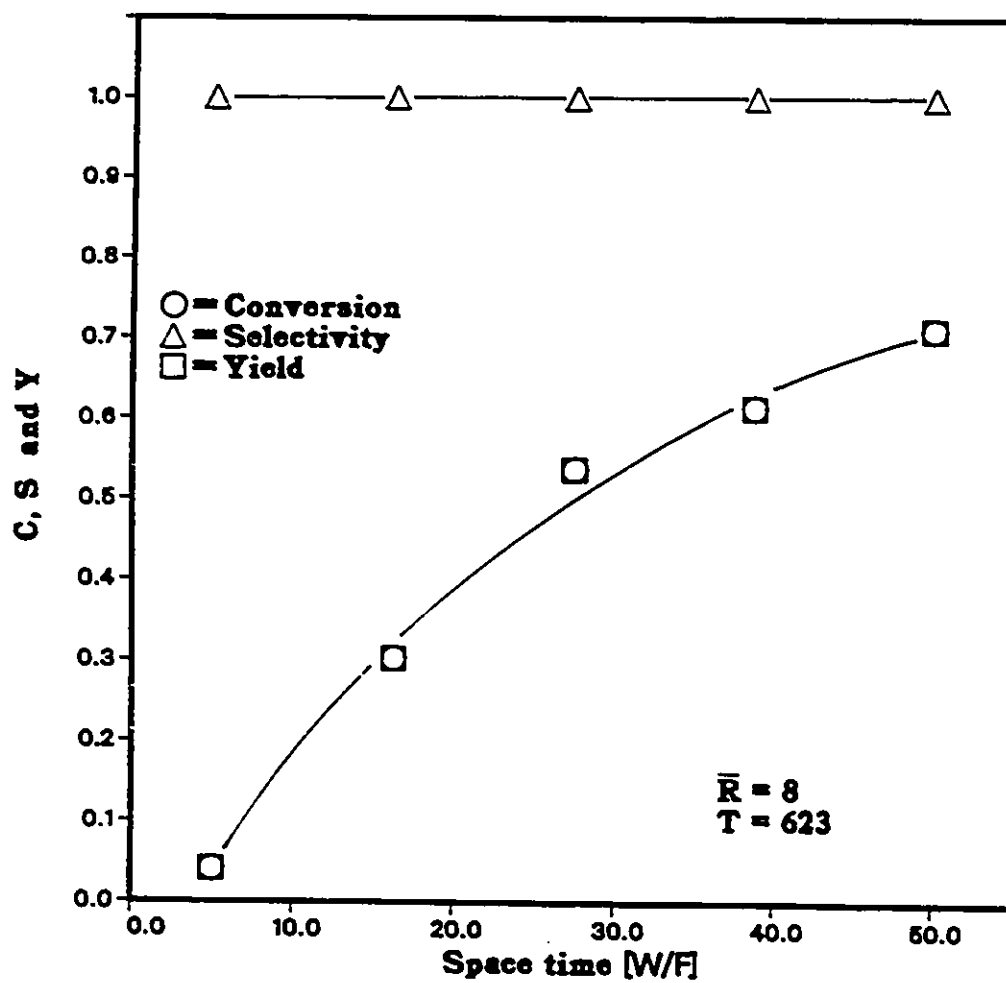


Figure C.23: W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 8

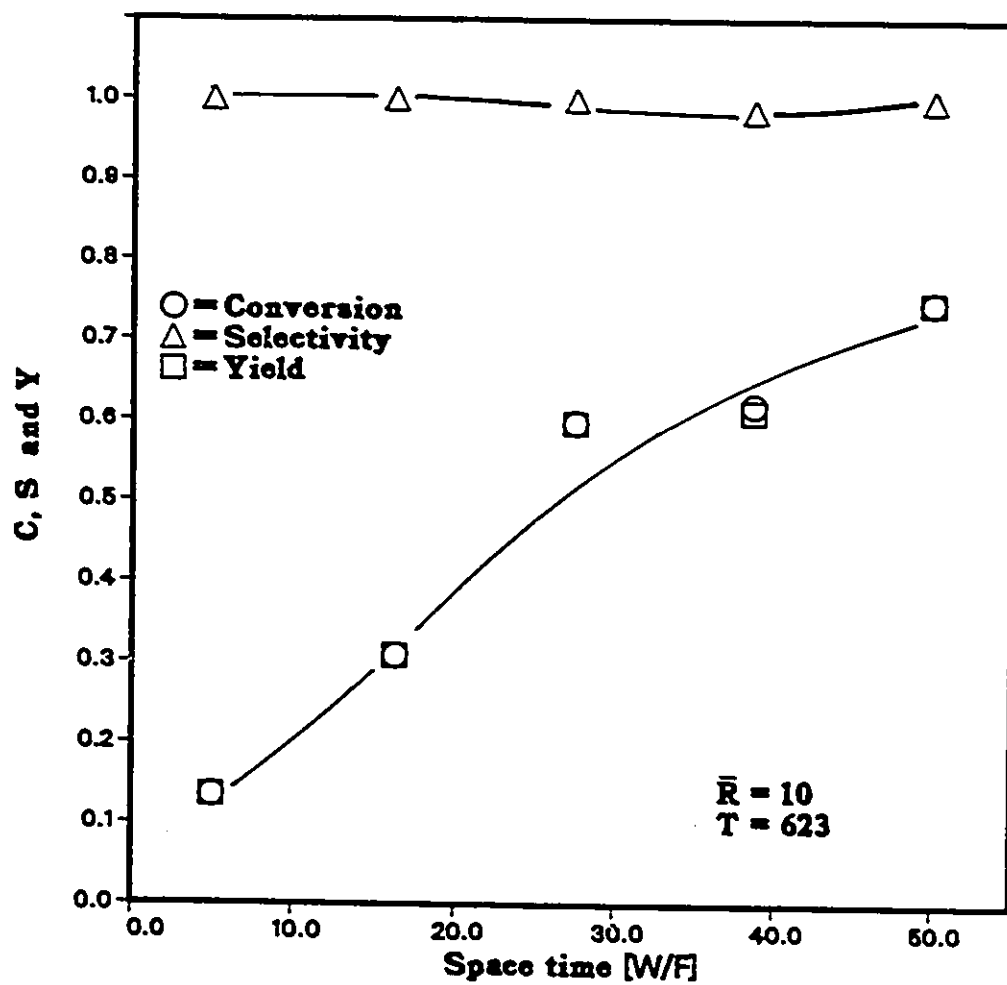


Figure C.24: W/F Effect on Conversion and Yield of HCHO at T of 623 K and $\bar{R}$ of 10

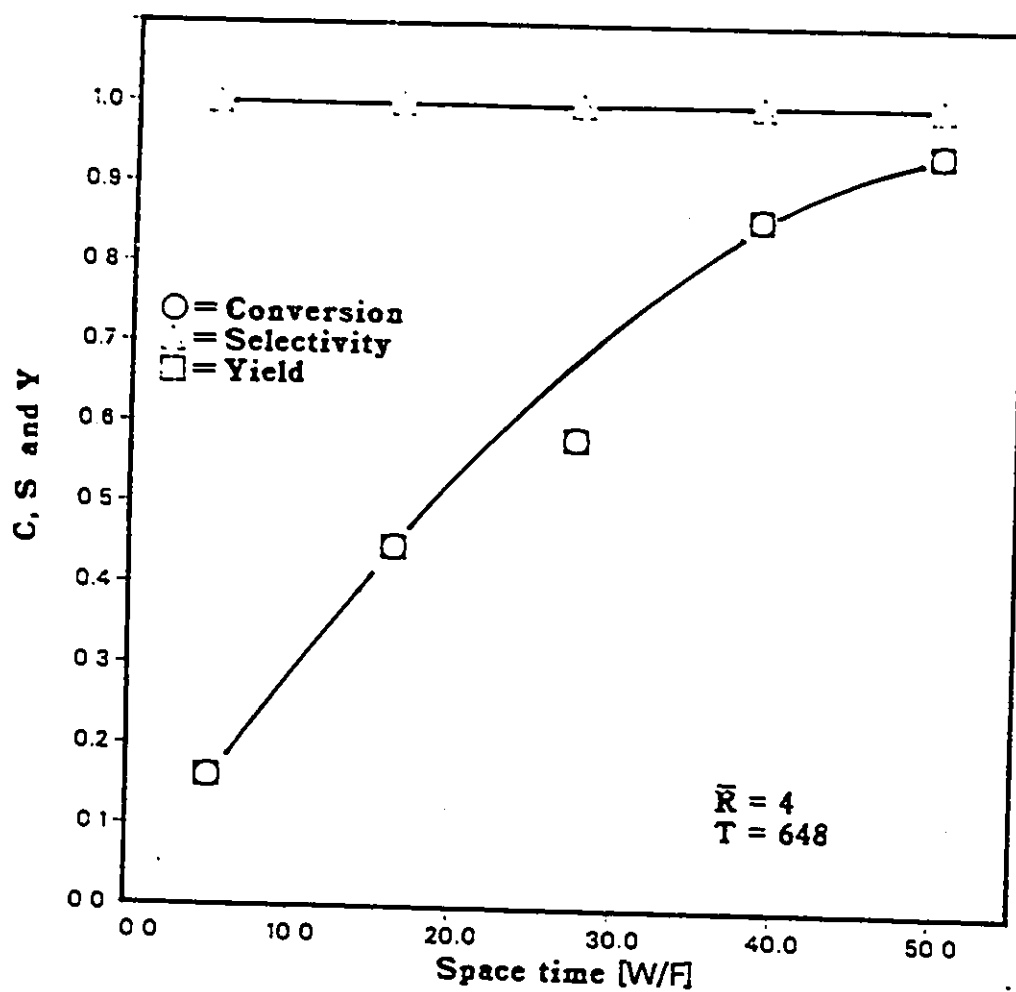


Figure C.25: W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 4

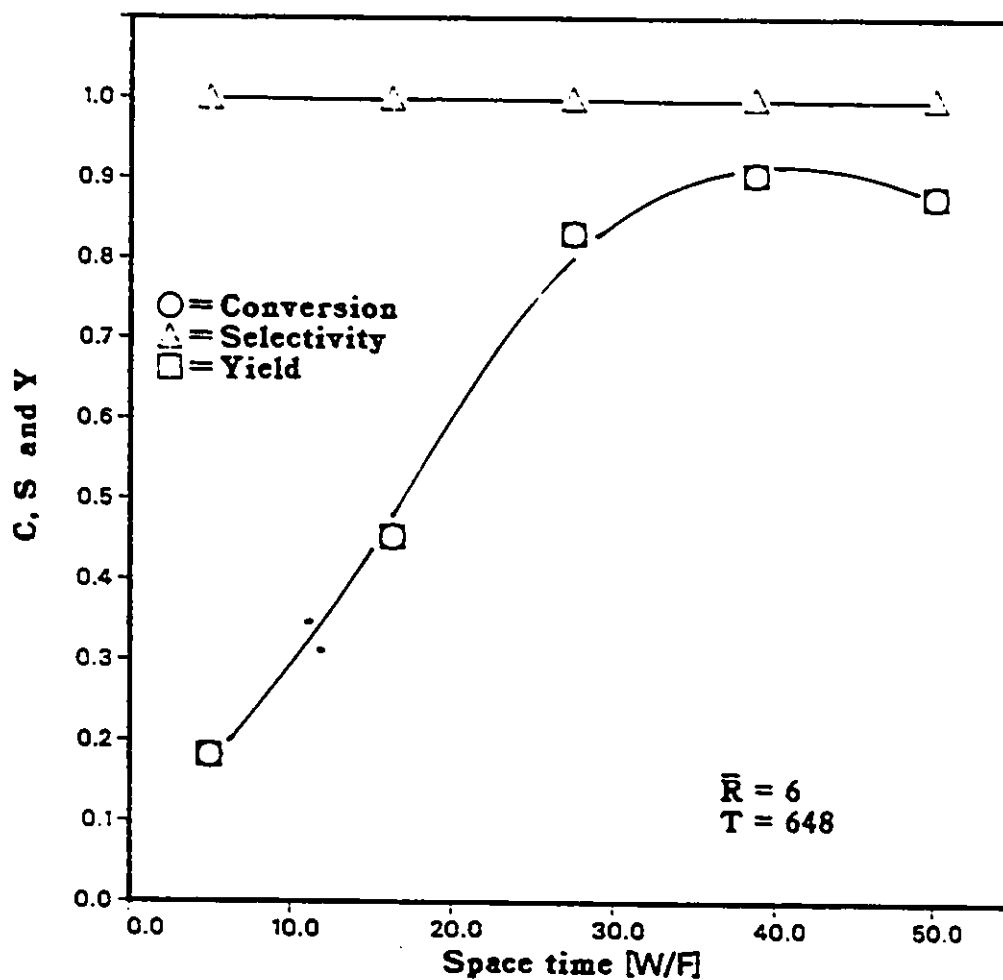


Figure C.26: W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 6

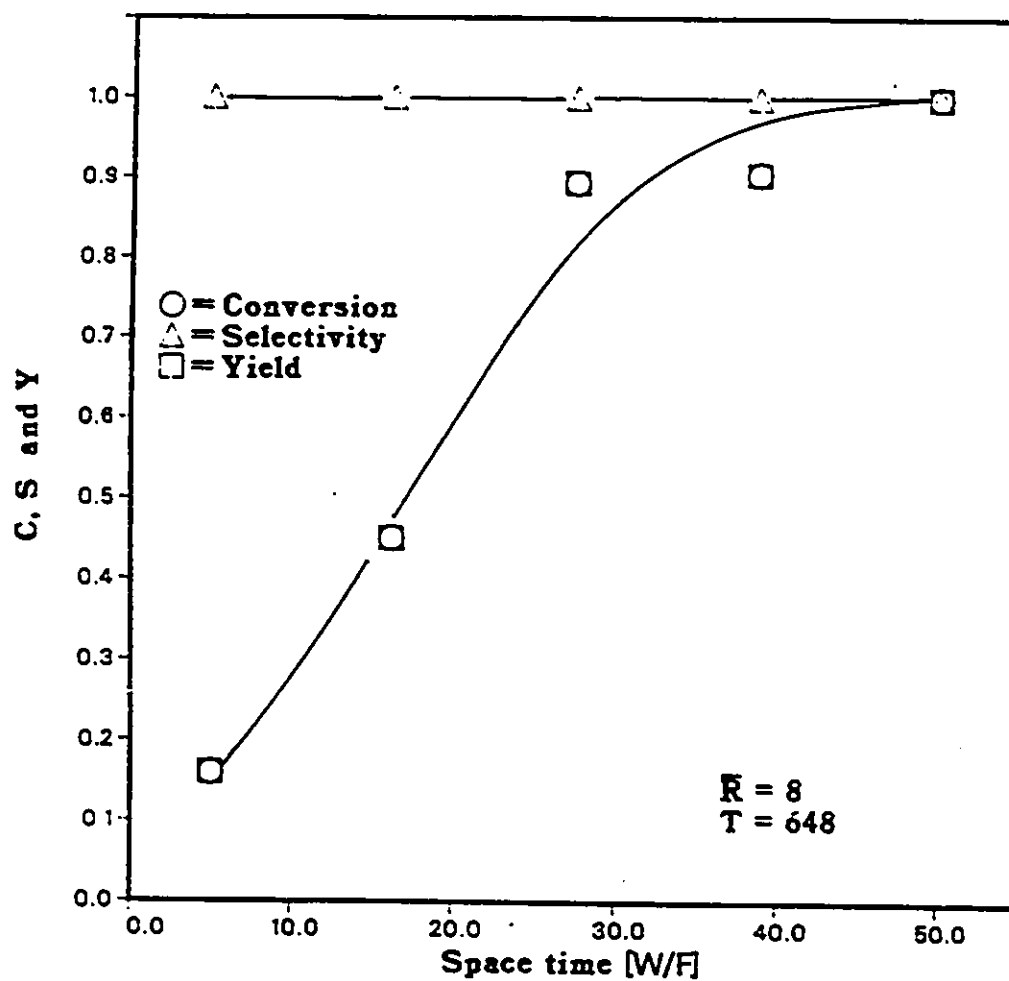


Figure C.27: W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 8

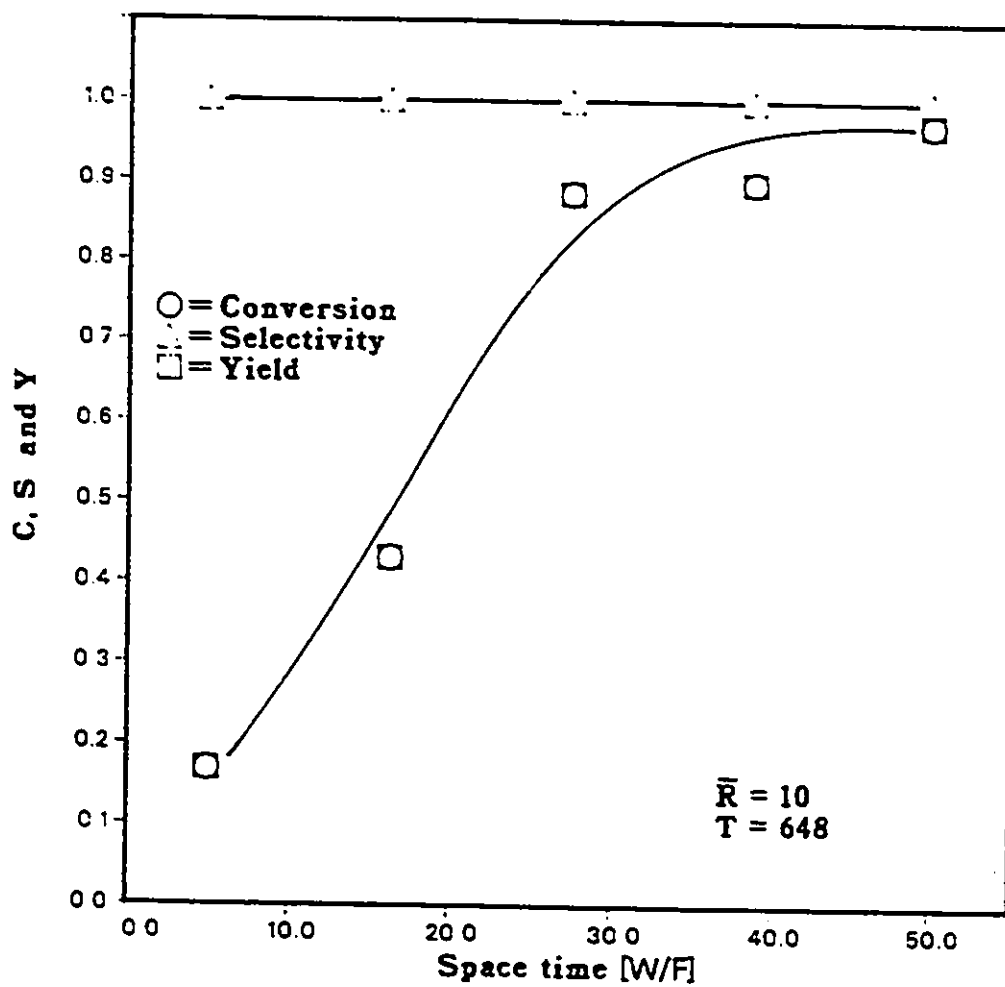


Figure C.28: W/F Effect on Conversion and Yield of HCHO at T of 648 K and $\bar{R}$ of 10

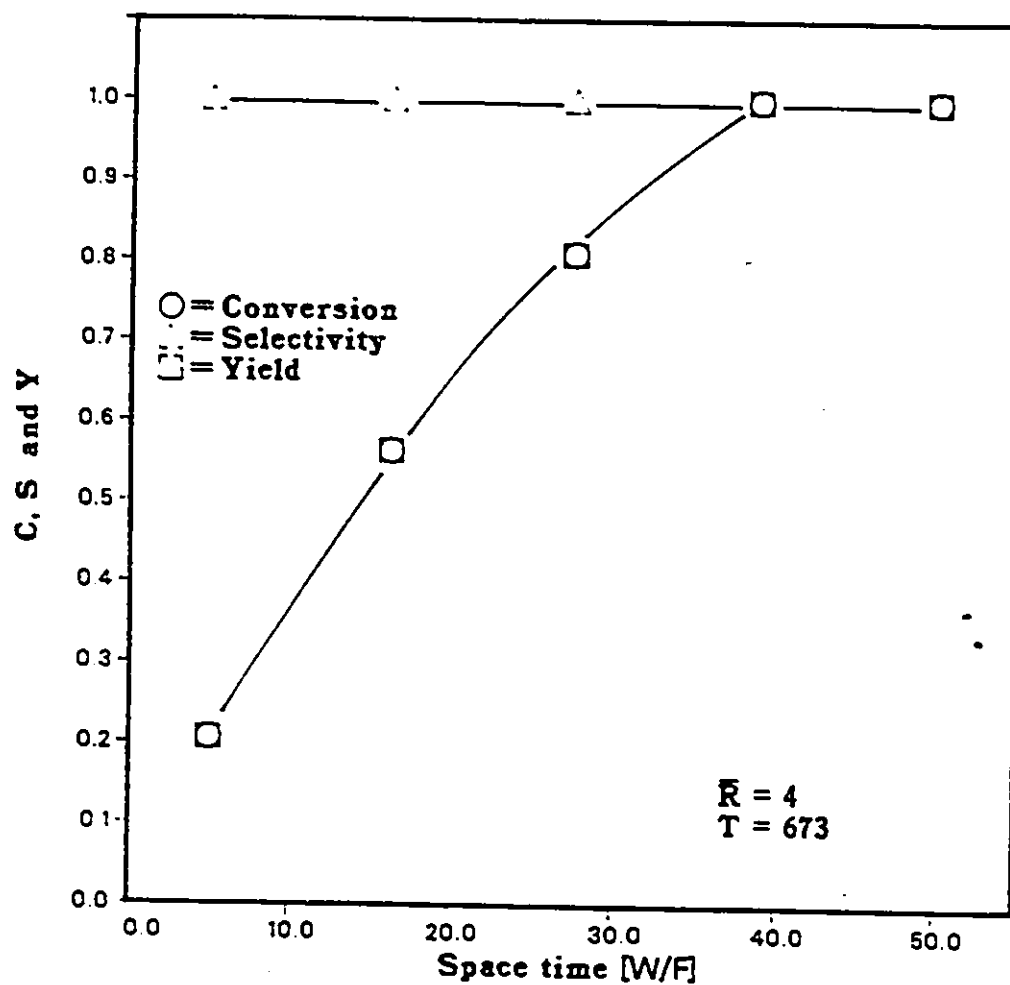


Figure C.29: W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 4

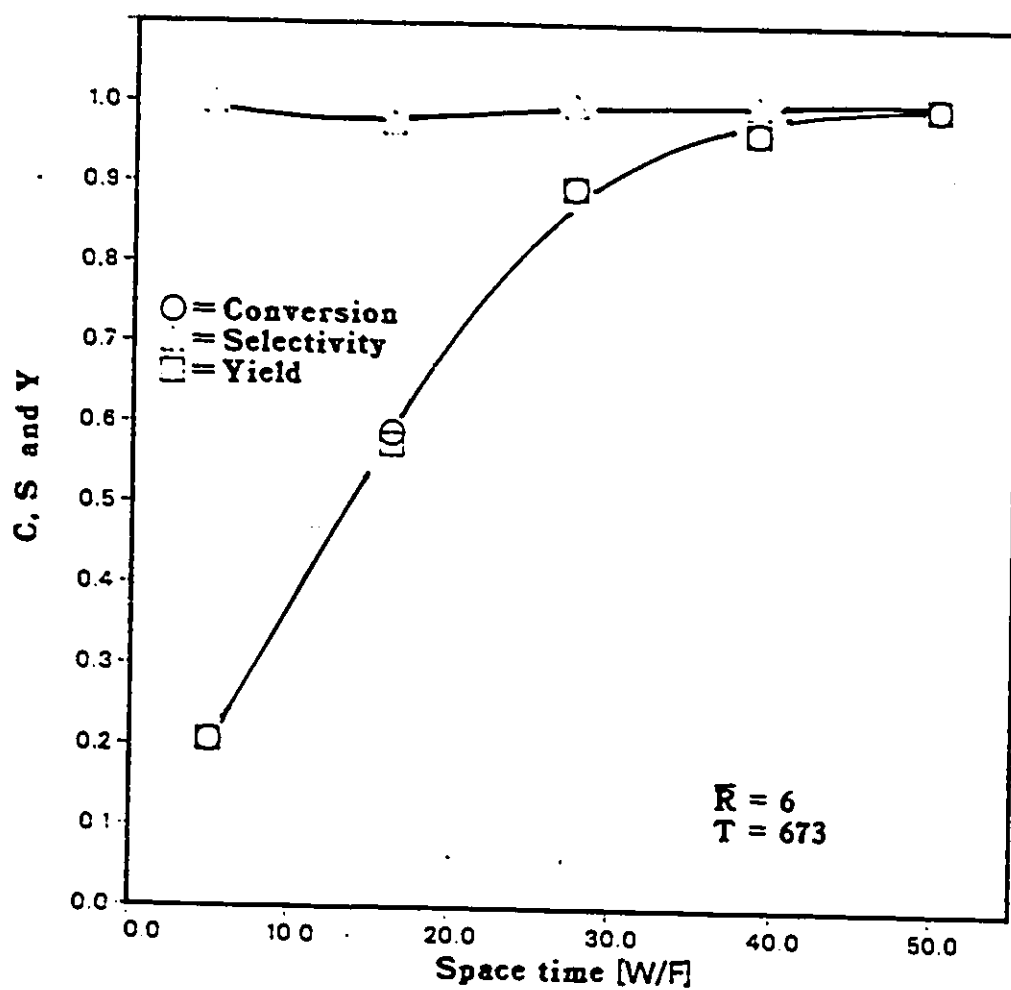


Figure C.30: W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 6

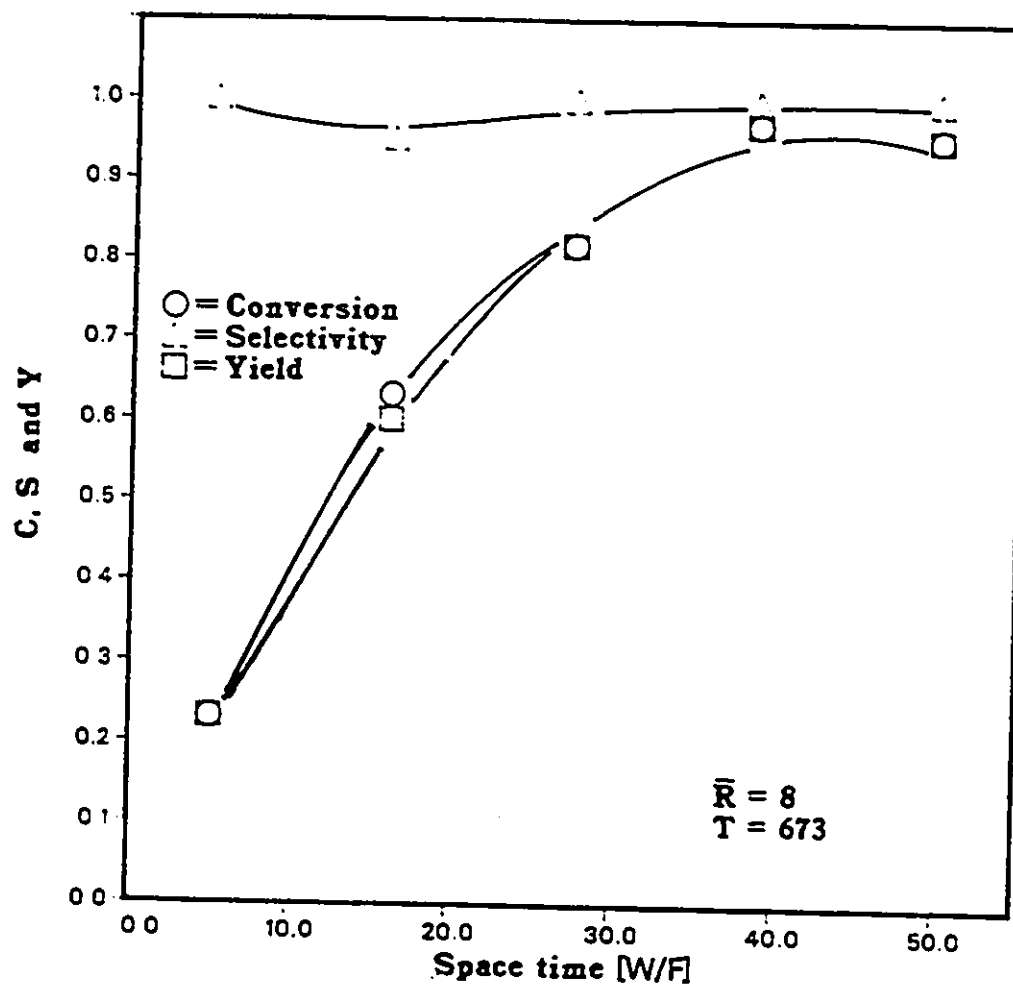


Figure C.31: W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 8

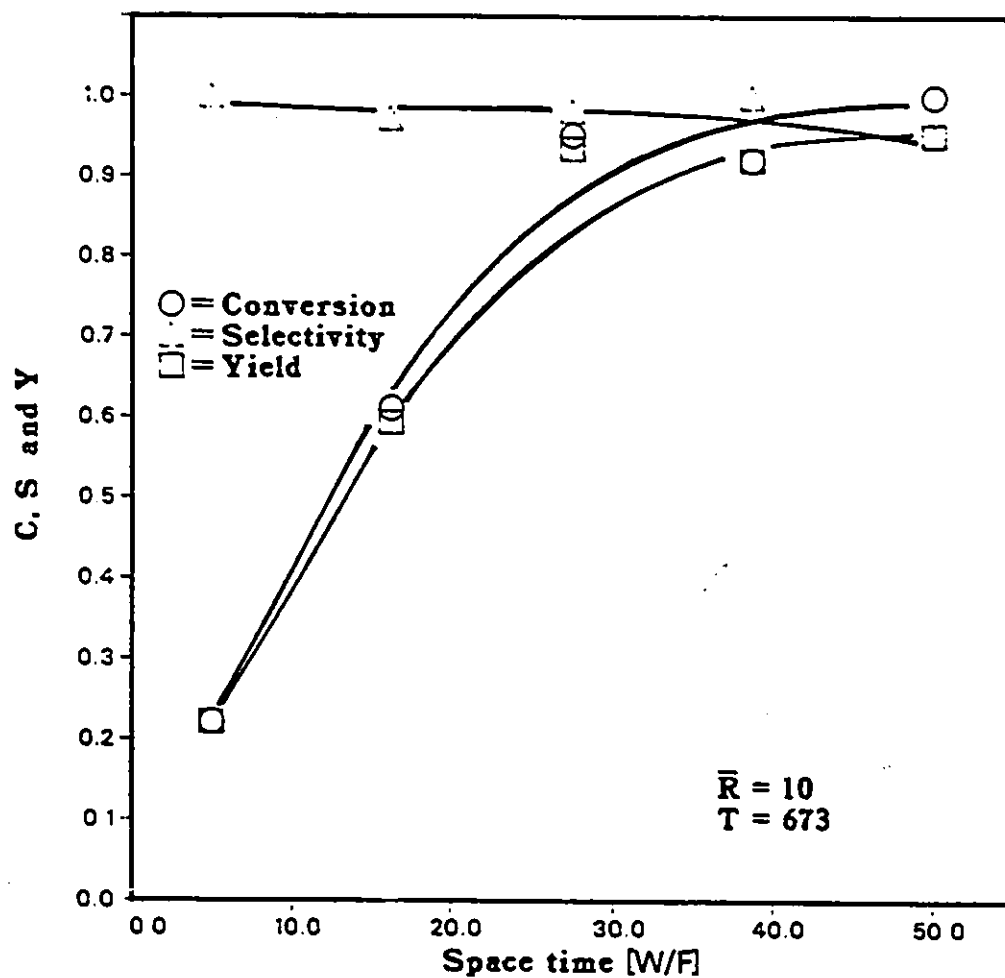


Figure C.32: W/F Effect on Conversion and Yield of HCHO at T of 673 K and $\bar{R}$ of 10

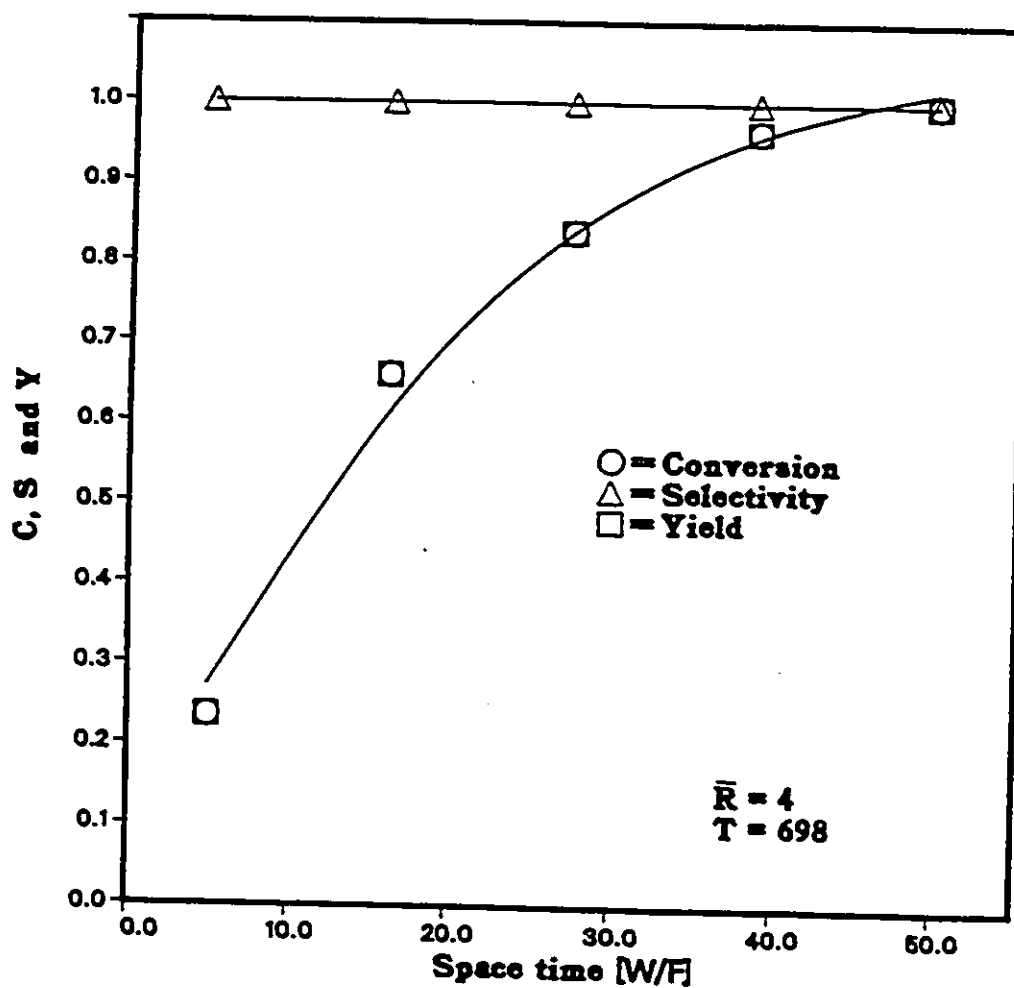


Figure C.33: W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 4

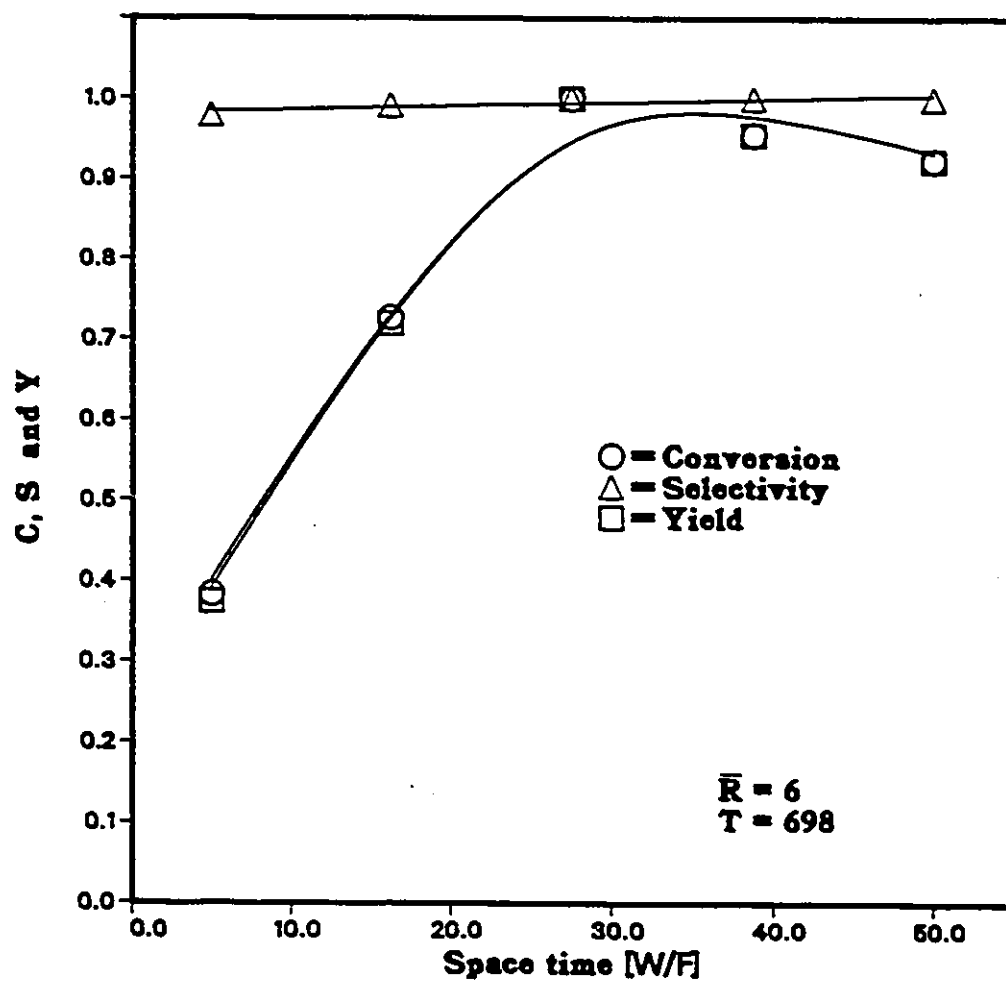


Figure C.34: W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 6

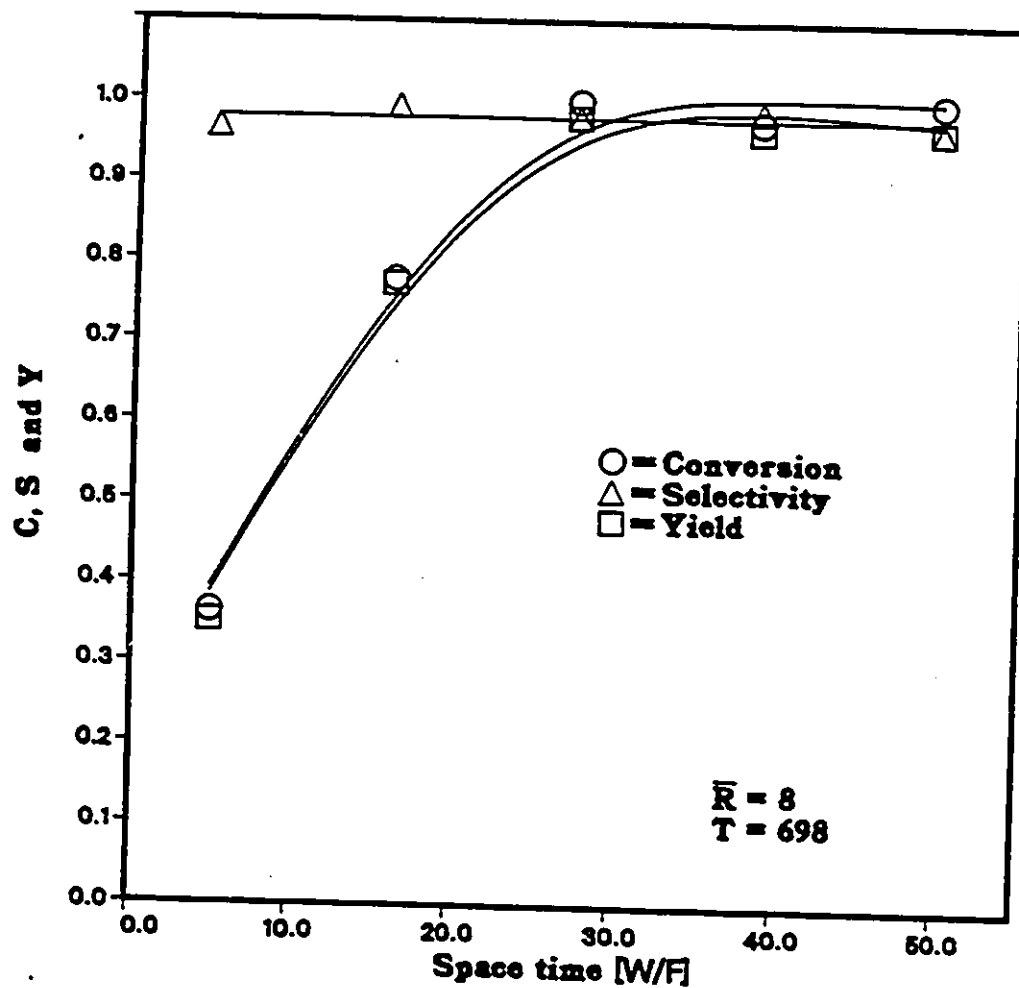


Figure C.35: W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 8

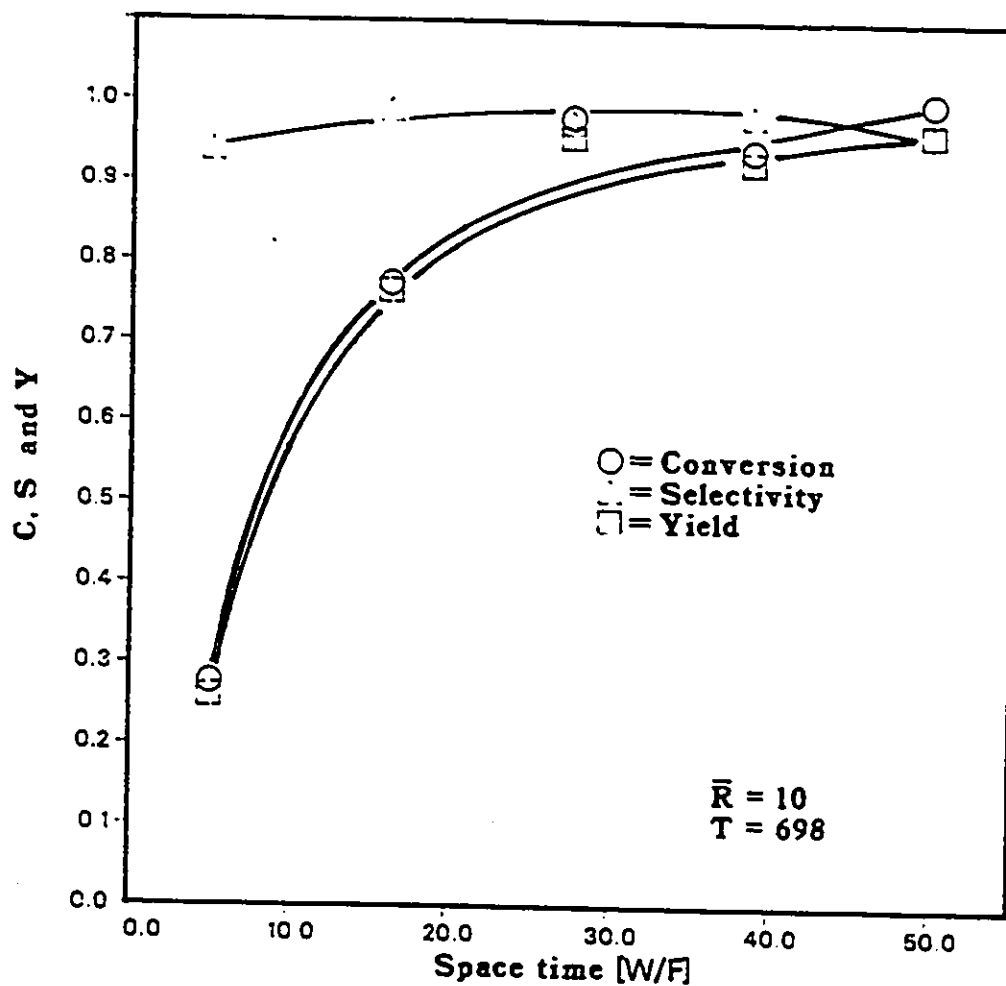


Figure C.36: W/F Effect on Conversion and Yield of HCHO at T of 698 K and $\bar{R}$ of 10

C.3 $\bar{R}$ Effect on Conversion and Yield of HCHO

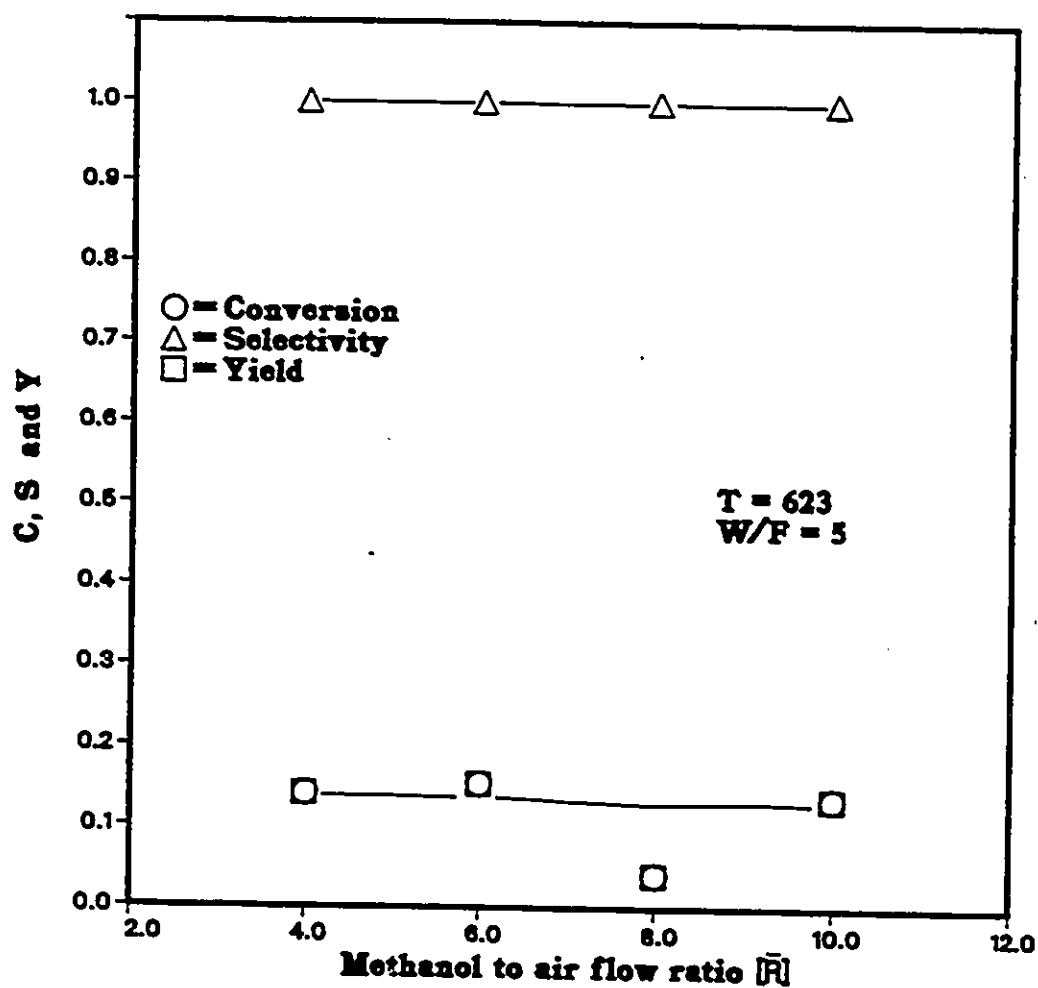


Figure C.37: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 5

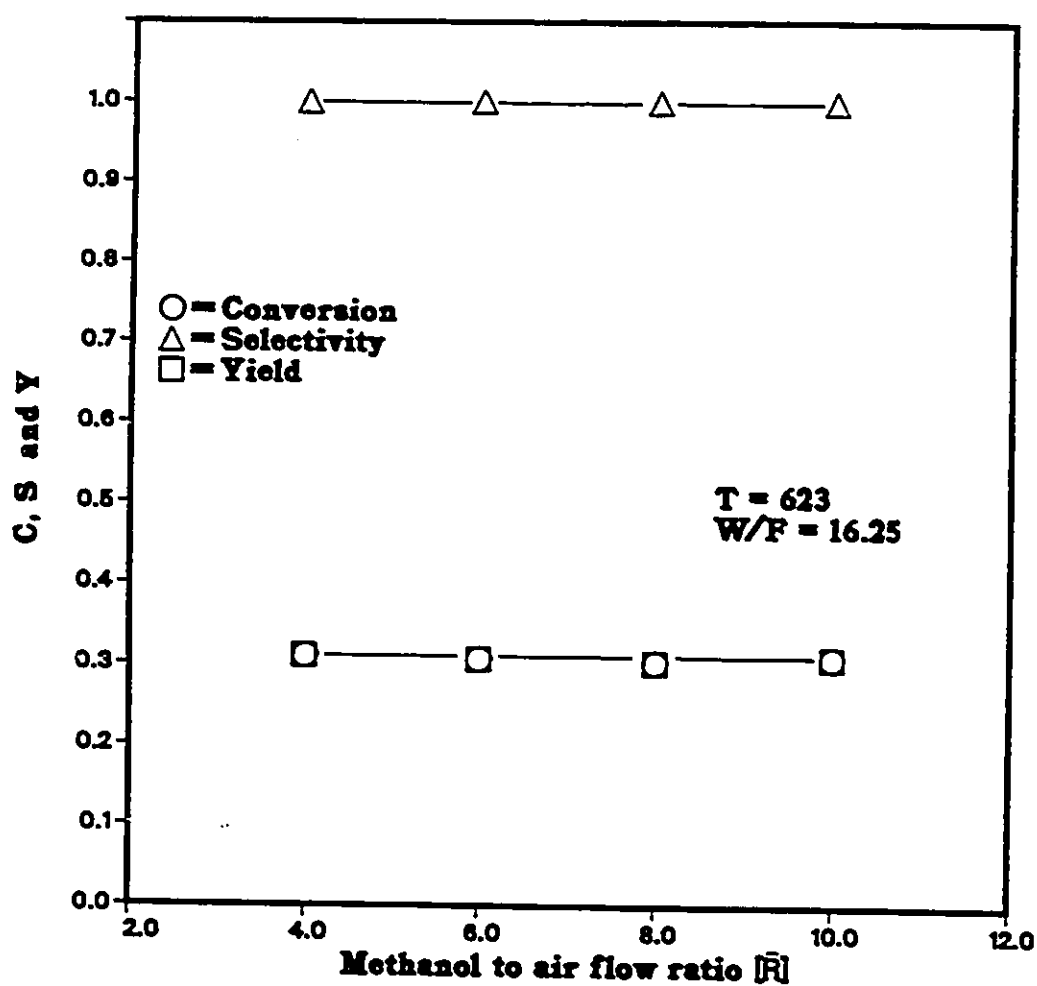


Figure C.38: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 16.25

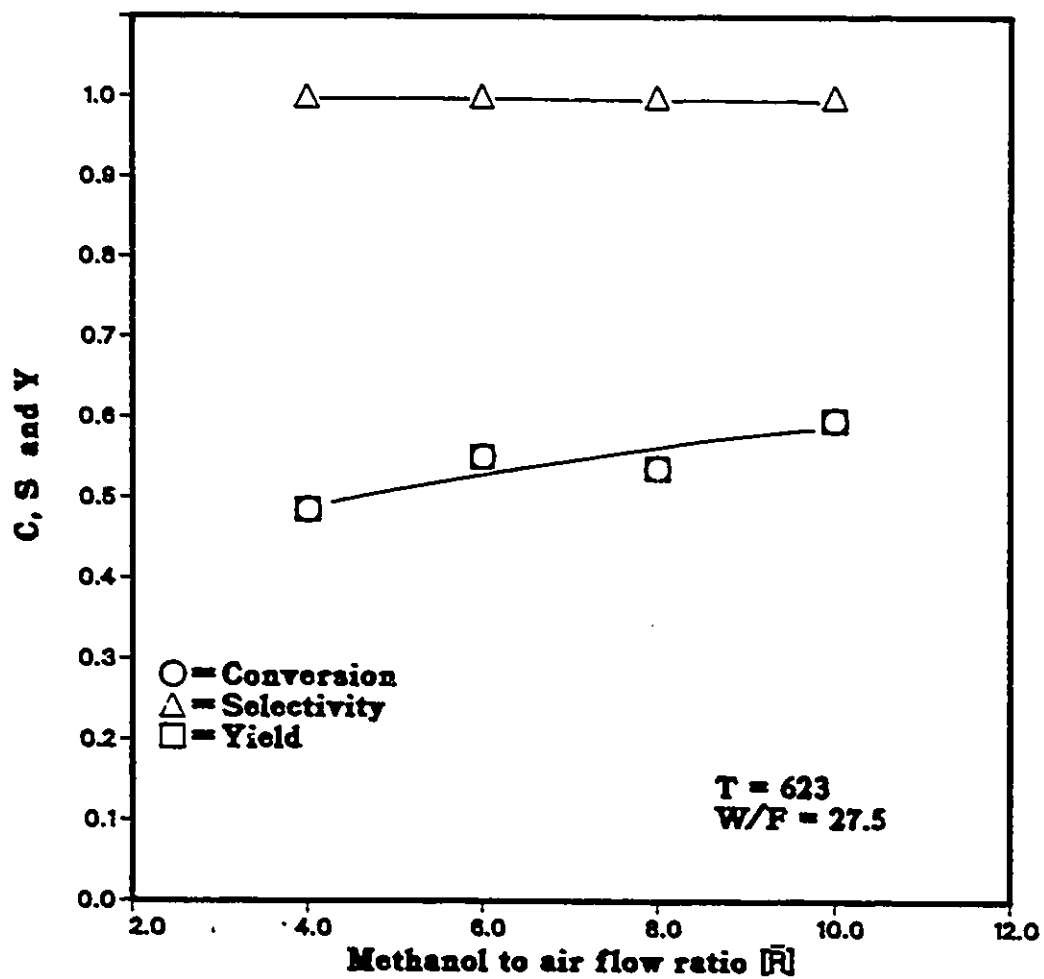


Figure C.39: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 27.5

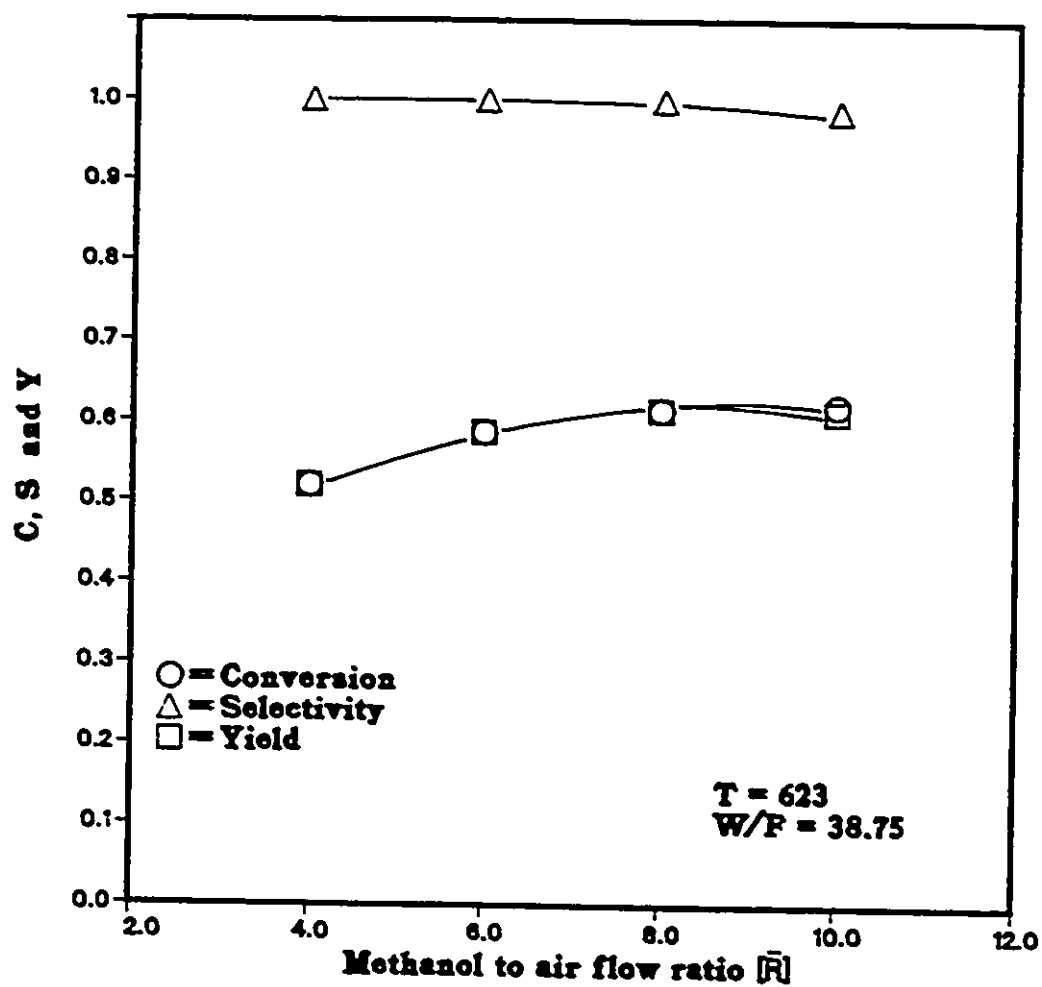


Figure C.40: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 38.75

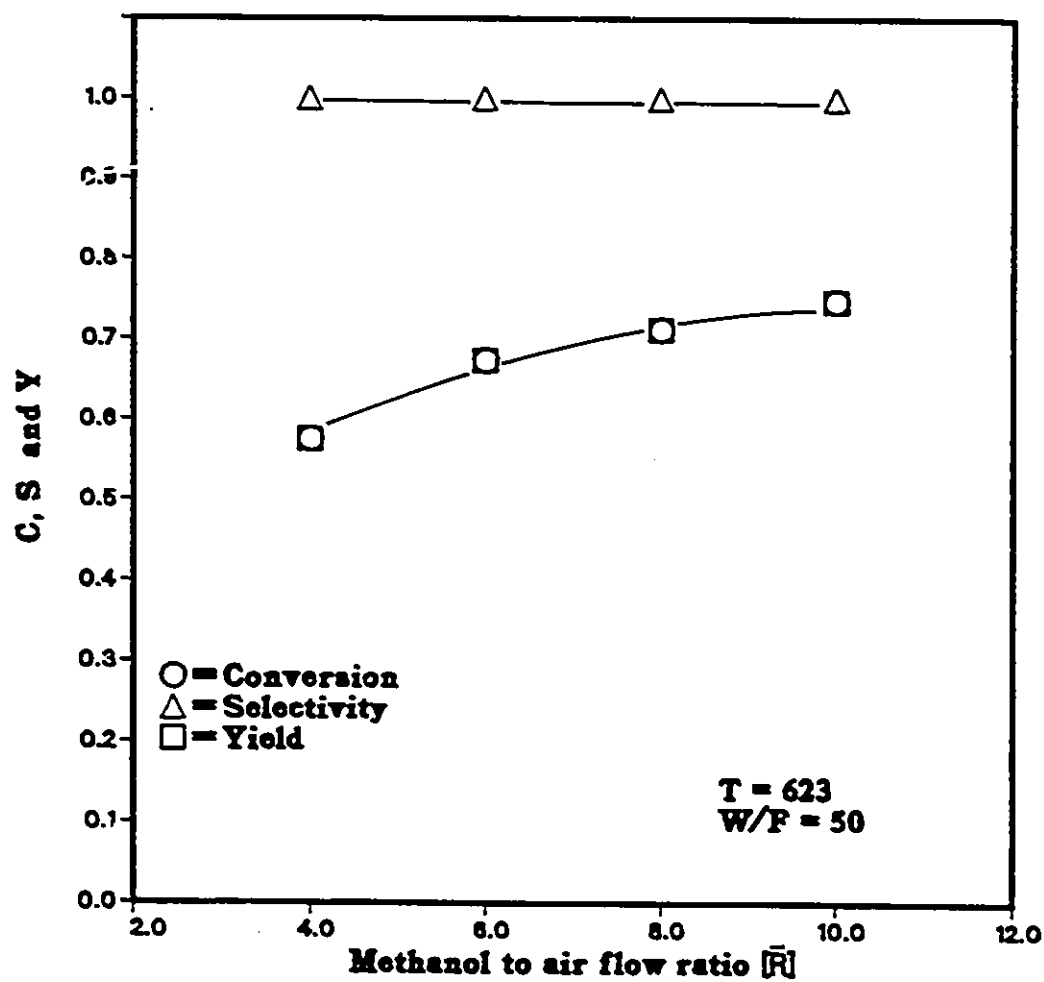


Figure C.41: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 623 K and W/F of 50

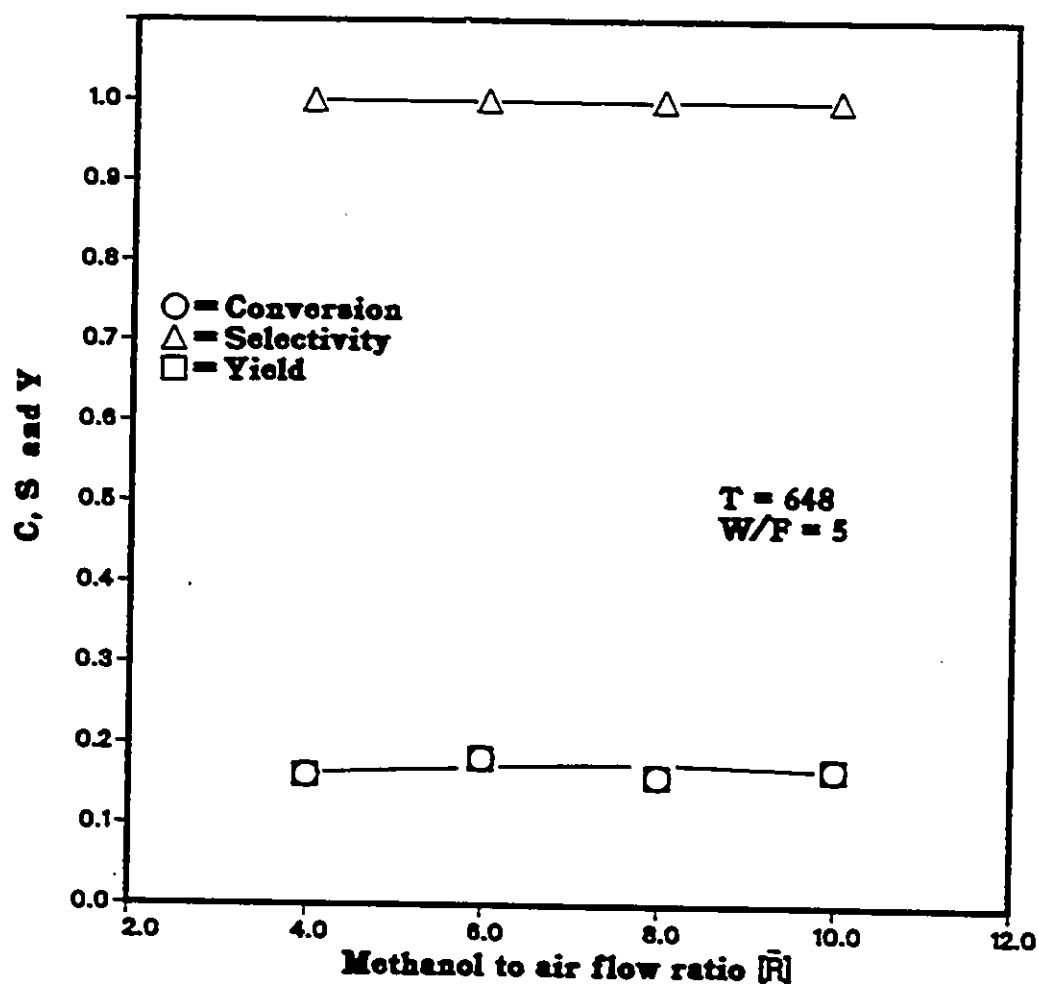


Figure C.42: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 5

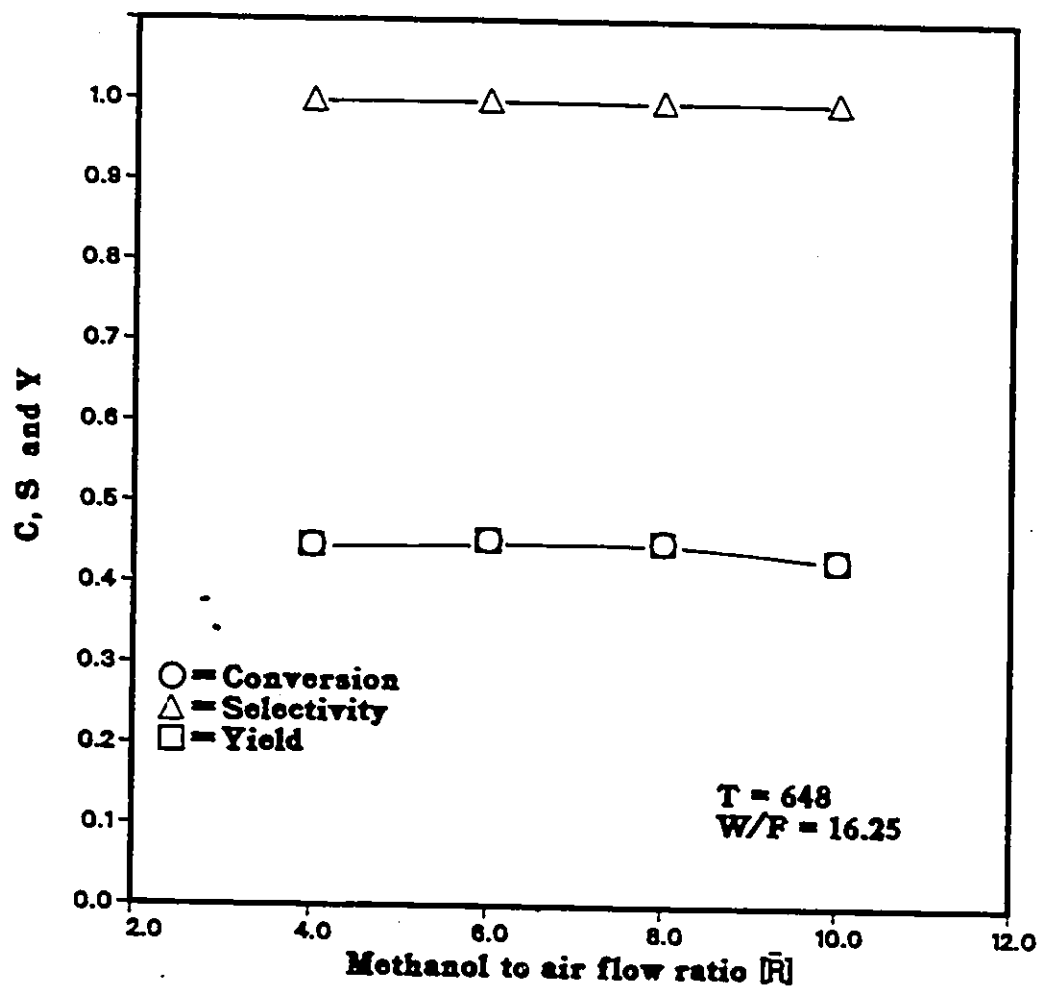


Figure C.43: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 16.25

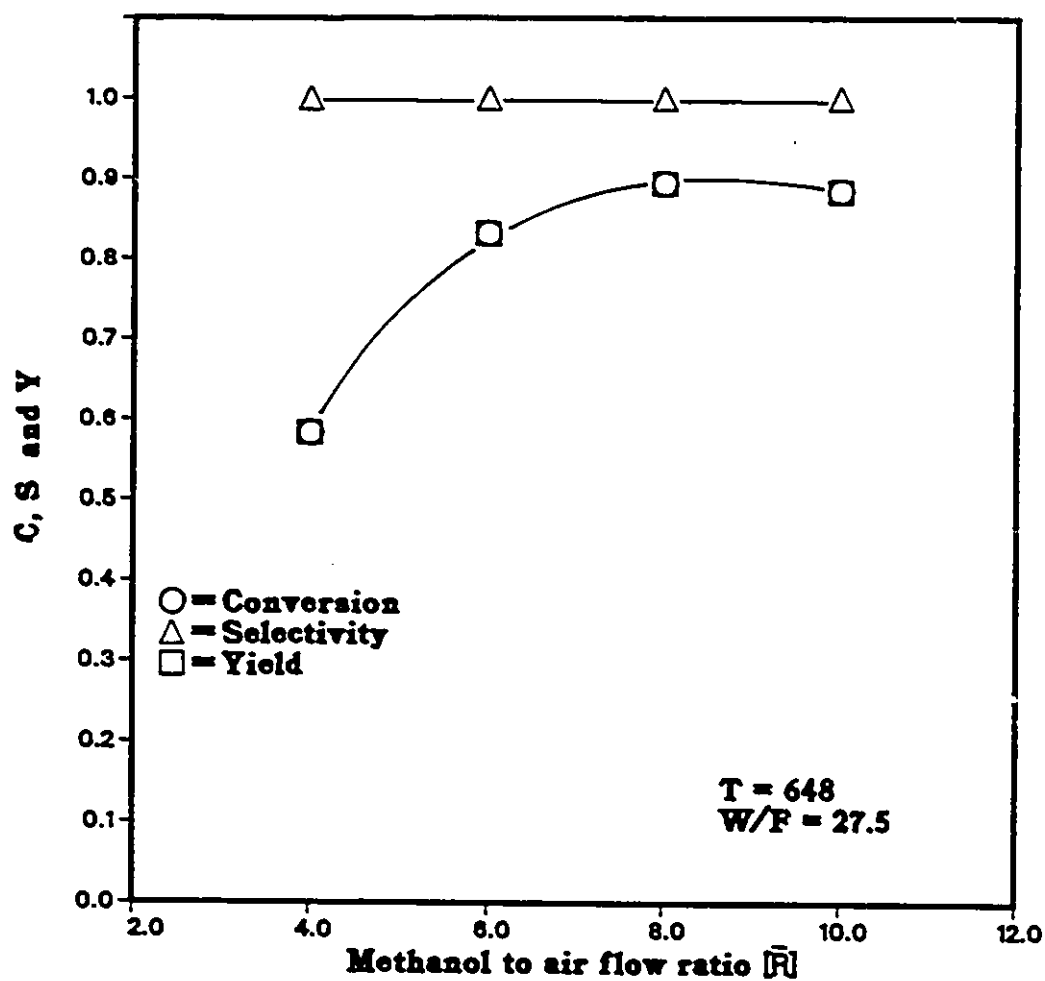


Figure C.44: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 27.5

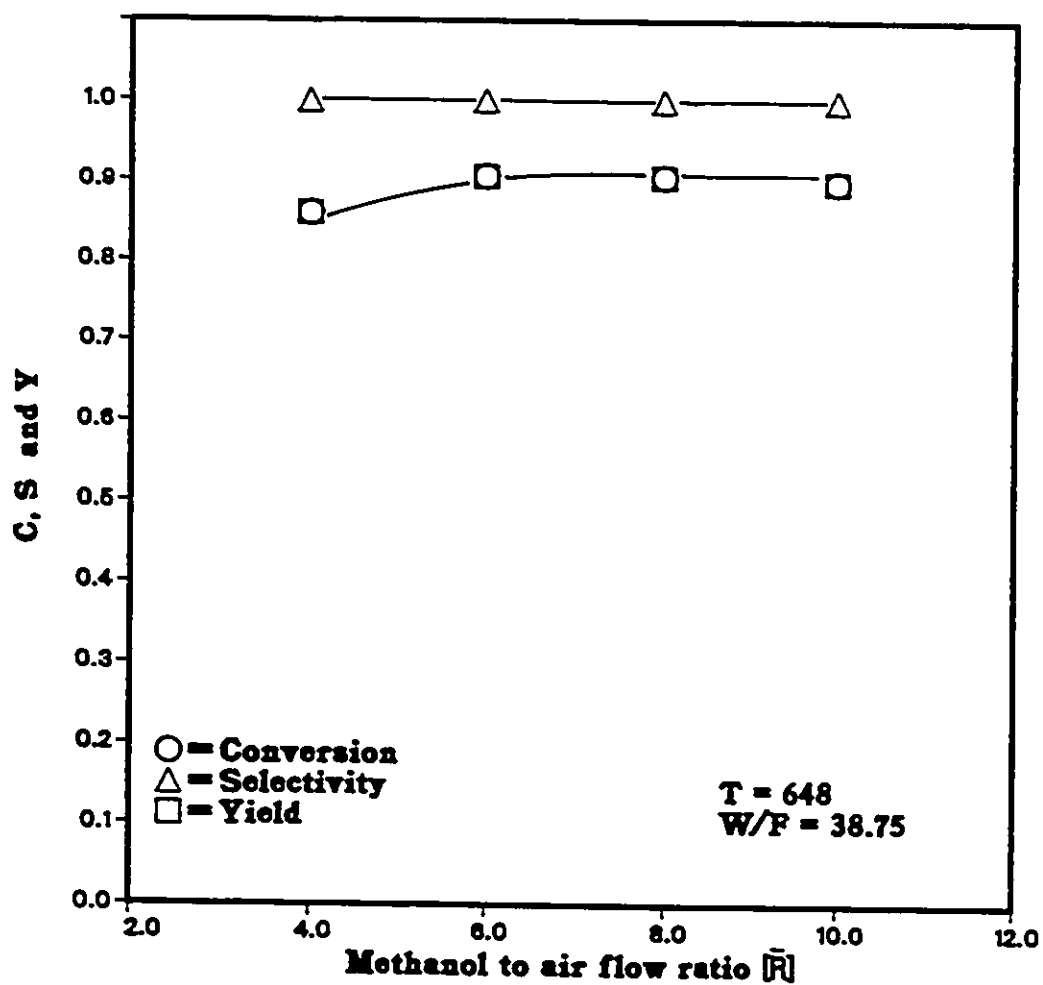


Figure C.45: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 38.75

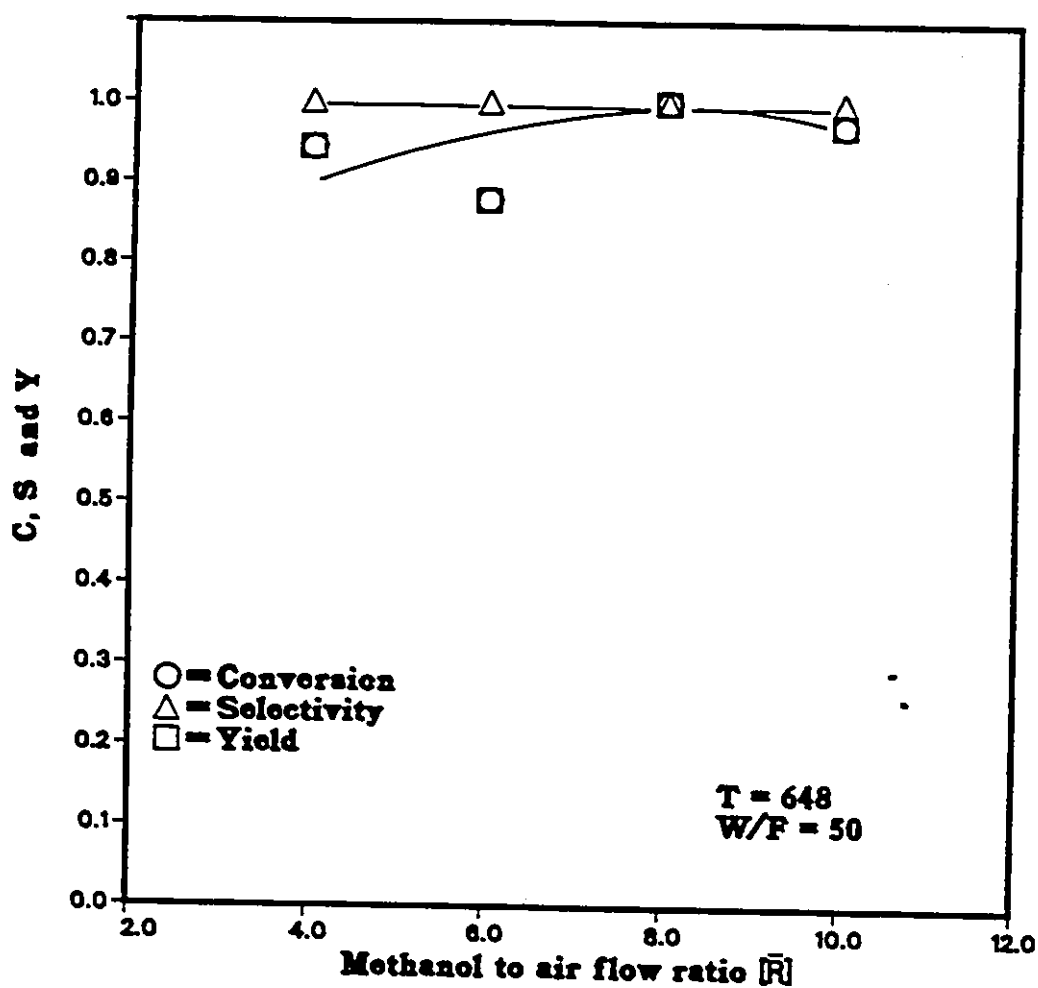


Figure C.46: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 648 K and W/F of 50

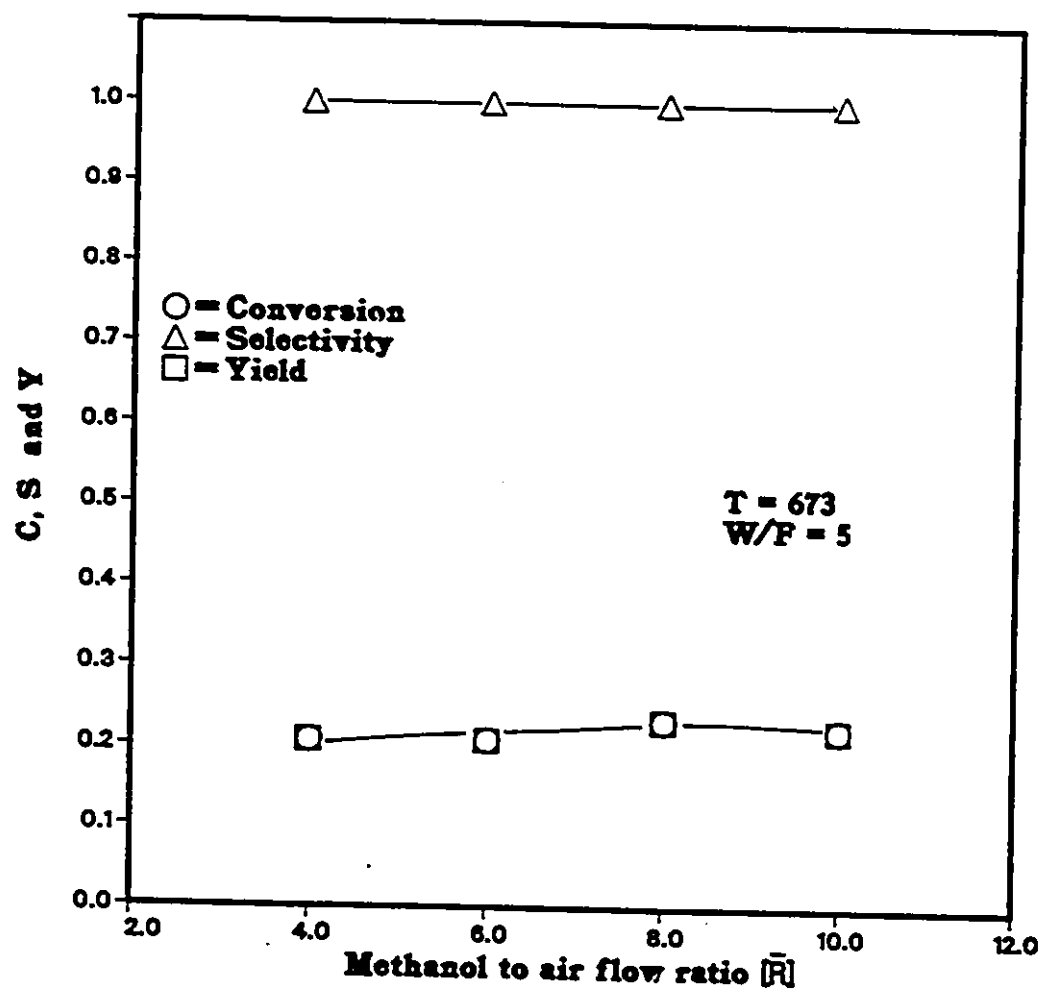


Figure C.47: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 5

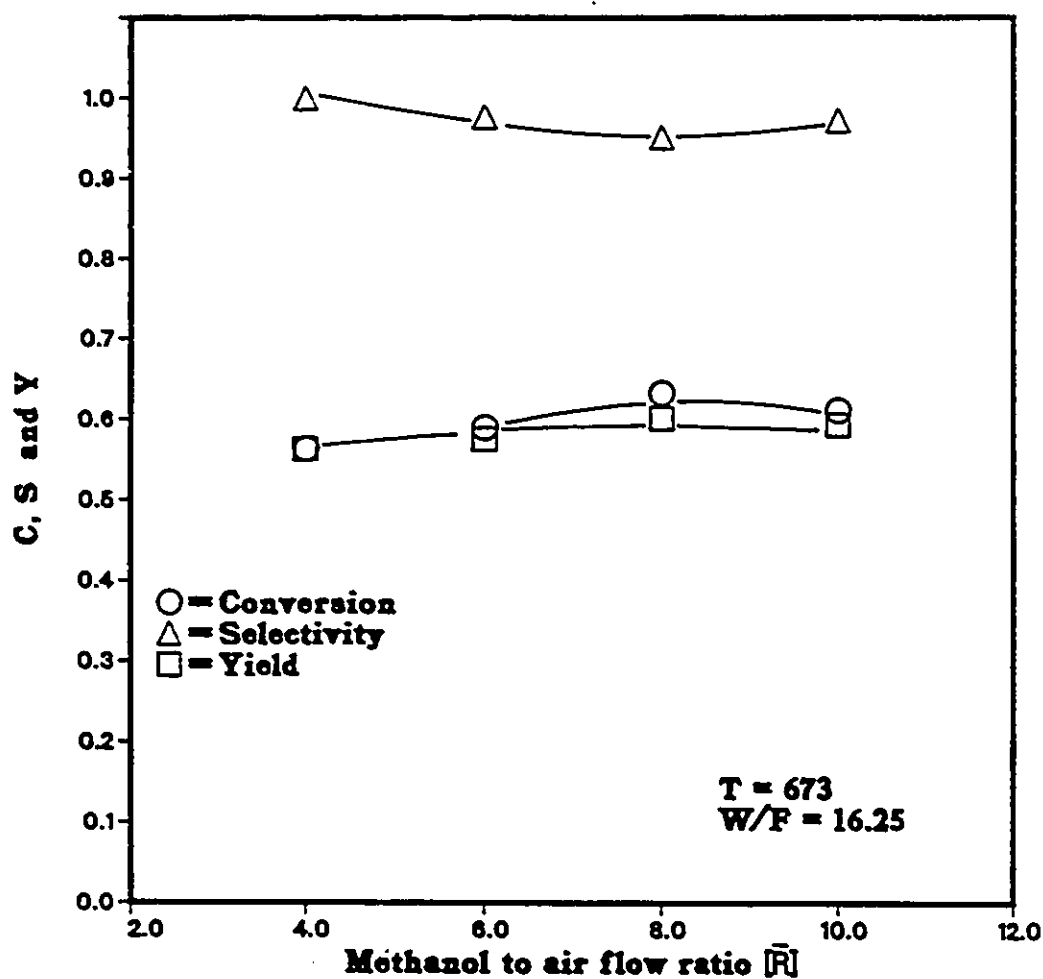


Figure C.48: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 16.25

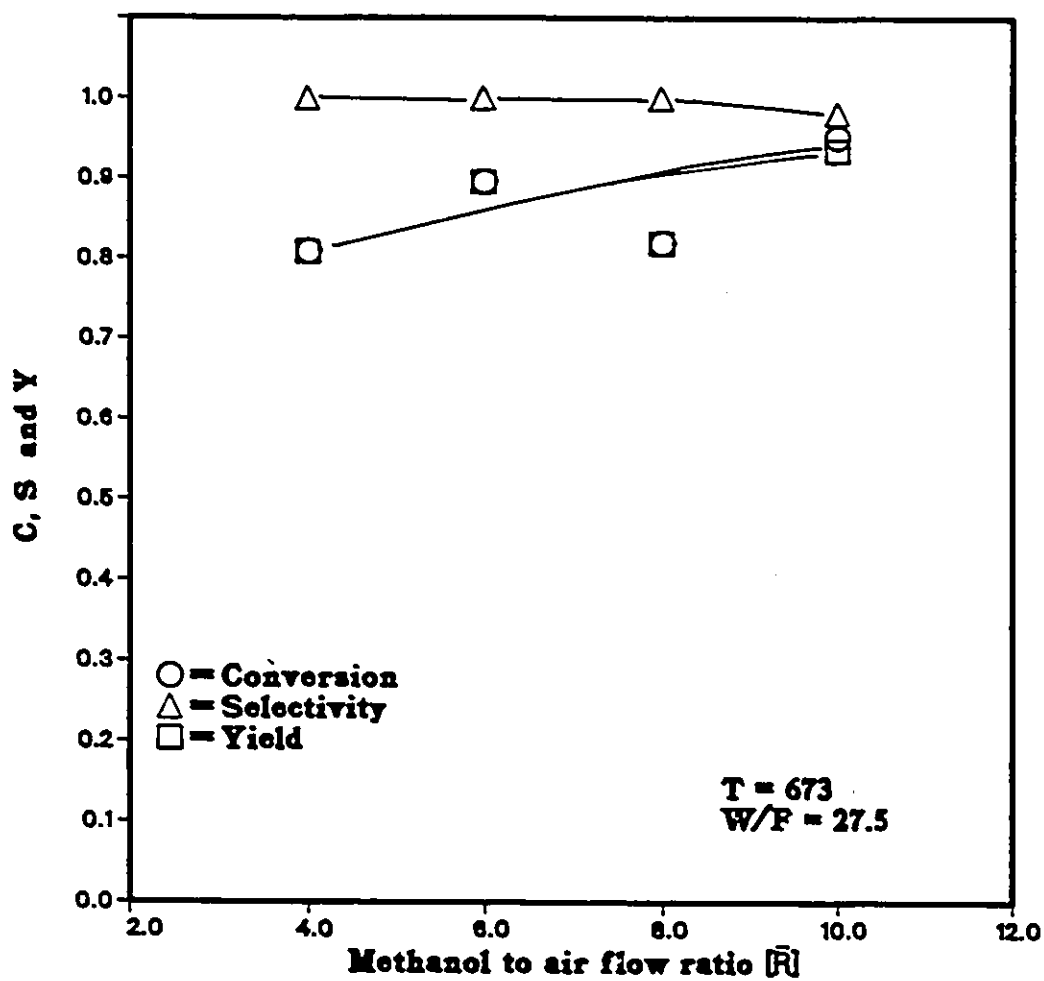


Figure C.49: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 27.5

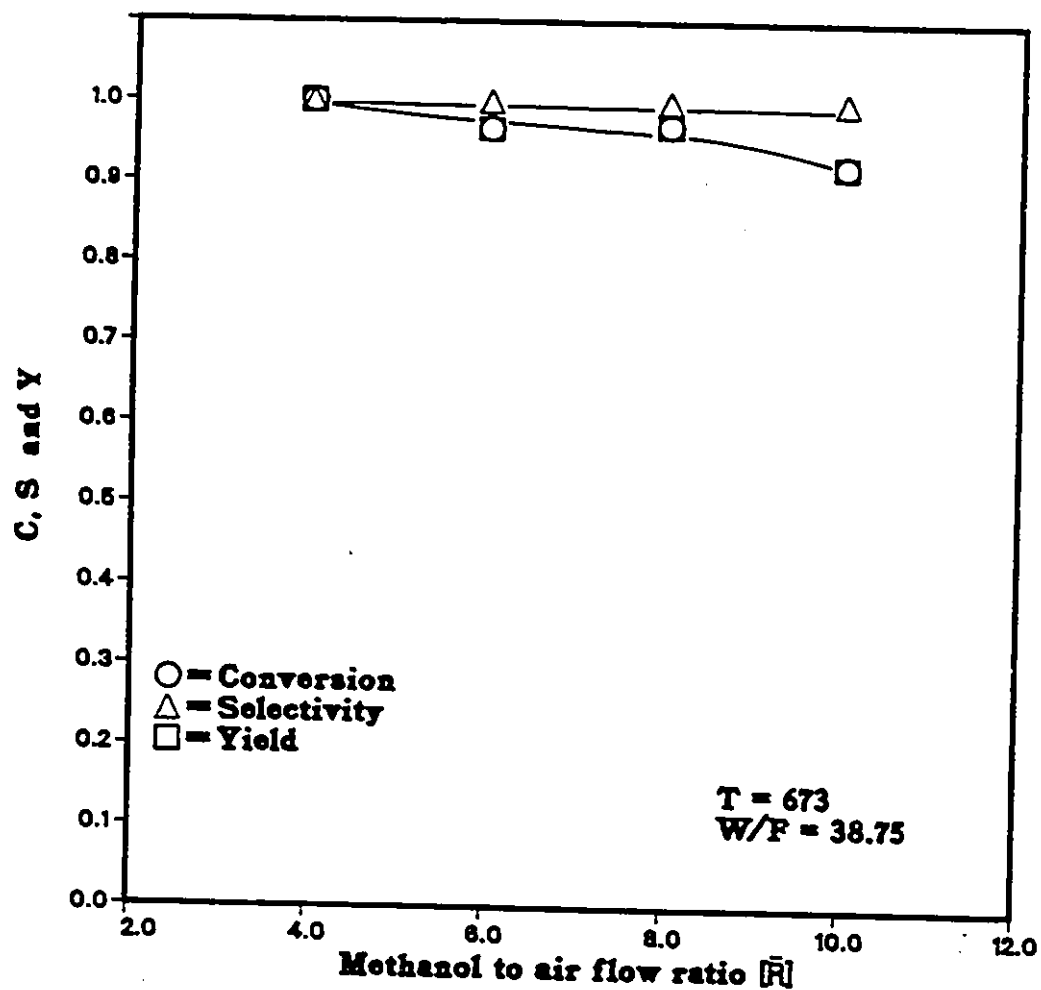


Figure C.50: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 38.75

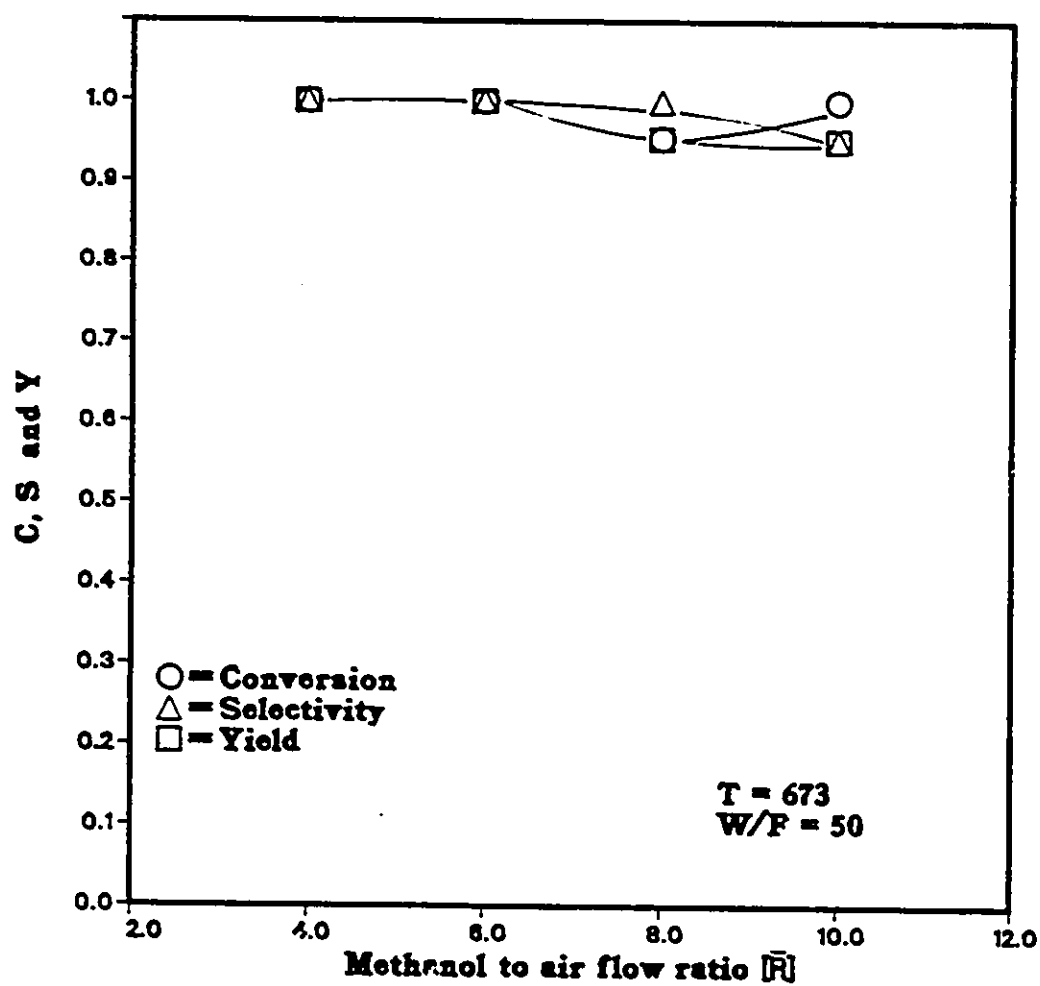


Figure C.51: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 673 K and W/F of 50

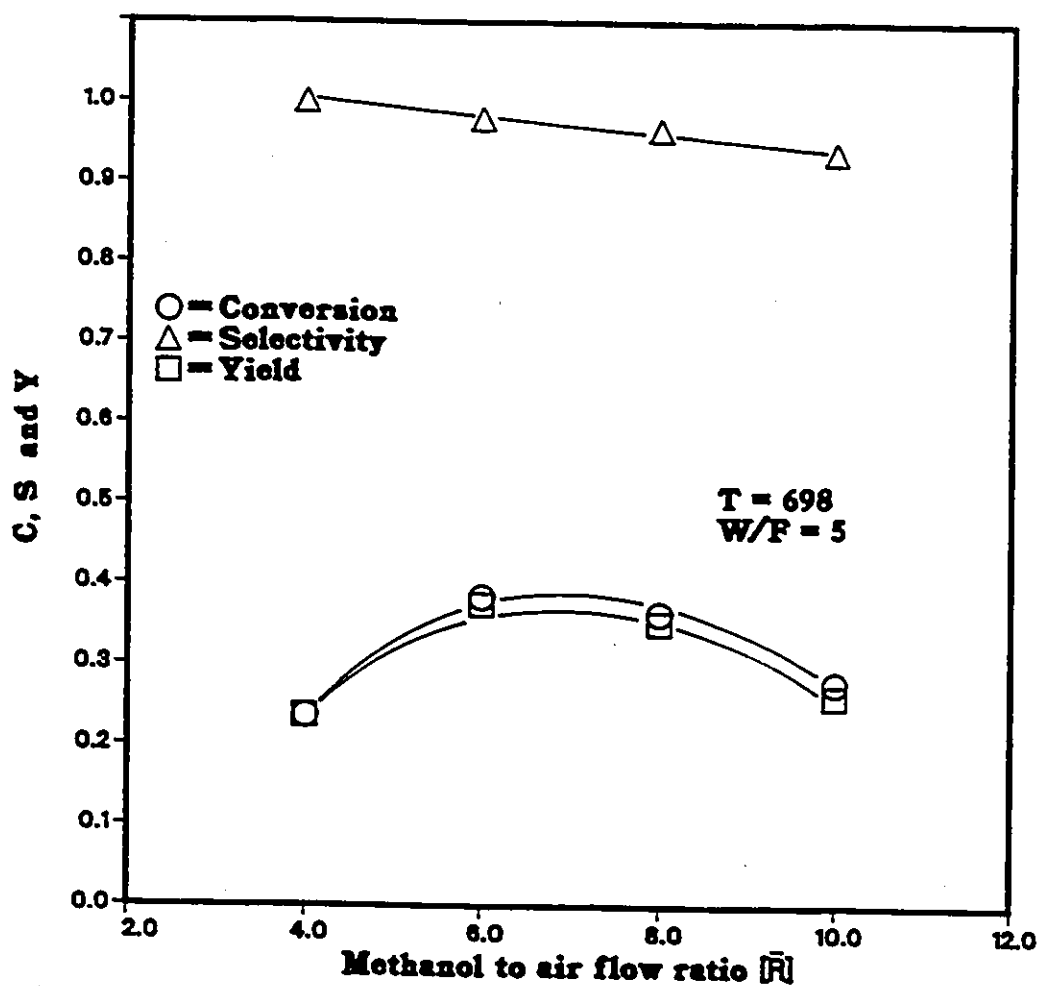


Figure C.52: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 5

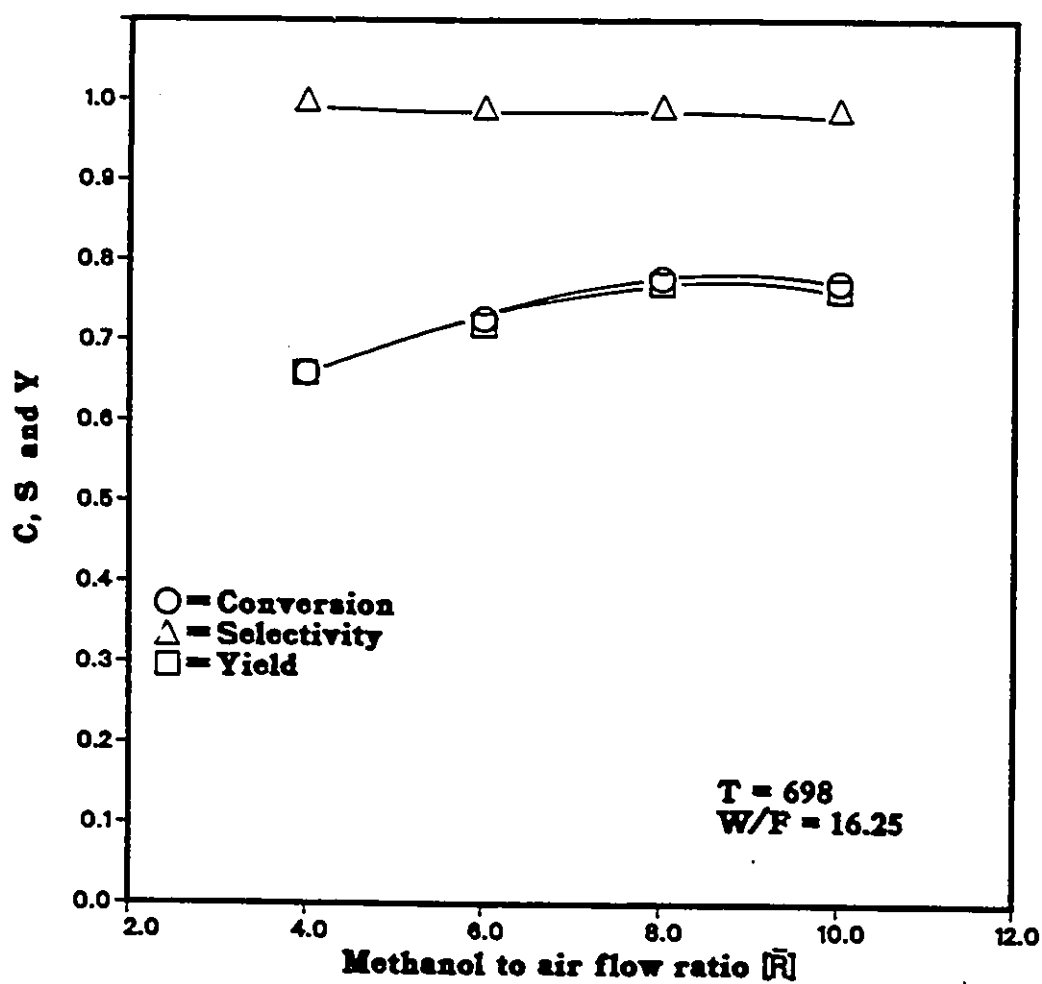


Figure C.53: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 16.25

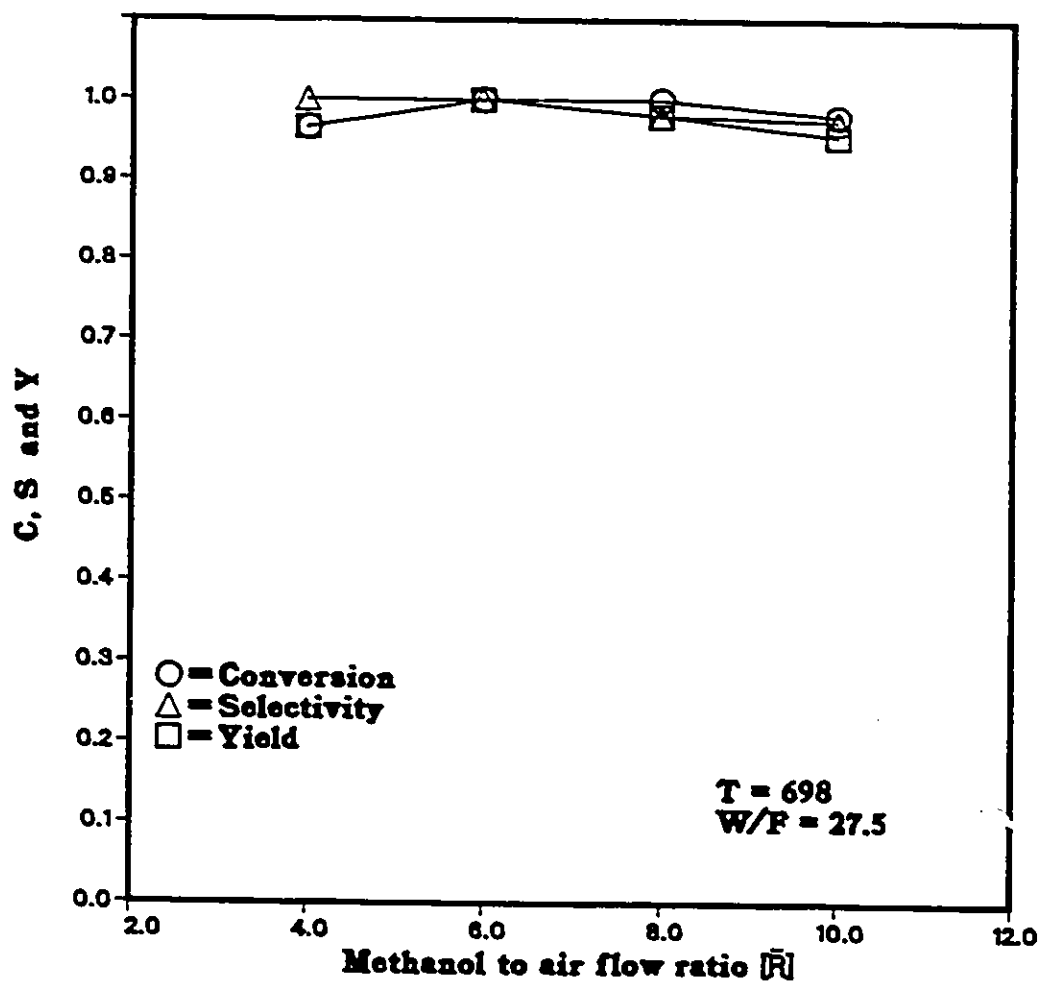


Figure C.54: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 27.5

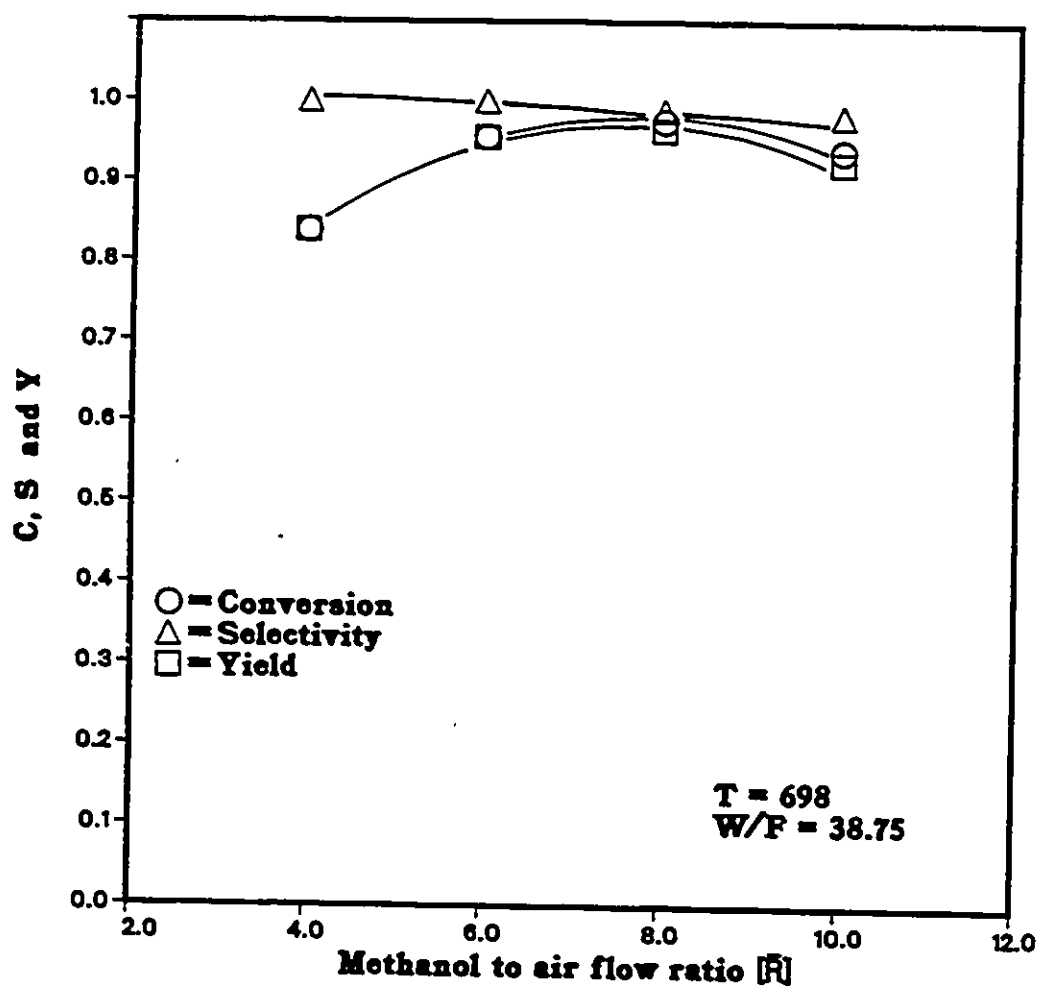


Figure C.55: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 38.75

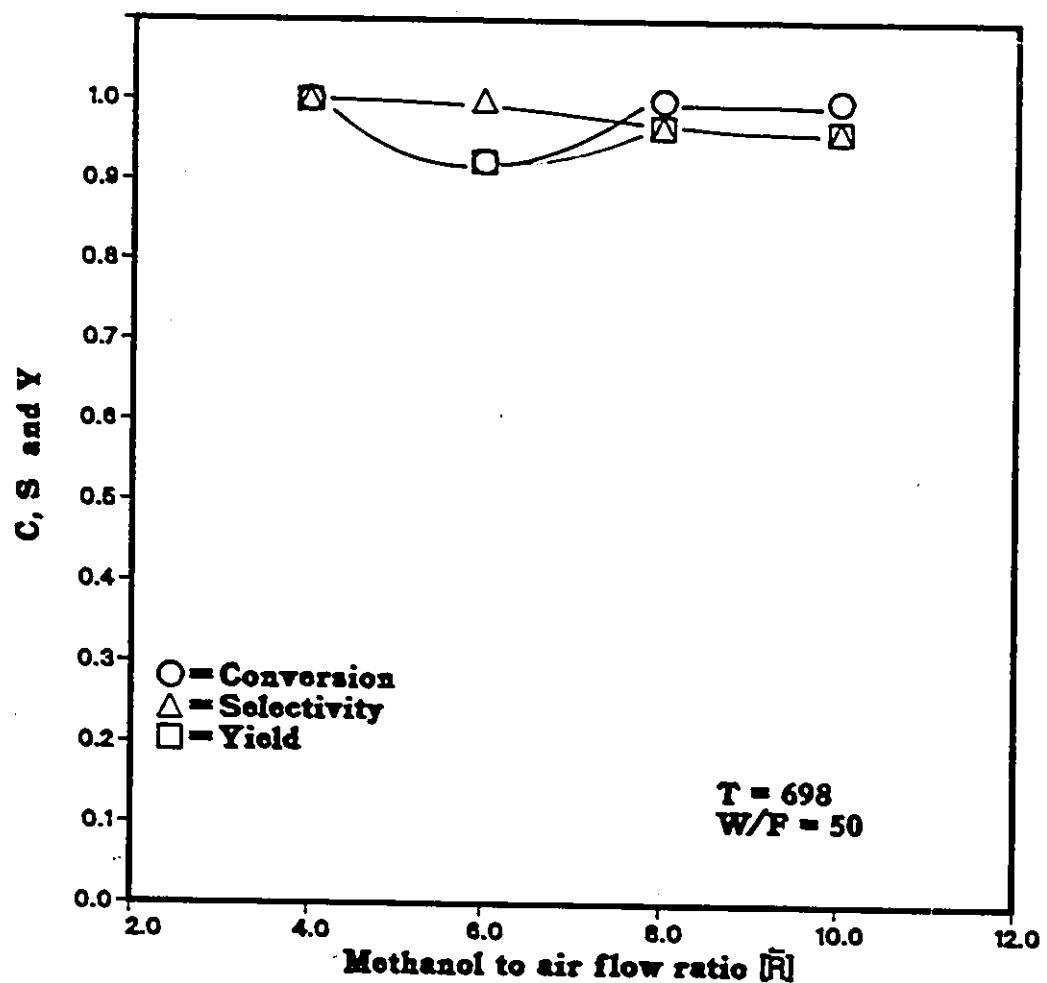


Figure C.56: $\bar{R}$ Effect on Conversion and Yield of HCHO at T of 698 K and W/F of 50

Appendix D

Mass Balance

The mass balance was performed based on carbon-containing products. A sample calculation is given in this appendix, as well as the results from the computer program. The latter being shown in Appendix B.

D.1 Sample Calculation

This calculation is based on the experimental data of run # J04.

From the gas analysis the mole ratios are:

$$\frac{\text{CO}_2}{\text{N}_2} = 0.0208$$

$$\frac{\text{O}_2}{\text{N}_2} = 0.1995$$

$$\frac{\text{CO}}{\text{N}_2} = 0.00237$$

As Nitrogen remains unreacted:

moles of N_2 in feed = moles of N_2 in product

moles of N_2 in feed = 0.586 moles/h

$$\begin{aligned}
 F_{\text{CO}_2} &= \text{moles of CO}_2 \text{ in product} \\
 &= 0.586 \times 0.0208 \\
 &= 1.2188 \times 10^{-2}
 \end{aligned}$$

$$\begin{aligned}
 F_{\text{O}_2} &= \text{moles of O}_2 \text{ unreacted} \\
 &= 0.586 \times 0.1995 \\
 &= 0.1169 \text{ moles/h}
 \end{aligned}$$

$$\begin{aligned}
 F_{\text{CO}} &= \text{moles of CO in product} \\
 &= 0.586 \times 0.00237 \\
 &= 1.3888 \times 10^{-3}
 \end{aligned}$$

From the liquid analysis the mole ratios are:

$$\frac{F}{W} = 0.2934$$

$$\frac{M}{W} = 0.1932$$

where F is the number of moles of formaldehyde in the liquid product, M is the number of moles of methanol in the liquid product and W is the number of moles of water in the liquid product.

Basing the moles of each product on T , the total number of moles of liquid product:

$$\begin{aligned}
 \frac{F}{T} &= \frac{F}{W} \times \frac{W}{T} \\
 \frac{M}{T} &= \frac{M}{W} \times \frac{W}{T} \\
 T &= F + M + W \\
 1 - \frac{W}{T} &= \frac{F}{T} + \frac{M}{T} \\
 \frac{W}{T} &= \frac{1}{1 + \frac{F}{W} + \frac{M}{W}} \\
 &= 0.6727 \\
 \frac{F}{T} &= 0.1974 \\
 \frac{M}{T} &= 0.1300
 \end{aligned}$$

Material Balance:

$\circ M$ = moles of methanol in feed

$$\circ M = M + F + F_{\text{CO}_2} + F_{\text{CO}} \quad (\text{D.1})$$

From stoichiometric relationships:

$$W = F + 2(F_{\text{CO}_2} + F_{\text{CO}}) \quad (\text{D.2})$$

$$T = M + W + F \quad (\text{D.3})$$

Placing values of F and W from relations D.1 and D.2 in D.3:

$$\begin{aligned} T &= \circ M + F + F_{\text{CO}_2} + F_{\text{CO}} \\ \frac{F}{T} &= \frac{F}{\circ M + F + F_{\text{CO}_2} + F_{\text{CO}}} \\ F &= \frac{F}{T} \times (\circ M + F + F_{\text{CO}_2} + F_{\text{CO}}) \end{aligned}$$

Rearranging:

$$\begin{aligned} F &= \frac{\frac{F}{T} \times (\circ M + F_{\text{CO}_2} + F_{\text{CO}})}{1 - \frac{F}{T}} \\ &= 0.01085 \text{ moles/h} \\ T &= 0.05495 \text{ moles/h} \\ M &= \frac{M}{T} \times T \\ &= 0.007141 \text{ moles/h} \end{aligned}$$

Carbon Balance Check :

$$\begin{aligned} \text{In feed} &= 0.030512 \text{ moles/h} \\ \text{In products} &= 0.01085 + 0.007141 + 0.012188 + 0.001388 \\ &= 0.03158 \text{ moles/h} \end{aligned}$$

Error in Material Balance: -3.498%

$$\begin{aligned}\text{Conversion} &= 1 - \frac{0.01085}{0.03158} \\ &= 77.4\%\end{aligned}$$

$$\begin{aligned}\text{Selectivity} &= \frac{F}{F+F_{\text{CO}_2}+F_{\text{CO}}} \\ &= 44.4\%\end{aligned}$$

$$\begin{aligned}\text{Yield} &= \text{Selectivity} \times \text{Conversion} \\ &= 34.3\%\end{aligned}$$

D.2 Results from Computer Program

MATERIAL BALANCE

RUN	ME (MOL/H)	GFR (MOL/H)	CO ₂ /N ₂	CO/N ₂	F/W	M/W
A01	.30512E-01	.520E+00	.000E+00	.000E+00	0.0490	9.6205
A02	.30512E-01	.513E+00	.744E-03	.000E+00	0.7107	2.3011
A03	.30512E-01	.510E+00	.123E-02	.164E-02	0.7840	1.5996
A04	.30512E-01	.520E+00	.130E-02	.200E-02	0.8684	1.0475
A05	.30512E-01	.501E+00	.221E-02	.206E-02	0.8807	0.8999
B01	.30512E-01	.523E+00	.523E-03	.000E+00	0.0203	12.6488
B02	.30512E-01	.516E+00	.128E-02	.000E+00	0.0285	7.9615
B03	.30512E-01	.509E+00	.198E-02	.000E+00	0.0558	7.1958
B04	.30512E-01	.516E+00	.239E-02	.000E+00	0.4981	3.7073
C01	.30512E-01	.510E+00	.231E-02	.000E+00	0.8638	1.1076
C02	.30512E-01	.377E+00	.260E-02	.000E+00	0.9573	2.4237
C03	.30512E-01	.714E+00	.120E-02	.000E+00	0.9502	1.2720
C04	.30512E-01	.691E+00	.833E-02	.000E+00	0.5116	0.4929
C05	.30512E-01	.382E+00	.135E-02	.000E+00	1.0472	0.9518
C06	.30512E-01	.499E+00	.104E-02	.000E+00	0.8568	2.0272
D01	.30512E-01	.515E+00	.199E-02	.000E+00	0.0110	9.8706

APPENDIX D. MASS BALANCE

268

D02	.30512E-01	.517E+00	.263E-02	.000E+00	0.0457	6.1769
D03	.30512E-01	.522E+00	.285E-02	.000E+00	0.0643	5.9442
D04	.30512E-01	.512E+00	.316E-02	.000E+00	0.4039	4.2619
D05	.30512E-01	.510E+00	.651E-02	.000E+00	0.5501	1.7382
E01	.30512E-01	.514E+00	.440E-02	.000E+00	0.6886	0.7444
E02	.30512E-01	.397E+00	.803E-02	.000E+00	0.0258	3.2477
E03	.30512E-01	.712E+00	.541E-02	.000E+00	0.4768	1.1843
E04	.30512E-01	.711E+00	.361E-02	.000E+00	0.0435	7.7358
E05	.30512E-01	.403E+00	.320E-02	.000E+00	0.3360	3.6888
E06	.30512E-01	.553E+00	.884E-02	.000E+00	0.7411	0.8677
F01	.30512E-01	.511E+00	.000E+00	.000E+00	1.1392	0.4340
F02	.30512E-01	.410E+00	.232E-02	.000E+00	0.8223	1.2051
F03	.30512E-01	.725E+00	.105E-02	.000E+00	1.0532	0.7369
F04	.30512E-01	.742E+00	.186E-01	.000E+00	0.3300	0.2320
F05	.30512E-01	.415E+00	.527E-01	.000E+00	0.1810	0.1940
F06	.30512E-01	.520E+00	.000E+00	.000E+00	1.0384	0.1668
G01	.30512E-01	.505E+00	.000E+00	.000E+00	1.0758	0.6547
G02	.30512E-01	.404E+00	.000E+00	.000E+00	0.9731	3.3407
G03	.30512E-01	.766E+00	.000E+00	.000E+00	1.1682	1.0270
G04	.30512E-01	.773E+00	.157E-01	.000E+00	0.3865	0.3210
G05	.30512E-01	.392E+00	.351E-01	.158E-02	0.2421	0.2654
G06	.30512E-01	.501E+00	.000E+00	.000E+00	1.1036	0.4501
H01	.30512E-01	.520E+00	.175E-02	.000E+00	0.9700	0.1814
H02	.30512E-01	.402E+00	.000E+00	.000E+00	1.0414	1.1493
H03	.30512E-01	.770E+00	.000E+00	.000E+00	1.1319	0.5090
H04	.30512E-01	.767E+00	.000E+00	.000E+00	1.0410	0.5269
H05	.30512E-01	.386E+00	.000E+00	.000E+00	1.0181	0.0000
H06	.30512E-01	.521E+00	.583E-03	.000E+00	1.0688	0.1712
I01	.30512E-01	.496E+00	.000E+00	.000E+00	1.0768	0.7329
I02	.30512E-01	.402E+00	.285E-01	.633E-02	0.2396	0.3405
I03	.30512E-01	.762E+00	.193E-01	.319E-02	0.2607	0.1711
I04	.30512E-01	.756E+00	.000E+00	.000E+00	1.0826	1.2908

APPENDIX D. MASS BALANCE

269

I05	.30512E-01	.400E+00	.000E+00	.000E+00	1.0886	0.0489
I06	.30512E-01	.502E+00	.000E+00	.000E+00	1.1409	1.7493
J01	.30512E-01	.530E+00	.174E-02	.000E+00	1.0438	0.2459
J02	.30512E-01	.402E+00	.000E+00	.000E+00	1.1476	1.0881
J03	.30512E-01	.749E+00	.000E+00	.000E+00	1.0979	0.3711
J04	.30512E-01	.742E+00	.208E-01	.237E-02	0.2934	0.1932
J05	.30512E-01	.394E+00	.522E-01	.116E-01	0.1001	0.1343
J06	.30512E-01	.501E+00	.112E-02	.000E+00	1.0573	0.3057
M101	.30512E-01	.756E+00	.000E+00	.000E+00	0.6850	4.1791
M102	.30512E-01	.517E+00	.000E+00	.000E+00	0.7691	4.2505
M103	.30512E-01	.367E+00	.000E+00	.000E+00	0.3977	9.3514
M104	.30512E-01	.296E+00	.000E+00	.000E+00	0.7510	4.8233
M105	.30512E-01	.514E+00	.000E+00	.000E+00	0.9026	1.9057
M201	.30512E-01	.769E+00	.000E+00	.000E+00	1.0622	5.5550
M202	.30512E-01	.496E+00	.000E+00	.000E+00	0.6865	3.0874
M203	.30512E-01	.386E+00	.000E+00	.000E+00	0.6854	3.6003
M204	.30512E-01	.301E+00	.000E+00	.000E+00	0.6780	3.3367
M205	.30512E-01	.496E+00	.000E+00	.000E+00	0.8464	2.8357
M301	.30512E-01	.769E+00	.000E+00	.000E+00	0.7112	2.7249
M302	.30512E-01	.489E+00	.000E+00	.000E+00	0.8029	3.0674
M303	.30512E-01	.390E+00	.000E+00	.000E+00	0.8435	2.7918
M304	.30512E-01	.302E+00	.000E+00	.000E+00	0.7634	2.6720
M305	.30512E-01	.508E+00	.000E+00	.000E+00	0.7548	3.1699
M401	.30512E-01	.752E+00	.000E+00	.000E+00	0.7673	2.4834
M402	.30512E-01	.496E+00	.582E-03	.000E+00	0.7914	1.3051
M403	.30512E-01	.391E+00	.116E-02	.000E+00	0.8487	1.5425
M404	.30512E-01	.302E+00	.208E-02	.000E+00	0.7618	2.1208
M405	.30512E-01	.499E+00	.000E+00	.000E+00	0.8103	4.2823
N101	.30512E-01	.776E+00	.000E+00	.000E+00	0.8432	1.8769
N102	.30512E-01	.505E+00	.000E+00	.000E+00	0.7998	1.8163
N103	.30512E-01	.402E+00	.000E+00	.000E+00	0.9160	2.1188

APPENDIX D. MASS BALANCE

270

N104	.30512E-01	.291E+00	.000E+00	.000E+00	0.8916	2.0056
N105	.30512E-01	.509E+00	.578E-03	.000E+00	1.0564	0.7408
N201	.30512E-01	.776E+00	.000E+00	.000E+00	1.0086	1.2502
N202	.30512E-01	.518E+00	.000E+00	.000E+00	1.0590	1.2787
N203	.30512E-01	.394E+00	.000E+00	.000E+00	1.0021	1.2174
N204	.30512E-01	.293E+00	.000E+00	.000E+00	1.0330	1.3667
N205	.30512E-01	.492E+00	.345E-02	.000E+00	0.8976	0.4221
N301	.30512E-01	.733E+00	.000E+00	.000E+00	0.9813	0.7618
N302	.30512E-01	.502E+00	.117E-02	.000E+00	1.0539	0.7537
N303	.30512E-01	.381E+00	.344E-02	.000E+00	1.0433	0.6389
N304	.30512E-01	.307E+00	.228E-02	.000E+00	1.0139	0.6656
N305	.30512E-01	.485E+00	.230E-02	.000E+00	0.9882	0.6144
N401	.30512E-01	.759E+00	.000E+00	.000E+00	0.9653	0.5000
N402	.30512E-01	.473E+00	.573E-03	.000E+00	1.0386	0.3957
N403	.30512E-01	.390E+00	.575E-03	.000E+00	1.0919	0.3161
N404	.30512E-01	.299E+00	.114E-02	.000E+00	1.0636	0.3184
N405	.30512E-01	.495E+00	.117E-02	.000E+00	1.0086	0.6315
O101	.30512E-01	.762E+00	.000E+00	.000E+00	0.9841	1.0453
O102	.30512E-01	.505E+00	.000E+00	.000E+00	1.0316	0.8397
O103	.30512E-01	.398E+00	.000E+00	.000E+00	1.1246	0.9713
O104	.30512E-01	.302E+00	.000E+00	.000E+00	1.1100	0.7480
O105	.30512E-01	.499E+00	.000E+00	.000E+00	1.0074	0.0631
O201	.30512E-01	.776E+00	.000E+00	.000E+00	1.0301	0.7370
O202	.30512E-01	.508E+00	.000E+00	.000E+00	1.1030	0.2240
O203	.30512E-01	.390E+00	.000E+00	.000E+00	1.0520	0.1246
O204	.30512E-01	.312E+00	.000E+00	.000E+00	1.0427	0.1369
O205	.30512E-01	.488E+00	.000E+00	.000E+00	1.0562	0.0842
O301	.30512E-01	.756E+00	.000E+00	.000E+00	1.0945	0.2596
O302	.30512E-01	.518E+00	.000E+00	.000E+00	1.0286	0.1212
O303	.30512E-01	.399E+00	.000E+00	.000E+00	1.0455	0.2307
O304	.30512E-01	.294E+00	.229E-02	.000E+00	0.9694	0.0495

APPENDIX D. MASS BALANCE

271

Q305	.30512E-01	.518E+00	.000E+00	.000E+00	1.0527	0.1045
Q401	.30512E-01	.745E+00	.000E+00	.000E+00	1.0280	0.1984
Q402	.30512E-01	.515E+00	.000E+00	.000E+00	1.0390	0.0000
Q403	.30512E-01	.370E+00	.229E-02	.000E+00	1.0469	0.0000
Q404	.30512E-01	.302E+00	.346E-02	.000E+00	1.0051	0.0209
Q405	.30512E-01	.490E+00	.000E+00	.000E+00	1.0028	0.0861
P101	.30512E-01	.776E+00	.000E+00	.000E+00	1.0476	0.9665
P102	.30512E-01	.496E+00	.000E+00	.000E+00	1.1431	0.8070
P103	.30512E-01	.371E+00	.000E+00	.000E+00	1.1260	0.7082
P104	.30512E-01	.298E+00	.115E-02	.000E+00	1.1283	0.7009
P105	.30512E-01	.490E+00	.000E+00	.000E+00	1.0487	0.0283
P201	.30512E-01	.749E+00	.000E+00	.000E+00	1.1021	0.1807
P202	.30512E-01	.447E+00	.000E+00	.000E+00	0.9265	0.0970
P203	.30512E-01	.392E+00	.000E+00	.000E+00	1.0812	0.1136
P204	.30512E-01	.310E+00	.000E+00	.000E+00	1.0569	0.1200
P205	.30512E-01	.517E+00	.000E+00	.000E+00	1.0308	0.0000
P301	.30512E-01	.776E+00	.000E+00	.000E+00	1.0518	0.0000
P302	.30512E-01	.502E+00	.000E+00	.000E+00	1.0144	0.0356
P303	.30512E-01	.390E+00	.000E+00	.000E+00	1.0738	0.0318
P304	.30512E-01	.290E+00	.225E-04	.000E+00	1.0843	0.0931
P305	.30512E-01	.496E+00	.000E+00	.000E+00	1.0220	0.0434
P401	.30512E-01	.751E+00	.000E+00	.000E+00	1.0236	0.0374
P402	.30512E-01	.511E+00	.000E+00	.000E+00	1.0407	0.0495
P403	.30512E-01	.391E+00	.114E-02	.000E+00	1.0603	0.0275
P404	.30512E-01	.296E+00	.224E-02	.000E+00	1.0612	0.0698
P405	.30512E-01	.495E+00	.000E+00	.000E+00	1.1059	0.3680
Q101	.30512E-01	.749E+00	.000E+00	.000E+00	1.0649	0.7870
Q102	.30512E-01	.511E+00	.000E+00	.000E+00	1.1247	0.5466
Q103	.30512E-01	.394E+00	.000E+00	.000E+00	1.0526	0.4263
Q104	.30512E-01	.306E+00	.000E+00	.000E+00	1.0102	0.3396
Q105	.30512E-01	.508E+00	.000E+00	.000E+00	1.0074	0.0000

APPENDIX D. MASS BALANCE

272

Q201	.30512E-01	.756E+00	.000E+00	.000E+00	1.0699	0.0641
Q202	.30512E-01	.499E+00	.000E+00	.000E+00	1.0818	0.1524
Q203	.30512E-01	.404E+00	.000E+00	.000E+00	1.0988	0.0000
Q204	.30512E-01	.312E+00	.000E+00	.000E+00	1.0124	0.0295
Q205	.30512E-01	.479E+00	.000E+00	.000E+00	1.0108	0.0000
Q301	.30512E-01	.716E+00	.000E+00	.000E+00	1.0845	0.0000
Q302	.30512E-01	.490E+00	.000E+00	.000E+00	1.0156	0.0000
Q303	.30512E-01	.396E+00	.000E+00	.000E+00	1.0809	0.0525
Q304	.30512E-01	.310E+00	.336E-02	.305E-02	0.9782	0.0000
Q305	.30512E-01	.526E+00	.000E+00	.000E+00	1.0118	0.1204
Q401	.30512E-01	.762E+00	.000E+00	.000E+00	1.0097	0.0000
Q402	.30512E-01	.523E+00	.000E+00	.000E+00	1.0008	0.0834
Q403	.30512E-01	.396E+00	.340E-02	.000E+00	0.9924	0.0000
Q404	.30512E-01	.303E+00	.335E-02	.152E-02	0.9340	0.0000
Q405	.30512E-01	.517E+00	.000E+00	.000E+00	1.0648	0.1629
R01	.30512E-01	.531E+00	.232E-02	.000E+00	1.0056	0.1078
R02	.30512E-01	.511E+00	.000E+00	.000E+00	0.9964	0.1324
S01	.30512E-01	.555E+00	.836E-02	.114E-01	0.4243	0.1647
S02	.30512E-01	.756E+00	.489E-02	.444E-02	0.5463	0.3507
S03	.30512E-01	.773E+00	.291E-02	.119E-01	0.4376	0.1428
S04	.30512E-01	.382E+00	.131E-01	.130E-01	0.4278	0.2979
S05	.30512E-01	.388E+00	.144E-01	.207E-01	0.4419	0.1382
S06	.30512E-01	.518E+00	.105E-01	.102E-01	0.4227	0.1696
S07	.30512E-01	.773E+00	.463E-02	.315E-02	0.6061	0.2197
S08	.30512E-01	.766E+00	.783E-02	.171E-01	0.2833	0.0459
S09	.30512E-01	.395E+00	.240E-01	.184E-01	0.2842	0.1759
S10	.30512E-01	.386E+00	.252E-01	.275E-01	0.2388	0.0261
S11	.30512E-01	.509E+00	.889E-02	.156E-01	0.4500	0.1084
T01	.15380E+00	.257E+01	.000E+00	.000E+00	0.9891	0.0701
T02	.76100E-01	.127E+01	.000E+00	.000E+00	1.0327	0.0954
T03	.15400E-01	.257E+00	.000E+00	.000E+00	1.0074	0.1022

RUN	N2(MOL/H)	W/T	F/T	M/T	T(MOL/H)	FF(MOL/H)	FM(MOL/H)	TMOL
A01	.411E+0	.9373E-1	.4593E-2	.9017E+0	.3065E-1	.1408E-3	.2764E-1	.2778E-1
A02	.406E+0	.2493E+0	.1772E+0	.5736E+0	.3745E-1	.6634E-2	.2148E-1	.2842E-1
A03	.403E+0	.2955E+0	.2317E+0	.4728E+0	.4122E-1	.9551E-2	.1949E-1	.3019E-1
A04	.411E+0	.3429E+0	.2978E+0	.3592E+0	.4538E-1	.1352E-1	.1630E-1	.3117E-1
A05	.396E+0	.3596E+0	.3167E+0	.3236E+0	.4713E-1	.1493E-1	.1525E-1	.3187E-1
B01	.413E+0	.7316E-1	.1485E-2	.9254E+0	.3077E-1	.4570E-4	.2848E-1	.2874E-1
B02	.407E+0	.1112E+0	.3170E-2	.8856E+0	.3113E-1	.9870E-4	.2757E-1	.2819E-1
B03	.402E+0	.1212E+0	.6762E-2	.8720E+0	.3152E-1	.2132E-3	.2749E-1	.2850E-1
B04	.407E+0	.1921E+0	.9569E-1	.7122E+0	.3482E-1	.3332E-2	.2480E-1	.2910E-1
C01	.403E+0	.3365E+0	.2907E+0	.3728E+0	.4433E-1	.1289E-1	.1653E-1	.3035E-1
C02	.298E+0	.2283E+0	.2185E+0	.5532E+0	.4004E-1	.8748E-2	.2215E-1	.3167E-1
C03	.564E+0	.3103E+0	.2949E+0	.3948E+0	.4423E-1	.1304E-1	.1746E-1	.3118E-1
C04	.546E+0	.4989E+0	.2552E+0	.2459E+0	.4707E-1	.1201E-1	.1158E-1	.2814E-1
C05	.302E+0	.3334E+0	.3492E+0	.3174E+0	.4751E-1	.1659E-1	.1508E-1	.3208E-1
C06	.394E+0	.2575E+0	.2206E+0	.5219E+0	.3967E-1	.8752E-2	.2071E-1	.2987E-1
D01	.407E+0	.9190E-1	.1011E-2	.9071E+0	.3135E-1	.3169E-4	.2844E-1	.2928E-1
D02	.408E+0	.1385E+0	.6327E-2	.8552E+0	.3179E-1	.2011E-3	.2718E-1	.2846E-1
D03	.413E+0	.1427E+0	.9175E-2	.8481E+0	.3198E-1	.2934E-3	.2712E-1	.2859E-1
D04	.404E+0	.1765E+0	.7129E-1	.7522E+0	.3423E-1	.2440E-2	.2575E-1	.2946E-1
D05	.403E+0	.3041E+0	.1673E+0	.5286E+0	.3979E-1	.6657E-2	.2104E-1	.3032E-1
E01	.406E+0	.4110E+0	.2830E+0	.3060E+0	.4505E-1	.1275E-1	.1378E-1	.2832E-1
E02	.314E+0	.2340E+0	.6037E-2	.7600E+0	.3323E-1	.2006E-3	.2525E-1	.2797E-1
E03	.562E+0	.3758E+0	.1792E+0	.4450E+0	.4088E-1	.7324E-2	.1819E-1	.2856E-1
E04	.562E+0	.1139E+0	.4955E-2	.8811E+0	.3271E-1	.1620E-3	.2862E-1	.3101E-1
E05	.318E+0	.1990E+0	.6687E-1	.7341E+0	.3379E-1	.2259E-2	.2481E-1	.2808E-1
E06	.436E+0	.3833E+0	.2841E+0	.3326E+0	.4801E-1	.1364E-1	.1597E-1	.3346E-1
F01	.404E+0	.3886E+0	.4427E+0	.1687E+0	.5475E-1	.2424E-1	.9234E-2	.3347E-1
F02	.324E+0	.3303E+0	.2716E+0	.3981E+0	.4292E-1	.1166E-1	.1709E-1	.2950E-1
F03	.573E+0	.3584E+0	.3775E+0	.2641E+0	.4998E-1	.1887E-1	.1320E-1	.3267E-1

APPENDIX D. MASS BALANCE

274

F04 .586E+0 .6402E+0 .2113E+0 .1485E+0 .5253E-1 .1110E-1 .7802E-2 .2982E-1
F05 .328E+0 .7273E+0 .1316E+0 .1411E+0 .5505E-1 .7246E-2 .7767E-2 .3230E-1
F06 .411E+0 .4535E+0 .4709E+0 .7564E-1 .5767E-1 .2715E-1 .4362E-2 .3152E-1

G01 .399E+0 .3662E+0 .3940E+0 .2398E+0 .5035E-1 .1984E-1 .1207E-1 .3191E-1
G02 .319E+0 .1882E+0 .1831E+0 .6287E+0 .3735E-1 .6840E-2 .2348E-1 .3032E-1
G03 .605E+0 .3130E+0 .3656E+0 .3214E+0 .4810E-1 .1758E-1 .1546E-1 .3304E-1
G04 .610E+0 .5857E+0 .2264E+0 .1880E+0 .5184E-1 .1173E-1 .9746E-2 .3108E-1
G05 .310E+0 .6634E+0 .1606E+0 .1761E+0 .4991E-1 .8016E-2 .8788E-2 .2819E-1
G06 .396E+0 .3916E+0 .4322E+0 .1763E+0 .5373E-1 .2322E-1 .9471E-2 .3269E-1

H01 .411E+0 .4648E+0 .4509E+0 .8432E-1 .5687E-1 .2564E-1 .4795E-2 .3116E-1
H02 .317E+0 .3134E+0 .3264E+0 .3602E+0 .4530E-1 .1478E-1 .1632E-1 .3110E-1
H03 .608E+0 .3787E+0 .4286E+0 .1927E+0 .5340E-1 .2289E-1 .1029E-1 .3318E-1
H04 .606E+0 .3894E+0 .4054E+0 .2052E+0 .5131E-1 .2080E-1 .1053E-1 .3133E-1
H05 .305E+0 .4955E+0 .5045E+0 .0000E+0 .6158E-1 .3106E-1 .0000E+0 .3106E-1
H06 .412E+0 .4464E+0 .4771E+0 .7643E-1 .5882E-1 .2806E-1 .4495E-2 .3280E-1

I01 .392E+0 .3559E+0 .3832E+0 .2608E+0 .4947E-1 .1896E-1 .1290E-1 .3186E-1
I02 .317E+0 .6329E+0 .1516E+0 .2155E+0 .4897E-1 .7426E-2 .1055E-1 .2902E-1
I03 .602E+0 .6984E+0 .1821E+0 .1195E+0 .5390E-1 .9815E-2 .6441E-2 .2983E-1
I04 .597E+0 .2964E+0 .3209E+0 .3826E+0 .4493E-1 .1442E-1 .1719E-1 .3161E-1
I05 .316E+0 .4678E+0 .5093E+0 .2288E-1 .6218E-1 .3167E-1 .1422E-2 .3309E-1
I06 .397E+0 .2571E+0 .2933E+0 .4497E+0 .4317E-1 .1266E-1 .1941E-1 .3208E-1

J01 .419E+0 .4367E+0 .4559E+0 .1074E+0 .5741E-1 .2617E-1 .6166E-2 .3307E-1
J02 .317E+0 .3091E+0 .3547E+0 .3363E+0 .4728E-1 .1677E-1 .1590E-1 .3267E-1
J03 .591E+0 .4050E+0 .4447E+0 .1503E+0 .5494E-1 .2443E-1 .8258E-2 .3269E-1
J04 .586E+0 .6727E+0 .1974E+0 .1300E+0 .5495E-1 .1085E-1 .7141E-2 .3158E-1
J05 .311E+0 .8101E+0 .8109E-1 .1088E+0 .5480E-1 .4444E-2 .5962E-2 .3025E-1
J06 .396E+0 .4232E+0 .4474E+0 .1294E+0 .5602E-1 .2507E-1 .7247E-2 .3275E-1

M101 .597E+0 .1705E+0 .1168E+0 .7127E+0 .3455E-1 .4036E-2 .2462E-1 .2866E-1
M102 .408E+0 .1661E+0 .1278E+0 .7061E+0 .3498E-1 .4469E-2 .2470E-1 .2917E-1
M103 .290E+0 .9303E-1 .3700E-1 .8700E+0 .3168E-1 .1172E-2 .2756E-1 .2874E-1
M104 .234E+0 .1521E+0 .1142E+0 .7337E+0 .3445E-1 .3935E-2 .2527E-1 .2921E-1
M105 .406E+0 .2626E+0 .2370E+0 .5004E+0 .3999E-1 .9478E-2 .2001E-1 .2949E-1

APPENDIX D. MASS BALANCE

275

M201	.608E+0	.1313E+0	.1394E+0	.7293E+0	.3546E-1	.4944E-2	.2586E-1	.3080E-1
M202	.392E+0	.2095E+0	.1438E+0	.6467E+0	.3564E-1	.5125E-2	.2305E-1	.2817E-1
M203	.305E+0	.1892E+0	.1297E+0	.6811E+0	.3506E-1	.4546E-2	.2388E-1	.2843E-1
M204	.238E+0	.1994E+0	.1352E+0	.6654E+0	.3528E-1	.4770E-2	.2348E-1	.2825E-1
M205	.392E+0	.2136E+0	.1808E+0	.6056E+0	.3724E-1	.6733E-2	.2256E-1	.2929E-1
M301	.608E+0	.2254E+0	.1603E+0	.6143E+0	.3634E-1	.5826E-2	.2232E-1	.2815E-1
M302	.386E+0	.2053E+0	.1649E+0	.6298E+0	.3654E-1	.6023E-2	.2301E-1	.2903E-1
M303	.308E+0	.2157E+0	.1820E+0	.6023E+0	.3730E-1	.6788E-2	.2247E-1	.2925E-1
M304	.239E+0	.2255E+0	.1721E+0	.6024E+0	.3686E-1	.6343E-2	.2220E-1	.2855E-1
M305	.401E+0	.2031E+0	.1533E+0	.6437E+0	.3604E-1	.5523E-2	.2319E-1	.2872E-1
M401	.594E+0	.2353E+0	.1805E+0	.5842E+0	.3723E-1	.6721E-2	.2175E-1	.2847E-1
M402	.392E+0	.3229E+0	.2556E+0	.4215E+0	.4129E-1	.1055E-1	.1740E-1	.2819E-1
M403	.309E+0	.2949E+0	.2503E+0	.4549E+0	.4117E-1	.1030E-1	.1873E-1	.2939E-1
M404	.239E+0	.2576E+0	.1962E+0	.5462E+0	.3858E-1	.7569E-2	.2107E-1	.2914E-1
M405	.394E+0	.1641E+0	.1330E+0	.7029E+0	.3519E-1	.4681E-2	.2474E-1	.2942E-1
N101	.613E+0	.2688E+0	.2267E+0	.5045E+0	.3945E-1	.8943E-2	.1991E-1	.2885E-1
N102	.399E+0	.2765E+0	.2212E+0	.5023E+0	.3918E-1	.8665E-2	.1968E-1	.2834E-1
N103	.317E+0	.2478E+0	.2270E+0	.5251E+0	.3947E-1	.8961E-2	.2073E-1	.2969E-1
N104	.230E+0	.2566E+0	.2288E+0	.5146E+0	.3956E-1	.9051E-2	.2036E-1	.2941E-1
N105	.402E+0	.3575E+0	.3777E+0	.2648E+0	.4940E-1	.1866E-1	.1308E-1	.3197E-1
N201	.613E+0	.3069E+0	.3095E+0	.3836E+0	.4419E-1	.1368E-1	.1695E-1	.3063E-1
N202	.409E+0	.2996E+0	.3173E+0	.3831E+0	.4469E-1	.1418E-1	.1712E-1	.3130E-1
N203	.311E+0	.3106E+0	.3113E+0	.3781E+0	.4430E-1	.1379E-1	.1675E-1	.3054E-1
N204	.231E+0	.2941E+0	.3039E+0	.4020E+0	.4383E-1	.1332E-1	.1762E-1	.3094E-1
N205	.389E+0	.4311E+0	.3869E+0	.1820E+0	.5196E-1	.2010E-1	.9454E-2	.3090E-1
N301	.579E+0	.3646E+0	.3577E+0	.2777E+0	.4751E-1	.1699E-1	.1319E-1	.3019E-1
N302	.397E+0	.3562E+0	.3754E+0	.2684E+0	.4959E-1	.1862E-1	.1331E-1	.3239E-1
N303	.301E+0	.3728E+0	.3890E+0	.2382E+0	.5163E-1	.2008E-1	.1230E-1	.3341E-1
N304	.243E+0	.3732E+0	.3784E+0	.2484E+0	.4998E-1	.1891E-1	.1241E-1	.3188E-1
N305	.383E+0	.3842E+0	.3797E+0	.2361E+0	.5061E-1	.1922E-1	.1195E-1	.3204E-1

N401	.600E+0	.4056E+0	.3916E+0	.2028E+0	.5015E-1	.1964E-1	.1017E-1	.2981E-1
N402	.374E+0	.4108E+0	.4267E+0	.1626E+0	.5359E-1	.2286E-1	.8711E-2	.3179E-1
N403	.308E+0	.4153E+0	.4534E+0	.1313E+0	.5615E-1	.2546E-1	.7371E-2	.3301E-1
N404	.236E+0	.4198E+0	.4465E+0	.1337E+0	.5561E-1	.2483E-1	.7434E-2	.3253E-1
N405	.391E+0	.3788E+0	.3820E+0	.2392E+0	.5011E-1	.1915E-1	.1199E-1	.3159E-1
O101	.602E+0	.3301E+0	.3248E+0	.3451E+0	.4519E-1	.1468E-1	.1559E-1	.3027E-1
O102	.399E+0	.3483E+0	.3593E+0	.2924E+0	.4762E-1	.1711E-1	.1393E-1	.3104E-1
O103	.314E+0	.3230E+0	.3633E+0	.3137E+0	.4792E-1	.1741E-1	.1503E-1	.3244E-1
O104	.239E+0	.3499E+0	.3884E+0	.2617E+0	.4989E-1	.1938E-1	.1306E-1	.3243E-1
O105	.394E+0	.4830E+0	.4865E+0	.3048E-1	.5943E-1	.2891E-1	.1811E-2	.3072E-1
O201	.613E+0	.3614E+0	.3723E+0	.2663E+0	.4861E-1	.1809E-1	.1295E-1	.3104E-1
O202	.401E+0	.4297E+0	.4740E+0	.9626E-1	.5801E-1	.2750E-1	.5584E-2	.3308E-1
O203	.308E+0	.4594E+0	.4833E+0	.5725E-1	.5905E-1	.2854E-1	.3381E-2	.3192E-1
O204	.246E+0	.4588E+0	.4784E+0	.6281E-1	.5850E-1	.2798E-1	.3674E-2	.3166E-1
O205	.385E+0	.4672E+0	.4935E+0	.3934E-1	.6024E-1	.2972E-1	.2370E-2	.3209E-1
O301	.597E+0	.4248E+0	.4649E+0	.1103E+0	.5702E-1	.2651E-1	.6288E-2	.3280E-1
O302	.409E+0	.4652E+0	.4785E+0	.5638E-1	.5850E-1	.2799E-1	.3298E-2	.3129E-1
O303	.315E+0	.4393E+0	.4593E+0	.1014E+0	.5643E-1	.2592E-1	.5720E-2	.3164E-1
O304	.232E+0	.4953E+0	.4802E+0	.2452E-1	.5972E-1	.2867E-1	.1464E-2	.3067E-1
O305	.409E+0	.4536E+0	.4880E+0	.4844E-1	.5959E-1	.2908E-1	.2887E-2	.3197E-1
O401	.589E+0	.4492E+0	.4617E+0	.8911E-1	.5669E-1	.2617E-1	.5051E-2	.3122E-1
O402	.407E+0	.4904E+0	.5096E+0	.0000E+0	.6221E-1	.3170E-1	.0000E+0	.3170E-1
O403	.292E+0	.4885E+0	.5115E+0	.0000E+0	.6382E-1	.3264E-1	.0000E+0	.3331E-1
O404	.239E+0	.4936E+0	.4961E+0	.1032E-1	.6219E-1	.3085E-1	.6416E-3	.3232E-1
O405	.387E+0	.4787E+0	.4801E+0	.4122E-1	.5868E-1	.2817E-1	.2419E-2	.3059E-1
P101	.613E+0	.3318E+0	.3476E+0	.3207E+0	.4677E-1	.1625E-1	.1500E-1	.3125E-1
P102	.392E+0	.3390E+0	.3875E+0	.2736E+0	.4981E-1	.1930E-1	.1363E-1	.3293E-1
P103	.293E+0	.3528E+0	.3973E+0	.2499E+0	.5062E-1	.2011E-1	.1265E-1	.3276E-1
P104	.235E+0	.3535E+0	.3988E+0	.2477E+0	.5120E-1	.2042E-1	.1268E-1	.3337E-1
P105	.387E+0	.4815E+0	.5049E+0	.1333E-1	.6163E-1	.3112E-1	.8397E-3	.3196E-1
P201	.591E+0	.4381E+0	.4828E+0	.7916E-1	.5899E-1	.2848E-1	.4670E-2	.3315E-1

APPENDIX D. MASS BALANCE

277

P202	.353E+0	.4942E+0	.4579E+0	.4794E-1	.5628E-1	.2577E-1	.2698E-2	.2847E-1
P203	.310E+0	.4556E+0	.4926E+0	.5176E-1	.6014E-1	.2962E-1	.3113E-2	.3274E-1
P204	.245E+0	.4594E+0	.4855E+0	.5512E-1	.5930E-1	.2879E-1	.3269E-2	.3206E-1
P205	.408E+0	.4924E+0	.5076E+0	.0000E+0	.6196E-1	.3145E-1	.0000E+0	.3145E-1
P301	.613E+0	.4874E+0	.5126E+0	.0000E+0	.6260E-1	.3209E-1	.0000E+0	.3209E-1
P302	.397E+0	.4878E+0	.4948E+0	.1737E-1	.6040E-1	.2989E-1	.1049E-2	.3094E-1
P303	.308E+0	.4749E+0	.5100E+0	.1510E-1	.6227E-1	.3175E-1	.9404E-3	.3269E-1
P304	.229E+0	.4593E+0	.4980E+0	.4276E-1	.6079E-1	.3027E-1	.2599E-2	.3288E-1
P305	.392E+0	.4842E+0	.4948E+0	.2101E-1	.6040E-1	.2989E-1	.1269E-2	.3116E-1
P401	.593E+0	.4852E+0	.4967E+0	.1815E-1	.6062E-1	.3011E-1	.1100E-2	.3121E-1
P402	.404E+0	.4784E+0	.4979E+0	.2368E-1	.6077E-1	.3026E-1	.1439E-2	.3170E-1
P403	.309E+0	.4790E+0	.5079E+0	.1317E-1	.6271E-1	.3185E-1	.8260E-3	.3303E-1
P404	.234E+0	.4693E+0	.4980E+0	.3275E-1	.6183E-1	.3079E-1	.2025E-2	.3334E-1
P405	.391E+0	.4042E+0	.4470E+0	.1488E+0	.5518E-1	.2467E-1	.8208E-2	.3287E-1
Q101	.591E+0	.3506E+0	.3734E+0	.2760E+0	.4869E-1	.1818E-1	.1344E-1	.3162E-1
Q102	.404E+0	.3743E+0	.4210E+0	.2046E+0	.5270E-1	.2219E-1	.1078E-1	.3297E-1
Q103	.311E+0	.4034E+0	.4246E+0	.1720E+0	.5303E-1	.2252E-1	.9120E-2	.3164E-1
Q104	.242E+0	.4256E+0	.4299E+0	.1445E+0	.5352E-1	.2301E-1	.7735E-2	.3074E-1
Q105	.401E+0	.4982E+0	.5018E+0	.0000E+0	.6125E-1	.3074E-1	.0000E+0	.3074E-1
Q201	.597E+0	.4686E+0	.5014E+0	.3004E-1	.6119E-1	.3068E-1	.1838E-2	.3252E-1
Q202	.394E+0	.4476E+0	.4842E+0	.6821E-1	.5915E-1	.2864E-1	.4035E-2	.3268E-1
Q203	.319E+0	.4765E+0	.5235E+0	.0000E+0	.6404E-1	.3353E-1	.0000E+0	.3353E-1
Q204	.246E+0	.4897E+0	.4958E+0	.1445E-1	.6052E-1	.3001E-1	.8743E-3	.3088E-1
Q205	.378E+0	.4973E+0	.5027E+0	.0000E+0	.6135E-1	.3084E-1	.0000E+0	.3084E-1
Q301	.566E+0	.4797E+0	.5203E+0	.0000E+0	.6360E-1	.3309E-1	.0000E+0	.3309E-1
Q302	.387E+0	.4961E+0	.5039E+0	.0000E+0	.6150E-1	.3099E-1	.0000E+0	.3099E-1
Q303	.313E+0	.4687E+0	.5067E+0	.2461E-1	.6185E-1	.3134E-1	.1522E-2	.3286E-1
Q304	.245E+0	.5055E+0	.4945E+0	.0000E+0	.6346E-1	.3138E-1	.0000E+0	.3295E-1
Q305	.415E+0	.4690E+0	.4745E+0	.5647E-1	.5807E-1	.2755E-1	.3279E-2	.3083E-1
Q401	.602E+0	.4976E+0	.5024E+0	.0000E+0	.6132E-1	.3081E-1	.0000E+0	.3081E-1
Q402	.413E+0	.4798E+0	.4802E+0	.4002E-1	.5870E-1	.2819E-1	.2349E-2	.3053E-1

Q403 .313E+0 .5019E+0 .4981E+0 .0000E+0 .6291E-1 .3133E-1 .0000E+0 .3240E-1
 Q404 .240E+0 .5171E+0 .4829E+0 .0000E+0 .6127E-1 .2959E-1 .0000E+0 .3076E-1
 Q405 .408E+0 .4489E+0 .4780E+0 .7312E-1 .5845E-1 .2794E-1 .4274E-2 .3221E-1

R01 .420E+0 .4732E+0 .4758E+0 .5101E-1 .6007E-1 .2858E-1 .3064E-2 .3262E-1
 R02 .404E+0 .4697E+0 .4681E+0 .6219E-1 .5736E-1 .2685E-1 .3567E-2 .3042E-1

S01 .439E+0 .6293E+0 .2670E+0 .1037E+0 .5345E-1 .1427E-1 .5541E-2 .2848E-1
 S02 .597E+0 .5271E+0 .2880E+0 .1849E+0 .5068E-1 .1459E-1 .9369E-2 .2954E-1
 S03 .610E+0 .6328E+0 .2769E+0 .9036E-1 .5469E-1 .1514E-1 .4942E-2 .2912E-1
 S04 .302E+0 .5795E+0 .2479E+0 .1726E+0 .5105E-1 .1266E-1 .8813E-2 .2935E-1
 S05 .307E+0 .6329E+0 .2797E+0 .8746E-1 .5728E-1 .1602E-1 .5010E-2 .3178E-1
 S06 .409E+0 .6280E+0 .2655E+0 .1065E+0 .5304E-1 .1408E-1 .5650E-2 .2818E-1
 S07 .610E+0 .5477E+0 .3320E+0 .1203E+0 .5279E-1 .1752E-1 .6352E-2 .2862E-1
 S08 .605E+0 .7523E+0 .2131E+0 .3453E-1 .5791E-1 .1234E-1 .2000E-2 .2940E-1
 S09 .312E+0 .6849E+0 .1946E+0 .1205E+0 .5432E-1 .1057E-1 .6543E-2 .3035E-1
 S10 .305E+0 .7906E+0 .1888E+0 .2063E-1 .5743E-1 .1084E-1 .1185E-2 .2810E-1
 S11 .402E+0 .6417E+0 .2888E+0 .6956E-1 .5673E-1 .1638E-1 .3946E-2 .3017E-1

T01 .203E+1 .4856E+0 .4803E+0 .3404E-1 .2960E+0 .1422E+0 .1008E-1 .1522E+0
 T02 .100E+1 .4699E+0 .4853E+0 .4483E-1 .1478E+0 .7174E-1 .6628E-2 .7837E-1
 T03 .203E+0 .4740E+0 .4775E+0 .4845E-1 .2948E-1 .1408E-1 .1428E-2 .1550E-1

RUN	T (K)	W/F	R	ERROR	CONV	SELECT	YIELD
A01	623.0	27.50	6.0	8.954	0.005	1.000	0.005
A02	648.0	27.50	6.0	6.872	0.244	0.956	0.233
A03	673.0	27.50	6.0	1.044	0.355	0.892	0.316
A04	698.0	27.50	6.0	-2.165	0.477	0.909	0.434
A05	723.0	27.50	6.0	-4.436	0.521	0.898	0.468
B01	648.0	27.50	6.0	5.811	0.009	0.174	0.002
B02	673.0	27.50	6.0	7.607	0.022	0.159	0.004
B03	698.0	27.50	6.0	6.599	0.035	0.211	0.007
B04	723.0	27.50	6.0	4.619	0.148	0.774	0.114
C01	673.0	27.50	6.0	0.546	0.455	0.933	0.425

APPENDIX D. MASS BALANCE

279

C02	648.0	16.25	8.0	-3.801	0.301	0.919	0.276
C03	698.0	16.25	4.0	-2.199	0.440	0.951	0.418
C04	648.0	38.75	4.0	7.783	0.589	0.725	0.427
C05	698.0	38.75	8.0	-5.123	0.530	0.976	0.517
C06	673.0	27.50	6.0	2.116	0.307	0.955	0.293
D01	623.0	27.50	6.0	4.035	0.029	0.038	0.001
D02	648.0	27.50	6.0	6.727	0.045	0.158	0.007
D03	673.0	27.50	6.0	6.287	0.051	0.200	0.010
D04	698.0	27.50	6.0	3.433	0.126	0.656	0.083
D05	723.0	27.50	6.0	0.638	0.306	0.717	0.220
E01	673.0	27.50	6.0	7.185	0.513	0.877	0.450
E02	648.0	16.25	8.0	8.320	0.097	0.074	0.007
E03	698.0	16.25	4.0	6.397	0.363	0.707	0.256
E04	648.0	38.75	4.0	-1.637	0.071	0.074	0.005
E05	698.0	38.75	8.0	7.964	0.117	0.689	0.080
E06	673.0	27.50	6.0	-9.676	0.523	0.779	0.408
F01	673.0	27.50	6.0	-9.707	0.724	1.000	0.724
F02	648.0	16.25	8.0	3.331	0.421	0.939	0.395
F03	698.0	16.25	4.0	-7.080	0.596	0.969	0.577
F04	648.0	38.75	4.0	2.280	0.738	0.504	0.372
F05	698.0	38.75	8.0	-5.864	0.760	0.295	0.224
F06	673.0	27.50	6.0	-3.291	0.862	1.000	0.862
G01	673.0	27.50	6.0	-4.581	0.622	1.000	0.622
G02	648.0	16.25	8.0	0.620	0.226	1.000	0.226
G03	698.0	16.25	4.0	-8.298	0.532	1.000	0.532
G04	648.0	38.75	4.0	-1.852	0.686	0.550	0.378
G05	698.0	38.75	8.0	7.611	0.688	0.413	0.284
G06	673.0	27.50	6.0	-7.144	0.710	1.000	0.710
H01	673.0	27.50	6.0	-2.116	0.846	0.973	0.823
H02	648.0	16.25	8.0	-1.926	0.475	1.000	0.475
H03	698.0	16.25	4.0	-8.741	0.690	1.000	0.690
H04	648.0	38.75	4.0	-2.685	0.664	1.000	0.664

APPENDIX D. MASS BALANCE

280

H05	698.0	38.75	8.0	-1.810	1.000	1.000	1.000
H06	673.0	27.50	6.0	-7.493	0.863	0.992	0.856
I01	673.0	27.50	6.0	-4.432	0.595	1.000	0.595
I02	648.0	16.25	8.0	4.902	0.636	0.402	0.256
I03	698.0	16.25	4.0	2.227	0.784	0.420	0.329
I04	648.0	38.75	4.0	-3.606	0.456	1.000	0.456
I05	698.0	38.75	8.0	-8.447	0.957	1.000	0.957
I06	673.0	27.50	6.0	-5.125	0.395	1.000	0.395
J01	673.0	27.50	6.0	-8.375	0.814	0.973	0.792
J02	648.0	16.25	8.0	-7.069	0.513	1.000	0.513
J03	698.0	16.25	4.0	-7.140	0.747	1.000	0.747
J04	648.0	38.75	4.0	-3.498	0.774	0.444	0.343
J05	698.0	38.75	8.0	0.862	0.803	0.183	0.147
J06	673.0	27.50	6.0	-7.348	0.779	0.983	0.765
M101	623.0	5.00	4.0	6.082	0.141	1.000	0.141
M102	623.0	5.00	6.0	4.398	0.153	1.000	0.153
M103	623.0	5.00	8.0	5.819	0.041	1.000	0.041
M104	623.0	5.00	10.0	4.276	0.135	1.000	0.135
M105	673.0	5.00	6.0	3.352	0.321	1.000	0.321
M201	648.0	5.00	4.0	-0.949	0.161	1.000	0.161
M202	648.0	5.00	6.0	7.670	0.182	1.000	0.182
M203	648.0	5.00	8.0	6.839	0.160	1.000	0.160
M204	648.0	5.00	10.0	7.425	0.169	1.000	0.169
M205	673.0	5.00	6.0	4.005	0.230	1.000	0.230
M301	673.0	5.00	4.0	7.753	0.207	1.000	0.207
M302	673.0	5.00	6.0	4.846	0.207	1.000	0.207
M303	673.0	5.00	8.0	4.127	0.232	1.000	0.232
M304	673.0	5.00	10.0	6.443	0.222	1.000	0.222
M305	673.0	5.00	6.0	5.880	0.192	1.000	0.192
M401	698.0	5.00	4.0	6.680	0.236	1.000	0.236
M402	698.0	5.00	6.0	7.620	0.383	0.979	0.374
M403	698.0	5.00	8.0	3.678	0.363	0.966	0.351

APPENDIX D. MASS BALANCE

281

M404	698.0	5.00	10.0	4.504	0.277	0.938	0.260
M405	673.0	5.00	6.0	3.591	0.159	1.000	0.159
N101	623.0	16.25	4.0	5.450	0.310	1.000	0.310
N102	623.0	16.25	6.0	7.109	0.306	1.000	0.306
N103	623.0	16.25	8.0	2.693	0.302	1.000	0.302
N104	623.0	16.25	10.0	3.607	0.308	1.000	0.308
N105	673.0	16.25	6.0	-4.789	0.591	0.988	0.584
N201	648.0	16.25	4.0	-0.382	0.447	1.000	0.447
N202	648.0	16.25	6.0	-2.589	0.453	1.000	0.453
N203	648.0	16.25	8.0	-0.095	0.451	1.000	0.451
N204	648.0	16.25	10.0	-1.394	0.430	1.000	0.430
N205	673.0	16.25	6.0	-1.263	0.694	0.938	0.651
N301	673.0	16.25	4.0	1.061	0.563	1.000	0.563
N302	673.0	16.25	6.0	-6.160	0.589	0.976	0.575
N303	673.0	16.25	8.0	-9.511	0.632	0.951	0.601
N304	673.0	16.25	10.0	-4.481	0.611	0.972	0.593
N305	673.0	16.25	6.0	-5.022	0.627	0.956	0.600
N401	698.0	16.25	4.0	2.313	0.659	1.000	0.659
N402	698.0	16.25	6.0	-4.190	0.726	0.991	0.719
N403	698.0	16.25	8.0	-8.184	0.777	0.993	0.771
N404	698.0	16.25	10.0	-6.623	0.772	0.989	0.763
N405	673.0	16.25	6.0	-3.531	0.621	0.977	0.606
O101	623.0	27.50	4.0	0.777	0.485	1.000	0.485
O102	623.0	27.50	6.0	-1.718	0.551	1.000	0.551
O103	623.0	27.50	8.0	-6.321	0.537	1.000	0.537
O104	623.0	27.50	10.0	-6.293	0.597	1.000	0.597
O105	673.0	27.50	6.0	-0.696	0.941	1.000	0.941
O201	648.0	27.50	4.0	-1.733	0.583	1.000	0.583
O202	648.0	27.50	6.0	-8.415	0.831	1.000	0.831
O203	648.0	27.50	8.0	-4.624	0.894	1.000	0.894
O204	648.0	27.50	10.0	-3.756	0.884	1.000	0.884

APPENDIX D. MASS BALANCE

2S2

0205	673.0	27.50	6.0	-5.184	0.926	1.000	0.926
0301	673.0	27.50	4.0	-7.502	0.808	1.000	0.808
0302	673.0	27.50	6.0	-2.551	0.895	1.000	0.895
0303	673.0	27.50	8.0	-3.697	0.819	1.000	0.819
0304	673.0	27.50	10.0	-0.513	0.952	0.982	0.935
0305	673.0	27.50	6.0	-4.771	0.910	1.000	0.910
0401	698.0	27.50	4.0	-2.336	0.838	1.000	0.838
0402	698.0	27.50	6.0	-3.900	1.000	1.000	1.000
0403	698.0	27.50	8.0	-9.178	1.000	0.980	0.980
0404	698.0	27.50	10.0	-5.928	0.980	0.974	0.955
0405	673.0	27.50	6.0	-0.258	0.921	1.000	0.921
P101	623.0	38.75	4.0	-2.420	0.520	1.000	0.520
P102	623.0	38.75	6.0	-7.919	0.586	1.000	0.586
P103	623.0	38.75	8.0	-7.376	0.614	1.000	0.614
P104	623.0	38.75	10.0	-9.380	0.620	0.987	0.612
P105	673.0	38.75	6.0	-4.736	0.974	1.000	0.974
P201	648.0	38.75	4.0	-8.647	0.859	1.000	0.859
P202	648.0	38.75	6.0	6.700	0.905	1.000	0.905
P203	648.0	38.75	8.0	-7.292	0.905	1.000	0.905
P204	648.0	38.75	10.0	-5.080	0.898	1.000	0.898
P205	673.0	38.75	6.0	-3.080	1.000	1.000	1.000
P301	673.0	38.75	4.0	-5.180	1.000	1.000	1.000
P302	673.0	38.75	6.0	-1.390	0.966	1.000	0.966
P303	673.0	38.75	8.0	-7.153	0.971	1.000	0.971
P304	673.0	38.75	10.0	-7.747	0.921	1.000	0.921
P305	673.0	38.75	6.0	-2.109	0.959	1.000	0.959
P401	698.0	38.75	4.0	-2.275	0.965	1.000	0.965
P402	698.0	38.75	6.0	-3.878	0.955	1.000	0.955
P403	698.0	38.75	8.0	-8.236	0.975	0.989	0.964
P404	698.0	38.75	10.0	-9.262	0.939	0.983	0.924
P405	673.0	38.75	6.0	-7.741	0.750	1.000	0.750

APPENDIX D. MASS BALANCE

283

Q101	623.0	50.00	4.0	-3.632	0.575	1.000	0.575
Q102	623.0	50.00	6.0	-8.063	0.673	1.000	0.673
Q103	623.0	50.00	8.0	-3.688	0.712	1.000	0.712
Q104	623.0	50.00	10.0	-0.761	0.748	1.000	0.748
Q105	673.0	50.00	6.0	-0.740	1.000	1.000	1.000
Q201	648.0	50.00	4.0	-6.569	0.943	1.000	0.943
Q202	648.0	50.00	6.0	-7.098	0.877	1.000	0.877
Q203	648.0	50.00	8.0	-9.880	1.000	1.000	1.000
Q204	648.0	50.00	10.0	-1.204	0.972	1.000	0.972
Q205	673.0	50.00	6.0	-1.080	1.000	1.000	1.000
Q301	673.0	50.00	4.0	-8.450	1.000	1.000	1.000
Q302	673.0	50.00	6.0	-1.560	1.000	1.000	1.000
Q303	673.0	50.00	8.0	-7.686	0.954	1.000	0.954
Q304	673.0	50.00	10.0	-7.986	1.000	0.952	0.952
Q305	673.0	50.00	6.0	-1.053	0.894	1.000	0.894
Q401	698.0	50.00	4.0	-0.970	1.000	1.000	1.000
Q402	698.0	50.00	6.0	-0.074	0.923	1.000	0.923
Q403	698.0	50.00	8.0	-6.181	1.000	0.967	0.967
Q404	698.0	50.00	10.0	-0.803	1.000	0.962	0.962
Q405	673.0	50.00	6.0	-5.572	0.867	1.000	0.867
R01	673.0	27.50	6.0	-6.910	0.906	0.967	0.876
R02	673.0	27.50	6.0	0.318	0.883	1.000	0.883
S01	673.0	27.50	6.0	6.649	0.805	0.622	0.501
S02	648.0	16.25	4.0	3.197	0.683	0.724	0.494
S03	698.0	16.25	4.0	4.565	0.830	0.626	0.520
S04	648.0	16.25	8.0	3.798	0.700	0.616	0.431
S05	698.0	16.25	8.0	-4.163	0.842	0.598	0.504
S06	673.0	27.50	6.0	7.642	0.800	0.625	0.500
S07	648.0	38.75	4.0	6.185	0.778	0.787	0.612
S08	698.0	38.75	4.0	3.640	0.932	0.450	0.420
S09	648.0	38.75	8.0	0.543	0.784	0.444	0.348
S10	698.0	38.75	8.0	7.906	0.958	0.403	0.386
S11	673.0	27.50	6.0	1.132	0.869	0.625	0.543

T01	673.0	27.50	6.0	1.019	0.934	1.000	0.934
T02	673.0	27.50	6.0	-2.985	0.915	1.000	0.915
T03	673.0	27.50	6.0	-0.671	0.908	1.000	0.908

D.3 Rate Constants for Several Reaction Mechanisms

RATE CONSTANTS FOR VARIOUS MECHANISMS

RATE CONSTANTS FOR MECHANISM # 1 FOR M = 1.0 N = 0.5

TEMPERATURE	R	K1	K2
(K)	(%)		

623.00

4.0	0.6050E-03	0.2805
6.0	0.4744E-03	0.2688
8.0	0.4283E-03	-.1268
10.0	0.3234E-03	1.0330

AVERAGE	0.4578E-03	0.3638
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648.00

4.0	0.1234E-02	-1.039
6.0	0.1177E-02	-.2846
8.0	0.1251E-02	-.1164
10.0	0.7043E-03	-.1413

APPENDIX D. MASS BALANCE

285

	AVERAGE	0.1092E-02	-.3953
673.00			
4.0	0.2629E-02	-.2976	
6.0	0.1641E-02	-.2269	
8.0	0.1126E-02	-.2447	
10.0	0.1010E-02	-.1413	

AVERAGE	0.1601E-02	-.2276
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698.00

4.0	0.3126E-02	-.3151
6.0	0.3144E-02	-.1980
8.0	0.1907E-02	-.2261
10.0	0.1385E-02	-.1263

AVERAGE	0.2391E-02	-.2164
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RATE CONSTANTS FOR MECHANISM # 2 FOR M = 1.0 N = 0.0

TEMPERATURE	R	K1	K2
(K)	(%)		

623.00

4.0	0.3235E-03	-.7558E-02
6.0	0.3795E-03	-.2410E-01
8.0	0.4885E-03	0.3949E-01
10.0	0.4083E-03	0.5368E-01

AVERAGE	0.4000E-03	0.1538E-01
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APPENDIX D. MASS BALANCE

286

648.00

4.0	0.2974E-02	0.2101E-01
6.0	0.2887E-02	0.2274E-01
8.0	0.5102E-02	0.1783E-01
10.0	-.1026E-01	0.1438E-01

AVERAGE	0.1759E-03	0.1899E-01
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673.00

4.0	0.1555E-01	0.1945E-01
6.0	0.3386E-02	0.2830E-01
8.0	0.2247E-02	0.3114E-01
10.0	0.3879E-02	0.2437E-01

AVERAGE	0.6266E-02	0.2581E-01
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698.00

4.0	0.1088E-01	0.2652E-01
6.0	0.1101E-01	0.3342E-01
8.0	0.3351E-02	0.4930E-01
10.0	0.2636E-02	0.3772E-01

AVERAGE	0.6969E-02	0.3674E-01
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RATE CONSTANTS FOR MECHANISM # 3. FOR M = 0.5 N = 0.0

TEMPERATURE	R	K1	K2
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(K)	(%)		
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623.00

4.0	-.6071E-01	0.6920E-02
6.0	-.5439E-01	0.7686E-02

	8.0	-.4046E-01	0.7299E-02
	10.0	-.7263E-01	0.8513E-02
	AVERAGE	-.5705E-01	0.7604E-02
648.00			
	4.0	-.1280	0.1086E-01
	6.0	-.1214	0.1275E-01
	8.0	-.1399	0.1235E-01
	10.0	-.3159	0.1445E-01
	AVERAGE	-.1763	0.1260E-01
673.00			
	4.0	-.1182	0.1390E-01
	6.0	-.1060	0.1434E-01
	8.0	-.5839E-01	0.1374E-01
	10.0	-.1227	0.1686E-01
	AVERAGE	-.1013	0.1471E-01
698.00			
	4.0	-.1915	0.1804E-01
	6.0	-.4237E-01	0.1806E-01
	8.0	-.4283E-01	0.1848E-01
	10.0	-.9817E-01	0.1904E-01
	AVERAGE	-.9373E-01	0.1841E-01

RATE CONSTANTS FOR MECHANISM # 4 FOR M = 1.0 N = 1.0

TEMPERATURE	R	K1	K2
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(K)	(%)		

623.00			
	4.0	0.6043E-03	-.5604E-01
	6.0	0.4738E-03	-.5415E-01
	8.0	0.4294E-03	0.2587E-01
	10.0	0.3233E-03	-.2126
	AVERAGE	0.4577E-03	-.7422E-01
648.00			
	4.0	0.1386E-02	0.1140
	6.0	0.1180E-02	0.5729E-01
	8.0	0.1180E-02	0.2485E-01
	10.0	0.7868E-03	0.2440E-01
	AVERAGE	0.1133E-02	0.5531E-01
673.00			
	4.0	0.2637E-02	0.5948E-01
	6.0	0.1646E-02	0.4577E-01
	8.0	0.1130E-02	0.4971E-01
	10.0	0.1848E-02	0.3842E-01
	AVERAGE	0.1575E-02	0.4834E-01
698.00			
	4.0	0.3595E-02	0.5427E-01
	6.0	0.3166E-02	0.4002E-01
	8.0	0.1916E-02	0.4620E-01
	10.0	0.1396E-02	0.2602E-01
	AVERAGE	0.2446E-02	0.4477E-01

RATE CONSTANTS FOR MECHANISM # 5 FOR M = 0.5 N = 0.5

TEMPERATURE	R	K1	K2
(K)	(%)		

623.00

4.0	0.2436E-02	-.5691E-02
6.0	0.2362E-02	-.4386E-02
8.0	0.1796E-02	-.2899E-02
10.0	0.1905E-02	-.2623E-02

AVERAGE	0.2125E-02	-.3900E-02
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648.00

4.0	0.5612E-02	-.1202E-01
6.0	0.4795E-02	-.2707E-02
8.0	0.4003E-02	-.6631E-02
10.0	0.5225E-02	-.6351E-02

AVERAGE	0.4909E-02	-.8426E-02
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673.00

4.0	0.9797E-02	-.1880E-01
6.0	0.5284E-02	-.1003E-01
8.0	0.4728E-02	-.7229E-02
10.0	0.5576E-02	-.7026E-02

AVERAGE	0.6346E-02	-.1077E-01
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698.00

4.0	0.1078E-01	-.2232E-01
6.0	0.1030E-01	-.1691E-01
8.0	0.6720E-02	-.1054E-01

APPENDIX D. MASS BALANCE

290

10.0	0.5226E-02	-.7255E-02
------	------------	------------

AVERAGE	0.8255E-02	-.1426E-01
---------	------------	------------

RATE CONSTANTS FOR MECHANISM # 6 FOR M = 2.0 N = 0.5

TEMPERATURE	R	K1	K2
-------------	---	----	----

(K)	(%)		
-----	-----	--	--

623.00

4.0	0.2944E-04	0.2412E-01
6.0	0.1808E-04	0.2422E-01
8.0	0.1406E-04	0.4558E-01
10.0	0.7930E-05	0.1920E-01

AVERAGE	0.1738E-04	0.2828E-01
---------	------------	------------

648.00

4.0	0.1090E-03	0.2979
6.0	0.9283E-04	-.2791
8.0	0.1262E-03	-.6582E-01
10.0	0.3541E-04	-.1228

AVERAGE	0.9085E-04	-.4245E-01
---------	------------	------------

673.00

4.0	0.3563E-03	-.1959
6.0	0.1646E-03	-.1451
8.0	0.7321E-04	-.1524
10.0	0.5043E-04	-.1144

APPENDIX D. MASS BALANCE

291

	AVERAGE	0.1611E-03	-.1520
698.00			
4.0	0.4411E-03	-.2321	
6.0	0.3502E-03	-.1118	
8.0	0.1600E-03	-.1091	
10.0	0.7512E-04	-.1108	
	AVERAGE	0.2566E-03	-.1410

RATE CONSTANTS FOR MECHANISM # 7 FOR M = 2.0 N = 1.0

TEMPERATURE	R	K1	K2
(K)	(%)		

623.00			
4.0	0.2907E-04	0.4765E-02	
6.0	0.1782E-04	0.4815E-02	
8.0	0.1396E-04	0.9211E-02	
10.0	0.7771E-05	0.3849E-02	
	AVERAGE	0.1716E-04	0.5660E-02

648.00			
4.0	0.1092E-03	0.6122E-01	
6.0	0.9348E-04	-.5473E-01	
8.0	0.1300E-03	-.1324E-01	
10.0	0.3617E-04	-.2386E-01	
	AVERAGE	0.9222E-04	-.7652E-02

673.00			
4.0	0.3601E-03	-.3878E-01	

APPENDIX D. MASS BALANCE

292

6.0	0.1666E-03	-.2894E-01
8.0	0.7422E-04	-.3008E-01
10.0	0.5153E-04	-.2264E-01

AVERAGE	0.1631E-03	-.3011E-01
---------	------------	------------

698.00

4.0	0.4453E-03	-.4613E-01
6.0	0.3570E-03	-.2259E-01
8.0	0.1626E-03	-.2221E-01
10.0	0.7628E-04	-.2254E-01

AVERAGE	0.2603E-03	-.2837E-01
---------	------------	------------

RATE CONSTANTS FOR MECHANISM # 8 FOR M = 2.0 N = 0.0

TEMPERATURE	R	K1	K2
-------------	---	----	----

(K)	(%)		
-----	-----	--	--

623.00

4.0	-.1428E-03	0.5561E-02
6.0	-.6200E-04	0.5826E-02
8.0	0.2151E-04	0.5083E-01
10.0	-.3833E-04	0.7000E-02

AVERAGE	-.5541E-04	0.1730E-01
---------	------------	------------

648.00

4.0	-.1861E-02	0.1163E-01
6.0	0.3542E-03	0.1927E-01
8.0	0.1373E-01	0.1536E-01

10.0	-.1260E-03	0.1210E-01
AVERAGE	0.3024E-02	0.1459E-01
673.00		
4.0	0.9762E-01	0.1726E-01
6.0	0.8050E-03	0.2081E-01
8.0	0.5622E-03	0.2002E-01
10.0	0.4558E-03	0.2129E-01
AVERAGE	0.2486E-01	0.1985E-01
698.00		
4.0	0.4328E-02	0.2288E-01
6.0	0.4446E-01	0.2787E-01
8.0	0.1046E-02	0.3037E-01
10.0	0.3209E-03	0.2826E-01
AVERAGE	0.1254E-01	0.2734E-01

RATE CONSTANTS FOR MECHANISM # 9 FOR M = 1.5 N = 0.0

TEMPERATURE	R	K1	K2
(K)	(%)		

623.00			
4.0	-.8892E-03	0.6166E-02	
6.0	-.5118E-03	0.6739E-02	
8.0	-.2826E-03	0.6255E-02	
10.0	-.4099E-03	0.7789E-02	
AVERAGE	-.5234E-03	0.6737E-02	

648.00

4.0	-.1730E-02	0.9586E-02
6.0	-.1103E-02	0.1104E-01
8.0	0.3124E-02	0.1661E-01
10.0	-.8703E-03	0.1262E-01

AVERAGE	-.1449E-03	0.1246E-01
---------	------------	------------

673.00

4.0	0.1677E-01	0.1786E-01
6.0	0.2109E-02	0.2017E-01
8.0	0.1274E-02	0.2058E-01
10.0	-.8446E-03	0.1518E-01

AVERAGE	0.4828E-02	0.1845E-01
---------	------------	------------

698.00

4.0	0.9054E-02	0.2255E-01
6.0	0.9082E-02	0.2930E-01
8.0	0.8672E-03	0.4480E-01
10.0	0.6591E-03	0.3407E-01

AVERAGE	0.4916E-02	0.3268E-01
---------	------------	------------

RATE CONSTANTS FOR MECHANISM # 10 FOR M = 1.5 N = 0.5

TEMPERATURE	R	K1	K2
-------------	---	----	----

(K)	(%)		
-----	-----	--	--

623.00

4.0	0.6869E-04	0.9740E-02
6.0	0.5056E-04	0.8968E-02
8.0	0.3991E-04	0.8895E-02
10.0	0.2914E-04	0.6771E-02

AVERAGE	0.4707E-04	0.8593E-02
---------	------------	------------

648.00

4.0	0.2285E-03	0.4464E-01
6.0	0.1933E-03	0.5500E-01
8.0	0.4268E-03	-.8190E-01
10.0	0.1129E-03	0.5574E-01

AVERAGE	0.2404E-03	0.1837E-01
---------	------------	------------

673.00

4.0	0.1144E-02	-.1654
6.0	0.3200E-03	0.1721
8.0	0.1908E-03	0.1032
10.0	0.1512E-03	0.9149E-01

AVERAGE	0.4515E-03	0.5036E-01
---------	------------	------------

698.00

4.0	0.8224E-03	1.463
6.0	0.1433E-02	-.9355E-01
8.0	0.3702E-03	-5.940
10.0	0.1850E-03	0.1030

AVERAGE	0.7026E-03	-1.117
---------	------------	--------

RATE CONSTANTS FOR MECHANISM # 11 FOR M = 1.5 N = 1.0

TEMPERATURE	R	K1	K2
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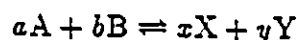
(K)	(%)		

623.00			
	4.0	0.6657E-04	0.1889E-02
	6.0	0.4856E-04	0.1736E-02
	8.0	0.3848E-04	0.1746E-02
	10.0	0.2739E-04	0.1300E-02
	AVERAGE	0.4525E-04	0.1668E-02
648.00			
	4.0	0.2270E-03	0.8913E-02
	6.0	0.1919E-03	0.1106E-01
	8.0	0.4407E-03	-.1599E-01
	10.0	0.1126E-03	0.1163E-01
	AVERAGE	0.2431E-03	0.3903E-02
673.00			
	4.0	0.1167E-02	-.3220E-01
	6.0	0.3206E-03	0.3584E-01
	8.0	0.1919E-03	0.2232E-01
	10.0	0.1519E-03	0.1981E-01
	AVERAGE	0.4580E-03	0.1144E-01
698.00			
	4.0	0.8271E-03	0.3411
	6.0	0.1478E-02	-.1877E-01
	8.0	0.3743E-03	-.4237
	10.0	0.1847E-03	0.2174E-01
	AVERAGE	0.7161E-03	-.1992E-01

Appendix E

Thermodynamic Aspects

The equilibrium constant of the gaseous reaction



is given by

$$K = \frac{P_X^x P_Y^y}{P_A^a P_B^b}$$

where A, B, X and Y are the chemical species involved, a , b , x and y are the respective quantities, in moles, taking part in the reaction, and P is the partial pressure of the reactant concerned.

At constant pressure $\ln K = \frac{-\Delta G^\circ}{RT}$ where $-\Delta G^\circ$ is the standard Gibbs function change. In the present case values for K are taken from literature.

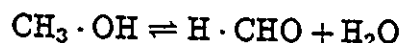
If one defines A and B as the original reactants and X and Y as the reaction products, it will be apparent that, when K is very large, the equilibrium mixture will contain very little of the original reactants and the reaction may be regarded as substantially complete and irreversible. On the other hand, when the value of K is near unity, the decomposition of the gas is very sensitive to variations in K , so that the reactions most likely to influence the quality of the product are those for which the value of $\log_{10} K$ passes through zero in the temperature range concerned.

Table E.1: Thermodynamic Equilibrium Constants ($\log_{10} K_p$) for Pyrolysis and Oxidation of Methanol

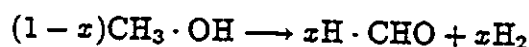
Chemical reaction	Temperature, K					
	600	700	800	900	1000	1100
$\text{CH}_3\cdot\text{OH} \rightleftharpoons \text{H}\cdot\text{CHO} + \text{H}_2$	-1.22	-0.14	+0.69	+1.35	1.86	2.28
$\text{H}\cdot\text{CHO} \longrightarrow \text{CO} + \text{H}_2$	5.16	5.34	5.48	5.62	5.70	5.78
$\text{CH}_3\cdot\text{OH} + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}\cdot\text{CHO} + \text{H}_2\text{O}$	17.41	15.44	13.98	12.83	11.92	11.16
$\text{H}\cdot\text{CHO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO} + \text{H}_2\text{O}$	23.79	20.92	18.77	17.12	15.76	14.65
$\text{CO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2$	20.06	16.54	13.90	11.84	10.20	8.86

E.1 Dehydrogenation Method

The first stage in the pyrolytic decomposition of methanol is



and the equilibrium mixture, corresponding to one mole of methanol originally, may be represented,



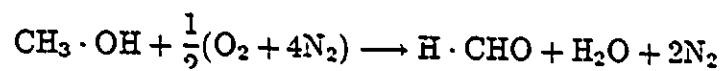
At atmospheric pressure, the equilibrium constant K is thus given by $K = \frac{x^2}{(1-x^2)}$, which reduces to $x^2 = \frac{K}{1+K}$. The values of $\log_{10} K$ at different temperatures are given in Table E.1, so that x can now be evaluated for any chosen temperature.

E.2 Oxidation Method

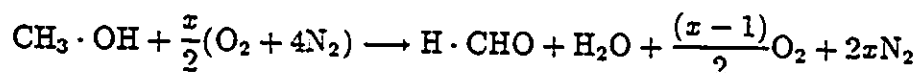
By using a catalyst the first stage becomes a heterogeneous reaction whereas the second one remains homogeneous. This second stage is the oxidation

of the hydrogen liberated in the pyrolytic decomposition of formaldehyde, so that the critical temperature for the second oxidation stage is that at which formaldehyde decomposes, i.e. 573 K.

Atmospheric oxygen is the obvious choice for use in a commercial oxidation process and can be considered to consist of one part of oxygen to four parts of nitrogen (for this analysis). The basic reaction may be represented:



The use of the reactants in these proportions is impracticable because the mixture is explosive. This can be inferred considering data from Table 4.5. The problem here is to bring the temperature of the products of this reaction down to the level at which decomposition of formaldehyde is negligible, i.e. 573 K. The preferred method in practice is to dilute the reactants until the reaction temperature drops to about its critical value -here taken as 573 K. The most convenient diluent is, of course, air, and if to each mole of methanol a volume of air equivalent to $\frac{1}{2}x(\text{O}_2 + 4\text{N}_2)$ is added, the result of the reaction would be



in which the products are assumed to be at 573 K.

The heats of reaction at different temperatures for this and other reactions of present interest are given in Table E.2, and the heat contents of the relevant gases and vapours are shown in Table E.3. With data from these tables the change in heat content of the reactants between 298 K and 573 K is given by

$$3.68 + \frac{x}{2}(2.007 + 4 \times 1.935) = 3.68 + 4.873x$$

This is the heat of reaction at 573 K, which is given as 36.7 kcal. On equating these two quantities one gets $x = 6.8$. If the assumption that the critical temperature used here, 573 K, is correct, the ideal mixture to use in a straight oxidation process is $\text{CH}_3 \cdot \text{OH} + 3.4(\text{O}_2 + 4\text{N}_2)$ or 5.6 % methanol in air.

Table E.2: Heats of Reaction (kcal) at Constant Pressure for Reactions Occurring in the Manufacture of Formaldehyde

Chemical reaction	Temperature, K						
	500	600	700	800	900	1000	1100
$\text{CH}_3\cdot\text{OH} \rightleftharpoons \text{H}\cdot\text{CHO} + \text{H}_2$	-21.5	-21.8	-22.0	-22.1	-22.2	-22.3	-22.4
$\text{H}\cdot\text{CHO} \longrightarrow \text{CO} + \text{H}_2$	-2.2	-2.6	-2.8	-3.0	-3.1	-3.1	-3.1
$\text{CH}_3\cdot\text{OH} + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}\cdot\text{CHO} + \text{H}_2\text{O}$	36.8	36.7	36.7	36.8	36.9	36.9	37.0
$\text{H}\cdot\text{CHO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO} + \text{H}_2\text{O}$	56.1	55.9	55.9	55.9	56.0	56.1	56.3
$\text{CO} + \frac{1}{2}\text{O}_2 \longrightarrow \text{CO}_2$	67.80	67.79	67.76	67.70	67.74	67.55	67.45

By repeating these calculations one can see that the temperature range 573–673 K corresponds to working mixtures in the range 5.5–8 % of methanol. Therefore, this study concentrates on this range.

Table E.3: Heat Contents (kcal/mol) of Gases and Vapours Involved in the Manufacture of Formaldehyde

Gas or vapour	Heat content (kcal/mol) at temperature, K								
	300	400	500	600	700	800	900	1000	1100
O ₂	2.083	2.792	3.524	4.279	5.058	5.856	6.670	7.497	8.335
H ₂	2.036	2.731	3.430	4.129	4.831	5.537	6.248	6.966	7.692
N ₂	2.085	2.282	3.485	4.198	4.925	5.669	6.428	7.203	7.992
H ₂ O	2.382	3.194	4.025	4.882	5.771	6.690	7.635	8.608	9.606
CO	2.086	2.784	3.490	4.210	4.946	5.700	6.471	7.257	8.056
CO ₂	2.254	3.195	4.223	5.323	6.481	7.690	8.939	10.222	11.535
CH ₃ OH	2.69	3.85	5.21	6.75	8.44	10.30	12.29	14.38	16.57
HCHO	2.410	3.299	4.289	5.386	6.587	7.876	9.258	10.707	12.22

Appendix F

Heat and Mass Transfer Effects

F.1 Mass Transfer Effects

The data for partial pressure drop to determine the maximum $\frac{\Delta P_i}{P_i}$ values are obtained from run Q104. If the $\frac{\Delta P_i}{P_i}$ is small the mass transfer effects on the catalyst surface can be neglected.

The calculation is based on the method of Yoshida *et al.*[172]. Figure 2 of their paper is used to determine the $\frac{R_i}{y_i}$ versus $\frac{\Delta P_i}{P_i}$ correlation. The results are recorded in Table F.1. The conditions which apply to this table are:

Temperature	= 623 K
W/F	= 50 g _{cat} /mol _{CH₃OH} h ⁻¹
$\bar{R}$	= 10 [100 × mol _{CH₃OH} h ⁻¹ /mol _{air} h ⁻¹]
ϕ	= Shape factor (0.9 for irregular particles)
G_m	= Molal mass velocity of gas based on the total cross section of the catalyst bed in $\frac{\text{gmol}}{\text{h-cm}^2}$
	= $\frac{F_M + F_{\text{air}}}{\pi r^2}$
	= $\frac{0.0305 + 0.306}{\pi \times 1^2} = 0.1071 \frac{\text{gmol}}{\text{h-cm}^2}$
W	= Weight of catalyst (1.5259 g)
a_m	= Surface area of catalyst per unit mass

	$= 61000 \text{ cm}^2/\text{g}$
$(y_j)_{\text{in}}$	= Mole fraction of component j in the feed
$(y_j)_{\text{out}}$	= Mole fraction of component j in the product
y_j	= Mole fraction of component j at the interface
	$= \frac{(y_j)_{\text{in}} + (y_j)_{\text{out}}}{2}$
r_{mj}	= Molal reaction rate of component j per unit mass of catalyst
$\dot{R}_j$	= Dimensionless term of component j
	$= \frac{r_{mj}}{a_m \phi G_m}$
	$= \frac{r_{mj}}{5379.79 \frac{\text{gmol}}{\text{g-h}}}$

For example in the case of formaldehyde:

$$r_{mF} = \frac{0.02301}{1.5259} = 0.01508 \frac{\text{gmol}}{\text{g-h}}$$

$$\dot{R}_F = \frac{0.01508}{5379.79} = 2.568 \times 10^{-6}$$

The values shown in Table F.1 can be obtained by following steps similar to those in the preceeding calculations, where

$(F_j)_{\text{in}}$ = Flow rate of component j in the feed

$(F_j)_{\text{out}}$ = Flow rate of component j in the product

From these results

$$\left(\frac{\Delta P_j}{P_j} \right)_{\text{max}} \ll 0.0001$$

hence, the effects of mass transfer can be neglected.

Table F.1: Data for Mass Transfer Effects

Component	$(F_j)_{in}$ gmol/h	$(F_j)_{out}$ gmol/h	$(y_j)_{in}$	$(y_j)_{out}$	y_j	$r_{mj} \times 10^2$ gmol/h	$\dot{R}_j$ $\times 10^6$	$\frac{R_i}{y_j}$ $\times 10^5$	$\left(\frac{\Delta P_i}{P_j}\right)_{max}$
O ₂	0.064	0.048	0.191	0.14	0.165	3.15	5.357	3.24	$\ll 0.0001$
N ₂	0.242	0.242	0.719	0.704	0.712	-	-	-	$\ll 0.0001$
CH ₃ OH	0.035	0.008	0.091	0.022	0.056	0.505	0.85	1.51	$\ll 0.0001$
HCHO	0.0	0.024	0.0	0.067	0.034	1.51	2.568	7.67	$\ll 0.0001$
H ₂ O	0.0	0.023	0.0	0.066	0.033	1.49	2.534	7.63	$\ll 0.0001$

F.2 Heat Transfer Effects

Calculation of temperature drop from catalyst particle to ambient gas stream was carried out by using the method of Yoshida *et al.*[172]. The values used, again from run Q104, are given in Table F.2.

From Section F.1 we have

$$\begin{aligned}
 G_m &= 0.1071 \text{ gmol/h-cm}^2 \\
 a_m &= 61000 \text{ cm}^2/\text{g} \\
 \phi &= 0.9 \\
 r_{mF} &= 0.0151 \text{ gmol/g-h} \\
 T &= 623 \text{ K}
 \end{aligned}$$

From the standard thermodynamics

$$C_p = \sum_{j=1}^n C_{p_j} \cdot y_j$$

thus,

$$C_p = 8.0076 \frac{\text{cal}}{\text{gmol} \cdot \text{K}}$$

Also to calculate the molal heat of reaction, $-\Delta H$, per mole of formaldehyde produced,

Table F.2: Data for Heat Transfer Effects

Component	y_j	C_{p_j} $\frac{\text{cal}}{\text{gmol-K}}$	$C_{p_j} \cdot y_j$	$\Delta H_f^\circ \dagger$ $\frac{\text{Kcal}}{\text{gmol-K}}$
O ₂	0.1653	7.94	1.3125	0.0
N ₂	0.7115	7.12	5.0658	0.0
CH ₃ OH	0.0564	16.8	0.9475	-48.08
HCHO	0.0335	11.6	0.3886	-28.29
H ₂ O	0.0332	8.83	0.2932	-57.8
CO	0.0	7.56	0.0	-26.41
CO ₂	0.0	12.32	0.0	-94.05

†: from reference [166]

- Heat of reaction for formaldehyde production

$$\Delta H_1 = -57.8 - 28.29 + 48.08 + 0.0 = -38.01$$

- Heat of reaction for formaldehyde conversion to CO

$$\Delta H_2 = -26.41 - 57.8 + 28.29 + 0.0 = -55.92$$

- Heat of reaction for formaldehyde conversion to CO₂

$$\Delta H_3 = -94.05 - 57.8 + 28.29 + 0.0 = -123.56$$

In the present case as selectivity is 100% no moles of CO or CO₂ were produced, therefore

$$\Delta H = \Delta H_1 = -38.01 \frac{\text{Kcal}}{\text{gmol}}$$

Hence,

$$Q_F = \frac{-\Delta H_{r_{mF}}}{a_m \phi C_p G_m}$$

$$Q_F = \frac{38010 \times 0.0151}{61000 \times 0.9 \times 8.007 \times 0.1071}$$

$$Q_F = 0.01219K$$

The maximum ΔT obtained from Figure 4 by Yoshida *et al.*[172] is 0.1 K.

Appendix G

Factorial Design Model

G.1 Sample Calculation of Model Building

The information obtained in data set J is used to perform the following calculations. Data set J can be found in Section D.2. Program MODEL FORTRAN obtains the following output.

CON	SEL	X1	X2	X3	TEMP	W/F	R
0.513	1.000	-1.0	-1.0	1.0	648.0	16.25	8.
0.747	1.000	1.0	-1.0	-1.0	698.0	16.25	4.
0.774	0.444	-1.0	1.0	-1.0	648.0	38.75	4.
0.803	0.183	1.0	1.0	1.0	698.0	38.75	8.

MATRIX: X

1.	-1.	-1.	1.
1.	1.	-1.	-1.
1.	-1.	1.	-1.
1.	1.	1.	1.

MATRIX: X TRANSPOSE

1.	1.	1.	1.
-1.	1.	-1.	1.
-1.	-1.	1.	1.
1.	-1.	-1.	1.

MATRIX: X TRANSPOSE X

4.	0.	0.	0.
0.	4.	0.	0.
0.	0.	4.	0.
0.	0.	0.	4.

MATRIX: X TRANSPOSE S

XTS(1) = 2.627
XTS(2) = -0.261
XTS(3) = -1.373
XTS(4) = -0.261

MATRIX: X TRANSPOSE C

XTC(1) = 2.837
XTC(2) = 0.263
XTC(3) = 0.317
XTC(4) = -0.205

MATRIX: (X TRANSPOSE X) INVERSE

0.25	0.00	0.00	0.00
------	------	------	------

0.00	0.25	0.00	0.00
0.00	0.00	0.25	0.00
0.00	0.00	0.00	0.25

MATRIX: (X TRANSPOSE X) INVERSE X TRANSPOSE C

C0 = 0.70925
C1 = 0.06575
C2 = 0.07925
C3 = -0.05125

MATRIX: (X TRANSPOSE X) INVERSE X TRANSPOSE S

S0 = 0.65675
S1 = -0.06525
S2 = -0.34325
S3 = -0.06525

YIELD 2ND ORDER EQUATION PARAMETERS

Y(1) = 0.4658
Y(2) = -0.0031
Y(3) = -0.1914
Y(4) = -0.0799
Y(5) = -0.0043
Y(6) = -0.0277
Y(7) = -0.0009
Y(8) = -0.0272
Y(9) = 0.0124
Y(10) = 0.0033

Taking data from these results our models result as follows:

$$y_1 = 0.7093 + 0.0657X_1 + 0.0792X_2 - 0.0512X_3 \quad (G.1)$$

$$y_2 = 0.6567 - 0.0652X_1 - 0.3432X_2 + 0.0652X_3 \quad (G.2)$$

$$\begin{aligned} Y_{\text{Sb}_2\text{O}_4-\text{MoO}_3} = & 0.4658 - 0.0031X_1 - 0.1914X_2 - 0.0799X_3 \\ & - 0.0043X_1^2 - 0.0277X_1X_2 - 0.0009X_1X_3 \\ & - 0.0272X_2^2 + 0.0124X_2X_3 + 0.0033X_3^2 \end{aligned} \quad (G.3)$$

G.2 Replicate Runs for Kinetic Analysis

The analysis of the replicate runs is based solely on the reaction yields obtained during the kinetic analysis, i.e. sets M, N, O, P, and Q. In Table G.1, $\bar{Y}$ represents the mean of the sample, s the standard deviation of the sample, s^2 its variance. The 95% confidence interval was calculated using the following formula [14]:

$$\bar{Y} \pm t_{v,\alpha/2} \frac{s}{\sqrt{n}} \quad (G.4)$$

where n is the number of replicates and α is the probability that this confidence interval does not contain the real mean. $t_{v,\alpha/2}$ is the t -probability density function with v degrees of freedom of the sample ($n-1$). In this case s^2 is an estimate of the real variance, because there are not enough data to justify it as the real variance.

The replicate data showed constant activity of the catalyst during the kinetic study. It is observed though, that at least one point may be good candidate for an outlayer. however more studies may be required as this happened at a large concentration of catalysts and it was not observed in other cases.

Table G.1: Replicate Runs for Kinetic Analysis

Set	M	N	O	P	Q
105	0.321	0.584	0.941	0.974	1.000
205	0.230	0.651	0.926	1.000	1.000
302	0.207	0.575	0.895	0.966	1.000
305	0.192	0.600	0.910	0.959	0.894
405	0.159	0.606	0.921	0.750	0.867
$\bar{Y}$	0.2218	0.6032	0.9186	0.9298	0.9522
s	0.0611	0.0294	0.0173	0.1017	0.0661
s ²	3.733×10^{-3}	8.643×10^{-4}	2.992×10^{-4}	1.034×10^{-2}	4.369×10^{-3}
$t_{\alpha/2, n}$	0.0758	0.0365	0.0214	0.1262	0.0820

Appendix H

Least Squares Criterion

H.1 Fitting a Straight Line

The simplest model for relating two variables is a straight line

$$E(Y) = \beta_0 + \beta_1 x \quad (\text{H.1})$$

where $E(Y)$ denotes the expected value of a random variable Y .

The assumptions associated with the form H.1 are as follows. First the “dependent” or “response” variable Y is a continuous random variable with probability density function $p(Y)$; so that

$$E(Y) = \int_{-\infty}^{\infty} Y p(Y) dY$$

The “independent” variable x is not a random variable. Its values are regarded as exact. In practice the interpretation of these assumptions is that any fluctuation associated with a value of x has a much smaller influence on Y than the fluctuation associated with Y itself. The postulated straight line relationship between $E(Y)$ and x is completely characterized by the two parameters β_0 and β_1 whose values are unknown. Estimates of β_0 and β_1 can be obtained by fitting model form H.1 to data for Y and x .

A measured value of Y is denoted by y and equation H.1 can be expressed equivalently as

$$y = \beta_0 + \beta_1 x + \varepsilon \quad (\text{H.2})$$

where ε is a random error term having probability density function $p(\varepsilon)$. If that straight line model H.1 does describe the relationship between $E(Y)$ and x adequately then the mean value of $p(\varepsilon)$ will be zero. ε can be expressed as representing the departures of a measured value y from its expected value which is given by the straight line form H.1.

In determining the particular values of β_0 and β_1 , departure of data points from the best fitting line can arise from two sources. One is experimental error, the lack of exact reproducibility in virtually all scientific measurements. The other is inadequacy of the selected model form.

In model form H.2 the values of the parameters β_0 and β_1 and the random error ε are unknown. However for any selected values $\tilde{\beta}_0$ and $\tilde{\beta}_1$ the error ε at datum u can be estimated by the residual e_u defined as

$$e_u = y_u - (\tilde{\beta}_0 + \tilde{\beta}_1 x_u) \quad (\text{H.3})$$

where

y_u	=	the measured response value for datum u
x_u	=	the independent variable value for datum u
$\tilde{\beta}_0, \tilde{\beta}_1$	=	selected values for the parameters

Several criteria can be used to determine the best fitting straight line, but the most common, and the most appropriate under the assumptions to be specified shortly, is the least squares criterion. If n data points are used to fit model H.2 then the values β_0 and β_1 for which $\sum_{u=1}^n e_u^2$ is minimized are called the least squares estimated of the parameters and are denoted by $\hat{\beta}_0$ and $\hat{\beta}_1$.

The distinction between ε and e is that ε involves the true but unknown values of the parameters β_0 and β_1 whereas e involves estimates of those parameters.

Even when the least squares estimates $\hat{\beta}_0$ and $\hat{\beta}_1$ are used the residuals e are not the random errors ε since the residuals in this case refer only to the data being used for the fit and not to other sets of data that can be obtained.

As stated above, least squares estimates $\hat{\beta}_0$ and $\hat{\beta}_1$ for the parameters in equation H.2 using data $(x_1, y_1), \dots, (x_n, y_n)$ are those values of β_0 and β_1 for which

$$\sum_{u=1}^n e_u^2 = \sum_{u=1}^n [y_u - (\beta_0 + \beta_1 x_u)]^2 \quad (\text{H.4})$$

is minimized. If no constraints are imposed on β_0 and β_1 then the minimum occurs at those values of β_0 and β_1 for which

$$\frac{\partial}{\partial \beta_0} \left[\sum_{u=1}^n e_u^2 \right] = 0 \quad (\text{H.5})$$

and

$$\frac{\partial}{\partial \beta_1} \left[\sum_{u=1}^n e_u^2 \right] = 0 \quad (\text{H.6})$$

Equations H.5 and H.6 can be expressed as

$$n\hat{\beta}_0 + \hat{\beta}_1 \sum_{u=1}^n x_u = \sum_{u=1}^n y_u \quad (\text{H.7})$$

$$\hat{\beta}_0 \sum_{u=1}^n x_u + \hat{\beta}_1 \sum_{u=1}^n x_u^2 = \sum_{u=1}^n x_u y_u \quad (\text{H.8})$$

and their unique solution is

$$\hat{\beta}_0 = \bar{y} - \hat{\beta}_1 \bar{x} \quad (\text{H.9})$$

$$\hat{\beta}_1 = \frac{\sum_{u=1}^n (x_u y_u) - n\bar{x}\bar{y}}{\sum_{u=1}^n x_u^2 - n\bar{x}^2} \quad (\text{H.10})$$

where $\bar{x} = \frac{1}{n} \sum_{u=1}^n x_u$ and $\bar{y} = \frac{1}{n} \sum_{u=1}^n y_u$.

Using the least squares estimated $\hat{\beta}_0$ and $\hat{\beta}_1$ from equations H.9 and H.10 the least squares straight line can be expressed as

$$\hat{y} = \hat{\beta}_0 + \hat{\beta}_1 x \quad (\text{H.11})$$

Table H.1: Collected Data for Least Squares Criterion

Data point number	Values of Independent Variables				Measured Response Values
u	x_1	x_2	$\cdots$	x_p	y
1	x_{11}	x_{12}	$\cdots$	x_{1p}	y_1
2	x_{21}	x_{22}	$\cdots$	x_{2p}	y_2
3	x_{31}	x_{32}	$\cdots$	x_{3p}	y_3
.	.	.		.	.
.	.	.		.	.
.	.	.		.	.
n	x_{n1}	x_{n2}	$\cdots$	x_{np}	y_n

H.2 Fitting Linear Models

A general linear model form can be written as

$$E(Y) = \beta_1 x_1 + \cdots + \beta_p x_p \quad (\text{H.12})$$

It is obvious that at least p data points must be available if unique estimates of p parameters are to be obtained. Suppose that there are n data points ($n > p$) which can be tabulated as indicated in Table H.1.

Let us now define the following matrices for this general case. The dimensions of each matrix are in parentheses below the matrix notation.

$$\underset{(n \times 1)}{\mathbf{Y}} = \begin{bmatrix} y_1 \\ \cdot \\ \cdot \\ \cdot \\ y_n \end{bmatrix}$$

$$\begin{matrix} \underline{\beta} \\ (p \times 1) \end{matrix} = \begin{bmatrix} \beta_1 \\ \cdot \\ \cdot \\ \cdot \\ \beta_p \end{bmatrix}$$

$$\begin{matrix} \underline{X} \\ (n \times p) \end{matrix} = \begin{bmatrix} x_{11} & \cdots & x_{1p} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ x_{n1} & \cdots & x_{np} \end{bmatrix}$$

For any selected values $\tilde{\beta} = (\tilde{\beta}_1, \dots, \tilde{\beta}_p)^T$, where superscript T denotes the transpose of a matrix, a matrix of residuals $\underline{e}$ can be constructed where

$$\begin{matrix} \underline{e} \\ (n \times 1) \end{matrix} = \begin{bmatrix} e_1 \\ \cdot \\ \cdot \\ \cdot \\ e_n \end{bmatrix} = \begin{bmatrix} y_1 - (\tilde{\beta}_1 x_{11} + \cdots + \tilde{\beta}_p x_{1p}) \\ \cdot \\ \cdot \\ \cdot \\ y_n - (\tilde{\beta}_1 x_{n1} + \cdots + \tilde{\beta}_p x_{np}) \end{bmatrix}$$

$$\underline{e} = \underline{Y} - \underline{X}\tilde{\beta}$$

Least squares estimated of the parameters $\underline{\beta}$ are obtained by minimizing $\underline{e}^T \underline{e}$, the sum of squares of residuals with respect to $\underline{\beta}$. The set of equations

$$\frac{\partial}{\partial \beta_1} (\underline{e}^T \underline{e}) = 0$$

·
·
·

$$\frac{\partial}{\partial \beta_p} (\underline{e}^T \underline{e}) = 0$$

can be written in matrix form as

$$\mathbf{X}^T \mathbf{X} \underline{\hat{\beta}} = \mathbf{X}^T \mathbf{Y} \quad (\text{H.13})$$

where $\underline{\hat{\beta}} = (\hat{\beta}_1, \dots, \hat{\beta}_p)^T$ are the least squares estimates of the parameters. The solution of equation H.13 is

$$\underline{\hat{\beta}} = (\mathbf{X}^T \mathbf{X})^{-1} \mathbf{X}^T \mathbf{Y} \quad (\text{H.14})$$

where superscript -1 denotes the inverse of a matrix. The fitted response values for the data points can be expressed as

$$\hat{\mathbf{Y}} = \begin{bmatrix} \hat{y}_1 \\ \cdot \\ \cdot \\ \cdot \\ \hat{y}_n \end{bmatrix} = \mathbf{X} \underline{\hat{\beta}} \quad (\text{H.15})$$

and the residuals from the least square fit as

$$\underline{\hat{\epsilon}} = \mathbf{Y} - \hat{\mathbf{Y}} \quad (\text{H.16})$$

Appendix I

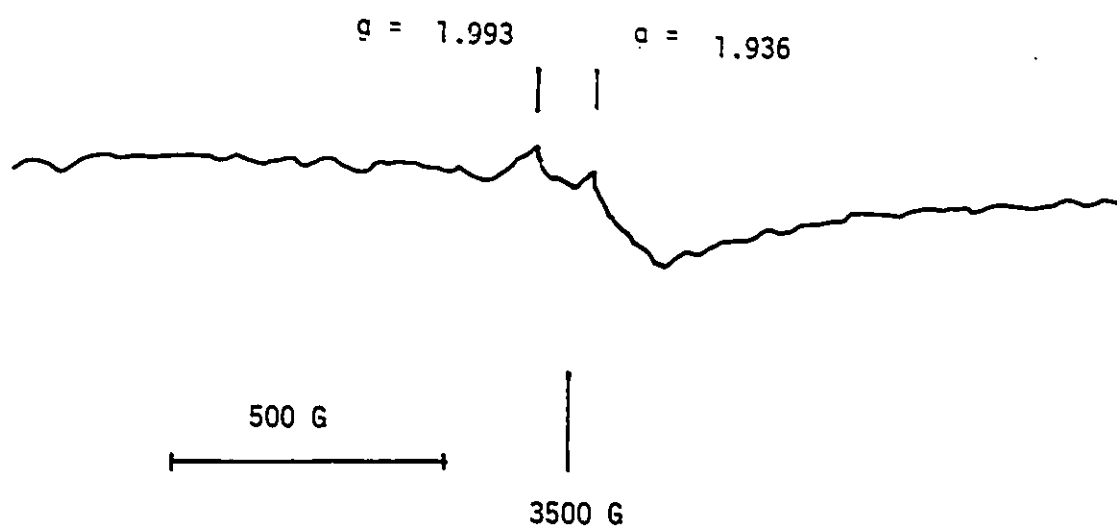
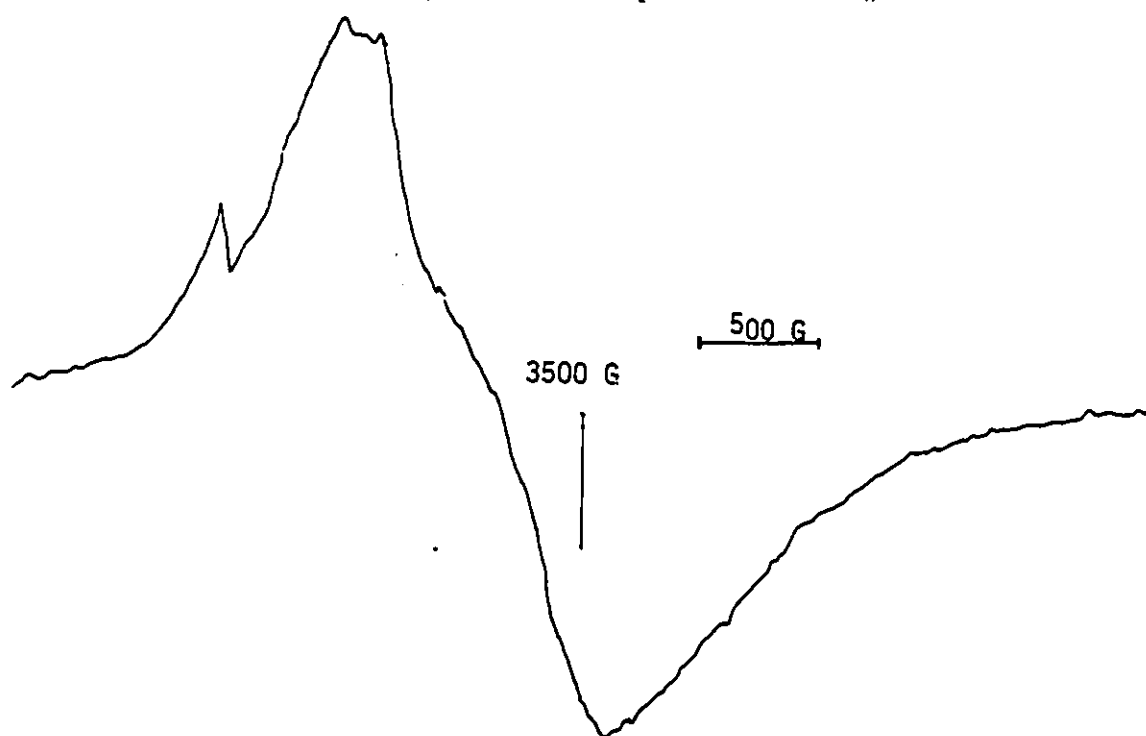
X-Ray Diffraction

Table I.1: Crystalline Structure of Different Oxides

Compound	Crystal	Space Group	a	b	c	β
$\text{Sb}_2\text{Mo}_{10}\text{O}_{31}$	Hexagonal	<i>Pma2</i>	20.03	8.08	7.17	-
$\beta\text{-Sb}_2\text{O}_4$	Monoclinic	<i>C2/c</i>	12.06	4.834	5.383	104°35'
$\alpha\text{-MoO}_3$	Cubic	<i>Fm3m</i>	5.549	-	-	-
$\beta\text{-MoO}_3$	Orthorombic	<i>PnMa</i>	13.85	3.696	3.966	-
Mo-doped Sb_2O_4	Monoclinic	<i>C2/c</i>	12.0571	4.8335	5.3838	105.579°
Mo_4O_{11}	Monoclinic	<i>P2_1/a</i>	24.52	5.439	6.701	94.28°
Mo_4O_{11}	Orthorombic	<i>Pnma</i>	24.49	5.457	6.752	-
$\text{Mo}_{17}\text{O}_{47}$	Orthorombic	<i>Pba2</i>	21.61	19.63	3.951	-
Mo_3Sb_7	Cubic	<i>Im3m</i>	9.5713	-	-	-
$\alpha\text{-Sb}_2\text{O}_4$	Orthorombic	<i>Pna2_1</i>	5.456	4.814	11.787	-

Appendix J

Electronic Spin Resonance

Figure J.1: ESR Spectrum of MoO_3 Figure J.2: ESR Spectrum of Sb_2O_3

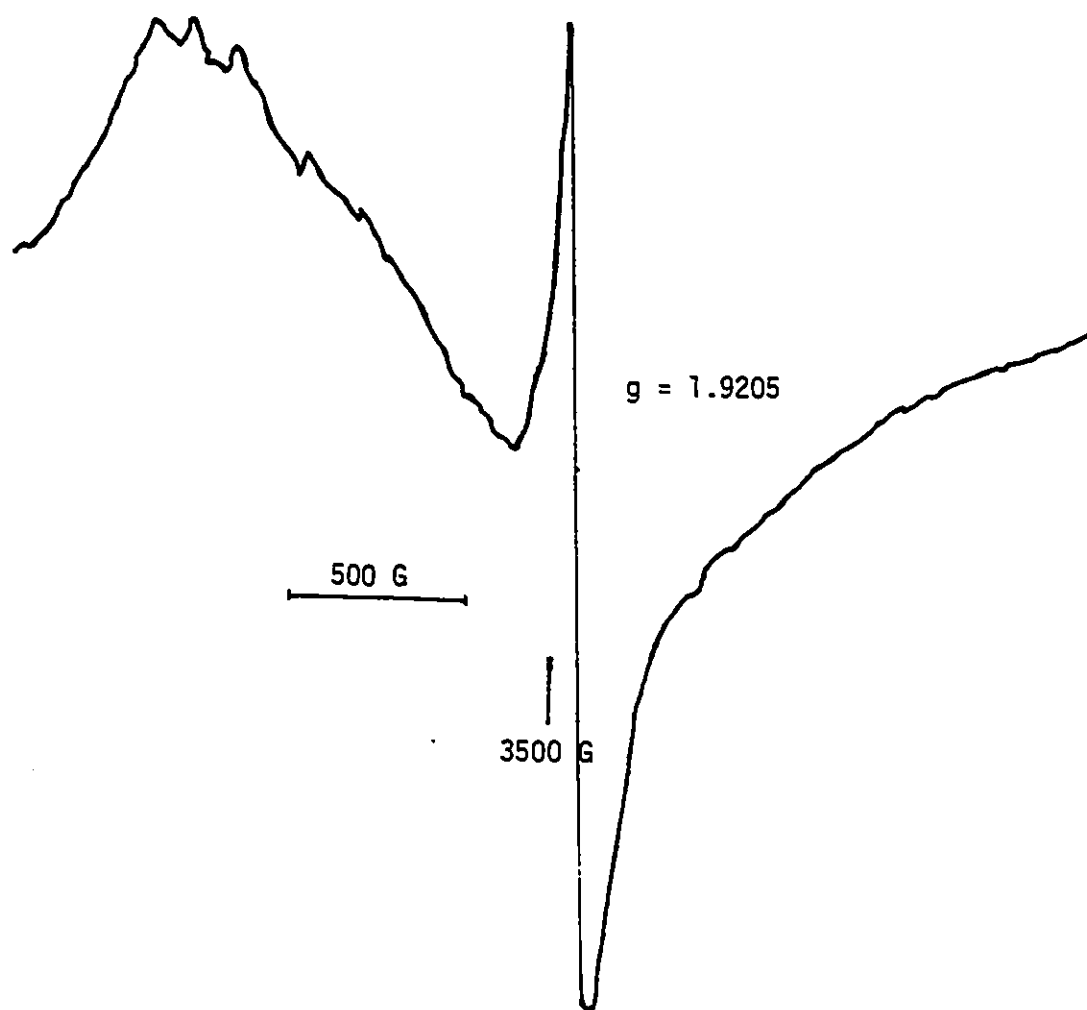


Figure J.3: ESR Spectrum of Catalyst Composition: 67% Sb_2O_3 , 33% MoO_3