



**REACTION ENGINEERING STUDIES IN
ION EXCHANGE RESIN CATALYZED
ESTERIFICATION REACTIONS**

**A THESIS
SUBMITTED TO THE**

UNIVERSITY OF PUNE

FOR THE DEGREE OF

**DOCTOR OF PHILOSOPHY
IN CHEMISTRY**

BY

CHARUBALA ANANDA PHALAK

**HOMOGENEOUS CATALYSIS DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE 411 008
INDIA**

FEBRUARY 2004



FORM – ‘A’

Certified that the work incorporated in the thesis entitled: “**REACTION ENGINEERING STUDIES IN ION EXCHANGE RESIN CATALYZED ESTERIFICATION REACTIONS**”, submitted by **Ms. Charubala Ananda Phalak** was carried under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

February, 2004

Pune (INDIA)

Dr. R.V.CHAUDHARI

(Supervisor / Research Guide)



Dedicated to

My Father & Mother

ACKNOWLEDGEMENT

I wish to express my sincere gratitude to Dr. R. V. Chaudhari, Head, Homogeneous Catalysis Division, National Chemical Laboratory (NCL) for his constant support and encouragement during my research work. I have high regards for his guidance, motivation and his dynamic presence as a guide.

I am grateful to Council of Scientific and Industrial Research (CSIR). India, for granting me the research fellowship. I am thankful to Dr. Sivram, Director, NCL, for allowing me to carry out research work and extending me all infrastructural facilities from time to time in this institute of research.

I take this opportunity to express my sincere gratitude to Dr. R. Jaganathan, for his valuable help and suggestions during this work. I sincerely acknowledge Dr. S. P. Gupte, Dr. R. M. Deshpande, Mr. Sunil Joshi, Dr. A. A. Kelkar, Dr. V. V. Ranade, Dr. C. V. Rode, Dr. V. H. Rane, Mr. Ozarde, Mr. P. B. Jadkar Dr. R. V. Naik for their valuable help and co-operation during my research stay in NCL.

I also thank all the staff member of library, RPBD administrative department and workshop staff for their co-operation. I am also thankful to Mr. David Solomon for his help in arranging the experimental setup. I am also grateful to office members of HCD, Mr. Raheja, Mr. Patne, Mr. Durai, Mr. Kedari and Mr. Kamble for their care, encouragement and support.

I also wish to thank my seniors and moreover my friends Dr. Shubhangi, Dr. S. Jayasree, Dr. A. Seayad, Dr. Vinid Nair, Dr. Suju Mathew for their helpful hand and sympathetic ear. I would also like to express my deep felt gratitude to my colleagues and friends Savita, Yogi, Sunil T., Vivek, Gunjal, Kaushik, Rajesh, Bibhas, Debu, Tushar, Anand, Shrikant, Mahesh, Makarand, Nandu, Manisha V., Manisha T., Rashmi, Rita, Anamika, Sunil S., Deepak, Pippalad, Nitin, Abhishek, Shashi, Ankush, Vikas, Prashant, Jayprakash, Atul, Sagar, Amit, Pankaj and many in NCL who are not named in person, for their valuable friendship and helping hand.

It is my immense pleasure to thank my husband Anant, who has encouraged and supported me for the completion of this thesis.

No thanks can be enough to acknowledge for the encouragement and support of my parents, sisters and brother. Needless to say it was because of the efforts of my parents and especially my late father today I stand where I am.

February 2004

Pune

Charubala Ananda Phalak

List of Contents

	Description	Page No.
	List of Tables	i
	List of Figures	ii
	Summery and Conclusions	v
Chapter 1	Introduction and Literature Survey	
1.1	Introduction	1
1.2	<i>Literature survey</i>	5
1.2.1	<i>Esterification catalysts and processes</i>	7
1.2.1.1	Homogeneous acid catalysis	7
1.2.1.2	<i>Heterogeneous acid catalysis</i>	9
1.2.1.2.1	Metal ion complexes as catalyst	9
1.2.1.2.2	Ion exchange resin as catalyst	10
1.2.1.2.3	Zeolites as catalysts	12
1.2.1.2.4	Enzymes as catalysts	12
1.2.2	Kinetic studies	14
1.2.2.1	<i>Kinetics of ion exchange catalysis</i>	14
1.2.2.2	<i>Kinetics and reaction engineering studies of esterification</i>	15
1.2.2.2.1	<i>Kinetics of esterification of monobasic acid</i>	16
1.2.2.2.2	<i>Kinetics of esterification of dibasic acid</i>	23
1.2.3	Reaction engineering studies	26
1.2.3.1	<i>Agitated slurry reactors</i>	26
1.2.3.2	Fixed bed reactor	27
1.2.3.2.1	Experimental studies in fixed bed reactor	29
1.2.3.3	Reactive distillation	30
1.3	Scope and objectives	31
1.4	References	32

Chapter 2 Esterification of Acetic Acid with Methanol using Dowex 50W Resin as a Catalyst

2.1	Introduction	42
2.2	Experimental	44
2.2.1	Material	44
2.2.2	Catalyst	44
2.2.3	Reactor setup	45
2.2.4	Experimental procedure	46
2.3	Analysis	46
2.4	Kinetics of esterification	47
2.4.1	Preliminary experiments	47
2.4.2	Kinetics of homogeneous reaction	48
2.4.3	Kinetics of ion exchange resin catalyzed esterification	58
2.4.3.1	Analysis of initial rate data	58
2.4.3.2	Analysis of mass transfer effects	59
2.5	Development of model for a first order reversible reaction	67
2.6	Kinetic model for the heterogeneous reaction	69
2.7	Conclusion	82
2.8	References	83

Chapter 3 Esterification of Acetic Acid with Butanol using Dowex 50W Resin as a Catalyst.

3.1	Introduction	85
3.2	Experimental	86
3.2.1	Materials	86
3.2.2	Catalyst	87
3.3	Analytical procedure	87
3.4	Kinetics of esterification of acetic acid and butanol	87
3.4.1	Preliminary experiments	887

3.4.2	Kinetics of homogeneous reaction	88
3.4.3	Kinetics of ion exchange resin catalyzed esterification	90
3.4.3.1	Analysis of initial rate data	90
3.4.3.2	Analysis of mass transfer effects	91
3.5	Reactor model	102
3.6	Kinetic model for the heterogeneous reaction	102
3.7	Conclusion	112
3.8	References	113

Chapter 4 Esterification of Maleic Acid with Methanol using Dowex 50W Resin as a Catalyst.

4.1	Introduction	114
4.2	Experimental	115
4.2.1	Materials	115
4.2.2	Reactor setup	115
4.2.3	Experimental procedure	116
4.3	Analysis	116
4.4	Kinetics of esterification	117
4.4.1	Preliminary experiments	117
4.4.2	Kinetics of homogeneous reaction	122
4.4.3	Kinetics of ion exchange resin catalyzed esterification reaction	123
4.4.3.1	Analysis of initial rate data	128
4.4.3.2	Analysis of mass transfer effects	128
4.5	Kinetic model for the heterogeneous reaction	132
4.6	Selectivity behavior of monomethyl maleate	134
4.7	Conclusion	147
4.8	References	148

Chapter 5 Performance of Trickle-bed Reactor for Esterification.

5.1	Introduction	149
5.2	Experimental	151
5.2.1	Materials	151
5.2.2	Catalyst	151
5.2.3	Reactor	151
5.2.4	Experimental procedure	153
5.3	Trickle bed reactor model	153
5.3.1	Reactor model for esterification of acetic acid with methanol/ butanol	153
5.3.2	Reactor model for esterification of maleic acid	156
5.4	Method of solution	158
5.4.1	Esterification of acetic acid with methanol/ butanol	158
5.4.2	Esterification of maleic acid with methanol	160
5.5	Results and discussion	160
5.5.1	Comparison with experimental data	160
5.6	Conclusion	172
5.7	References	173

List of Tables

Table No.	Description	Page No.
1.1	Some important commercial processes catalyzed by cation exchange resin	4
1.2	Catalysts used for esterification reactions	8
1.3	Ion exchange resin catalyzed esterification processes	13
1.4	Literature survey on esterification of monocarboxylic acids with alcohols	17
1.5	Literature survey on esterification of dicarboxylic acids with alcohols	24
1.6	Some batch reactor modeling and reaction engineering studies of esterification reactions	28
2.1	Specifications of Dowex 50W resin catalyst	45
2.2	Range of operating conditions	47
2.3	Homogeneous reaction rate constants	51
2.4	Initial rate data for ion exchange resin catalyzed esterification of acetic acid with methanol	60
2.5	Diffusivity of acetic acid in methanol	66
2.6	Reaction rate constants for heterogeneous catalyzed esterification	74
3.1	Range of operating condition	88
3.2	Homogeneous reaction rate constants	89
3.3	Initial rate data for ion exchange resin catalyzed esterification of acetic acid with butanol	101
3.4	Diffusivity of acetic acid in butanol	101
3.5	Heterogeneous reaction rate constant	112
4.1	Range of operating conditions	118
4.2	Homogeneous reaction rate constants	123
4.3	Initial rate data for ion exchange resin catalyzed esterification of maleic acid with methanol	131
4.4	Diffusivity of maleic acid in methanol	131
4.5	Heterogeneous reaction rate constants	133
5.1	Catalyst specifications	151
5.2	Reactor details	151
5.3	Range of operating conditions	153

5.4	Dimensionless parameters used in the model	159
5.5	Summary of various correlations used in this work	171

List of Figures

Figure No.	Description	Page No.
1.1	Several routes for synthesis of esters	6
1.2	Types of resin catalyzed reactions	11
2.1	Experimental setup of a batch slurry reactor for esterification reaction	45
2.2	Effect of catalyst recycle at 318 K	50
2.3	Concentration-Time profile at 308 K for AcOH-MeOH molar ratio of 1:2	52
2.4	Concentration-Time profiles at 318 K for AcOH-MeOH molar ratio of 1:2	53
2.5	Concentration-Time profiles at 328 K for AcOH-MeOH molar ratio of 1:2	54
2.6	Concentration-Time profiles at 318 K for AcOH-MeOH molar ratio of 1:1	55
2.7	Concentration-Time profile at 318 K for AcOH-MeOH molar ratio of 1:4	56
2.8	Effect of temperature on homogeneous reaction rate constants	57
2.9	Effect of catalyst loading on rate of reaction	61
2.10	Effect of agitation on rate of reaction at 318 K	62
2.11	Effect of methanol concentration on the rate of reaction	63
2.12	Effect of particle size on rate of reaction	64
2.13	Concentration-time profile at 308 K	71
2.14	Concentration-time profile at 318 K	72
2.15	Concentration-time profile at 328 K	73
2.16	Concentration-time profiles for various particle sizes at 308 K	75
2.17	Concentration-time profiles for various particle sizes at 318 K	76
2.18	Concentration-time profiles for various particle sizes at 328 K	77
2.19	Concentration-time profiles for various temperatures with acid-alcohol molar ratio of 1:1	78
2.20	Concentration-time profiles for various temperatures with acid-alcohol molar ratio of 1:4	79

2.21	Concentration-time profiles for various catalyst loadings at 318 K	80
2.22	Effect of temperature on heterogeneous catalyzed reaction rate constants	81
3.1	Concentration-Time profile at 353 K	92
3.2	Concentration-Time profile at 343 K	93
3.3	Concentration-Time profile at 363 K	94
3.4	Concentration-Time profile at 353 K for acid-alcohol molar ratio of 1:1	95
3.5	Concentration-Time profile at 353 K for acid-alcohol molar ratio of 1:0.5	96
3.6	Effect of temperature on rate constants of homogeneous esterification reaction	97
3.7	Effect of catalyst loading on rate of reaction	98
3.8	Effect of butanol concentrations on rate of reaction	99
3.9	Effect of particle size on rate of reaction	100
3.10	Concentration-Time profile at 343 K	103
3.11	Concentration-Time profile at 353 K	104
3.12	Concentration-Time profile at 363 K	105
3.13	Concentration-Time profile for various catalyst loading at 353 K	107
3.14	Concentration-Time profile for various reactant concentrations at 353 K	108
3.15	Concentration-Time profiles for temperatures at $d_p = 7.8 \times 10^{-4}$ m	109
3.16	Concentration-Time profiles at $d_p = 3.75 \times 10^{-4}$ m at 328 K	110
3.17	Effect of temperature on heterogeneous reaction rate constants	111
4.1	Concentration-Time profile at 308 K	119
4.2	Concentration-Time profile at 318 K	120
4.3	Concentration-Time profile at 328 K	121
4.4	Concentration-Time profile at 308 K for maleic acid-methanol molar ratio of 1:6	124
4.5	Concentration-Time profile at 318 K for maleic acid-methanol molar ratio of 1:6	125
4.6	Concentration-Time profile at 328 K for maleic acid-methanol molar ratio of 1:6	126
4.7	Effect of temperature on homogenous reaction rate constants	127

4.8	Effect of catalyst loading on rate of reaction	129
4.9	Effect of particle size on rate of reaction	130
4.10	Concentration-Time profile at 308 K	135
4.11	Concentration-Time profile at 318 K	136
4.12	Concentration-Time profile at 328 K	137
4.13	Concentration-Time profile at 308 K for maleic acid-methanol molar ratio of 1:6	138
4.14	Concentration-Time profile at 318 K for maleic acid-methanol molar ratio of 1:6	139
4.15	Concentration-Time profile at 328 K for maleic acid-methanol molar ratio of 1:6	140
4.16	Concentration-Time profile for catalyst loading at 318 K for maleic acid:methanol of 1:4	141
4.17	Concentration-Time profile for particle sizes at 318 K for maleic acid:methanol of 1:4	142
4.18	Effect of temperature on heterogeneous rate constants	143
4.19	Selectivity behavior of monomethyl maleate in homogeneous reactions	144
4.20	Selectivity behavior of monomethyl maleate in heterogeneous reactions	145
4.21	Selectivity behavior of monomethyl maleate at different catalyst loading	146
5.1	Exit concentrations for esterification of acetic acid with methanol at different temperatures	162
5.2	Exit concentrations for esterification of acetic acid with butanol at 353 K	163
5.3	Exit concentrations for esterification of maleic acid with methanol at 318 K	164
5.4	Conversion of acetic acid for esterification with methanol for different reactant concentrations at 318 K	165
5.5	Conversion of acetic acid for esterification with methanol for different reactant concentration at 328 K	166
5.6	Conversion of acetic acid for esterification with methanol for different reactant concentrations at 308 K	167
5.7	Conversion of acetic acid for esterification with butanol for different reactant concentration at 353 K	168
5.8	Conversion of acetic acid for esterification with butanol for different temperature	169
5.9	Conversion of maleic acid for esterification with methanol different temperatures	170

Summary and Conclusions

Introduction:

Esterification is a well-known process and a number of industrially important chemicals such as methyl, ethyl and butyl esters, alkyl t-butyl ethers (MTBE and ETBE) are produced using esterification reactions. Esterification represents one of the most important reactions in chemical industry and the esters produced have applications in a variety of areas such as plasticizers, flavors and fragrances, pesticides, solvents, medicinal and surface active agents. Some esters are converted into their derivatives, which are useful as chemical intermediates and monomers for resins and high molecular weight polymers (McKetta, 1983). Catalytic esterification can be carried out in liquid phase as well as in vapor phase and higher levels of conversions have been generally obtained in vapor phase esterification (Kirk-Othmer, 1992). Esterification reactions are equilibrium processes and must be displaced toward the desired ester by use of an excess of one of the reactants or by continuous removal of water by azeotropic distillation. These reactions are generally carried out in batch reactors in the presence of homogeneous or heterogeneous catalysts and also with supported heterogeneous catalysts in a fixed bed reactor with cocurrent down-flow of the liquid phases. Homogeneous acid catalyzed reactions generate side products posing environmental and corrosion problems. In addition, separation of the pure product from the homogeneous catalyst is a very difficult task. Hence, heterogeneously catalyzed esterification reactions are gaining more attention. They provide cleaner routes for chemicals due to ease of separation of the products without contamination. Therefore, studies on heterogeneously catalyzed esterification reactions are extremely important in developing cleaner and economically improved processes for a wide variety of industrial products. The choice of a method to achieve complete esterification depends on the boiling points of the alcohol, the carboxylic acid, the ester produced, catalyst used and the reactor type. A systematic study of the effect of reaction parameters and reaction engineering aspects is useful to develop an optimum process. The aim of this thesis is to investigate reaction-engineering studies of esterification reactions, using ion exchange resin catalyst in slurry and fixed bed reactors. The following reaction systems have been investigated: Esterification of Acetic acid with Methanol in the presence of Dowex 50W catalyst.

1. Esterification of Acetic acid with Butanol in the presence of Dowex 50W catalyst.
2. Esterification of Maleic acid with Methanol in the presence of Dowex 50W catalyst.

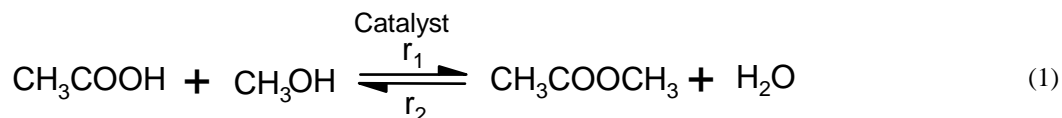
For all the systems under consideration, rate equations have been developed using extensive experimental data obtained over a wide range of operating conditions. In evaluating the kinetics, the contributions of both homogeneous and heterogeneous reactions have been taken into account. Batch and fixed bed reactor models have also been developed, and the model predictions compared with experimental data. The thesis is presented in five chapters:

Chapter 1: Introduction and Literature Survey

A detailed literature review on esterification of carboxylic acids with different alcohols has been made. The type of catalysts used, their activity, selectivity, kinetic modeling and reaction engineering aspects have been discussed. A general review of the esterification of carboxylic acid with alcohol in presence of mineral acid or heterogeneous acid catalyst have been presented. Critical analyses of reaction engineering aspects such as external and intraparticle mass transfer effects and reactor performance models have been presented and scope and objective of the present thesis outlined.

Chapter 2: Esterification of Acetic Acid with Methanol using Dowex 50W Resin as a Catalyst

A detailed study on the ion exchange resin (Dowex 50W) catalyzed esterification of acetic acid with methanol in a batch slurry reactor was undertaken. The reaction scheme is:



Since, esterification can also take place in the homogeneous phase, the kinetics of homogeneous reaction was investigated separately to assess its contribution. For this purpose, the experiments were carried out in a mechanically agitated slurry reactor of 500 cm³ capacity at 308, 318 and 328 K with a molar ratio of acetic acid and methanol as 1:2 at a stirring speed of 450 rpm. In each experiment, concentration-time profiles were observed for all the reactants and products. The following form of rate equation was proposed assuming a first order dependence of the rate for both forward and reverse reactions.

$$r_1 = k_1 C_1 \cdot C_2 \quad (2)$$

$$r_2 = k_2 C_3 \cdot C_4 \quad (3)$$

Where r_1 and r_2 are forward and backward reaction rates respectively (kmol/m³/sec.), and C_1 , C_2 , C_3 , and C_4 are concentrations (kmol/m³) of Acetic acid, Methanol, Methyl acetate and water respectively.

For interpretation of the kinetics, the observed concentration-time data were used and the rate parameters evaluated at each temperature using a batch reactor model. The activation energies for homogeneous forward and backward reactions were evaluated as 115.18 and 43.82 kJ/mol.

The ion exchange catalyzed heterogeneous reaction was studied in the same reactor. The effect catalyst concentration, particle size and initial concentration of reactants was studied at 308, 318 and 328 K. The concentration-time profiles were observed for different sets of conditions (Molar ratio of acetic acid and methanol of 1:05-1:2, Catalyst loading, 8.14-48.82 kg/m³ and stirring speed of 450 rpm). For the present case, the reaction rates will be the sum of homogeneous and heterogeneous reactions. Hence,

$$r_3 = k_1 C_1 \cdot C_2 + w\eta_c k_3 C_1 \cdot C_2 \quad (4)$$

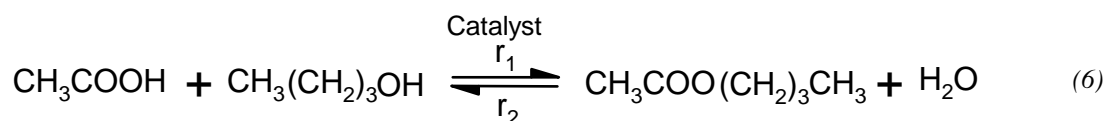
$$r_4 = k_2 C_3 \cdot C_4 + w\eta_c k_4 C_3 \cdot C_4 \quad (5)$$

where r_3 and r_4 represent overall rates for forward and backward reactions, w is the catalyst loading in kg/m³ and η_c is the catalytic effectiveness factor. An analytical

solution has been developed for evaluating η_c for a 1,1 order reversible reaction incorporating intraparticle diffusional resistances. The rate parameters for the heterogeneous reaction (k_3 and k_4) were estimated by simulation of the experimental batch reactor data. The activation energies for heterogeneous forward and backward reactions were evaluated as 38.69 and 46.27 kJ/mol.

Chapter 3: Esterification of Acetic Acid with Butanol using Dowex 50W catalyst.

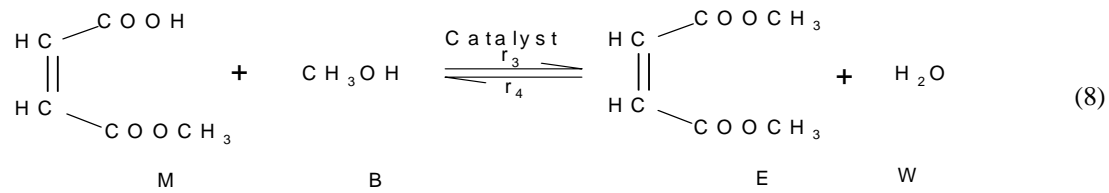
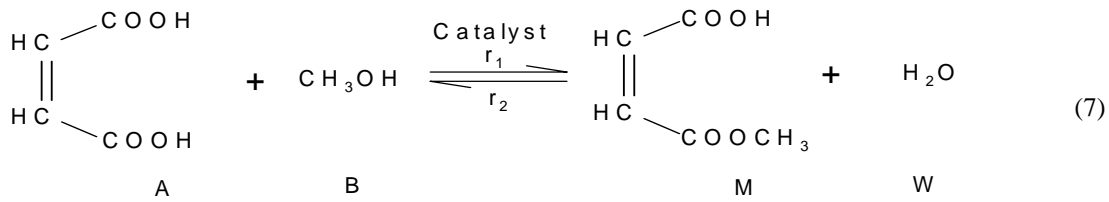
The liquid phase esterification of acetic acid with butanol in a batch slurry reactor was also studied. The autocatalyzed (homogeneously catalyzed) and ion exchange resin catalyzed reactions were studied separately. The reaction scheme is:



The effect of concentration of the reactants and catalyst loading was studied at temperatures of 343, 353 and 363 K and the concentration-time profiles were obtained under these conditions. Again, a first order rate equation was proposed and the rate parameters were evaluated by following the same methodology described earlier in Chapter 2. From the temperature dependence of the rate constants, the values of activation energies for homogeneous forward and backward reactions were evaluated as 53.83 and 43.68 kJ/mol. Similarly, the values of activation energies for heterogeneous forward and backward reactions were found to be 49.42 and 91.95 kJ/mol respectively.

Chapter 4: Esterification of Maleic Acid with Methanol in Presence of Dowex 50W as a catalyst.

The liquid phase esterification of maleic acid with methanol in a batch slurry reactor was studied. The esterification of maleic acid is an example of a multistep catalytic reversible reaction. The first reaction involves formation of a monoester (monomethyl-maleate) which further reacts with methanol to form a di-ester (dimethyl-maleate). The reactions involved are:



For this system, the homogeneous and the heterogeneous reactions were studied separately and the concentration-time profiles were obtained over a wide range of operating conditions. For the heterogeneous reaction, a smaller particle size (0.46 μm) of the ion exchange resin was used where the intraparticle diffusion resistances were negligible. One interesting observation was that the homogeneous reaction rate was significantly higher for this system. This is due to the catalytic effect of the maleic acid. The homogeneous rate of reaction was represented as:

$$r_1 = k_1 C_1 \cdot C_2 \quad (9)$$

$$r_2 = k_2 C_4 \cdot C_5 \quad (10)$$

$$r_3 = k_3 C_4 \cdot C_2 \quad (11)$$

$$r_4 = k_4 C_3 \cdot C_5 \quad (12)$$

Where r_1 and r_2 represent forward and backward reaction rates for step-I respectively and r_3, r_4 for step-II and C_1 to C_5 are concentrations (kmol/m^3) of Maleic acid, Methanol, and Mono-methyl maleate, Di-methyl maleate and water respectively. The rate constants k_1 to k_4 for the homogeneous reaction were evaluated by the same procedure described **earlier** in Chapter 2. The overall reaction rate was represented as:

$$r_5 = k_1 C_1 \cdot C_2 + w k_5 C_1 \cdot C_2 \quad (13)$$

$$r_6 = k_2 C_4 \cdot C_5 + w k_6 C_4 \cdot C_5 \quad (14)$$

$$r_7 = k_3 C_4 \cdot C_2 + w k_7 C_4 \cdot C_2 \quad (15)$$

$$r_8 = k_4 C_3 \cdot C_5 + w k_8 C_3 \cdot C_5 \quad (16)$$

The kinetic parameters were evaluated by simulation of the experimental data using a batch reactor model at different temperatures.

Chapter 5: Performance of a Trickle-bed Reactor for Esterification.

A trickle bed reactor model was developed for the Esterification reactions studied. This model incorporates the contribution of intraparticle mass transfer resistances. The kinetic equations already developed were used for the respective esterification reactions. Experimental data were obtained in a 25 mm diameter glass trickle bed reactor at different concentrations of reactants, flow rates and temperatures. The performance of the reactor was measured in terms of the conversions of the acids obtained at the exit of the reactor. The model predictions were compared with experimental data at different operating conditions. This model would be useful in predicting the performance of a trickle bed reactor for esterification reactions in general.

Thus, this thesis presents a detailed investigation on kinetic modeling and experimental verification of batch and continuous reactor data for mono and diesterification reactions. Such information is of immense value in design and scale-up of esterification reactors.

Kirk Othmer, "Encyclopedia of Chemical Technology", V-9, 4th Ed.(1992)

Mcketta John J., "Encyclopedia of Chemical Processing and Design", V-19 (1983)

Rajashekheram M. V., Jagganathan R. and Chaudhari R. V., A trickle-bed reactor model for hydrogenation of 2,4 dinitrotoluene : experimental verification., Chem. Eng. Sci., 53(4), 787(1998).

Chapter 1

Introduction and Literature Survey

1.1 Introduction

Catalysts are extremely important materials of commerce. Most of the industrial reactions pertaining to the chemical, petrochemical, and pharmaceutical sector and almost all-biological reactions are catalytic in nature. Products like food, clothing, drugs, fuels etc., which drive today's economy involve catalysis in some way or the other. Catalysts also form an integral part of environmental protection and emission control strategies. Catalysts have been used commercially for more than a century dating from the Deacon and Contact process for sulfuric acid, used in the late 1800s to the latest FCC processes for petrochemical cracking. Firtz Habers ammonia synthesis process of 1908 can be considered as the process that heralded the birth of modern industrial catalysts.

Majority of chemical reactions use catalysts to enhance the reaction rates in order to obtain the desired products in an economical way. Catalysts in general are classified into two types, depending on the phase in which the catalyst is present. Homogeneous catalysis, in which reactants, products as well as catalysts are present in a single phase, and heterogeneous catalysis in which, the catalyst is present in a different phase than that of the reactants. Some general features of the homogeneous catalysts are: mild reaction conditions, high activity and selectivity, difficult and expensive catalyst-product separation, better mechanistic understanding etc. Some examples of the processes involving homogeneous catalysts are carbonylation, hydroformylation, oxidation, telomerization, co-polymerization, metathesis etc. (Parshall (1980)). In homogeneous catalysis, a small catalyst molecule or ion is consumed in an early reaction step and is restored in a later step. The main drawback of homogeneous catalysts is in the difficulty separation of catalyst and product.

Heterogeneous catalysts are preferred over the soluble acid catalysts due to easier separation of the products without contamination, ease of handling, higher rates of reaction, high selectivity, reusability of catalyst and minimum corrosion of equipment. Heterogeneous catalysts, by virtue of their surface properties, accelerate gas-phase, liquid-phase, or multi-phase reactions. The chemistry concerned is controlled by the chemical reactivities of both the reactants and the catalyst surface. In heterogeneous catalysis the use of solid acid catalysts have wide ranging applications in the petrochemical industry, where they have largely replaced traditional liquid phase acid

catalysts for hydrocarbon transformations. Besides being convenient to handle, solid catalysts can be used at higher temperatures and often give enhanced product selectivity. They are also finding increasing use in the production of organic chemicals and syntheses of fine chemicals. A review by Tanabe and Holderich (1999) summarized over 90 acid-catalyzed processes that are either being exploited commercially or are likely to be commercialized. The solid acid catalysts can be used in vapor phase or multiphase (slurry, fixed bed etc.) modes and have made significant impact in improving conventional organic synthesis processes. Since these systems involve multiple phases like solid (catalyst) and one or more liquid phases, the role of different reaction engineering process parameters assumes importance. The analysis and design of multiphase catalytic reactors had been reviewed by Ramchandran and Chaudhari (1992), Doraiswamy and Sharma (1984), Mills and Chaudhari (2000).

The processes using ion exchange resin as catalysts represent important examples of solid acid catalysis. In heterogeneous catalysis, the forces active at a solid surface can distort or even dissociate an absorbed reactant molecule and affect the rate of reaction (Helfferich and Hawang (1988)). The synthesis of ion exchangers was first reported in 1935 and was used as heterogeneous catalyst (Adsmid and Homes (1954)). The use of ion-exchange catalysis should now be regarded not merely as an elegant preparative technique but also as a potential method in modern chemical technology, combining simplicity in the design and operation of the plant with high yields of valuable products. Strong acid cation exchange resins have been used commercially as solid acid catalysts in many areas. For example, (1) Etherification of olefins with alcohols, e.g. the coupling of isobutene with methanol to form methyl t-butyl ether (MTBE). (2) Dehydration of alcohols to olefins or ethers, e.g. t-butanol dehydration to form isobutene. (3) Alkylation of phenols to alkyl phenols. (4) The condensation reactions, e.g. manufacture of bisphenol-A from phenol and acetone (5) Olefin hydration to form alcohols, e.g. propene hydration to form 2-propanol. (6) Purification of the phenol stream after the decomposition of cumene hydroperoxide to phenol and acetone. (7) Ester hydrolysis and other reactions. Doraiswamy and Sharma (1984) and Olaha (1994) reviewed the use of ion exchange resin catalysts for a wide variety of reactions ranging from alkylation with olefins, alkyl halides, and alkyl esters; isomerisation; transalkylation; acylation;

nitration; ether and ester synthesis; acetals, thioacetals hydration and rearrangement chemistry. Doraiswamy and coworkers (1995) give detailed applications of polystyrene-based ion-exchanged resins with approximately 300 different reactions. Bhagade and Nageshwar (1977, 1978, 1980, 1981) reviewed the use of resin catalysts for hydration, dehydration, esterification, ester hydrolysis and alkylation. Widdecke's (1999) review discussed the design and industrial applications of polymeric acid catalysts. Albright (1987) analyzed various aspects of the fundamentals of the catalysis by acidic ion-exchange resins. Neier (1991) has published a comprehensive review on the ion exchange catalyzed reactions. A recent review by Harmer (2001) described new developments in the catalytic application of ion-exchange resins and micro structural features of polystyrene-based sulfonic acid resin catalysts and perfluorinated sulfonic acid resin nanocomposite catalysts. Ion exchange resin producers like Rohm and Hass, Dow Chemical, also provide very useful literature for handling and use of ion-exchange resins as catalysts. A list of some of the important ion exchange resin catalyzed processes in industry is presented in Table 1.1.

Esterification of carboxylic acids on solid acid catalysts is a well-studied subject as is evident by a large number of established industrial applications. Though several reports have addressed important issues concerning product distribution, catalyst activity, stability and kinetic studies, a few important aspects have still not been well understood. For example, for the solid acid catalyzed esterification reactions, the homogeneous esterification reaction is also significant and the kinetic modeling must incorporate the contribution of homogeneous reaction. The question of diffusional limitation in ion exchange resin catalyzed reactions requires a quantitative evaluation before the data are used for development of rate equations. Similarly the detailed information on kinetics of esterification of dicarboxylic acid is very limited in the literature. Considering the growing importance of esterification reactions in the industry, the objective of the present work was to investigate the kinetic and reaction engineering aspects of esterification of monobasic and dibasic carboxylic acids. Therefore, the aim of this thesis is to investigate kinetics of the homogeneous (non-catalytic) and ion exchanged resin catalyzed esterification reactions of aliphatic carboxylic acids in batch slurry and fixed bed reactors. The following reaction systems have been investigated:

- Esterification of Acetic acid with Methanol using Dowex 50W catalyst.
- Esterification of Acetic acid with Butanol using Dowex 50W catalyst.
- Esterification of Maleic acid with Methanol using Dowex 50W catalyst.

Table 1.1: Some important commercial processes catalyzed by cation exchange resins

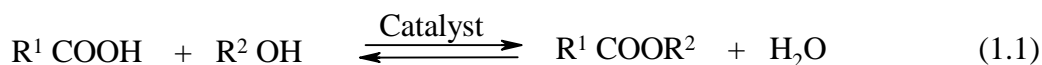
Name of the product	Key reactants	Reference
Methyl <i>tert</i> -butyl ether (MTBE)	Methanol + Isobutylene	Inst. Fr. Petrole tech. (1991), Melpolder (1980)
Ethyl <i>tert</i> -butyl ether (ETBE)	Ethanol + Isobutylene	Inst. Fr. Petrole tech. (1991)
<i>tert</i> -Amyl methyl ether (TAME)	Methanol + Isoamylene	Inst. Fr. Petrole tech. (1991)
Isobutylene	<i>tert</i> -Butanol	Vora et. al. (1990), Chem. Econ. Eng. Rev. (1983), Armor (1991)
<i>tert</i> -Butanol	Isobutylene + Water	Chem. Econ. Eng. Rev. (1983), Armor (1981)
Isopropanol	Propylene + Water	Brandes et al. (1973), (1974)
<i>Sec</i> -Butanol	<i>n</i> -butenes + Water	Webers et. al. (1976) and Neier et. al. (1982)
Isopropyl ester	Isopropanol + carboxylic acid	Leupold et.al. (1974)
<i>Sec</i> -Butyl acetate	Butene + Acetic acid	Ancillotti et. al. (1980)
<i>Sec</i> -Butyl acrylates	Butene + Acrylic acid	Perez and Albertos (1991)
Acrylates and Methacrylates	Acrylic acid or Methacrylic acid + Alcohols	Lohma et. al (1973) and Matsumura et. al. (1980)
Allylphenols	Phenols + Olefins	Helmut (1991)
Bisphenol A	Phenol + Acetone	Helmut (1991)
Methyl glucoside	Dextrose + Methanol	Anon (1955)
Methyl isopropenyl ketone	Methyl ethyl ketone + Formalin	Rheinpreussen (1964)

For all the systems under consideration, rate equations have been developed using extensive experimental data obtained over a wide range of operating conditions. In evaluating the kinetics, the contributions of both homogeneous (non-catalytic) and heterogeneous reactions have been taken into account. Batch and fixed bed reactor models have also been developed, and the model predictions have been compared with

experimental data. While the first two reaction systems were chosen to illustrate the experimental kinetics of homogeneous and heterogeneous reactions of the esterification of monocarboxylic acid, the third case represent an example of esterification of a dicarboxylic acid. The relevant literature on these reactions, catalysts used, kinetic modeling and reaction engineering aspects is presented below.

1.2 Literature survey on esterification of carboxylic acids

Esterification of carboxylic acids is an important class of reactions, the kinetics and equilibrium of which have been investigated throughout the history of physical chemistry, the dating back to pioneering efforts of Berthelot and Gilles (1863). In 1914 at the beginning of the World War I, amyl acetate in the form of fusel oil acetate was the best known ester solvent. The demand for airplane dope and the corresponding need for cellulose nitrate and cellulose acetate solvents increased rapidly during the war period. The only ester that was developed on a large scale during the war to replace amyl acetate was methyl acetate, thus esterification of acetic acid with methanol got a boost as an important process. Esters can be produced by different approaches on both laboratory and commercial scales. There are several routes given by Ogliaruso and Wolfe (1991) for the synthesis of esters as described in Fig. 1.1. Among all these, the simplest route to produce esters with high yield is the direct esterification of acids with alcohol in presence of mineral acid or a heterogeneous catalyst.



Esterification reactions are equilibrium processes and must be displaced toward the desired ester by the use of excess of one of the free reactants or by continuous removal of water by azeotropic distillation. Removal of water by chemical or adsorptive binding is also possible in preparative chemistry, while calcium carbide, calcium hydride and calcium and magnesium sulfate have proved successful in industrial application.

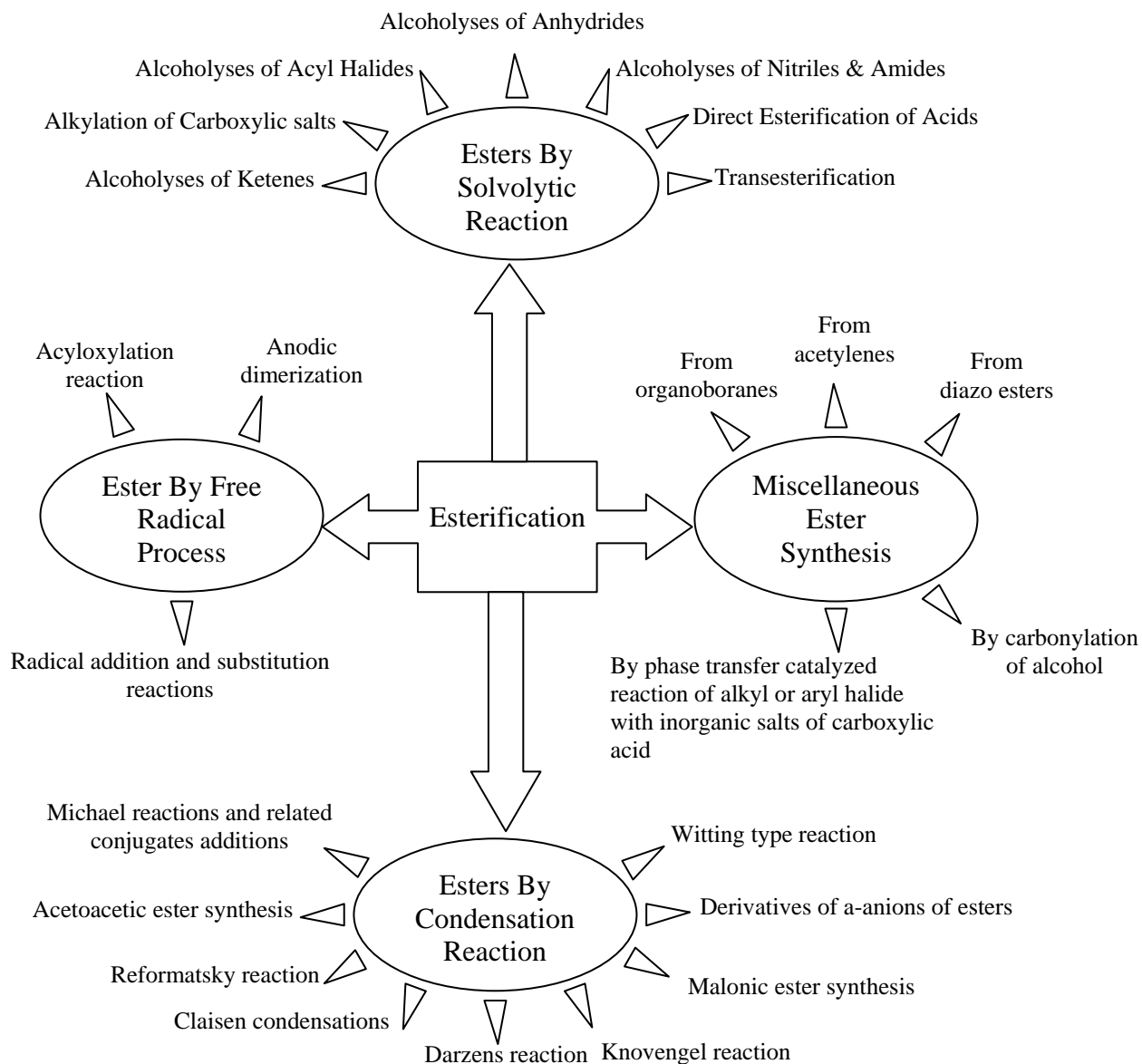


Fig. 1.1: Several routes for synthesis of esters

The rate of ester formation depends on the carboxylic acid and the alcohol used. The lowest members, i.e. methanol and formic acid, react most readily. Primary alcohols react faster than secondary alcohols and the latter react faster than tertiary ones. Within each series, the reaction rate generally decreases with increasing molecular mass. Straight-chain acids react more readily than branched ones; particularly branching in the α -position lowers the rate of esterification. Esterification of aromatic acids, e.g. benzoic

acid, is generally slow. Experiments with primary and secondary alcohols containing ^{18}O have shown that the oxygen in the water formed during acid-catalyzed esterification originates from the acid, not from alcohol (Roberts (1938)). The reactions of tertiary alcohols are more complex and do not proceed clearly via a tertiary carbonium ion. The mechanism of esterification reactions has been discussed in detailed by Zimmermann and Rudolf (1965).

Generally, in industrial processes refluxing the reaction mixture until all the water has been split off facilitates esterification. The water or the esters formed are removed from the equilibrium mixture by distillation. The choice of a method to achieve complete esterification depends on the boiling points of alcohols, acids, and esters. With high boiling esters (esters of polyhydric alcohols), the water of reaction may either be removed by evaporation or by means of inert gases. Steam distillation can also be used to remove excess alcohol after the esterification is complete. Esterification is usually carried out in a batch or continuous mode depending on the scale of operation. It can also be carried out in the vapor phase by heating a mixture of acid, alcohol, ester, and catalyst to the desired temperature.

1.2.1 Esterification catalysts and processes

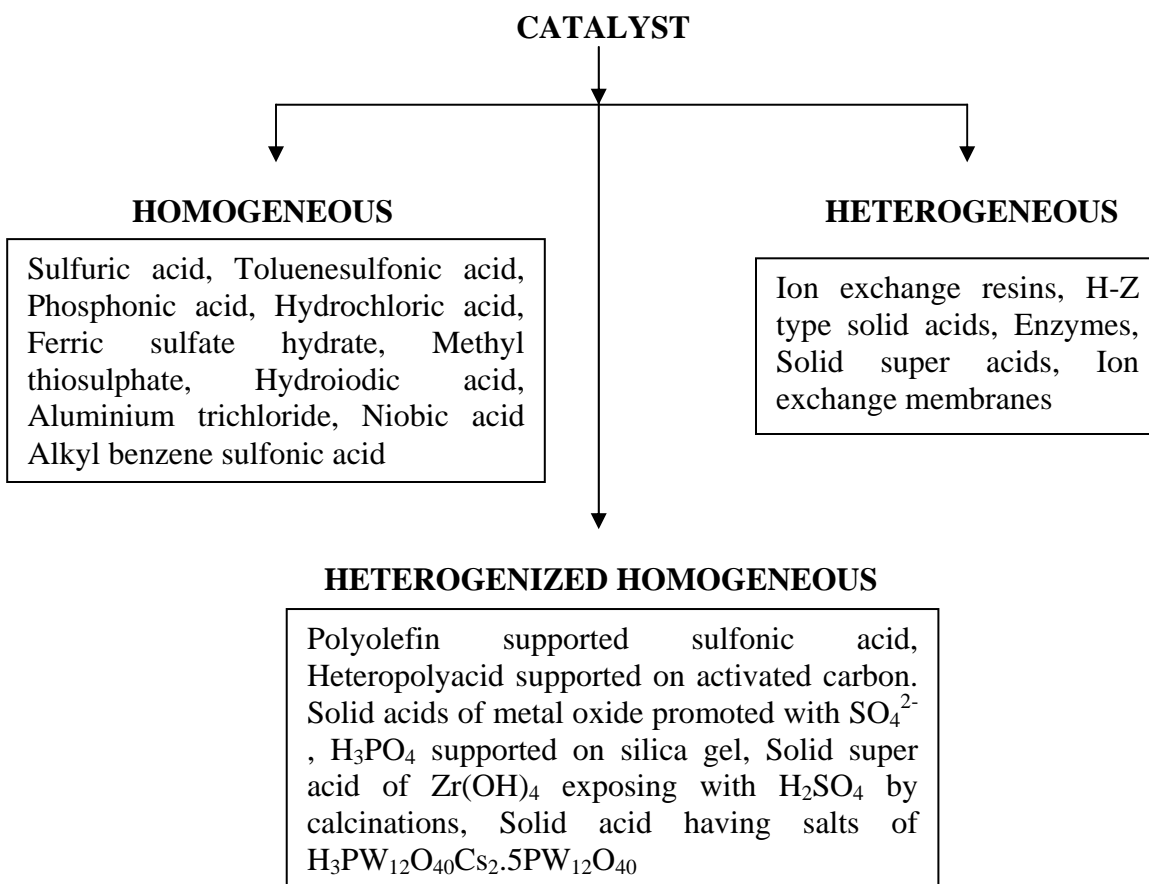
Esterification reactions proceed with or without a catalyst. In the absence of a catalyst, the reaction is, however, extremely slow, since its rate depends on the autoprotolysis of the carboxylic acid. Therefore, esterification is carried out in the presence of an acid catalyst, which acts as a proton donor to the carboxylic acid. Different catalysts used for esterification reactions are listed in Table 1.2.

1.2.1.1 Homogeneous acid catalysts

Catalysis by mineral acids has emerged as a field of growing interest and importance in the last three decades with respect to new applications and detailed investigations on catalysis and reaction engineering. Generally homogeneous acid catalysts consist of inorganic mineral acids and heteropoly acids. Typical examples include sulfuric acid, hydrochloric acid, arylsulfonic acids such as *p*-toluenesulfonic acid

and chlorosulfuric acid. Phosphoric acid, polyphosphoric acids and mixtures of acids are also recommended (Bader and Kontowicz (1953)). Smith, (1939) studied esterification of

Table 1.2: Catalysts used for esterification reactions



different aliphatic carboxylic acids with methanol in the presence of 1% hydrochloric acid as a catalyst. Keys (1932) pointed out the desirability of carrying out esterification reactions in the presence of sulfuric acid catalyst. Leyes and Othmer (1945) used sulfuric acid catalyst for esterification of acetic acid and butanol. Ronnback et al. (1997) studied the esterification kinetics of acetic acid with methanol in presence of hydroiodic acid. But the disadvantage of mineral acids is their miscibility with the reaction medium leading to corrosion hazards and separation problems. Hence heterogeneous or heterogenized acid catalysts provide an attractive alternative to homogeneous catalyst.

1.2.1.2 Heterogeneous acid catalysis

1.2.1.2.1 Metal ion complexes as catalysts

Metallic oxides and hydroxides of magnesium, zinc, titanium, zirconium and metal oxide complexes have been used as catalysts for esterification reactions. Nozawa (1975) and Putzing (2000) described a catalyst composition for production of polyalkylene terephthalates. The composition comprises of titanium or a titanium compound, a complexing agent, hypophosphorous acid or a salt thereof and optionally a solvent. Water compatible titanates, such as titanium bisammonium lactate, bis-triethanolamine titanate or the titanium sodium citrate catalysts have been reported by Ridland (1997) as polyesterification catalysts. Lindall (2002) reported novel organotitanium, organozirconium or organoaluminium compounds in combination with other metal compounds for esterification of hydroxy carboxylic acids. Balkrishnan and Rajendran (2000), prepared insoluble poly(4-vinylpyridine-co-styrene) beads using divinylbenzene as the crosslinking agent to convert into poly(4-vinylpyridine-N-oxide) (PVPNO) under peracetic acid conditions. The resulting polymer was functionalized with titanium tetrachloride (TiCl_4) to form the corresponding PVPNO- TiCl_4 complex, which showed good catalytic activity for esterification reactions.

Xin Chen et al. (1999) and Arabi (2003) proposed the use of heteropolyacids as catalysts for both homogeneous and heterogeneous acid-catalyzed esterification reactions. Some heteropoly-compounds have been utilized in industrial chemical processes like esterification, etherification, hydration of olefin, de-esterification, dehydration of alcohol and polymerization of tetrahydrofuran. They give product with higher yields than sulfuric acid and *p*-toluenesulfonic acid. The acidic properties of heteropolyacids can be controlled by the substitution of constituent elements without changing the fundamental structure. Okuhara et. al. (1998) observed that solid acid heteropoly acids are water-tolerant catalysts for various reactions such as hydrolysis of esters, hydration of alkenes and esterification. Supporting metal on oxides improved stability of these catalysts in water. Timofeeva (2003) presented a review on the achievements in the field of acid catalysis by heteropoly acids. Due to their unique physicochemical properties, heteropoly acids can be profitably used in homogeneous, biphasic and heterogeneous systems. The catalytic effect of heteropoly acids in acidic-

type reactions depends mainly on three factors, namely, the acidity, heteropolyanion structure and type of reaction. The catalytic activity is more dependent on the heteropoly acid structure rather than its composition.

1.2.1.2.2 Ion exchange resins as catalysts

Ion exchange resin catalysts have been used for several years in esterification reactions. Ion exchange material may be broadly defined as an insoluble matrix containing labile ions capable of exchanging with ions in the surrounding medium without major physical change in its structure (Streat, (1988)). Typical resin catalysts are sulphonic acids fixed to a polymer carrier, such as polystyrene crosslinked with divinylbenzene (DVB). Several types of catalysts are commercially available like Amberlyst resins (e.g. Amberlyst –15, Amberlite IR-120 etc.). The principal differences between catalysis by dissolved electrolytes and by resins are i) With resins as catalysts, the catalysis overlaps with diffusion, adsorption and desorption processes (Neumann (1959)) and the concentration of the reactants inside the catalyst (where the reaction takes place) may be different from that in the bulk solution, depending on the nature of the matrix, fixed ionic group, the reactants, and the solvents. ii) The matrix with the fixed ionic group may have some influence (which is not purely physical) on the course of the reaction. Depending on the nature of the reactants and solvents, all the resin-catalyzed reactions are divided into two groups type A and type B as shown in Fig. 1.2, (Pitochelli (1980))

Hellmuth (1953) developed the first commercial process, for esterification and ester hydrolysis over Wofatit, phenolsulphonic acid-formaldehyde condensation polymers, in the 1940s in the context of the German war effort. Kemp (1972) describe an approach to reduce the amount of byproduct produced in an esterification reaction, in which isobutene was esterified with a carboxylic acid in the presence of a macroporous, acidic cation-exchange resin having a limited cation-exchange capacity (0.4-0.5 meq/g, compared with the usual 4-6 meq/g for fully functionalized microporous cation-exchange resins).

The capacity of this microreticular resin was reduced by partially neutralizing it with sodium ions. Although surface functionalized cation-exchange resins have been

produced by Hansen (1966) and McMaster (1972), who controlled the depth of sulfonation to as little as 15% of the total bead diameter by carefully limiting the sulfonation time. Widdecke (1984) had also sulfonated the surface of macroporous resins, but such resins have largely remained a laboratory tool for investigation of reaction kinetics. Partially sulfonated cation exchange resins having a cation-exchange capacity between 0.1 and 0.6 meq/g were shown to produce negligible byproducts when used to selectively decompose methyl t-butyl ether to isobutylene and methanol. Inorganic oxides with modified surfaces have been employed as esterification catalysts for fatty acids (Scharmer (1989)).

Resin Catalyzed Reactions

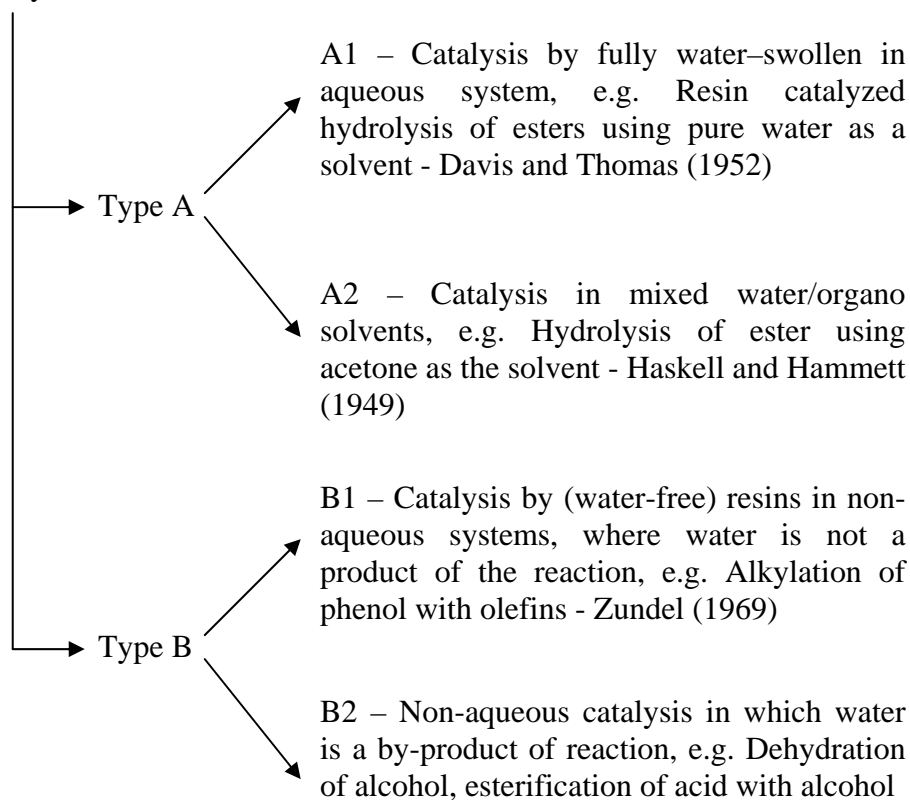


Fig. 1.2: Types of resin catalyzed reactions

Lundquist (1999) described a process for esterification and transesterification, particularly of, organic acids with alcohols, or of, esters with alcohols catalyzed with surface-functionalized, crosslinked vinylaromatic polymer beads. Zupan and Segatin

(1991) have described the effect of polymer catalyst structure (polarity, crosslinking etc.) on the esterification of acids (acetic acid, benzoic acid) with n-butanol in the presence of solvents (n-octane, toluene, n-butanol). Some examples of ion exchange resin catalyzed esterification processes are summarized in Table 1.3.

1.2.1.2.3 Zeolites as catalysts

Zeolites are also used as esterification catalysts (Bergk (1978)). The rare earth-exchanged RE H-Y zeolite is the best of the various zeolites catalysts. The $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ catalyst is claimed to be more active than cation-exchange resin, SiO_2 , Al_2O_3 and solid super acids (Otera 2003). Nagaraju and Mehboob (1996) compared the catalytic activity of zeolites of the types of NaX, NaY and NaZSM-5 and their protonated forms with some conventional Lewis acids such as anhydrous ZnCl_2 , AlCl_3 , and H_2SO_4 in the esterification reaction between isoamyl alcohol and acetic acid. They observed that zeolites were more active than the conventional Lewis acid catalyst.

1.2.1.2.4 Enzymes as catalysts

Enzymes have been widely used in esterification technology. In particular, lipase enzymes are used for the resolution of racemic alcohols and carboxylic acids through asymmetric hydrolysis of the corresponding esters. Yeast lipase (*Candida cylindracea*), completely converts a carboxylic acid and an alcohol into the corresponding ester in organic solvents, in a highly stereoselective manner (Kirchner et al. (1985)). Enzymes are highly stable in organic solvents compared to water. To predict the behavior of batch enzymatic reactors, Mensah (1998) developed a model incorporating reaction kinetics, water partitioning, and mass transfer effects. He also conducted experimental and theoretical studies on immobilized enzyme catalyzed esterification of propionic acid with isoamyl alcohol in presence of hexane as solvent to understand the dynamic behavior of a continuous-flow fixed-bed reactor.

Table 1.3: Ion exchange resin catalyzed esterification reactions

System	Catalyst	Reference
Propene + Acetic acid	Lewatit SPC	Sante-Ollalo (1982) and Tokumoto (1990)
<i>n</i> -Butenes + Acetic acid	KU-23	Stepanova (1977)
1 Butene, Isobutylene } 1-Octene, 1-Dodecene } Acetic acid	Amberlyst-15	Patwardhan (1990)
Cyclohexene + Acetic acid	001 x 7 (Cation exchanger)	Yu (1991)
Cyclohexene + Acetic acid	Amberlyst-15	Chakrabarti (1992)
Cyclohexene + Acetic acid + Water	Lewatit SPC 118	Fukuhara (1989)
Camphene + Acetic acid and Formic acid	Cation exchange resin	Nigam (1984)
Dihydromyrcene + Acetic acid	Cation exchange resin	Nigam (1984)
Styrene + Acetic acid	Ostion KS	Cervený (1988)
Styrene + Acetic acid	Amberlyst-15, Amberlyst XN-1010, Nafion NR 50, Monodisperse K2661, K2631	Chakrabarti (1991/1992)
Propylene + Chloroacetic acid	Amberlyst-15	Patwardhan (1990)
1-Butene + Acrylic acid	Lewatit SPC 118	Perez (1991)
Camphene + Methacrylic acid		Yang (1990)
Dicyclopentadiene + Acetic acid	Lewatit SPC 108	Kiein (1987)
2- Methyl-1-butene Isoprene + } Cyclopentadiene } Acetic acid	Lewatit SPC 118 (45% neutralized with K ⁺)	Schleppinghoff (1983)
Propylene + Myristic acid	Amberlyst-15	Chakrabarti (1992)
Isopropanol + Acetic acid	Diaien HPK 55 (Modified to get corresponding fluorinated ion exchange resin)	Okazaki (1988)
Hexyl alcohol + Acetic anhydride	Ion exchanger	Cornea (1982)

System	Catalyst	Reference
Glycerol + Acetic anhydride	EX 14611	Yamata (1988)
Glycerol + Acetic and propionic acid	D61, D72, Amberlyst -15	Yu (1988)
Ethanol + Oxalic acid	Amberlite IR-120	Capecetti (1979)
C ₆₋₁₂ Alcohols + Maleic anhydride	Vionit	Ciobann (1987)
Methanol + Methacrylic acid	Cation exchange resin	Chi (1991)
2-Ethyl hexanol + Methacrylic acid	Cation exchange resin	Kamioka (1991)
2-Ethyl hexanol + Acrylic acid	Diaion PK 208	Nakashimo (1988)
Ethylene glycol (Di, Tri and Tetra-Ethylene glycol) + Acrylic acid	Strongly acidic cation exchanger	Ding (1991)
Methanol + Fatty acid	Lewatit	Jeromia (1986)
Oleic acid and Malonic acid monoethyl ester + Methanol	Amberlyst-15	Petrini (1988)
Phenol + Methacrylic acid	Amberlyst-15	Iwasaki (1988)
Ring opened adduct of cyanoethyl alcohol and ϵ -Caprolactone + Acrylic acid	Amberlyst-15	Tono (1990)
Lipids + Acetic anhydride	Cation exchange resin	Totani (1981)
Pyrrole diacids + Methanol	Amberlite IR-120	Wiison (1980)
Ethylene glycol monoethyl ether + Acetic acid + Acetic acid	H ⁺ form cation exchanger	Rataj (1987)
Dimethylphosphoramidothioate + Acetic anhydride	Amberlyst 15	Platt (1973)
Trioxane + Carbon monoxide + Methanol	Strongly acidic cation exchanger	Mitsubishi (1982)

1.2.2 Kinetic studies

1.2.2.1 Kinetics of ion exchange catalysis

Chakrabarti and Sharma (1993) reviewed the kinetics of ion exchange resin catalyzed reactions. They pointed out that most of the resin-catalyzed reactions can be

classified either as quasi-homogeneous or as quasi-heterogeneous. The idealized homogeneous state requires complete swelling of the resin and total dissociation of the polymer-bound $\text{-SO}_3\text{H}$ group. They described that in all cases which have so far been studied, and in which limitations due to slow diffusion process could be ruled out, the kinetic order of the chemical reaction in the particles was found to be the same as that observed in the homogeneous catalysis by a dissolved electrolyte. However, there were differences in the reaction rates, even when the amount of catalyst (in counter-ion equivalents) was the same in both cases. A significant difference in the reaction rates of homogeneous catalysis and heterogenized homogeneous catalysis was due to the presence of diffusional limitations in the later case. Three phenomena have been found to affect the rate of overall reaction (i) diffusion of reactants and products across the film (Nernst diffusion layer) surrounding the catalyst particle (ii) diffusion of the reactants and products in the interior of the catalyst particle and (iii) chemical reaction at the active sites. If the film diffusion is sufficiently fast, the process is controlled by chemical reaction at the surface. Intraparticle diffusion can affect the overall rate of reaction, but it can never be the sole rate-determining step, as diffusion and chemical reaction are parallel steps, occurring simultaneously within the resin bead. These considerations suggest that, in the limiting cases, the overall rate of any ion exchange resin catalyzed reaction is controlled by i) film diffusion ii) intraparticle diffusion with reaction throughout the particle, and iii) chemical reaction at the active sites. Doraiswamy and Sharma (1984) have discussed the procedures for discerning the controlling mechanism in ion exchange resin catalyzed liquid/solid reactions.

1.2.2.2 Kinetics and reaction engineering of esterification

Kinetics of esterification between organic acids and alcohols have been extensively studied. There are two different opinions about the ways in which H^+ performs its catalytic effect. One of the opinions is that the organic acid is activated initially, (Royals (1954)) i.e. the organic acid molecule gets a hydrogen ion from the catalyst before it is esterified with a molecule of primary or secondary alcohol. In the case of tertiary alcohol, such as *t*-butyl alcohol, the hydroxyl group of the alcohol, rather than that of the acid is eliminated. The other opinion was introduced by Goldschmidt

(1908) and further explored by Smith (1939). During the period of 1895-1928 Goldschmidt demonstrated the fact that in acid catalyzed esterification reactions, the H^+ ions from the catalyst forms complexes with the alcohol molecules, and that the esterification proceeds through interaction of molecules of the complex with the molecules of organic acid. The rate of formation of ester in this case is thus proportional to the momentary concentration of the organic acid. Smith (1939) studied the kinetics of hydrogen ion catalyzed esterification of seven *n*-organic acids in methyl alcohol. He has discussed the influence of acids and the length of the carbon chain of the acid on the rate of its esterification.

1.2.2.2.1 Kinetics of esterification of monobasic acid

A detailed literature survey on esterification of different monobasic carboxylic acids with alcohols is presented in Table 1.4. The kinetics of esterification of monobasic carboxylic acids with alcohols in the presence of homogeneous catalysts has been investigated to some extent in the past. Leyes and Othmer (1945) investigated the sulfuric acid catalyzed esterification of acetic acid with butanol. They found the reaction to be second order with respect to acetic acid concentration up to 75 to 85 %, in a temperature range of 373 K-393 K. The rate was a linear function of the catalyst concentration and the molar ratio of butanol to acetic acid. They also found that the logarithm of the rate constant was proportional to the reciprocal of absolute temperature as per Arrhenius law of temperature dependence. Ronnback et al. (1997) developed a kinetic model for the esterification of acetic acid with methanol in the presence of hydrogen iodide as homogeneous acid catalyst at 303 K- 323 K. Plausible reaction mechanisms for methyl acetate and methyl iodide formation were proposed. Rate equations, concentration-based as well as activity-based, with UNIFAC activity coefficient estimations were derived and the kinetic and equilibrium parameters included in the rate equations were estimated from experimental data with regression analysis.

Shimizu and Hirai (1987) studied the solvent effect on the kinetics of resin catalyzed esterification of octanoic acid with 1-butanol catalyzed by macroreticular sulfonic acid resin (Amberlyst 15) in the presence of various organic solvents and water. They concluded that the extent of the selectivity of the resin catalyst depend on the alkyl

Table 1.4: Literature survey on esterification of monocarboxylic acids with alcohols

Substrate	Catalyst	Reaction Condition	Reference
Acetic acid, n-butanol and 2-ethyl 1-hexanol	Sulfuric acid, Amberlyst 200, 15, IR120, Nefion NR 50, SO ₄ -zirconia	Dilute tow phase system T= 150 °C	Bianchi (2003)
Propionic acid, n-butanol	Amberlyst 35	Fixed bed reactor, T= 353-373 K.	Lee (2002)
Acetic acid, methanol	Amberlyst 15	Fixed bed reactor Magnetic resonance tech. is used. T= 22 °C	Yuen (2002)
Acetic acid, 1-butanol	Ion exchange resin	Fixed bed reactor, T=75 °C	Smejkal (2002)
Tertiary alc., Acid anhydride	Solid acid	T=10-50 °C	Chaudhary US6420596 (2002)
Acetic acid, Iso-pentyl alcohol	Amberlyst 15	Contineous flow reactor. T= 40 °C	Kabza (200)
Isopropyl lactate synthesis	Ion exchange resin	T= 85 °C	Yadav (2000)
Acetic acid, Amyl alcohol	Dowex 50W	T= 323-393 K Kinetic study	Lee (2000)
Acetic acid, Methanol.	Monometalic Ru & heterometalic complexes	Ligand effect	Robles-Dutenhefner (2002)
Acetic acid, n-butanol & iso amyl alcohol.	Indion 130	Recovery of dilute acid, T= 473 K	Saha (2000)
Acetic acid, Methanol	Homogeneous acetic acid itself and heterogeneous Amberlyst-15	T = 30-40 °C, Concentrations are from stoichiometric to dilute regime	Popken (2000)
Acetic acid, Methanol	[(η^5 -C ₅ H ₅)(Phosphine) ₂ RuX] and [(η^5 -C ₅ H ₅)(Phosphine) ₂ Ru(SnX ₃)] (X=F,Cl,Br)	Glass tube reactor with vacuum valve and manipulate under nitrogen atm is used for reactions	Robels-Dutenhefner (2000)
Dilute acetic acid recovery	Indion 130		Saha and Mahajani (2000)

with butanol			
Acrylic acid, 1-butanol	Solid acid including salt of $H_3PW_{12}O_{40}Cs_{2.5}PW_{12}O_{40}$	T= 353 K. Water tolerant property of catalyst	Chen (1999)
n-Octyl acetate synthesis	Titanium tetrachloride supported on styrene DVB	T= 40-60 °C Catalyst prep. and activity	Balakrishnan (1999)
Hexanoic acid, 1-propanol	MCM-41 supported heteropoly acid	Reflux temp, Vapor phase exp. At 110 °C, In fixed bed reactor	Verhoef (1999)
Acetic acid, Methanol	Polyolefin supported sulfonic acid	T = 55°C	Maki-Arvela (1999)
Acetic acid, Propionic acid, Methanol		T = 60-90 °C.	Wolfgang (1999)
Acrylic acid, n-butanol in water	Solid acid including salt of $H_3PW_{12}O_{40}Cs_{2.5}PW_{12}O_{40}$	Water tolerant catalyst	Okuhara (1998)
Acetic acid, Butanol	Microporous strong acidic cationic exchange resin. 2,5gm/mol acetic acid	Alcohol : Acid = 1:1 T = 110-120 °C	Jinlong (1998)
Propionic acid with isoamyl alcohol in hexene	Mix of Immobilized enzymes + ion ex. resin in organic solvent medium	Fixed bed reactor	Paul (1998)
Anthranilic acid, Methanol	Ion ex. resin	T= 120 °C. Parr reactor	Yadav (1998)
Acetic acid, Methanol	Amberlyst15	T = 45 °C	Song (1998)
Acetic acid, Ethanol	Amberlyst 15	T= 25 °C. Kinetics and sorption equilibria	Mazzotti (1997)
Acetic acid, Butanol	Modified ion exchange resin	T = 124 °C	Liao (1997)
Acetic acid, Methanol	Hydrogen Iodid. 0.05-10 wt%	T = 30-60 °C	Ronnback (1997)
Dilute Acetic acid, Methanol	Amberlyst15 1.5 mass%	Dilute Acetic acid 0.00863, methanol 0.00925 (mole fraction), T = 94 °C	Xu (1997)
Acetic acid, Methanol			Chuang US 18309 (1996)
Acetic acid, Butanol	A- weakly basic resin D370, B-	Acetic acid : butanol = 1:13	Huang (1996)

	ferric chloride hexahydrate prepared from A and HCl. C-quarter ammonium resin from D370		
Dilute Acetic acid, Methanol	Amberlyst15, 1.5 mass%	Dilute Acetic acid 0.00863, methanol 0.00925 (mole fraction) T = 94 °C	Xu (1996)
Aromatic carboxylic acid, alcohols	Thionyl chloride		Bhaskar (1996)
Carboxylic acid, alcohol	Triphenylphosphine and N-bromo/Iodo succinamide		Sucheta (1994)
Acetic acid, Methanol	MeSO ₃ H	T = 90-120 °C	Perry EP 529868 (1993)
Acrylic acid, Butanol	Amberlyst-15 cation exchange resin	Batch reactor, Temp = 333-364 K	Darge (1993)
Acetic acid, n-butanol	HZSM-5, 4 wt%	Alcohol : Acid = 1:10, T = 135 °C	Lu (1992)
Acetic acid, benzoic acid, n-octane, toluene, n-butanol	Dowex 20M with hydrogen halide	T=50-100 °C. Effect of polymer catalyst structure	Zupan (1991)
AcOH, a-olofins and isobutylene	Amberlyst 15	T = 10-100 °C	Patwardhan (1990)
AcOH, BuOH	H ₃ PO ₄ supported on silica gel	BuOH:AcOH = 4:1, dp = -8 to +100 BS mesh, T = 165 °C	Thakar (1990)
Acetic acid, Methanol	H ₂ SO ₄	Series of countercurrent flashing reactors was used	Agreda (1990)
Acetic acid, Methanol		Acetic acid : Methanol = 1.5-3:1, Reflux ratio = 0.75-1.5:1	Erpenbach EP 387674 (1990)
AcOH, BuOH	Cation exchange resin 732 and D 72. 36g/mol AcOH	AcOH : BuOH = 1:1.2	Li (1989)
AcOH, C3-C5 alcohols	Lewatit SPC 118 cation exchange resin	T = 50-100 °C, AcOH : Alcanol = 5-12	Helmut, DE 3636754 (1988)
Acetic acid, Ethanol	Comparision betwn. Gel and	Vapour phase esterification.	Gimenez (1987)

	microporous resin	T= 85-150 °C	
Acetic acid, n-butanol	SiO ₂ – Al ₂ O ₃	T = 230 and 290 °C, AcOH : BuOH : 1:1 and 1:2	Elorriaga (1984)
Acetic acid, n-butanol	Heteropoly acids 10.8 wt% (Tungstosilicic acid on act. C)	EtOH : AcOH = 2.5:1, T = 150 °C	JP 57130954 (1982)
Carboxylic acid, alcohol	Benzene and methane-sulfonyl chlorides as coupling agent		Dharmaratne (1982)
Acetic acid, Methanol, Ethanol, Propanol, Butanol, and iso-butyl alc.	Solid superacid catalyst obtained by exposing Zr(OH) ₄ to 1N H ₂ SO ₄ and then calcining in air at 500- 750°C	T = 30-45 °C	Makoto (1981)
Propionic acid,1-butanol	AlCl ₃ , 0-3 wt.%	T = 70-90oC. Alc. : Acid = 1-3:1	Rao (1979)
AcOH, BuOH	H ₃ PO ₄ -Silica gel	BuOH:AcOH = 4:1, T = 165 °C	Thakur (1973)
Acetic acid, Ethanol	Dowex 50	Fixed bed reactor, T= 30-70 °C	Saletan, Symposium
Acetic acid, Methanol	Sulphuric acid 0.03-0.13%	Acetic acid : Methanol = 1:5, T = 0 to 120° C (at temp sets 0-13, 25-30, 100 and 115)	Leys and Othmer (1945)
Methanol, Formic, Acetic, propionic, Butyric Valeric, Capronic and pelargonic acid	Hydrochloric acid , conc.: 0.005M	Acid conc, 0.5M in Methanol	Smith (1939)

chain length of *n*-fatty acids. When solvents with a strong electron donor property were employed as diluents in the esterification with the macroreticular sulfonic acid resin, they donor property of solvents, diminished the number of unionized sulfonic acid groups, which act as catalytic species for the heterogeneous reaction, and, consequently, a decrease in the total catalytic activity was observed. Elewady et al. (1987), studied the esterification of formic, propionic, butyric and valeric acids with ethanol in the presence of Amberlite IR-120 as a catalyst. The activation energy of esterification reaction was found to increase with increase in the size of the alkyl group in the acid moiety.

Bhatnagar et al. (1994) investigated the kinetics of esterification of *n*-butanol with butyric acid in a batch reactor using Amberlyst-15 macroporous cation exchange resin as a catalyst. The effects of variables such as mole ratio of *n*-butanol to butyric acid (2:1 to 8:1), catalyst concentration (2-15 wt%), resin particle size (0.25-0.45mm), and reaction temperature (338-358 K) were studied. They correlated the rate data with integral kinetic model based on homogeneous reaction. The apparent activation energy was found to be 52 kJ mol⁻¹ for the formation of *n*-butyl butyrate. The resin catalyst showed absence of deactivation and diffusional effects.

Dakshinamurthy et al. (1992) studied the kinetics of esterification of *n*-propanol with acetic acid in a batch stirred tank reactor using a solid cation exchange resin, CXC 125 as a catalyst. He observed that the conversion of acid increased with increase in temperature, catalyst concentration and molar ratio of alcohol to acid. The reaction was found to be second order with respect to acid and zero order with respect to alcohol. An empirical correlation for the estimation of specific reaction rate constant was developed incorporating different variables studied. The Langmuir-Hinshelwood and Hougen-Watson models were used to determine the rate-controlling step.

Kumbhar and Yadav (1989) proposed a model for solid-catalyzed liquid phase reactions. A power law model was used to describe the surface reaction. Later, Yadav and Mehta (1994) applied this model to heterogeneous catalytic esterification. Patwardhan and Sharma (1990) also used the power law model to fit their experimental data for the esterification of carboxylic acids with olefins using cation ion exchange resins. They found that Amberlyst 15 had the highest activity among various catalysts.

Venimadhavan (1994) presented the heterogeneous kinetics for methyl acetate synthesis. He has developed a Langmuir - Hinshelwood - Hougen-Watson model to represent reaction kinetics. Isothermal batch kinetic experiments were performed using heterogeneous catalyst (Amberlyst 15) at temperatures of 313 K - 323 K. Also, independent binary adsorption experiments were performed to estimate the adsorption equilibrium constants.

Xu and Chang (1996), have conducted kinetic measurements in a batch reactor for the esterification of dilute acetic acid with methanol in presence of Amberlyst 15 at 367 K. The internal mass transfer resistance was found to be insignificant. A kinetic equation was developed and used in the simulation and design of a catalytic distillation column for removing dilute acetic acid from wastewater. Xu and Chang (1997) have also presented a theoretical analysis to determine the effect of internal diffusion on second order reversible esterification. The results of the analysis showed that the catalyst effectiveness factors were above 0.94 for beads smaller than 0.6 mm diameter at a temperature lower than 353 K. However, the effectiveness factors were lower than 0.77 for the beads larger than 1.0 mm diameter at reaction temperature higher than 367 K.

Maki-Arvela (1999) has developed a new polyolefin supported sulphonic acid catalyst for esterification of acetic acid with methanol. The esterification kinetics (pseudo-homogeneous) was modeled with a mechanistic rate equation, the parameters of which were determined by non-linear regression. The esterification rate constant of the most active modification of the new catalyst was $9.6 \times 10^{-10} \text{ dm}^3/(\text{mol}^2 \text{ g min})$ at 328 K, which clearly exceeds the corresponding value obtained with a traditional (Amberlyst 15) polyvinyl benzene supported catalyst, $1.5 \times 10^{-10} \text{ dm}^3/(\text{mol}^2 \text{ g min})$.

Yadav and Kulkarni (2000) have studied the esterification of lactic acid with isopropanol in presence of various ion exchange resin catalysts (Indion-130, Amberlyst-36, Amberlyst-15, Amberlite-120, Dowex 50W, Filtrol-44, 20% DTPA/K-10 and 20% DTPA/Filtrol-44) A theoretical kinetic model was developed for evaluation of this slurry reaction. The effects of various parameters on the rate of reaction were evaluated. The reaction was found to be kinetically controlled and there were no intraparticle as well as interparticle mass transfer limitations on the rate of reactions.

Popken (2000) investigated the reaction kinetics and chemical equilibrium of homogeneously (autocatalyzed) and heterogeneously catalyzed acetic acid esterification with methanol and methyl acetate hydrolysis. The chemical equilibrium composition was measured for various temperatures and starting compositions of the reactants and products. Kinetic information was obtained at temperatures between 303.15 K and 343.15 K at various starting compositions covering concentration ranges from the stoichiometric regime to the dilute regions. A simple power law model was proposed to study the kinetics.

Sanz (2002) investigated the esterification kinetics of homogeneously and heterogeneously (Dowex 50W, ion exchange resin) catalyzed lactic acid esterification with methanol. The effect of catalyst type, stirrer speed, catalyst size, catalyst loading, reactant ratio and temperature on reaction kinetics was evaluated. Experimental reaction rates were correlated by some models based on homogeneous and heterogeneous (dual and single site mechanisms) catalytic reactions. Non-ideality of the liquid phase was taken into account by using activities instead of mole fractions. Prediction of the activity coefficients was made by UNIFAC. Parameters of the different models were obtained by the simplex search method.

Altiokka et al. (2003) obtained the kinetics data on the esterification of acetic acid with isobutanol from both homogeneously (autocatalyzed) and heterogeneously catalyzed reactions using dioxane as a solvent in a stirred batch reactor. The uncatalyzed reaction was found to be second-order reversible. In the presence of the catalyst, on the other hand, the reaction was found to occur between an adsorbed alcohol molecule and a molecule of acid in the bulk fluid (Eley-Rideal model). It was also observed that the initial reaction rate decreased with alcohol and water concentrations and linearly increased with that of acid. The temperature dependency of the constants appearing in the rate expression was also determined.

1.2.2.2.2 Kinetics of esterification of dibasic acid

In the esterification of a dibasic acid with alcohol, monoester should be the only primary product at the early stage of reaction. As the monoester is produced to a certain amount, it begins to react with another mole of alcohol to form diester, while rest of the

Table 1.5: Literature survey on esterification of dicarboxylic acids with alcohols

Substrate	Catalyst	Reaction Condition	Reference
Maleic acid, Ethanol	Ion exchange resin	T= 80°C	Yadav (2002)
Lactic acid, Methanol	Autocatalyzed and Dowex 50W	T= 353 K	Sanz (2002)
Phthalic, adipic, Sebacic, Maleic with alcohol	Titanium	T= 170°C	US28963 (2002)
Isopropyl lactate synthesis	Ion exchange resin	T=85°C	Yadav (2000)
Phthalic anhydride, 2-ethyl hexanol give dioctyl phthalate	Solid superacidic catalyst	At T= 140 monoester, T=195 Diester	Thorat (1992)
Acetic acid, n-butanol	HZSM-5 , 4 wt%	Alcohol : Acid = 1:10, T = 135°C	Lu (1992)
Maleic & Oxalic acid, Isopropanol & Isobutanol	SBPF resin	T = 60°C	Aboul-Magd (1988)
Oleic acid, Butanol	Dowex 50W-X8	T = 90-110°C	Rajkhowa (1975)
Salicylic acid, Methanol	Zeokarb 225	T= 68-69°C	Satyanarayana (1970)
Salicylic acid, Methanol, water 0.6 mol/lit	Dowex 50W (X-8)	T = 68-69 ° C	Bochner et. al. (1965)
Maleic anhydride, Maleic acid, Methanol	H ₂ SO ₄	T = 90-140°C	Makowka DE 3711155 A1 (1988)

acid is still reacting to produce the monoester. The detailed literature survey on esterification of different dibasic carboxylic acids with alcohols is presented in Table 1.5.

Huang (1967) studied the kinetics of esterification succinic acid with various alcohols, such as n-butanol, isobutanol, n-octyl alcohol, sec-nutanol, tert- butanol and iso-amyl alcohol with various compounds, such as benzoic acid, maleic anhydride, oxalic acid, itaconic acid, and adipic acid in the presence of sulfuric acid or Dowex 50 W as catalysts at different temperatures. The activation energies and the thermodynamic quantities such as ΔH , ΔG and ΔS of esterification have also been evaluated and discussed. They suggested that if the rate-determining step of esterification is the formation of the activated complex between acid (or alcohol) and hydrogen ion from the catalyst, the activation energies of a certain acid with various alcohols (or a given alcohol with various acids) should give similar values. But the experimental data showed that the activation energy varied with various acids, alcohols, and catalysts. This indicated that the activation process among the reactants and catalyst was not of a simple form and any one of the reactants may be activated by hydrogen ion before it proceeds to esterification. The various values of activation energies obtained in this work may also be interpreted on the basis of formation of activated complex of acid, alcohol and hydrogen ion. Hence the activated complex formation was regarded as the rate-controlling step, and was affected by both structures of acid and of alcohol.

Levesque and Craig (1948) carried out the esterification of oleic acid with n-butanol using cation exchanger as catalyst. They observed that the reaction rate was proportional to the external surface area of the particles, and the reaction, owing to the slow diffusion rate of the large molecules of the acid, appeared to occur only at or near the surface of the resin particles. The esterification of salicylic acid with methanol in presence of Dowex 50 W resin as catalyst in a batch stirred reactor was studied by Bochner (1965). The rate of conversion of salicylic acid was found to be unaffected by the stirring rate and the catalyst particle size. It was also observed that neither bulk, nor pore diffusion was the rate-determining step, but the initial water concentration had a marked influence on the reaction. Satynarayana and Verma (1970) concluded from their studies that in the esterification of salicylic acid with methanol using the acid form of Zero-Karb 225, the presence of water in the equilibrated solution lowers the percentage

conversion appreciably. Abul-Magd and Hassan (1988) studied the kinetics of liquid phase esterification of iso-propanol and isobutanol with maleic and oxalic acid using their laboratory made styrene butadiene phenolformaldehyde sulphonic acid resin as a catalyst. They concluded that the rate of esterification of maleic acid was lower than that of oxalic acid under same reaction conditions. Chawla and Hussain (1982) studied the Sulphuric acid catalyzed esterification of maleic anhydride with ethanol at 333 K – 353 K. Rode et al. studied Indion 130 cation exchange resin catalyzed esterification of maleic anhydride with ethanol at 343 K- 36 K. They analyzed the initial rate data were for the significance of mass transfer, which showed that all the rate data were in kinetic regime. Yadav and Thathagar (2002) described the efficacy of several heterogeneous catalysts in the esterification of maleic acid with ethanol. They employed the pseudo-homogeneous kinetic model to fit the experimental data and the activation energy calculated was 14.3 kcal/mol, which suggested that this reaction was intrinsically kinetically controlled.

1.2.3 Reaction engineering studies

Esterification of organic compounds often involves multiphase catalytic reactions in which contact of liquid (organic substrate) and solid (catalyst) phases are involved. The most common esterification processes fall into the category of two phase (liquid-solid) reactions. Both slurry and fixed bed reactors can be used for ion exchange resin catalyzed esterification reactions. The overall performance of these reactors depends on the inter phase mass transfer, intrinsic kinetics of reaction, physicochemical properties and mixing of the fluid phases. For a continuous process, fixed bed reactors should be preferred, however, in fixed bed reactors small catalyst particles cause higher pressure drop. Special type of support trays may also be required to support small catalyst particles in fixed bed reactors.

1.2.3.1 Agitated slurry reactors

The agitated slurry reactors are most commonly used on industrial scales in liquid phase esterification processes. In agitated reactors, the catalyst particles are used in a smaller form and kept in suspension by means of mechanical agitation. Due to smaller catalyst particle size, intraparticle diffusional effects are negligible in these reactors. Also

the overall mass and heat transfer efficiency is better than fixed bed reactors and these reactors are preferred for reactions with mass transfer limitation and those with high level of exothermicity. Many variations of these agitated slurry reactors are used in industry, e.g. stirred reactors with multiple impellers, and with multiple temperature control systems etc. The agitated slurry reactors can also be operated in a semi-batch or continuous mode depending on the process requirement. Several studies on reaction engineering aspects of esterification reactions are published previously as summarized in Table 1.6.

1.2.3.2 Fixed bed reactor

In this type of reactors, the gas and the liquid phase flow over a fixed bed of catalysts. The fixed bed reactors can be mainly classified into three types, (i) co-current down-flow of both gas and liquid phases (ii) downward flow of liquid with gas in the countercurrent upward direction and (iii) co-current up-flow of both gas and liquid. Reactors with co-current down-flow of gas and liquid is called as trickle bed reactors (TBR) and the co-current up-flow reactors are also referred to as packed bubble column reactors. Trickle bed reactors, wherein, the liquid reactant trickles down concurrently along with the gaseous reactant, over a fixed bed of catalyst pellets finds its application in wide variety of chemical, petrochemical and biochemical processes along with its application in waste water treatment. The examples of application of trickle bed reactors are given in detail in several monographs. (Satterfield (1975), Shah (1979), Al-Dahhan (1997) and Saroha (1996)). These include oxidation, hydrogenation, isomerisation, hydrodesulfurisation, hydroprocessing. These types of reactors are also applicable for esterification reactions (Hanika (2003)).

Table 1.6: Some batch reactor modeling and reaction engineering studies of esterification reactions

System	Catalyst	Remark	Reference
Octanoic acid + 1-butanol	Amberlyst-15	Kinetic and reactor modeling	Shimizu and Hirai (1987)
Acetic acid + n-propanol	Indian CXC-125	Kinetic and reactor modeling	Dakshinamurty (1992)
Butyric acid + n-butanol	Amberlyst-15	Kinetic and reactor modeling	Bhatnagar et al. (1994)
Acetic acid + Methanol	Amberlyst-15	Kinetic and batch reactor model	Xu and Chuang (1996)
Acetic acid + Methanol	Amberlyst-15	Batch reactor modeling with Intraparticle diffusional effect	Xu and Chuang (1997)
Acetic acid + Ethanol	Amberlyst-15	Kinetic and reactor model with multicomponent sorption equilibria	Xu and Chuang (1997)
Acetic acid + Methanol	Hydrogen iodide	Kinetic and reactor modeling	Ronnback et al. (1997)
Acetic acid + Methanol	Amberlyst-15	Kinetic and reactor modeling with reactive distillation	Song et al. (1998)
Acetic acid + Methanol	Polyolefin supported sulphonic acid	Kinetic and batch reactor model	Maki-Arvelds et al. (1999)
Acetic acid + Methanol	Amberlyst-15	Homogeneous, Heterogeneous kinetics	Popken et al. (2000)
Lactic acid + iso-propanol	Heterogeneous	Kinetic and reactor modeling	Yadav & Kulkarni (2000)
Lactic acid + Methanol	Dowex 50W, Amberlyst –15 and –36	Homogeneous, Heterogeneous kinetic model	Sanz et al. (2002)
Acetic acid + iso-butanol	Amberlite IR-120	Homogeneous, Heterogeneous kinetics	Altiokka and Citak (2003)

1.2.3.2.1 Experimental studies in fixed bed reactors

The kinetic behavior of the heterogeneous esterification of acetic acid with amyl alcohol over Dowex 50 Wx8-100 resin and propionic acid with n-butanol over Amberlyst 35 was investigated by Lee and Lin (2000/2002) in a fixed bed reactor at temperatures from 323 K to 393 K and molar ratios of feed (amyl alcohol to acetic acid) from 1 to 10 and the molar ratios of feed (n-butanol to propionic acid) from 0.5 to 2. The equilibrium conversions of acid were found to increase with an increase in the reaction temperature. The kinetic data was correlated with the quasi-homogeneous, Langmuir-Hinshelwood, Eley-Rideal and modified Langmuir-Hinshelwood models.

Hanika et al. (2003) investigated the esterification of acetic acid and butanol in a trickle bed reactor, packed with a strong acid ion-exchange resin (Purolite 151) at 343 K – 393 K. Experimental data illustrate the benefit of simultaneous esterification and partial evaporation of the reaction products in the multi-functional trickle bed reactor. In case of total wetting of the catalyst bed, contact of vaporized products (ester and water) with catalyst was naturally limited and thus, the backward reaction i.e. ester hydrolysis was suppressed. This phenomenon shifted the chemical equilibrium conversion to high values. Saletan (1952) obtained quantitative reaction rate data for the formation of ethyl acetate from ethanol and acetic acid in fixed beds of cation exchange resin catalyst. The complex interaction of diffusion and reaction kinetics within the resin, which determine over-all esterification rate, has been resolved mathematically.

The simulated moving-bed absorber has been successfully applied to the continuous chromatographic separation of two components from a large amount of feedstock. As a new application of the simulated moving-bed absorber, a simultaneous reaction and separation process was carried out in a simulated moving-bed apparatus. The simulated moving bed reactors involve various fixed beds, which are operated in a periodic mode. In particular the location of the inlet streams and of the outlet streams are continuously moved from one bed to the next one at a fixed velocity in the same direction of the fluid flow. The advantage is that this unit behaves exactly as a continuous countercurrent unit, even though the sorbent remains immobile. This technology finds wide application in the petrochemical industry (Sorbex process for the separation of

xylene isomers) and for the separation of various mixtures (of sugars, fine chemicals, enantiomers and others).

Mazzotti et al. (1996) studied the esterification of acetic acid with ethanol on a highly cross-linked sulphonic ion exchange resin (Amberlyst-15) in a continuous simulated moving bed reactor. The resin acted as catalyst as well as a selective sorbent simultaneously. They have studied the multicomponent sorption equilibria and swelling of the resin, as well as esterification kinetics with appropriate models. The thermodynamic and kinetic descriptions of the system have been combined to develop a fully predictive mathematical model of the chromatographic reactor.

Kawase (1966) used simulated moving-bed reactor for production of phenethyl acetate from acetic acid and phenethyl alcohol with ion exchange resin Amberlyst 15 as catalyst. They proved that flow rates and temperature were the most important factors to achieve almost 100% conversion. Lode et al. (2001) used a simulated moving-bed reactor for recovery of dilute acetic acid from wastewater, by esterification with methanol in presence of ion exchange resin catalyst. They found that the overall efficiency of acetic acid recovery was about 96 percent.

1.2.3.3 Reactive distillation

A chemical reaction and multistage distillation can be carried out simultaneously and this combined unit operation is called reactive distillation. The technique was first applied in the 1920's, to esterification processes using homogeneous catalyst (Keyes, 1932). Employing reactive distillation for reactions that rely on a solid heterogeneous catalyst is a more recent development. There is considerable academic and industrial interest in the area of reactive distillation. Overcoming equilibrium limitations on conversion, suppressing side reactions to reduce undesired byproducts, and overcoming azeotropic limitations on achievable separation are some additional advantages offered by reactive distillation. The above-listed advantages have led to commercial applications of reactive distillation in the chemical, petrochemical and polymer industry, with the most well known examples of methyl tert-butyl ether (MTBE) process and the Eastman Chemical Company process for methyl acetate.

Venimadhavan et. al. (1999) developed batch reactive distillation model for production of butyl acetate in presence of sulfuric acid catalyst. They also studied the kinetics of esterification of acetic acid with butanol and calculated the thermodynamic equilibrium constant in a temperature range of 373 K- 393 K. They found that the equilibrium constant did not vary strongly with temperature.

The recovery of acetic acid from its dilute aqueous solutions is a major problem in both petrochemical and fine chemical industries. Saha, et al. (2000) developed conventional methods of recovery of 30% acetic acid by reaction with n-butanol and iso-amyl alcohol in a reactive distillation column using macroporous ion-exchange resin, Indion 30, as a catalyst bed, confined in stainless steel wire cages. They found that recovery of acetic acid was enhanced by reactive distillation compared to the batch operation. Hanika et al. (1999) studied the esterification butyl alcohol with acetic acid in a pilot plant using a reactive distillation column packed with commercial catalysts (KATPAK and CY). It was found that butylacetate could be recovered in very high purity. This study had resulted in the development of a new technology for the manufacture of butylacetate.

1.3 Scope and objective of the thesis

The review of literature on esterification of monobasic and dibasic acid presented above indicates the wide-ranging applications of these reactions in industry. Being an equilibrium reaction, removal of one of the products, mainly water, to shift the equilibrium to the right side is a major challenge in this technology. To achieve the best performance, novel concepts like reactive distillation and moving bed reactors have been commercially established. In order to understand the reactor design aspects for esterification reactions it is most essential to have the knowledge of intrinsic kinetics of the reaction. From the review of literature it was evident that in spite of several published reports on this subject, there was a need to undertake a detailed study on features like kinetics of homogeneous-heterogeneous catalytic esterification. Therefore, the objective of the present thesis was to study homogeneous-heterogeneous kinetics for reactions described below:

- Kinetics of esterification of acetic acid with methanol to methyl acetate.
- Kinetics of esterification of acetic acid with butanol to butyl acetate.
- Kinetics of esterification of maleic acid with methanol to mono and diethyl maleate.

While the first two reactions were used as case studies of esterification reactions to account for the homogeneous reaction in simultaneous homogeneous-heterogeneous catalytic reaction, the third problem was challenging as it involves esterification of a dibasic acid, which has commercial value. The results presented in this thesis would be very valuable as a basic information in the design of esterification reactions and processes.

1.4 References

- Abul-Magad A.S., Kamal F.H., Hassan E.A., *Indian J. of Technology*, 26, 133 (1988)
- Adsmid B. A., Homes E. L., *J. Soc. Chem. Ind. I*, 54 (1954)
- Agarda V.H., Partin, L.R., Helse, W.H., *Chem. Eng. Prog.* 86,40 (1990)
- Albright R. L., *Supported Catal.*, 159 (1987)
- Altiokka M. R., *Appl. Catal. A: General*, 239, 141 (2003)
- Ancillotti F., Mauri M. M., Pescarollo E., *J. Catal.*, 46, 49 (1977)
- Ancillotti F., Gioacchino S. D., Costa G., *Ger. Offen.* 3,003,126 (1980)
- Anon., *Chem. Eng. News*, Oct 24, 4592 (1955)
- Arabi M., Amini Mohammadpour, Abedini M., Nemat A. and Alizadeh M., *J.Mol. Catal.: A*, 16, 3977 (2003)
- Armor J.N., *Appl. Catal.*, 78, 141 (1991)
- Baba S. , Ono Y., *Appl. Catal.*, 22, 321 (1986)
- Bader R., Kontowicz A. D., *J. Am. Chem. Soc.*, 75, 5116 (1953)
- Balakrishnan T. , Rajendran V., *J. Appl. Polym. Sci.*, 78, 2075 (2000)
- Bart, H.J. , Landschutzer, H. *Chem. Eng. Tech.*, 68, 944 (1996)
- Beasley G.H , Jakovac I.J., Ion exchange resin catalysts having improved catalytic activity and enhanced thermal stability, in D. Naden and M.Streat (Eds.), *Ion Exchange Technology*, Horwood, Chichester, 440 (1984)
- Bergk, *Z. Chem.* 18, 22 (1978)

Berthelot M. , Aaint-Gilles L. P., *Ann. Chim. Phys.* 68, 225 (1863)

Bhagade S. S., Nageshwar G. D., *Chem. Petro-Chem. J.*, 9, 3 (1978)

Bhagade S. S., Nageshwar G. D., *Chem. Petro-Chem. J.*, 9, 21 (1978)

Bhagade S. S., Nageshwar G. D., *Chem. Petro-Chem. J.*, 8, 9 (1977)

Bhagade S. S., Nageshwar G. D., *Chem. Petro-Chem. J.*, 12, 21 (1981)

Bhagade S. S., Nageshwar G. D., *Chem. Petro-Chem. J.*, 11, 23 (1980)

Bhatnagar R., Arvind, R., , Bhatia, S., *Indian Chem. Eng. Sect. A*, 36(3) , 120 (1994)

Bhaskar D., *Tetrahedron Lett.*, 37, 6375 (1996)

Bianchi C. L., Ragaini V., Pirola C., Carvoli G., *Appl. Catal. B: Environ.*, 40, 93 (2003)

Bilbao E. J., *An. Quim., Ser. A*, 80(1), 155 (Spanish) (1984)

Bochner M. B., Gerber S. M., *Ind. Eng. Chem. Fundamentals*, 4(3) (1965)

Brandes G., Neier W., Woellner J., Webers W., Hoppe A., *DE* 21,47,739 (1973)

Brandes G., Neier W., Woellner J., Webers W., Hoppe A., *DE* 21,47,740 (1973)

Brandes G., Neier W., Woellner J., Webers W., Hoppe A., *DE* 22,33,967 (1974)

Buttersack C. Widdecke H., Klein J., *H. React. Polym.*, 5, 181 (1987)

Buttersack C., *React. Polym.*, 10, 143 (1989)

Caapeletti R. A., Chialvo A. A., *Rev. Fac. Ing. Quim.*, 43, 155 (1979)

Carrigan T. E., Ferris W. R., *Can. J. Chem. Eng.*, 47(1969)

Cervený L., Marhoul A., Kozel J., *React. Kinet. Catal. Lett.*, 37, 337 (1988)

Chakrabarti A. , Sharma M. M., *React. Polym.*, 16, 15 (1991/1992)

Chakrabarti A. , Sharma M. M., *React. Polym.*, 18, 107 (1992)

Chakrabarti A. , Sharma M. M., *J. Am. Oil Chem. Soc.*, 69, 1251 (1992)

Chakrabarti A. , Sharma M. M., *React. Polym.*, 20, 1 (1993)

Chaudhary V. R., *US* 6420596 (2002)

Chawla H. S. , Hussain S. Z., *Chem. Econ. Eng. Rev.*, 15, 16 (1983)

Chawla H. S., Hussain Z. S., *Ind. J. Tech.*, 20, 22 (1982)

Chen X., Xu Z., Okuhora T., *App. Cat. A*, 180, 261-269, (1999)

Chi H. Cui Y., Wang Z., *Faming Zhuanli Shenqing Gongkai Shuoningshu* CN 1,052,848 (1991)

Ciobann A., Nicolae A., Malinetescu M., *Rev. Chem.*, 38, 29 (1987)

Cornea F., Ciobanu A., Nicolae A. R. , Petrescu, *Rom. RC* 80,597 (1982)

Cunill F., Toral L., Izquiordo J. F., Tejero J. , Iborra M., *React. Polym.*, 10, 175 (1989)

Dakshinamurty P., Hanuma G., Ramchandramurty C. V., *Indian Chem. Eng.*, 34(4), (1992)

Darge Olivier and Thyron Fernand C., *J.Chem. Technol.Biotechnol.*, 38,4, 351 (1993)

Davies C. W., Thomas G. G., *J. Chem. Soc.*, 1607 (1952)

Dharmaratne H. R. W., *Ind. J. Chem.* 21, 39 (1982)

Ding Z., Wu M., *Shanghal Keji Daxue Xuebao*, 14, 100 (1991)

Doraiswamy L. K. , Sharma M. M., “Heterogeneous Reactions: Analysis. Examples, and Reactor Design”, Vol.2, *Wiley-Interscience*, New York, 254 (1984)

Doraiswamy L. K. , Sharma M. M., “Heterogeneous Reactions: Analysis. Examples, and Reactor Design”, Vol.2, *Wiley-Interscience*, New York, 280, 307 (1984)

Dierichs, Report PB 866, Office of Technical Services, Dept. of Commerce, Washington, (1945)

Edward S., *J. Chem. Edu.*, 796 (1990)

Edwin-Haslam, *Tetrahedron*, 36, 2409 (1980)

Elewady Y.A., Mel -Nahas , Mnh Moussa., *Indian J. Chem.*, 26A, 63 (1987)

Ellenberger J., Krishna R.; *Chem.Eng. Sci.* 54, 1339 (1999)

Elorriaga Bibao J., Gonzalez-Velasco J.R., Gonzalez J.A., Aguaya A.T., *An. Quim. Ser.A.*, 80,1,155 (1984)

Erpenbach H., Gehrman K., Joest H., Zerres P., *Ger. Offen.* 2,449,811 (1976)

Erpenbach, H.; *EP* 387674 A2 (1990)

Farbenindustrie I.G. *Ger. Pat. DE* 882,091 (1958)

Fukuhara H., Matsunaga F., *JP* 01,254,634 (1989)

Gates B. C., Johanson L. N., *J. Catal.*, 14, 69 (1969)

Gates B. C., “Catalytic Chemistry”, *Wiley, New York* (1992)

Gimenez J., Costa J. , March C. S., *Appl. Cat.*, 31, 221 (1989)

Grequel A. , Torek B, *J. Catal.*, 83, 9 (1983)

Goldschmidt H., Udby O. Z., *Phy. Chem.* 60, 728 (1908)

Haag W. O., *Chem. Eng. Prog. Symp. Ser.*, 63, 140 (1967)

Harmer M. A., Sun Qun, *Appl. Catal. A: General*, 221, 45 (2001)

Hanika Jiri, Kolena Jiri, Kucharova Magdalen, Havlickova Karla, Tatranske Matliare, Slovak Republic, 30 (2003)

Hanika Jiri, Kucharova Magdalena, Kolena Jiri and Smejkal Quido, *Catalysis Today* 79-80, 83-87 (2003)

Haskell V. C., Hammett L. P., *J. Am. Chem. Soc.*, 71, 1284 (1949)

Hansen R. D., *US* 3,252,921 (1966)

Helfferrich F. G. and Hawang Y., "Ion Exchangers as Catalysts", in "Ion Exchange for Industry", M. Streat, Ed., Ellis Horwood, New York (1988)

Helmut Zinke-Allmang, Hofmann Herwing, Scheidmeir Walter, Schaefer Eberhard, Mueller Guenther, *DE* 3636754 A1 (1988)

Helmut F., Phenol derivatives in B. Elvers, S. Hawkins , G. Schulz (Eds.). *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 19, VCH. Weinheim, 313 (1991)

Hepplewhite Iain Wesley and Ridland John, *WO* 99/28033 (2000)

Huang, W.; Lizi J.; Yu X.; *12(6)*, 510 (Chinese) (1996)

Huang T., Wan J., Tsai L., *J. Chin. Chem. Soc.* 14(2-3), 72 (1967)

Ihm S. K., Suh S. S. , Ch I. H., *J. Chem. Eng. Jpn.* 15, 206 (1982)

Iwasaki H., Kobayashi M., *JP* 63,57,554 (1988)

Izum Yuusuke, *JP* 57130954 (1982)

Jeromia L, Peakart E. , Wollmann G., *Ger. Offen. DE* 3,501,761 (1986)

Jinlong Z.; Xuebao X. D., *Kexueban Ziran*, 37(2), 224 (chinese) (1998)

Jagannadha R.; Chand, K. M. K.; *Indian Chem. Eng.*, 32(3), 92 (1990)

Kabza K. G., Chapados B. R., Gestwicki J. E., Mcgrath J. L., *J. Org. Chem.* 65, 1210-1214 (2000)

Kawase M., Suzuki T. B., Inoue K., Yoshimoto K., Hasimoto K., *Chem. Eng. Sci.*, 51 (11), 2971-2976, 1996

Kemp, *US* 3,678,099 (1972)

Keys D. B., *Ind. Eng. Chem.*, 24, 1096 (1932)

Kiein H. W., *Ger. Offen. DE* 3,619,797 (1987)

Kirk Othmer Encycl., Section: Catalysis, 320, (1993)

Kirk R. E, Othmer D. F., *Encycl. Chemical Technology*, 5, 789 (1953)

Komioka M., Matsumoto S., Yoshida H. , Baba M., *JP* 03,52,842 (1991)

Kumbhar P. S. , Yadav G. D., *Chem. Eng. Sci.*, 44 (11), 2535 (1989)

Lee M., Wu H., Lin H., *Ind. Eng. Chem. Res.*, 39, 4094 (2000)

Lee M., Wu H., Lin H., *Ind. Eng. Chem. Res.*, 41, 2882 (2002)

Leupold E. I., Arpe H. J., *Ger. Offen.* 2,306,586 (1974)

Levesque C. L., Craig A. M., *Ind. Eng. Chem.*, 40, 95 (1948)

Leyes C. E. , Othmer D. F., *Ind. Eng. Chem.*, 36-37, 968-977 (1945)

Liao Shijun, Zang Xiaoling, Huanan Ligong Ligong Daxue Xuebao, *Ziran Kexueban* 25,11,88 (1997)

Li B., Chin, *J.Catal.*, 10, 331 (1989)

Lindall C. M., *US Pat.* 0087027 A1 (2002)

Lode F., Mazzotti M., Morbidelli M., *Chimia.* 55, 883-886, (2001)

Lohma E., Ohorodink A., Gehrman K. , Stutzke P., *Ger. Offen.*, 2,226,829 (1973)

Lundquist E. G.; *US Pat.* 5,426, (1999)

Mazzotti M., Neri B., Gelosa D., Kruglov A., Morbidelli M., *Ind. Eng. Chem. Res.*, 36, 3 (1997)

Maki-Arvela P., Salmi T., Sundell M., Ekman K., Peltonen R., Lehtonen J., *Appl. Catal. A: General* 184, 25 (1999)

Mensah P., *Biotech. & Bioengg.*, 60, 445 (1998)

MCMaster., *Ind. Eng. Chem. Prod. Res. Develop.*, 11 (1), 97 (1972)

Makoto H.; *Chem. Lett.*, 12, 1671 (1981)

Makowka, Bernd; *DE* 3711155 A1 (1988)

Matsumura H., Murakami F., Sonobe H., *EP* 10,953 (1980)

Mazzotti M., Kruglov A., Neri B., Gelosa D., Morbidelli M., *Chem. Eng. Sci.*, 51(10), 1827-1836, 1996

Melpolder F. W. , Wentzheimer W.W., *US* 4198530 (1980)

Mills P. L., Chaudhari R. V., *La Chimica e l'Industria*, 82, 539 (2000)

Mitsubishi Chemical Industries Co. Ltd., *JP* 8228015 (1982)

MTBE, ETBE, TAME: IFP etherification technology, inst. Fr. Petrole-Direction *Ind. Bull.*, 12 (1991)

Mueller G., Schaefer E., Zinke A. H., Hoffmann H., Scheidmeir W., *DE* 3636754 (1988)

Nakashimo S., Sogabe H., Yoshida H., Okubo A., *WO* 8800,180 (1988)

Nagaraju N., Mehboob P., *Indan J. Chem. Tech.*, 3, 253 (1996)

Neier W., Ion exchangers as catalysts, in K. Dorfner (Ed.), "Ion Exchangers", *Walter de Gruyter, Berlin* 981 (1991)

Neier W., Webers W., Ruckhaber R., Osterberg G., Ostwald W., *DE* 30,40,997(1982)

Neumann R., Sasson Y., *Ind. Eng. Chem. Process Des. Dev.*, 23 (4), 654 (1984).

Neumann G., *Chem. Tech.*, 11, 18 (1959)

Nigam S. C., Bannore H. N., Aubbarao S., *Indian Pat.* 154862 (1984).

Nozawa R., *Chem. Econ. Eng. Rev.*, 7(10), 26 (1975)

Obenaus F., Greving B., Nalke H. , Scholz B., *DE* 3,151,446 (1983)

Okazaki S., Kokoma M., Kaneko T. , Sakai K., *JP* 63,297,340 (1988)

Okuhara T., Kimura M., Kawai T., Xu Z., Nakato T., *Catal. Today*, 45, 73 (1998)

Olah G.A., Iyer P. S., Prakash G. K. S., *Synthesis*, 513 (1986)

Olah G.A., "Catalytic chemistry of perfluorinated resinsulfonic acids: reactions, mechanistic aspects and superelectrophilic activation", in: *J. Fraissard, L. Petrakis (Eds), Acidity and Basicity of Solids*, 305 (1994)

Olivier D.; Thyron, F. C.; *J. Chem. Technol. Biotechnol.*, 58(4), 351 (1993)

Ogliaruso M. A. , Wolfe J. F., *John Wiley and Sons: Chichester*, (1991)

Parshall G.W., "Homogeneous catalysis", *Wiley-Interscience*, New York, (1980)

Patwardhan, A.A; Sharma M.M; *React. Polym.*, 13(1-2), 16176 (1990)

Perez Pascual M. A. , de-Benito Albertos F., *EP* 445,859 (1991)

Perez Pascual M. A. , Albertas de Benito F, *Span. ES* 2,019,052 (1991)

Perry A. R., Pummell D. W., Thomson A. I. *EP* 529868 (1993)

Petrini M., Ballini R. , Marcantoni E., *Synth. Commun.*, 18, 847 (1988)

Petrus L., Roo R. W. De, Stamhuis E. J., Joosten G. E. H., *Chem. Eng. Sci.*, 39, 433 (1984)

Petrus L., Roo R. W. De, Stamhuis E. J., Joosten G. E. H., *Chem. Eng. Sci.*, 41, 217 (1986)

Pipus G., Plazl I., Koloini T., *Ind. Eng. Chem. Res.*, 41, 1129-1134, (2002)

Pitochelli A. R., "Ion exchange catalysis and matrix effects", *Rohm and Hass, Philadelphia*, (1980)

Platt L. L. Jr., *US* 3732344 (1973)

Popken T., Gotze L. , Gmehling J., *Ind. Eng. Chem. Res.*, 39, 2601 (2000)

Putzing D. E., *US* 6,166,170 (2000)

Rajkhowa, P.; *Indian Chem. Eng.*, 17(3), 41 (1975)

Ramchandran P. A., Chaudhari R. V., “Three Phase Catalytic Reactor”, *Gorden and Breach Science Publishers*, Paris (1992)

Rao B. A.; *Chem. Petro-Chem. J.*, 10(3), 7 (1979)

Rataj A., Kulidcki and Krogulocki A., *Pol.* PL 837483 (1987)

Rehfinger A., Hoffmann U., *Chem. Eng. Sci.*, 45, 1605 (1996)

Rehfinger A., Hoffmann U., *Chem. Eng. Sci.*, 45, 1619 (1996)

Rehfinger A., Hoffmann U., *Chem. Eng. Technol.*, 13, 150 (1990)

Rheinpreussen AG Fur Bergbau und Chemie, *Fr. Pat.* 1,383,548 (1964)

Ridland J. D., *EP* 812,818 (1997)

Robels-Dutenhefner ; *J. Mol. Catal. A: Chem.*, 164, 39 (2000)

Roberts I., Urey H. C., *J. Am. Chem. Soc.*, 60, 2391 (1938)

Robert Perry, Adam; *E P.529868 A2* (1993)

Robles-Dutenhefner P.A., Moura E. M., Gama G. J., Siebald H. G. L., Gusevskaya E. V., *J. Mol. Cat. A*, 164, 39-47, (2000)

Ronnback R., Salmi T., Vuori A., Haario H., Lehtonen J., Sundqvist A., Tirronen E., *Chem. Eng. Sci.*, 52(19), 3369 (1997)

Rohm and Hass, “Amberlyst 15-Ion exchange resin for Catalyst”, *Rohm and Hass Company encyclopedia* (1990)

Royals E. E., *Advanced Org. Chem.*, 600 (1954)

Saletan D. I. , White R. R., *Ind. Eng. Chem., Symposium series no.4* (1952)

Sante-Ollalo Gadea J., *EP* 54,576 (1982)

Sanz M. T., Murga R., Beltran S. , Cabezas J. L., *Ind. Eng. Chem. Res.*, 41, 512 (2002)

Sarobha A. K. and Nigam K.D.P., *Rev. Chem. Eng.*, 3-4, 12 (1996)

Satynarayana B. , Verma Y. G. B., *Indian J. Technol*, 8, 312 (1970)

Satterfield C. N., *A.I.Ch.E.J.*, 21(2), 209 (1975)

Schleppinghoff B., Leblane H. , Mallmann K. H., *Ger. Offen. DE* 3,105,399 (1983).

Scharmer Klaus, *EP* 310 843 (1989)

Saha B., Chopade S.P. , Mahajani S. M., *Catal. Today*, 60(1-2), 147 (2000)

Shah N. E. , Sharma M. M., *React. Polym.*, 19, 181 (1993)

Shah T.Y., “Gas liquid-solid reactor design, *McGraw-Hill*, New York (1979)

Sharma M. M., *Reactive and Functional Polymers*, 26, 3 (1995)

Shimizu S., Hirai C., *Bull. Chem. Soc. Jpn.*, 60,1975 (1987)

Shijun L.; Hauanan L. Dacue X., *Ziran Kexueban*, 25(11), 88 (Chinese) (1997)

Smith A. , Hilton By, *J. Am. Chem. Soc.*, 61, 254 (1939).

Smith L.A., *US* 4,307,254 (1981)

Sidney S., *Ind. Eng. Chem.*, 38(12), 1228 (1946)

Stepanova I. P., Obukhov V. M., Bondarenko A. V., Farberov M. I., *Zh. Pr. Khim.*, 50, 640 (1977)

Streat M., “Ion Exchange for Industry”, *Ellis Horwood*, Chichester (1988)

Subramaniam C., Bhatia S., *Can. J. Chem. Eng.*, 65, 613 (1987)

Sucheta K., *Tetrahedron Lett.*, 35, 4415-4416 (1994)

Sundmacher K. , Hoffmann U., *Chem. Eng. Sci.*, 47, 2733 (1992)

Song W.; Venimadhavan G., Manning J. M., Malone M. G., Doherty M. F., *Ind. Eng. Chem. Res.*, 37(5), 1917 (1998)

Tanabe K. , Holderich W. F., *Appl. Catal. A: General* 181, 399 (1999)

Tang D., *J. Mol. Cat. A: Chem.*, 147, 159 (1999)

Thakar, H.P.; Gade, V.N.; *Chem. Eng. Div*, 70(1), 26 (1990)

Thakur, D. S.; *J. Inst. Eng., Part CH*, 58(2), 24 (1973)

Thorat T. S., Yadav V. M., Yadav G. D., *Appl. Catal. A: General*, 90, 73 (1992)

Timofeeva M.N., *Applied Catalysis A : General* 256, 19-35 (2003)

Tian Z.; *Jingxi Huagong*, 17(6), 334 (Chinese) (2000)

Tokumoto Y., Sakamoto K., Sasaki K., Shimizu I., *EP*. 483826 (1990)

Tono I., Kamezawa M. , Hayashi T., *JP* 02,160,753 (1990)

Totani N. , Muramatsu T., *Chem. Phys. Lipids*, 29, 375 (1981)

Tokuyama Soda Co. Ltd., Japan, *JP* 57130954 A2 (1982)

Tze-Tang Chuang, Karl; *US* 96,18309 (1996)

VanGulijk C., *Computers in Chemical Engineering*, 22, S767 (1998)

Venimadhavan G., Buzad G. Doherty M. F., Malone M. F., *A.I.Ch.E. J.* 40, 1814 (1994)

Vora B., Pujado P., Imai T. , Fritsch T., *Chem. Ind.*, 19, 187 (1990)

Voioch M., Ladisch M. R. , Tsao G. T., *React. Polym.*, 4, 91 (1986)

Verhoef M. J., *Microporous & Mesoporous Mater.*, 27, 365 (1999)

Webers W., Sandhack L. , Neier W., *DE* 24,29,770 (1976)

Wesley R. B. , Gates B. C., *A.I.Ch.E. J.*, 20, 933 (1974)

Widdecke., *Macromol. Chem. Phys. Suppl.*, 6, 211 (1984)

Widdecke H., Design and industrial application of polymeric acid catalysts, in D. C. Sherrington , P. Hodge (Eds.), *Syntheses and Separations using Functional Polymers*, Wiley, Chichester, 149 (1988)

Widdecke H., Design and industrial application of polymeric acid catalysts, in D. C. Sherrington , P. Hodge (Eds.), *Syntheses and Separations using Functional Polymers*, Wiley Chichester, 149 (1999)

Wiison M. I., Chen J. C., *Ger. Offen.* 2,942,186 (1980)

Woellner J., Neier W., *Ger. Offen.* 1,260,454 (1968)

Wolfgang A., *Fluid Phase Equilib.*, 158-160, 973-977, (1999)

Xin C., Zheng Xu , Toshio O., *Appl. Catal. A: General*, 180, 261 (1999)

Xiuzhen Lu; Lai, S.; *J. Nat. Gas. Chem.*, 1(4), 375 (1992)

Xu Z.P., Chuang K.T., *Can. J. Chem. Eng.*, 74, 493, (1996)

Xu Z.P., Chuang K.T., *Chem. Eng. Sci.*, 52(17), 3011,(1997)

Xu, X., Zhao, Z., Tian, S.J., *Trans. I. Chem. E. Part A*, 75, 625 (1997)

Yadav G. D. , Kulkarni H. B., *React. Funct. Polym.*, 44, 153 (2000)

Yadav G. D. , Thathagar M. B., *React. Funct. Polym*, 52, 99 (2002)

Yadav G. D. and Mehta P. H., *Ind. Eng. Chem. Res.*, 33, 9 (1994)

Yadav G.D.and Krishnan M.S., *Organic Process Research and Development*, 2, 86 (1998)

Yamata Y., Murata T., Takagi Y., *JP* 63,297,340 (1988)

Yang Z., Hu W., Xie Y., *Lizi Jiaohuan Yu Xifu*, 6, 178 (1990)

Yongguang Li, Wang, *Jingmin Riyong Huaxue Gongye*, (2), 54 (Chinese) (1989)

Yu S., *Lizi Jiaohuan Yu Xifu*, 7, 219 (1991)

Yu Y., Wei R., Lian Y., Che R., *Lizi Jiaohuan Xu Xifu*, 4, 305 (1988)

Yuen E. H. L., *Appl. Catal.A: General*, 232, 29 (2002)

Zimmermann H., Rudolf J., *Angew. Chem.* 77, 65 (1965); *Angew. Chem. Int. Ed. Engl.* 4, 40 (1965)

Zinke-Allmang H.; Hiffnabb H.; *DE* 3636754 (1988)

Zupan M., Segatin N., *Synth. Commun.*, 21(4), 597 (1991)

Zundel G., "Hydration and Intermolecular Interaction Infrared Investigations with Polyelectrolyte Membranes", *Academic Press*, New York (1969)

2.1 Introduction

Methyl acetate forms as an intermediate in the acetic acid synthesis from methanol and carbon monoxide and is used as a solvent for cellulose, nitrates, esters and ethers. When this ester is produced via esterification of acetic acid with methanol, generally mineral acids like sulfuric acid, hydrogen chloride and aryl sulfonic acid (such as *p*-toluenesulfonic acid) are used as homogenous acid catalysts, while cation exchange resin and zeolites are used as heterogeneous catalysts. The relevant literature on this subject is summarized in Chapter-1. Some important studies on esterification of acetic acid with methanol are summarized below.

The kinetics of homogeneous esterification of acetic acid with methanol has been investigated in the past. Agreda et. al. (1990) have studied the kinetics of esterification of acetic acid with methanol in presence of sulfuric acid as a catalyst. They described an automated plant for the production of methyl acetate comprising a reactive distillation unit with countercurrent operation. Ronnback et. al. (1997) studied the esterification of acetic acid with methanol in the presence of hydrogen iodide as a catalyst in a batch reactor at 30-60°C. They proposed a reaction mechanism with methyl acetate and methyl iodide formation as rate determining steps, and proposed rate equations. The literature on esterification of acetic acid with methanol reveals that the ion-exchange resin catalyst is commonly used compared to mineral acid catalysts due to some advantages, like catalyst separation, minimizing corrosion problems etc.

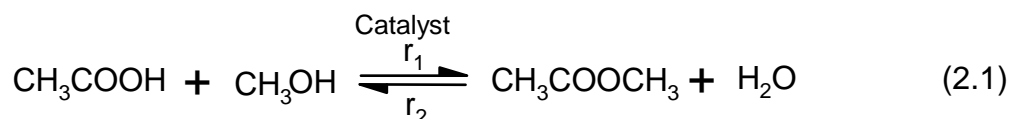
The kinetics of esterification of acetic acid with methanol in presence of ion exchange resin for recovery of dilute acetic acid from wastewater is reported by Neumann and Sasson (1984) and Xu and Chuang (1996/ 1997). Neumann and Sasson (1984) used a chemorectification column packed with an acidic organic polymer catalyst for kinetic studies. They observed that both diffusion and the chemical reaction were partially controlling the overall reaction rates. The reaction was found to be second order in acetic acid and zero order in methanol. Xu and Chuang (1996) found Amberlyst-15 to be effective as a catalyst for the aqueous phase reaction of acetic acid and methanol at lower reactant concentrations. They found that the internal mass transfer resistance was not significant. A kinetic equation was developed and used in the design of a catalytic distillation column. Xu and Chuang (1997) analyzed the effect of internal diffusion on the

catalytic esterification of acetic acid. The intraparticle diffusion resistance was shown to be insignificant for the second order reversible esterification of acetic acid with methanol using commercial catalyst Amberlyst-15, because of the relatively small size of the catalyst particles and the high activation energy of the reaction observed.

The kinetics and equilibrium of autocatalyzed and ion exchange resin (Amberlyst-15) catalyzed esterification of acetic acid with methanol and hydrolysis of methyl acetate were studied by Popken et. al. (2000) in a temperature range of 303 - 343 K. The homogeneous reaction has been described with a simple power-law model. To compare pseudo-homogeneous and adsorption-based kinetic models for the heterogeneously catalyzed reaction, independent binary liquid phase adsorption experiments were used to estimate the adsorption equilibrium constants to keep the number of adjustable parameters the same for each model.

From the literature survey, it was observed that the kinetics of esterification of acetic acid with methanol has been investigated extensively. It is well known that a homogeneous esterification always occurs even in the presence of solid acidic ion-exchange resin catalysts. Though, there are many studies on the esterification of acetic acid with methanol in the presence of ion exchange resin catalysts, there are no studies wherein the simultaneous homogeneous and heterogeneous reactions have been taken into consideration. In the present work, the example of an esterification reaction, which simultaneously occurs homogeneously in the liquid phase and heterogeneously at the catalyst surface, has been analyzed. Theoretical models incorporating the mass transfer effects for the overall rate of reaction has been developed. These studies would be useful in the analysis of experimental data in a fixed bed reactor for this system and also for reactive distillation.

The reaction involving esterification of acetic acid with methanol is described below:



Experimental studies on homogeneous reaction were carried out over a temperature range of 308-328 K. For the heterogeneous catalytic esterification reaction,

the effect of temperature, catalyst loading, and catalyst particle size and reactant concentrations on the initial rate of reaction were also studied in a temperature range of 308-328 K. These data were used to develop intrinsic kinetics of homogeneous and heterogeneous reactions. A rate model has been developed incorporating the effect of intraparticle diffusion for [1,1] order reversible reaction. The model predictions for different operating conditions are compared with experimental data.

2.2 Experimental

2.2.1 Materials

The reactants methanol and acetic acid used were of A.R. grade (99.8%) and were obtained from S.D. Fine Chemicals, India. Purity was determined by gas chromatography. The chemicals were used without further purification.

2.2.2 Catalyst

The cation exchange resin Dowex 50W (Dow Chemical Co.) used as the catalyst was procured from Vijay Chemicals, India. Before using for experiments, the resin was pretreated using standard procedures (Helfferich, 1962). First, the resin was washed with water, followed by hydrochloric acid and sodium hydroxide wash. For this purpose, the catalyst was packed in a glass column of 10 mm, inner diameter and 1000 mm height. The catalyst was soaked in distilled water for 15 minutes and then charged into the column. Then, one liter of 0.1 M hydrochloric acid solution and 0.1 M sodium hydroxide solution was passed through the catalyst bed to remove acid soluble and alkali soluble impurities. After acid and alkali treatment each time, the resin was washed with water to ensure complete removal of chloride and sodium ions from the catalyst bed. This was ensured by litmus paper test. Finally 0.1 M hydrochloric acid solution was passed through the column to convert all the resin to H^+ form and the free acid was washed with water. The resin was then dried in an oven at 100°C. The ion exchange capacity of the resin was determined by total exchange with sodium chloride solution and subsequent titration. The dry weight capacity of the resin was found to be 4.3 meq./ g. This compared well with the value of 4.4 meq./ g. given by the Dow Chemical Company. The specifications of ion exchange resin catalyst are shown in Table 2.1.

Table 2.1: Specifications of Dowex 50W resin catalyst

Structure	Macroporous Cross-linked Styrene-DVB
Particle size range, mm	0.4 – 1.0
Moisture content, % (w/w)	20
Form	-SO ₃ H
Bulk density, gm/ml	0.5-0.6
H ⁺ conc, meq/gm, dry	4.3.
Particle density, kg/m ³	1.37 X 10 ³

2.2.3 Reactor Setup

A schematic diagram of the experimental setup is shown in Fig. 2.1.

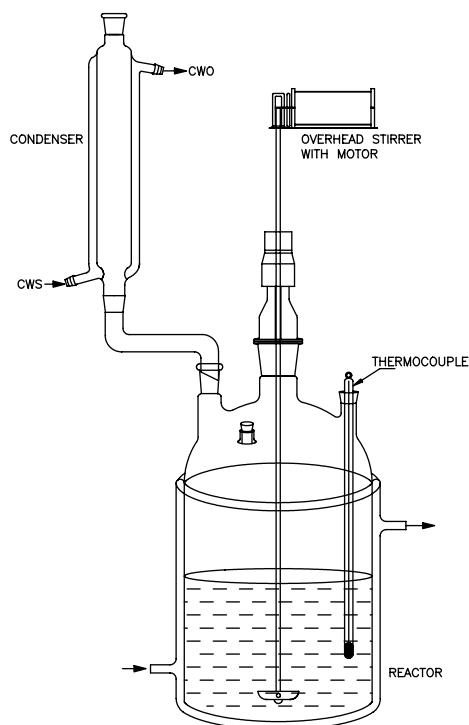


Fig. 2.1: Experimental setup of a batch slurry reactor for esterification reaction

The esterification of acetic acid with methanol was carried out in a glass reactor of 10-cm i. d. and 16-cm height. An outer jacket was provided to the reactor through which water at a constant temperature could be circulated. The temperature in the jacket was maintained within $\pm 0.1^\circ\text{C}$ using a thermostat. A glass stirrer with four blades, turbine type impeller (1 cm in width), was used for agitation. The agitation speed could be varied using a constant speed regulator.

2.2.4 Experimental procedure

In all the experiments, a known amount of acetic acid was charged to the reactor and heated to the desired temperature. When the temperature remained constant, the required amount of methanol was added under constant stirring. It was observed that the temperature fall as a result of this addition was not significant and the temperature equilibrium was reached in a short time. A sample was removed for analysis. This was taken as the starting point of homogeneous (uncatalyzed) reaction. For the catalytic reaction, after attaining the desired temperature, a known quantity of ion exchange resin along with methanol was added to the reactor. The moment of resin addition was taken as the starting time of reaction. Samples were withdrawn at regular time intervals for analysis. The volume of sample withdrawn from the reactor during a run was negligible compared with the total volume of the system. The total volume of reactants was 120 cm^3 in all the experiments.

2.3 Analysis

The analysis of reactants and products was carried out using gas chromatography. The gas chromatograph used for analysis was a Hewlett-Packard model no. HP 5890. A FFAP (cross linked polyethylene glycol-TPA as the stationary phase) column (diameter: 0.53 mm, film thickness: $1\ \mu\text{m}$, length: 30 m) was used for separating the reactant and products. The conditions of GC analysis were:

Column temperature	: 50-200°C (Programmed at 20°C /min)
Injector temperature	: 250°C
Detector (FID) temperature	: 250°C
Carrier gas (He) flow	: 35 ml/min

By this procedure, the concentration change of the reactants/ products species with time was recorded in all the experiments. Methanol, acetic acid and methyl acetate were analyzed in each sample.

2.4 Kinetics of esterification

2.4.1 Preliminary Experiments

Some preliminary experiments were carried out to select a range of reaction conditions suitable for studying the reaction kinetics and establish the product distribution, material balance etc. The range of reaction conditions under which the present study was carried out is given in Table 2.2.

Table 2.2: Range of operating conditions

Reaction temperature, K	308, 318 and 328
Agitation speed, rpm	800 - 1200
Catalyst loading, kg/m ³	8.14, 16.3, 32.08 and 48.82
Acetic acid: methanol ratio	1:1, 1:2 and 1:4
Particle size, mm.	0.458, 0.74 and 1.0

Initial experimental data on concentration-time profiles (Figs. 2.3-2.5) showed that the material balance of methanol and acetic acid consumed matched up to 95% with methyl acetate formed.

For the heterogeneous reaction using ion exchange catalyst, it should be ensured that the catalyst is uniformly suspended in the reaction medium. Zweitering (1958) has proposed a correlation to predict the minimum speed of agitation required to keep the solid particle in complete suspension. The correlation is

$$N_m = \frac{B_2 d_p^{0.2} \mu_L^{0.1} g^{0.45} (\rho_p - \rho_L)^{0.45} w^{0.13}}{\rho_L^{0.55} d_i^{0.85}} \quad (2.2)$$

Where, N_m = required for complete suspension and minimum speed of agitation (Hz).

Using the above correlation, it was found that the minimum agitation speed required for the highest catalyst loading (48.82 kg/m³) was 140 Hz. Hence, all the heterogeneous reactions were carried out at 167 Hz (1000 rpm).

$$B_2 = \text{constant} = 2 \left(\frac{d_T}{d_1} \right)^{1.33} \quad (2.3)$$

It was also important to ensure that the catalyst activity did not vary during the course of a run. To confirm this, a few experiments on the reusability of the catalyst were carried out. Initially the reaction with the fresh catalyst was carried out for 5 hours. The change of concentration as a function of time was observed. At the end of the reaction the catalyst was separated from the reaction mixture by filtration and then charged again to the reactor. The new esterification run with the recycled catalyst was completed, exactly in the same manner as the first run. The concentration-time profile obtained for fresh and third recycle of catalyst were identical as shown in Fig. 2.2, indicating the constancy of the catalyst activity during a particular experiment.

2.4.2 Kinetics of homogeneous reaction

For the kinetic study of the homogeneous esterification reaction, (without ion exchange resin catalyst) the experiments were carried out at 308, 318 and 328 K at molar ratios of acetic acid to methanol of 1:1, 1:2 and 1:4 at a stirring speed of 1000 rpm respectively. Since esterification of acetic acid is a reversible reaction, evaluation of rate parameters using initial rate data may not be appropriate. Hence, it was decided to use the integral rate data for developing a suitable kinetic model. In each experiment, the concentration of reactants and products were measured as a function of time to obtain the concentration-time profiles for each species. The results are presented in Figs. 2.3-2.5. The following forms of rate equations were assumed

$$r_1 = k_3 C_1 \cdot C_2 \quad (2.4)$$

$$r_2 = k_4 C_3 \cdot C_4 \quad (2.5)$$

Where, r_1 and r_2 are the rate of forward reaction and backward reaction respectively with units of $\text{kmol/m}^3/\text{sec}$; C_1, C_2, C_3, C_4 are concentrations of acetic acid, methanol, methyl acetate and water respectively in kmol/m^3 .

In order to evaluate the rate parameters in the kinetic model, the observed concentration time data were simulated using a batch reactor model under isothermal conditions as described below:

$$\frac{dC_1}{dt} = r_2 - r_1 \quad (2.6)$$

$$\frac{dC_2}{dt} = r_2 - r_1 \quad (2.7)$$

$$\frac{dC_3}{dt} = r_1 - r_2 \quad (2.8)$$

$$\frac{dC_4}{dt} = r_1 - r_2 \quad (2.9)$$

The initial conditions are:

$$\text{at } t=0; C_1=C_{A0}, C_2=C_{B0} \text{ and } C_3, C_4=0 \quad (2.10)$$

Where, C_{A0} and C_{B0} are the initial concentrations of acetic acid and methanol respectively.

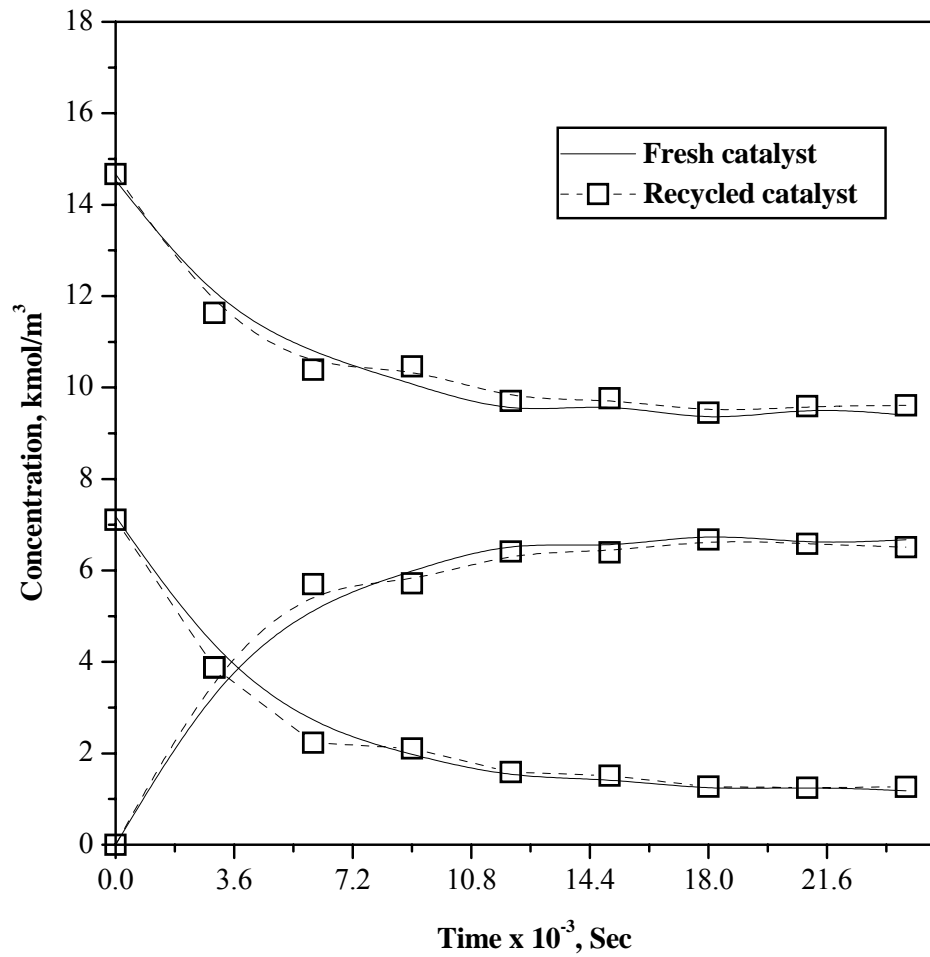


Fig. 2.2: Effect of catalyst recycle at 318 K
Reaction conditions: $C_{A0} = 7.485 \text{ kmol/m}^3$, $C_{B0} = 14.011 \text{ kmol/m}^3$, $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$

By solution of equation 2.6 to 2.10 with these initial conditions, and fitting the experimental concentration-time data in Figs. 2.3-2.5 the kinetic parameters were determined. A nonlinear regression analysis was used to obtain the best-fit values of the parameters. For this purpose, an optimization program based on Marquart's method combined with a Runge-Kutta method was used to solve the above set of equations (2.6-2.10). The model parameters were estimated by minimizing the following objective function:

$$\phi_{\min} = \sum_{i=1}^4 \sum_{1}^n (Y_{i\text{exp}} - Y_{i\text{mod}})^2 \quad (2.11)$$

Where $Y_{i\text{exp}}$ is the measured concentration of component i , $Y_{i\text{mod}}$ is the calculated concentration of component i and n is the number of samples. The kinetic parameters evaluated for 308, 318 and 328 K, are presented in Table 2.3.

Table 2.3: Homogeneous reaction rate constants

Temp., K	$k_3 \times 10^6$ $\text{m}^3 / \text{kmol} / \text{sec}$	$k_4 \times 10^6$ $\text{m}^3 / \text{kmol} / \text{sec}$
308	0.211	0.101
318	0.564	0.476
328	0.939	1.338

A comparison of the model predictions with experiments is shown in Figs. 2.3-2.5 for 308, 318 and 328 K respectively. It was found that the agreement of model predictions with experiments was very good with an average error of < 5%. The results for acetic acid and methanol with 1:1 and 1:4 molar ratios, at 318K are shown in Figs. 2.6 and 2.7 respectively. The effect of temperature on the rate constants is shown in Fig. 2.8 in form of Arrhenius plots and the activation energies for the homogeneous forward and backward reactions were evaluated to be 65.15 and 109.17 kJ/mol respectively.

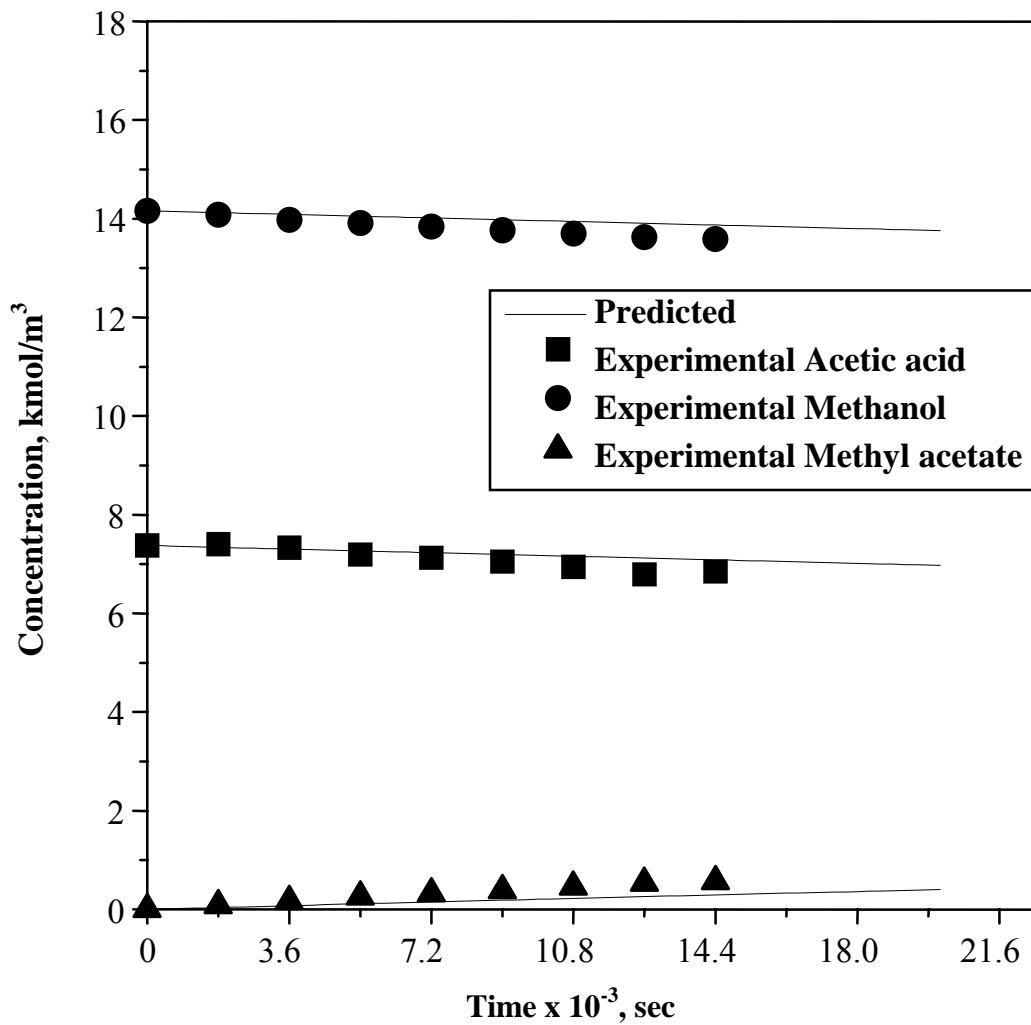


Fig. 2.3: Concentration-time profile at 308K for AcOH-MeOH molar ratio of 1:2

Reaction Conditions: $C_{A0} = 7.485 \text{ kmol/m}^3$, $C_{B0} = 14.011 \text{ kmol/m}^3$

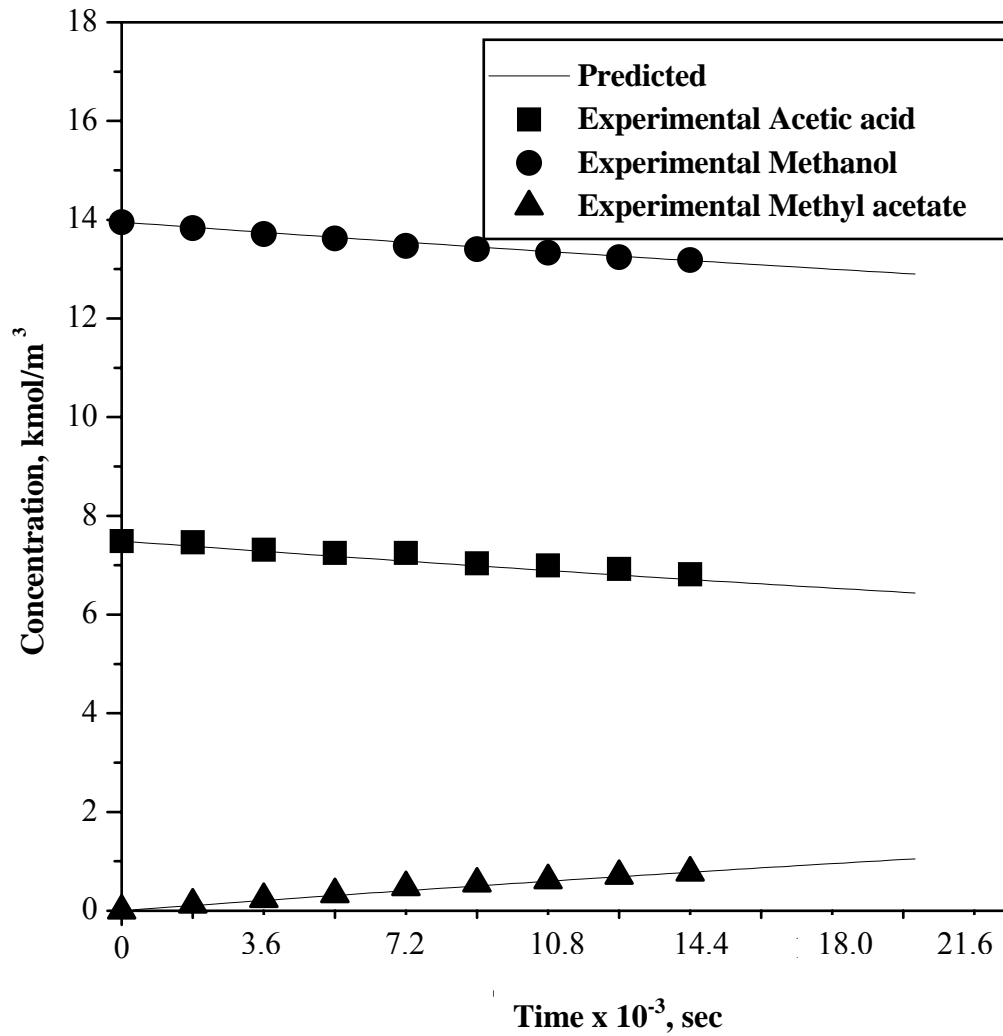


Fig. 2.4: Concentration-time profile at 318K for AcOH-MeOH molar ratio of 1:2
Reaction Conditions: $C_{A0} = 7.485 \text{ kmol/m}^3$, $C_{B0} = 14.011 \text{ kmol/m}^3$

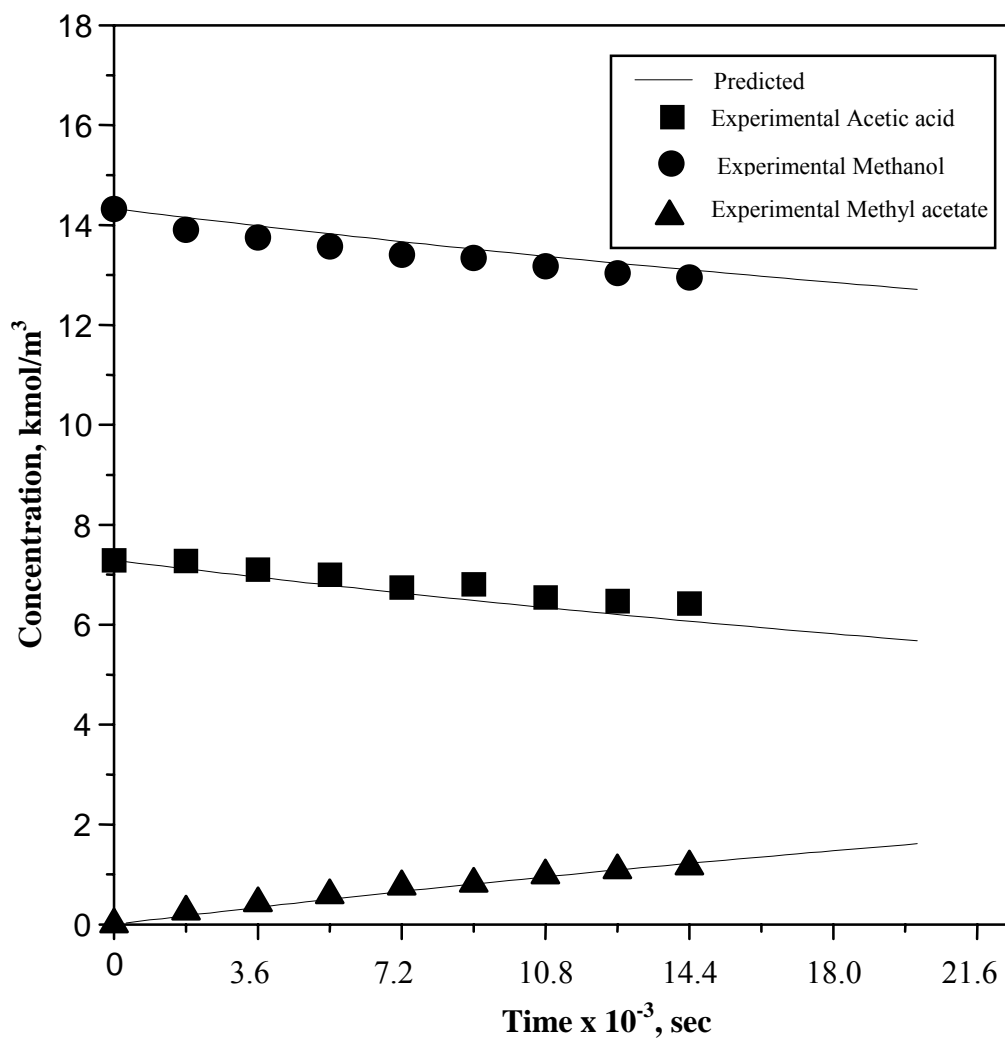


Fig. 2.5: Concentration-time profile at 328K for AcOH-MeOH molar ratio of 1:2
Reaction Conditions: $C_{A0} = 7.485 \text{ kmol/m}^3$, $C_{B0} = 14.011 \text{ kmol/m}^3$

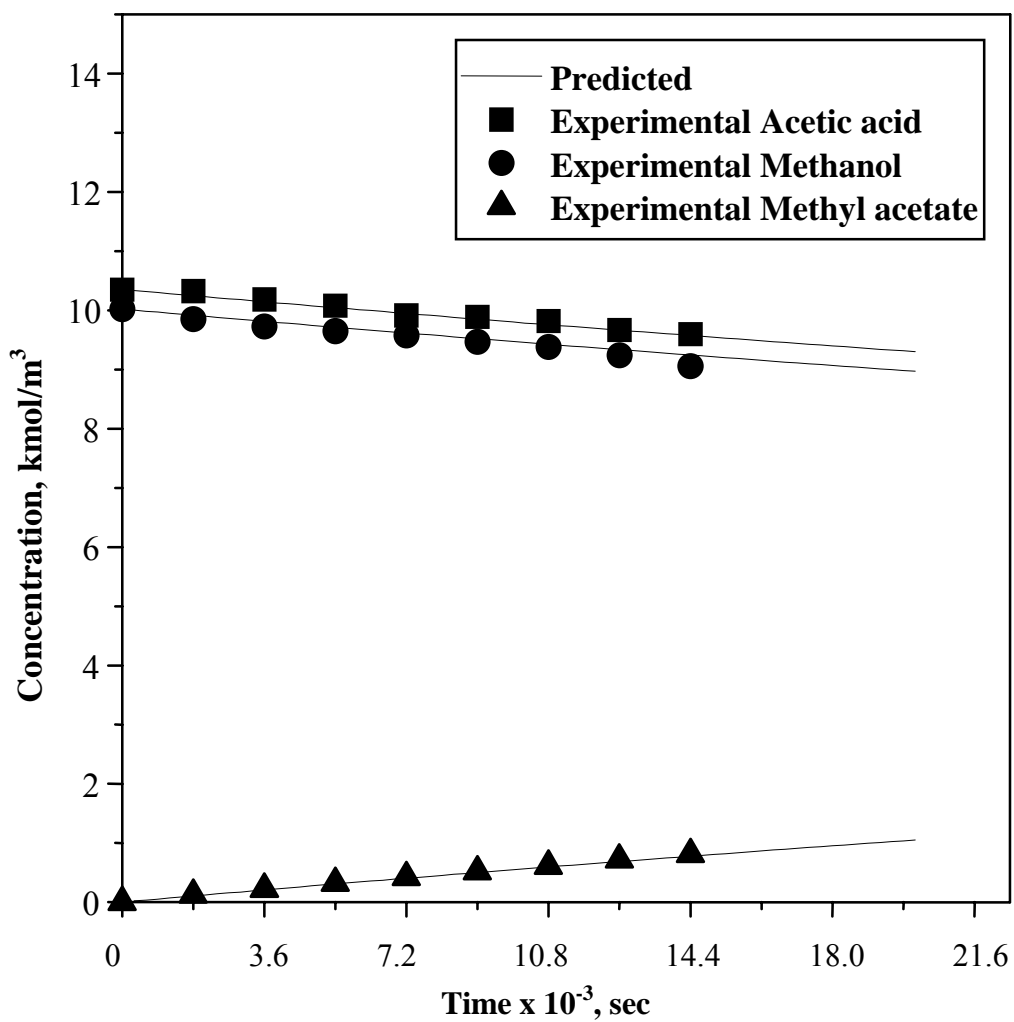


Fig. 2.6: Concentration-time profiles at 318 K for AcOH-MeOH molar ratio of 1:1
Reaction Conditions: $C_{A0} = 10.350 \text{ kmol/m}^3$, $C_{B0} = 10.020 \text{ kmol/m}^3$

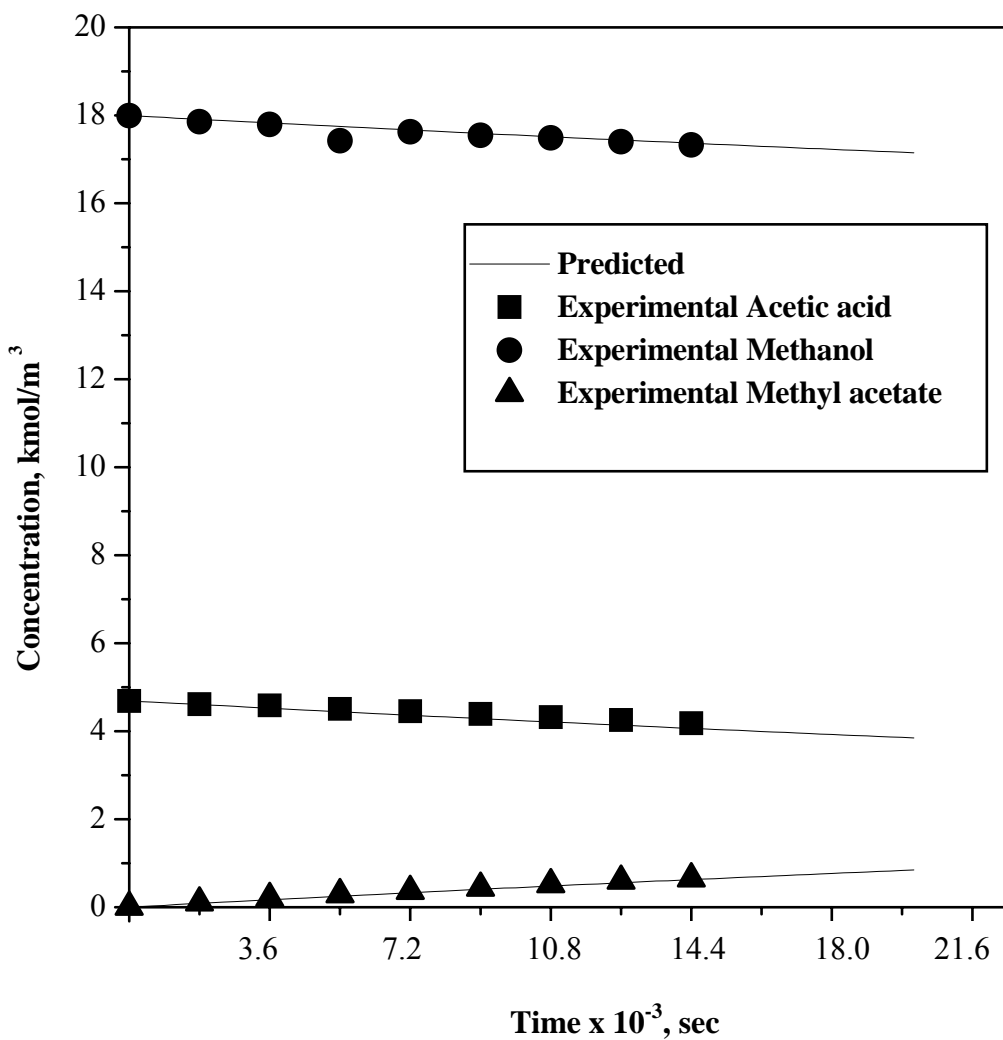


Fig. 2.7: Concentration-time profile at 318 K for AcOH: MeOH molar ratio of 1:4
Reaction Conditions: $C_{A0} = 4.707 \text{ kmol/m}^3$, $C_{B0} = 17.961 \text{ kmol/m}^3$

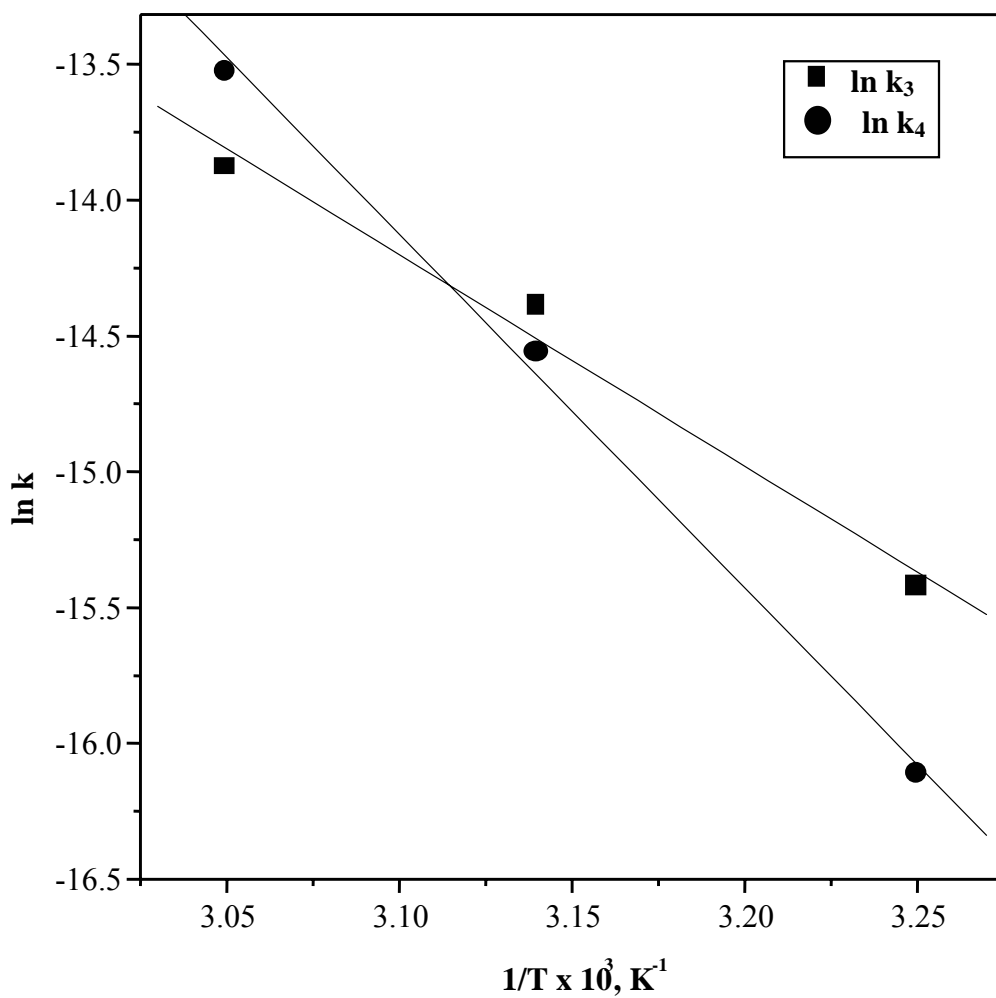


Fig. 2.8: Effect of temperature on homogeneous reaction rate constants

2.4.3 Kinetics of ion exchange resin catalyzed esterification

Esterification of acetic acid with methanol was studied using ion exchange resin catalyst. The effect of catalyst loading, initial concentrations of reactants, temperature, and particle size on the concentration-time profiles were studied. In each experiment, the concentration of reactants and products were recorded as a function of time.

2.4.3.1 Analysis of initial rate data

For calculating the rate of reaction at any given time, the concentration-time data observed under different conditions were fitted by a second-degree polynomial as:

$$C_i = a_1 + b_1t + c_1t^2 \quad (2.12)$$

Where C_i is the concentration of i^{th} component, kmol/m^3 ; t the time, sec and a_1 , b_1 , and c_1 are constants. These constants were evaluated by linear regression analysis for the different curves. The rate of reaction at any time can then be calculated as

$$r_i = - \frac{dC_i}{dt} = - b_1 - 2 c_1t \quad (2.13)$$

Initial rate of reaction r_{i0} can then be calculated by substituting $t = 0$ in the above equation as

$$r_{i0} = - \frac{dC_i}{dt} \Big|_{t=0} = - b_1 \quad (2.14)$$

The analysis of initial rate data is useful in understanding the dependence of the reaction rate on individual reaction parameters and also in the evaluation of mass transfer effects. The initial rates of the reaction were calculated from the concentration time data, based on consumption of acetic acid concentration in the reaction. The initial rate data for all the runs at different reaction conditions are presented in Table 2.4.

The effect of catalyst loading on the initial rate was found to be linear as shown in Fig. 2.9. It is interesting to note that the line-graph has a significant intercept on the Y-axis (corresponding to zero catalyst loading). This corresponds to the homogeneous rate of reaction. For the reaction conditions as shown, the rate was found to be 6.69×10^{-4}

kmol/m³/sec. The experimental reaction rate for homogeneous reaction under identical conditions was observed to be 6.81×10^{-4} kmol/m³/sec (Fig. 2.4), showing a good agreement.

The agitation speed also showed no influence on the initial rate in the range of 900-1200 rpm as shown in Fig. 2.10. This indicated that the external mass transfer resistance is negligible in this case.

The effect of methanol concentration on the initial rate of reaction showed that the rate decreases with increase in methanol concentration as shown in Fig 2.11. However, in these experiments, a change in methanol concentration resulted in a change in acetic acid concentration as the volume of liquid phase was kept constant. Since, the densities of methanol and acetic acid are different, a decrease in the molar concentration of acetic acid was more significant and not linearly proportional to increase in methanol concentration. Therefore, the rate was found to decrease as a result of changes in both methanol and acetic acid concentration (see data in Table 2.4).

In order to study the effect of particle size, the resin was sieved to obtain average particle sizes of 0.458, 0.7 and 1.0 mm diameters respectively. The effect of particle size on initial rate of reaction is shown in Fig. 2.12, indicates a decrease in the rate with increase in catalyst particle size. This clearly showed that intraparticle diffusion resistance was significant.

2.4.3.2 Analysis of mass transfer effects

A detailed analysis to check the role of external and intraparticle mass transfer is necessary before proceeding to evaluate kinetics. The quantitative criteria involve evaluation of factors, α_2 and ϕ_{exp} (experimental Thiele parameter), which are defined as the ratios of observed rates of esterification to the maximum rates of liquid-solid and intraparticle mass transfer respectively (Ramchandran and Chaudhari, 1983).

Table 2.4: Initial rata data for ion exchange resin catalyzed esterification of acetic acid with methanol

Temp. K	d_p $\times 10^3$, m	Catalyst loading, kg/m^3	Initial AcOH conc., kmol/m^3	Initial MeOH conc., kmol/m^3	Initial rate \times 10^4 , $\text{kmol/m}^3/\text{sec}$	α_2 $\times 10^6$	ϕ_{exp}
308	0.458	16.3	10.251	10.207	7.699	0.7985	0.229
	0.458	16.3	7.520	13.944	7.617	1.08	0.266
	0.458	16.3	4.690	17.993	5.033	1.14	0.274
	0.74	16.3	8.735	11.666	6.397	0.7787	0.346
	1.00	16.3	8.694	11.743	5.050	0.6175	0.308
318	0.458	16.3	10.350	10.020	10.5	1.08	0.262
	0.458	16.3	7.386	14.197	9.619	1.39	0.297
	0.458	16.3	4.707	17.961	6.559	1.48	0.307
	0.74	16.3	8.616	11.890	6.682	0.825	0.350
	1.00	16.3	8.413	12.271	5.785	0.731	0.329
328	0.458	16.3	10.274	10.163	10.9	1.13	0.264
	0.458	16.3	7.485	14.011	10.0	1.42	0.296
	0.458	16.3	4.711	17.953	7.370	1.66	0.320
	0.74	16.3	7.192	14.897	7.088	1.05	0.411
	1.00	16.3	7.097	14.689	6.009	0.900	0.571
	0.458	8.14	7.127	14.632	7.809	1.17	0.379
	0.458	32.08	7.315	14.279	14.0	2.04	0.252
	0.458	48.82	7.381	14.155	15.7	2.26	0.216

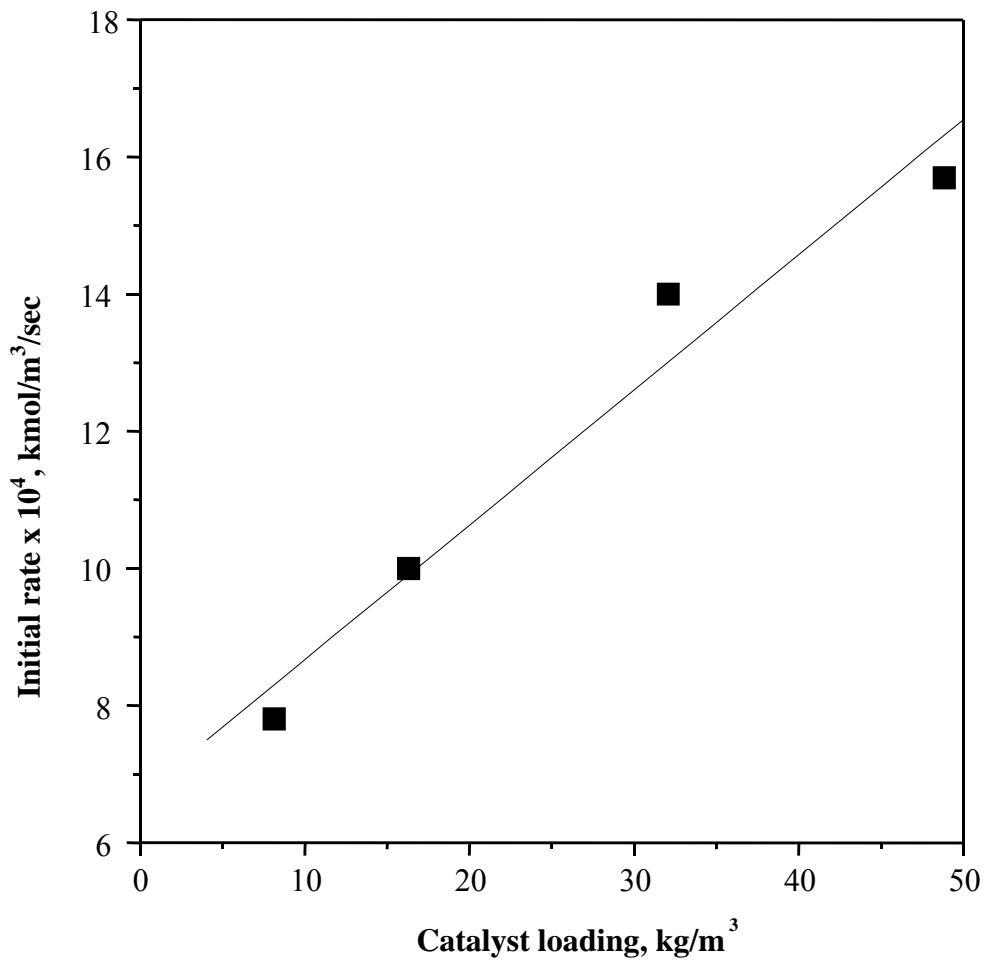


Fig. 2.9: Effect of catalyst loading on rate of reaction
Reaction Conditions: $C_{A0} = 7.485 \text{ kmol/m}^3$, $C_{B0} = 14.011 \text{ kmol/m}^3$,
Temp. = 318 K, $d_p = 4.58 \times 10^{-4} \text{ m}$

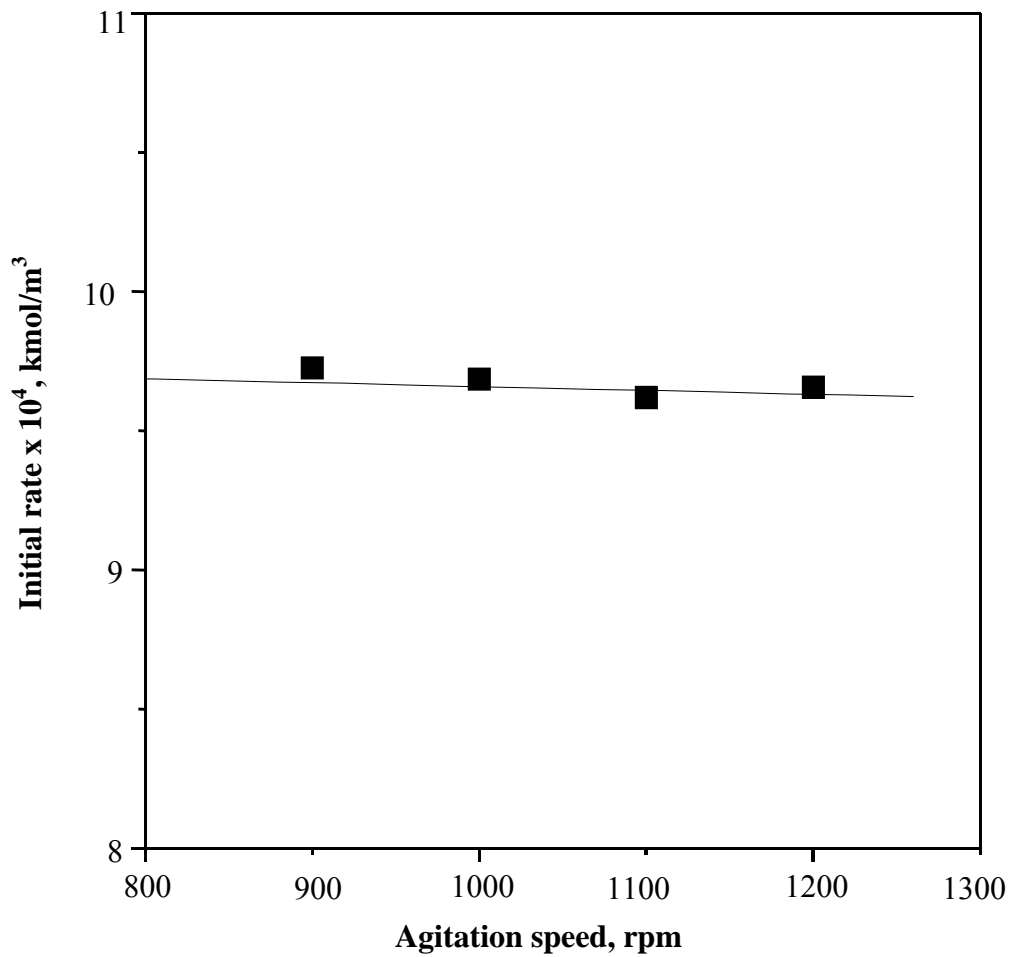


Fig. 2.10: Effect of agitation on rate of reaction at 318 K
Reaction conditions: $C_{A0} = 7.386 \text{ kmol/m}^3$, $C_{B0} = 14.197 \text{ kmol/m}^3$,
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$

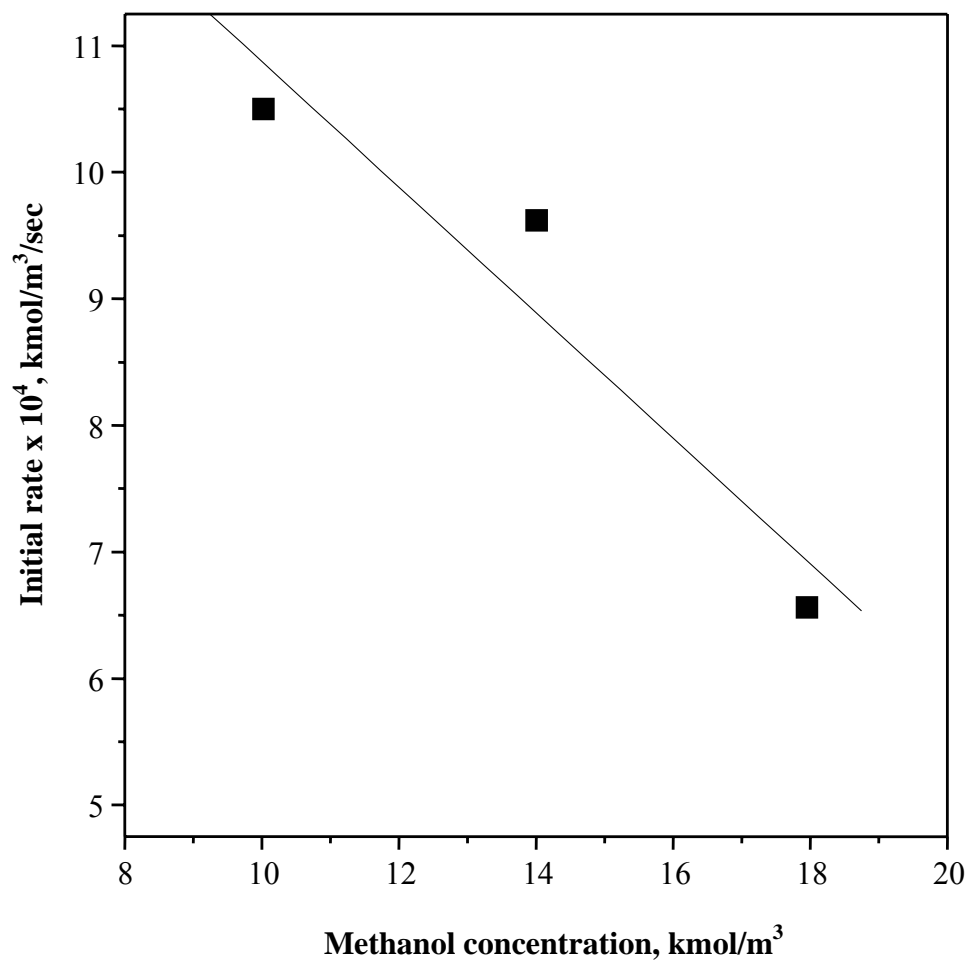


Fig. 2.11: Effect of methanol concentration on rate of reaction

Reaction conditions: Temp. = 318 K, $w = 16.3 \text{ kg/m}^3$,
 $d_p = 4.58 \times 10^{-4} \text{ m}$

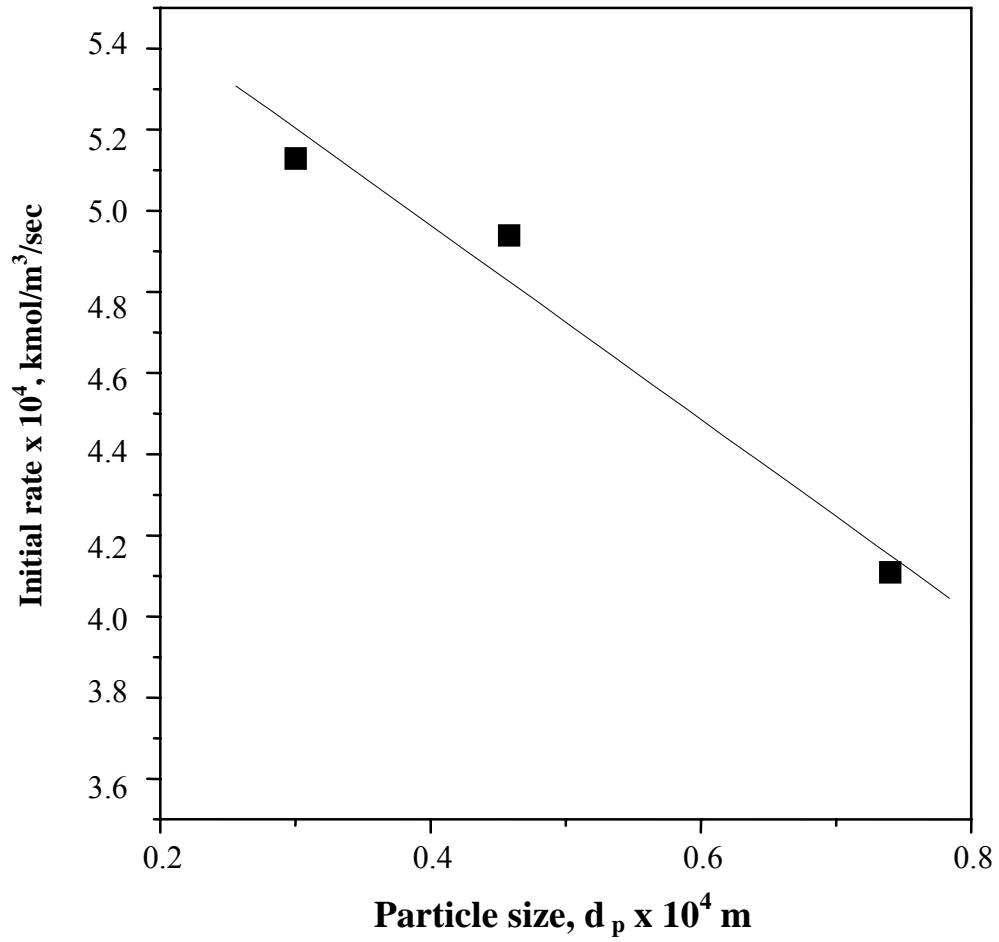


Fig. 2.12: Effect of particle size on rate of reaction
Reaction Conditions: Temp. = 318 K, Acetic acid: MeOH = 1:2,
 $w = 16.3 \text{ kg/m}^3$

Criteria for Liquid – Solid mass transfer resistance to be negligible

$$\alpha_2 = \frac{r_A}{k_s a_p C_i} < 0.1 \quad i = 1, 2 \quad (2.15)$$

Where, k_s is the liquid-solid mass transfer coefficient (m/sec); r_A is the initial rate (kmol/m³/sec); C_i is the initial concentration of reactant acetic acid (kmol/m³) and a_p is the effective liquid-solid interfacial area of catalyst particles per unit volume of slurry (m²/m³), given as,

$$a_p = \frac{6w}{\rho_p d_p} \quad (2.16)$$

In which, w is the catalyst loading (kg/m³), ρ_p is the particle density (kg/m³) and d_p is the particle diameter (m)

To evaluate α_2 , the knowledge of liquid–solid mass transfer coefficient, k_s , is essential, which was evaluated using the following correlation proposed by Sano et al. (1974)

$$\frac{k_s d_p}{DF_c} = 2 + 0.4 \left[\frac{e d_p^4 \rho_L^3}{\mu_L^3} \right]^{1/4} \left[\frac{\mu_L}{\rho_L D} \right]^{1/3} \quad (2.17)$$

Where, F_c is the shape factor assumed to be unity for spherical particles and e , the energy supplied to the liquid was calculated by the following correlation described by Calderbank (1958).

$$e = \frac{8 N^3 d_i^5 \psi}{d_T^2 L} \quad (2.18)$$

Here, N is the Speed of agitation of slurry (Hz); d_i is the diameter of impeller (m); d_T is the diameter of the slurry reactor (m); L is the total height of the slurry (m); ψ is the

correction factor for the presence of gas bubbles. In the present case since, there is no gas phase, so the factor ψ was assumed to be unity.

Criteria for intraparticle diffusion to be negligible

$$\phi_{\text{exp}} = \frac{d_p}{6} \left[\frac{r_A \rho_p}{w D_e [A_0]} \right]^{0.5} < 0.2 \quad (2.19)$$

d_p = particle size (m)

ρ_p = density of catalyst (kg/m³)

w = Catalyst Loading (kg/m³)

A_0 = initial concentration of acetic acid (kmol/m³)

D_e = effective diffusivity (m²/sec)

The effective diffusivity D_e was calculated as

$$D_e = D \varepsilon_p / \tau \quad (2.20)$$

Where, D is the molecular diffusivity calculated from Wilke-Chang equation (1955). ε_p is the porosity of catalyst and τ is the tortosity factor. For the present case the value of ε_p was taken as 0.5 and τ was taken as 2.4 (Satterfield, 1970). The diffusivity values calculated are presented in Table 2.5.

Table 2.5 Diffusivity of acetic acid in methanol

Temperature K	Molecular Diffusivity D x 10⁹, m²/s	Effective Diffusivity D_e x 10¹⁰, m²/s
308	3.369	7.018
318	3.478	7.246
328	3.587	7.474

The values of α_2 and ϕ_{exp} , as calculated above are also presented in Table 2.4. The α_2 values were in a range 1×10^{-4} to 8×10^{-5} indicating the absence of liquid-solid mass transfer resistance, for the range of operating conditions used in this work. The value of ϕ_{exp} varied between 0.2 to 0.6 indicating that the intraparticle diffusion is significant for

most of the experiments. Considering the significant contribution of intra particle diffusion, a rate model is necessary to account for it for the interpretation of experimental data.

2.5 Development of a rate model for a first order reversible reaction

Consider a first order reversible reaction with the following stoichiometry in the presence of a solid catalyst.



For isothermal conditions and absence of external (liquid-solid) mass transfer resistance the diffusion reaction model for reactions within the porous ion exchange catalyst particles can be written as (Ramachandran and Chaudhari, 1983)

$$\frac{D_{e1}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_1}{dr} \right) = \rho_p \Omega_1 \quad (2.22)$$

$$\frac{D_{e2}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_2}{dr} \right) = \rho_p \Omega_2 \quad (2.23)$$

$$\frac{D_{e3}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_3}{dr} \right) = - \rho_p \Omega_1 \quad (2.24)$$

$$\frac{D_{e4}}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_4}{dr} \right) = - \rho_p \Omega_1 \quad (2.25)$$

where, C_1, C_2, C_3 and C_4 are concentrations of A, B, C and D respectively in kmol/m^3 and $\Omega_1 = (k_1 C_1 C_2 - k_2 C_3 C_4)$ (2.26)

The boundary conditions are

$$\text{at } r = 0, \quad \frac{dC_1}{dr} = \frac{dC_2}{dr} = \frac{dC_3}{dr} = \frac{dC_4}{dr} = 0$$

$$\text{or } r = R, C_1 = C_{1,l}, C_2 = C_{2,l}, C_3 = C_{3,l} \text{ and } C_4 = C_{4,l} \quad (2.27)$$

From the above equations, we have:

$$D_{e1} \frac{d^2C_1}{dr^2} = D_{e2} \frac{d^2C_2}{dr^2} = D_{e3} \frac{d^2C_3}{dr^2} = D_{e4} \frac{d^2C_4}{dr^2} \quad (2.28)$$

Integrating the above equations and simplifying we get:

$$\begin{aligned} C_2 &= C_{2,l} - \frac{D_{e1}}{D_{e2}} (C_{1,l} - C_1) \\ C_3 &= C_{3,l} - \frac{D_{e1}}{D_{e3}} (C_1 - C_{1,l}) \\ C_4 &= C_{4,l} - \frac{D_{e1}}{D_{e4}} (C_1 - C_{1,l}) \end{aligned} \quad (2.29)$$

The overall rate of reaction of acetic acid (reactant A) can be described as

$$r_1 = \eta_c w \Omega_1 = \eta_c w k_1(C_1 C_2 - k_2' C_3 C_4) \quad (2.30)$$

with

$$k_2' = k_2/k_1$$

and

$$\eta_c = \frac{1}{\phi} \left[\coth \left(3\phi - \frac{1}{3\phi} \right) \right] \quad (2.31)$$

The solution of Φ , the Thiele parameter was obtained following the Bischoff's approximation (1965). Accordingly ϕ in this case is given by

$$\Phi = \frac{R}{3\phi} \rho_P (\Omega_1)_l \left[\int_0^{C_{1,l}} 2 D_e \rho_P \Omega_1 dC_1 \right]^{-1/2} \quad (2.32)$$

Therefore,

$$\Phi = \frac{R}{3} \rho_p k_1 [C_{1,1} C_{2,1} - C_{3,1} C_{4,1}] \left[\int_0^{C_{1,1}} 2 D_e \rho_p k_1 [C_1 C_2 - k' C_3 C_4] dC_1 \right]^{-1/2} \quad (2.33)$$

In order to integrate the above equation, C_2 , C_3 and C_4 have to be expressed in terms of C_1 . This can be done by using a set of equations 2.29. Integrating equation 2.33 and simplifying we get the expression for ϕ as

$$\Phi = \frac{R}{3} \left[\frac{\rho_p k_1 C_{2,1} \left(1 - k' \frac{C_{3,1} C_{4,1}}{C_{1,1} C_{2,1}} \right)}{D_e \left[\left(1 - \frac{D_{e1} C_{1,1}}{3 C_{2,1}} \right) + k' \left(\frac{D_{e1} C_{1,1}}{D_{e3} C_{2,1}} - \frac{2 D_{e1}^2 C_{1,1}}{3 D_{e3} D_{e4} C_{2,1}} - \frac{D_{e1} C_{3,1}}{D_{e4} C_{2,1}} - \frac{2 D_{e1} C_{4,1}}{D_{e3} C_{2,1}} - \frac{2 C_{3,1} C_{4,1}}{C_{1,1} C_{2,1}} \right) \right]} \right]^{-1/2} \quad (2.34)$$

2.6 Kinetic model for the heterogeneous reaction

In this case, the experiments were carried out using ion exchange resin catalyst in the same reactor following the procedures described for the homogeneous reaction. For interpretation of the kinetics, several experiments were carried out in which observed concentration time data were used over a range of condition given in Table 2.1. The concentration-time profiles for standard experimental conditions (acetic acid: methanol 1:2, particle size 4.58×10^{-4} m., catalyst loading 16.3 kg/m^3) at 308, 318 and 328 K are shown in Figs. 2.13 to 2.15 respectively.

For the present case the reaction rates will be the sum of homogeneous and heterogeneous reaction rates.

The forward reaction rate is,

$$r_3 = k_3 C_1 \cdot C_2 + w \eta_c k_1 C_1 \cdot C_2 \quad (2.35)$$

Reverse reaction rate is,

$$r_4 = k_4 C_3 \cdot C_4 + w \eta_c k_2 C_3 \cdot C_4 \quad (2.36)$$

Where, w is the weight of catalyst in kg/m^3

The batch reactor model at isothermal conditions for each species can now be written as

$$\frac{dC_1}{dt} = r_4 - r_3 \quad (2.37)$$

$$\frac{dC_2}{dt} = r_4 - r_3 \quad (2.38)$$

$$\frac{dC_3}{dt} = r_3 - r_4 \quad (2.39)$$

$$\frac{dC_4}{dt} = r_3 - r_4 \quad (2.40)$$

The initial conditions are,

$$\text{at } t=0, C_1=C_{A0}, C_2=C_{B0} \text{ and } C_3, C_4=0 \quad (2.41)$$

Here, C_{A0} and C_{B0} are the initial concentrations of acetic acid and methanol in kmol/m^3 respectively.

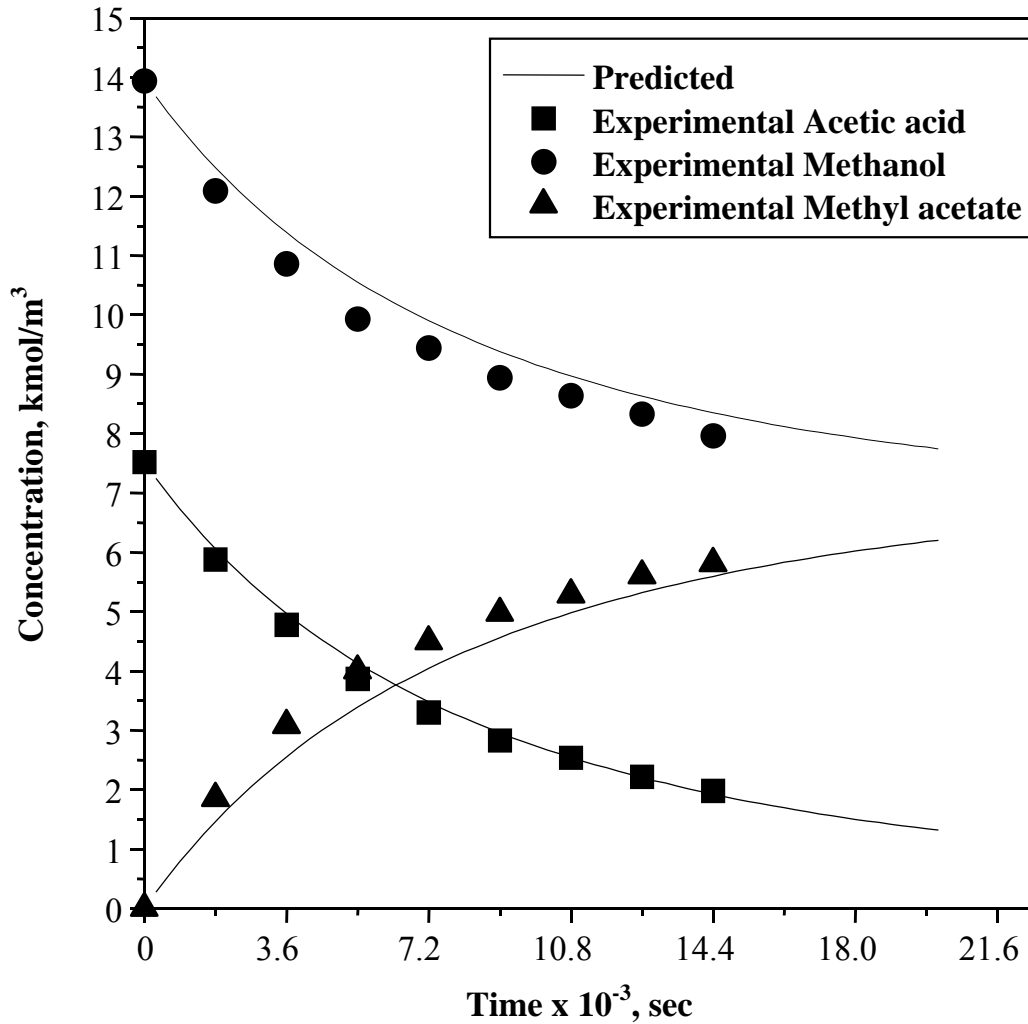


Fig. 2.13: Concentration-time profile at 308 K
Reaction Conditions: $C_{A0} = 7.520 \text{ kmol/m}^3$, $C_{B0} = 13.944 \text{ kmol/m}^3$,
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$

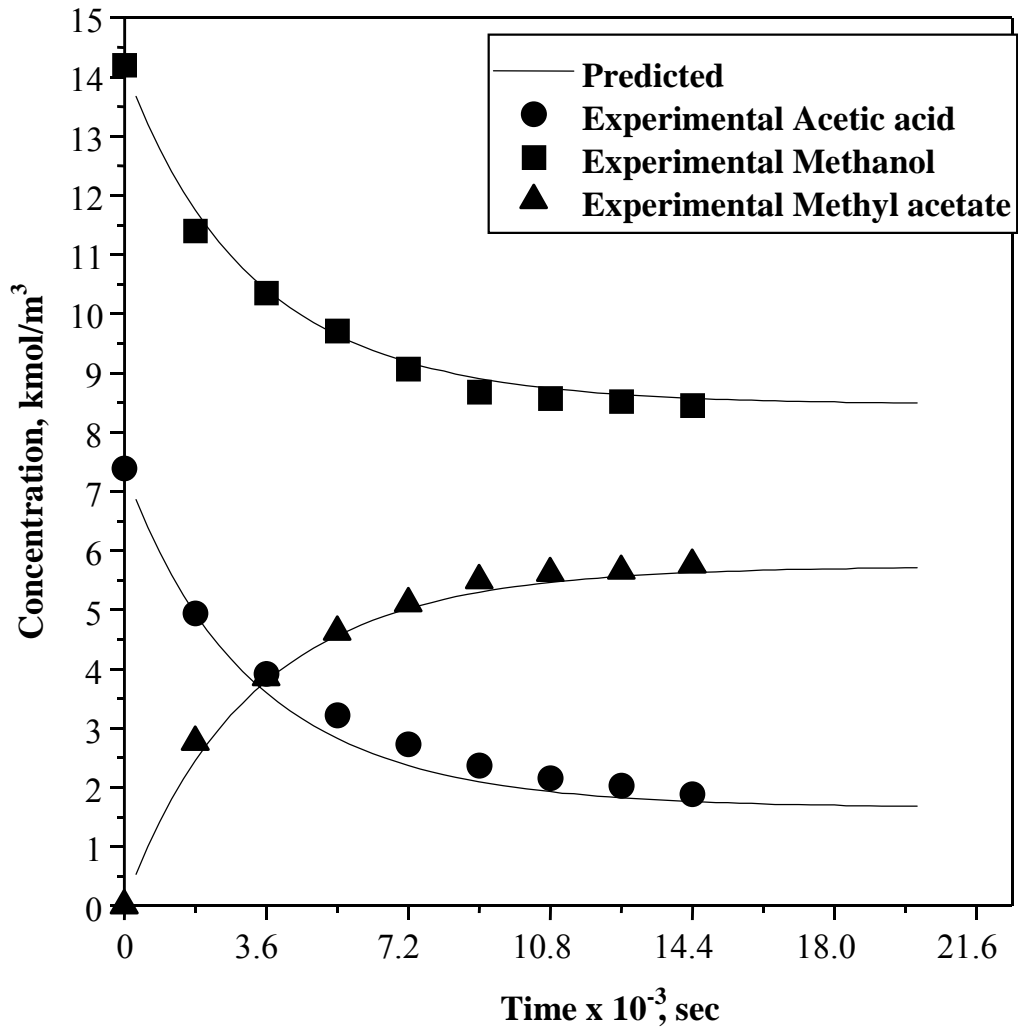


Fig. 2.14: Concentration-time profile at 318 K
Reaction conditions: $C_{A0} = 7.386 \text{ kmol/m}^3$, $C_{B0} = 14.197 \text{ kmol/m}^3$,
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$

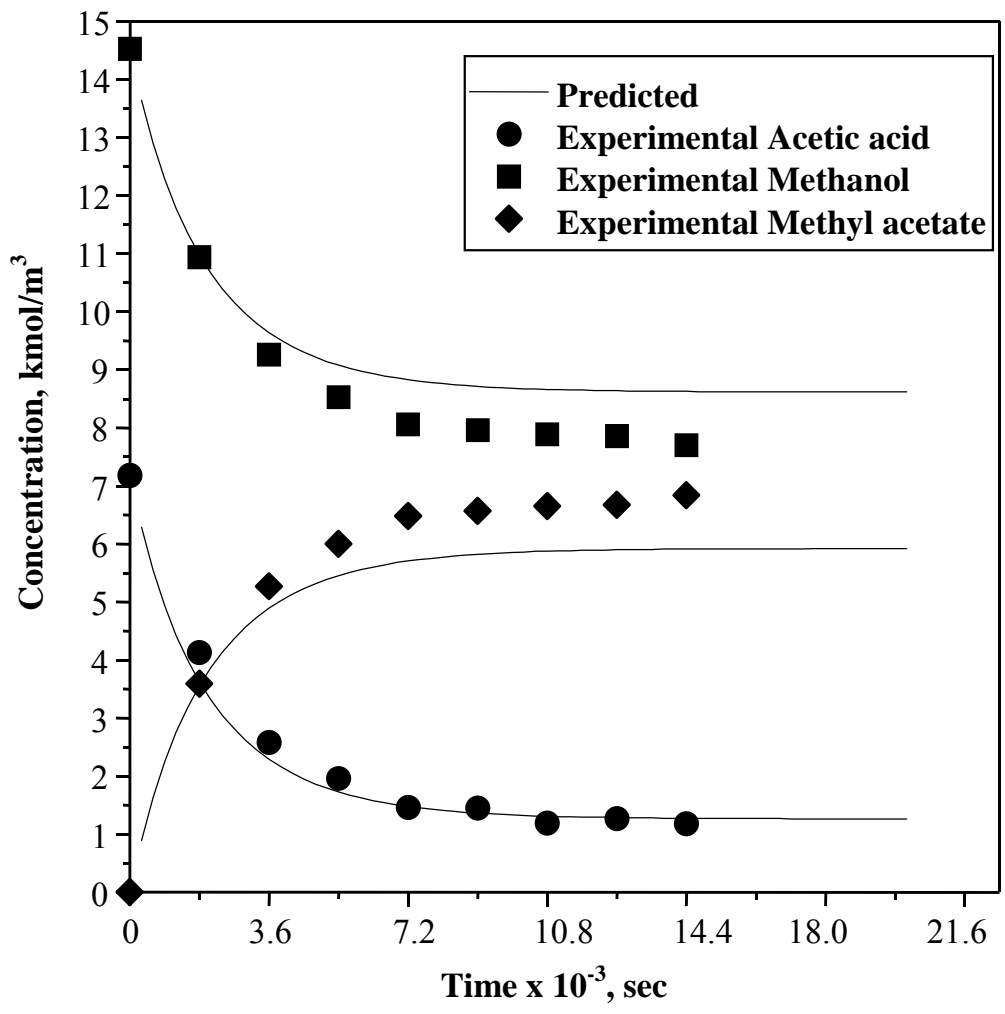


Fig. 2.15: Concentration-time profile at 328 K

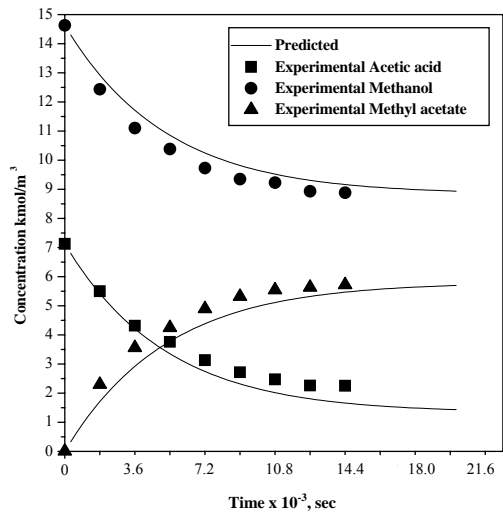
Reaction conditions: $C_{A0} = 7.485 \text{ kmol/m}^3$, $C_{B0} = 14.011 \text{ kmol/m}^3$,
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$

The approach followed to evaluate the kinetic parameters for the overall rate of reaction was the same as described earlier (Section 2.4.2) for the homogeneous reaction. A nonlinear regression analysis combined with a Runge-Kutta method was used to solve the equations 2.38 to 2.42 to obtain the best-fit values of the parameters. At each stage of integration the effectiveness factor η_c was calculated using equations 2.31 and 2.34. Only the parameters k_1 and k_2 in equations 2.36 and 2.37 were optimized. The homogeneous rate constants k_3 and k_4 determined earlier (Table 2.3) were used in these calculations. The optimized values of the heterogeneous reaction rate constants are presented in Table 2.6. From Figs. 2.13 to 2.15 it can be seen that the agreement between the model predictions and experimental observations is excellent.

Using these parameters the concentration-time profiles at different operating conditions were also predicted. For example, the effect of particle size on the concentration-time profile at acetic acid to methanol ratio 1:2 at temperature 308, 318 and 328 K are presented in Figs. 2.16 to 2.18 while the model predictions for the effect of temperature at acetic acid to methanol ratio 1:1 and 1:4 are shown in Figs. 2.19 and 2.20. Also the effect of catalyst loadings at 318 K is shown in Fig. 2.21. Again in all the cases the model predictions agree well with the experimental observations. The temperature dependence of the rate parameters k_3 and k_4 is shown in Fig. 2.22. From this, the value of activation energy for the forward and the reverse heterogeneous reaction were evaluated as 44.47 and 56.55 kJ/mol respectively.

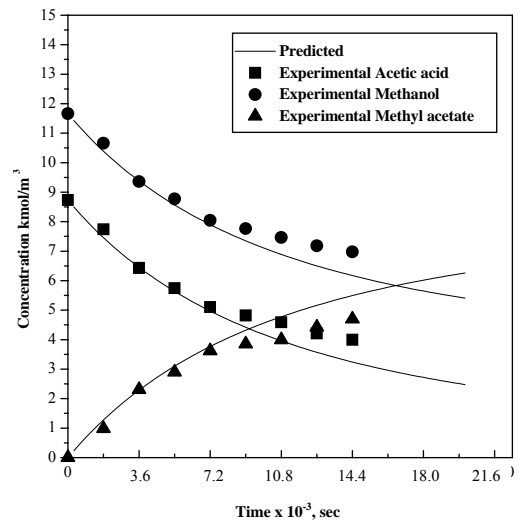
Table 2.6: Reaction rate constants for heterogeneous catalyzed esterification

Temp., K	$k_1 \times 10^6$ m ³ / kmol/sec. m ³ /kg	$k_2 \times 10^6$ m ³ / kmol/sec. m ³ /kg
308	0.649	0.135
318	1.051	0.341
328	1.877	0.518



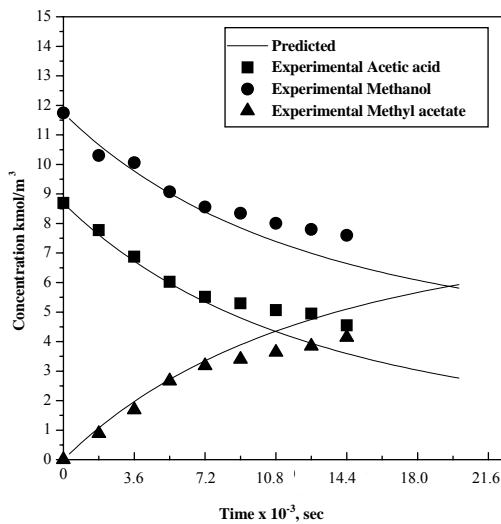
Reaction Condition:

$w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 7.52 \text{ kmol/m}^3$, $C_{B0} = 16.779 \text{ kmol/m}^3$



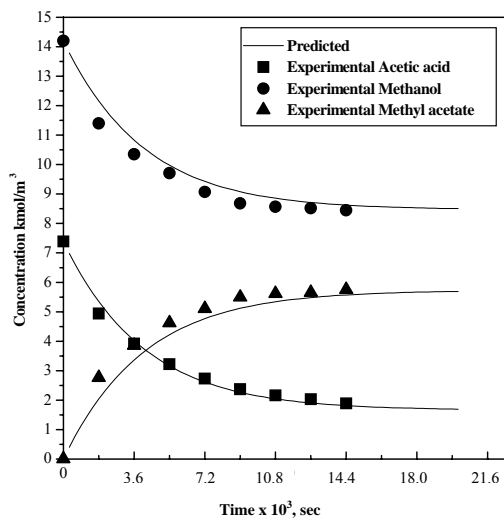
Reaction Condition:

$w = 16.3 \text{ kg/m}^3$, $d_p = 7.4 \times 10^{-4} \text{ m}$
 $C_{A0} = 8.735 \text{ kmol/m}^3$, $C_{B0} = 11.66 \text{ kmol/m}^3$



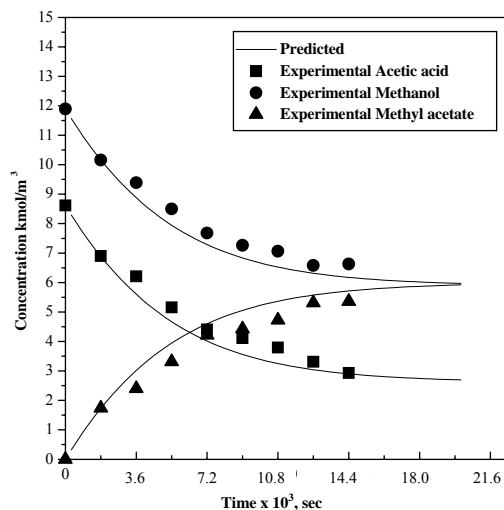
Reaction Condition: $w = 16.3 \text{ kg/m}^3$, $d_p = 1.0 \times 10^{-3} \text{ m}$
 $C_{A0} = 8.69 \text{ kmol/m}^3$, $C_{B0} = 11.74 \text{ kmol/m}^3$

Fig. 2.16: Concentration-time profiles for various particle sizes at 308 K



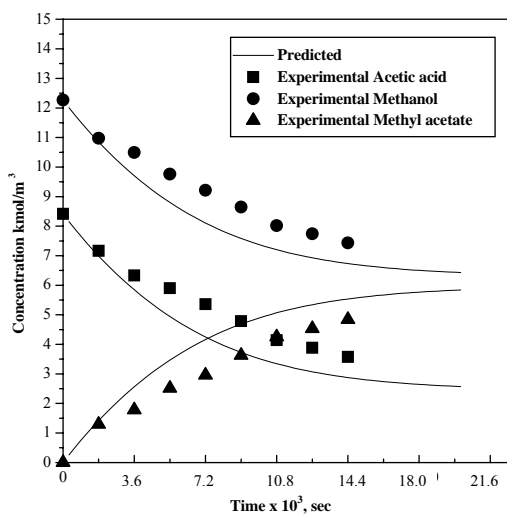
Reaction Condition:

$w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 7.386 \text{ kmol/m}^3$, $C_{B0} = 14.197 \text{ kmol/m}^3$



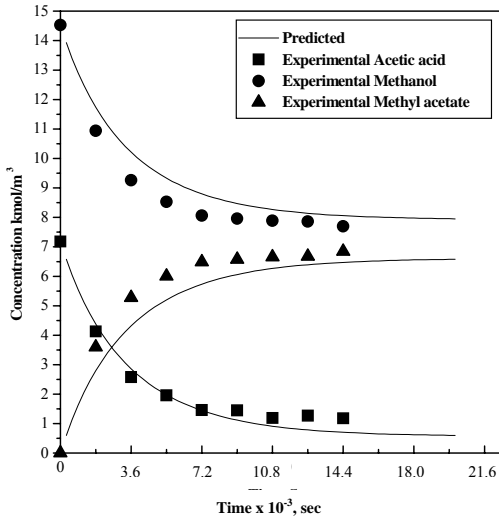
Reaction Condition:

$w = 16.3 \text{ kg/m}^3$, $d_p = 7.4 \times 10^{-4} \text{ m}$
 $C_{A0} = 8.616 \text{ kmol/m}^3$, $C_{B0} = 11.89 \text{ kmol/m}^3$



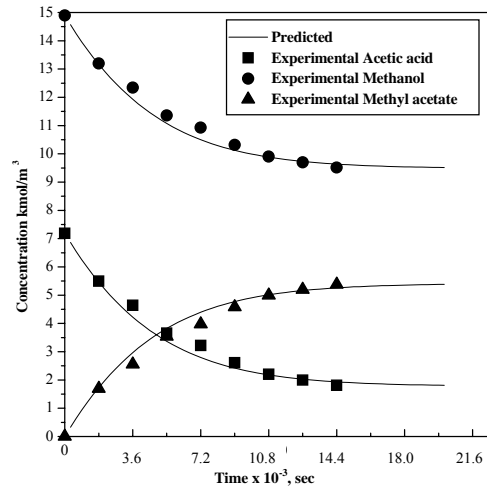
Reaction Condition: $w = 16.3 \text{ kg/m}^3$, $d_p = 1.0 \times 10^{-3} \text{ m}$
 $C_{A0} = 8.413 \text{ kmol/m}^3$, $C_{B0} = 12.27 \text{ kmol/m}^3$

Fig. 2.17: Concentration-time profiles for various particle sizes at 318 K



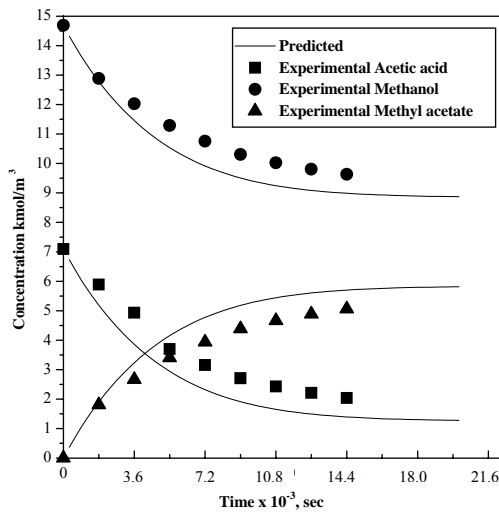
Reaction Condition:

$w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 7.185 \text{ kmol/m}^3$, $C_{B0} = 14.81 \text{ kmol/m}^3$



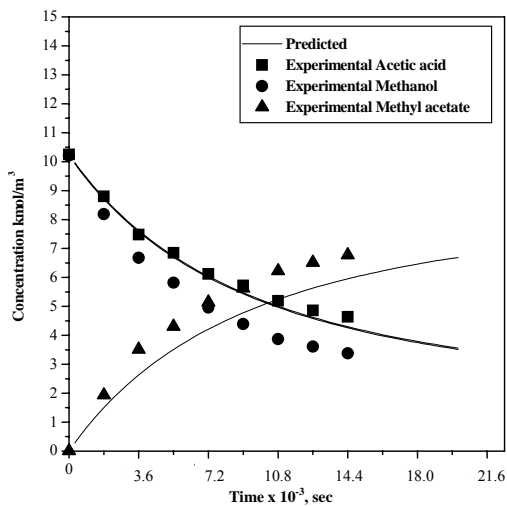
Reaction Condition:

$w = 16.3 \text{ kg/m}^3$, $d_p = 7.4 \times 10^{-4} \text{ m}$
 $C_{A0} = 7.19 \text{ kmol/m}^3$, $C_{B0} = 14.897 \text{ kmol/m}^3$

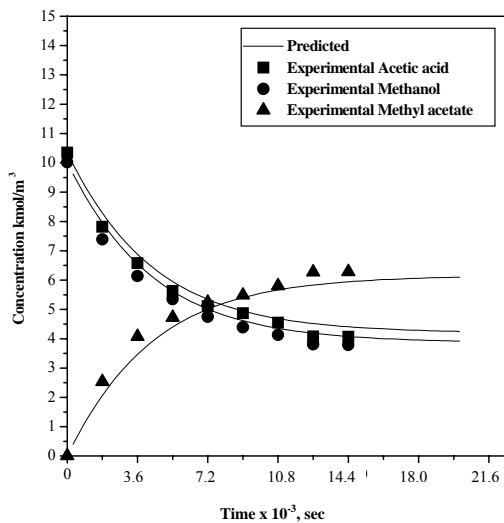


Reaction Condition: $w = 16.3 \text{ kg/m}^3$, $d_p = 1.0 \times 10^{-3} \text{ m}$
 $C_{A0} = 7.096 \text{ kmol/m}^3$, $C_{B0} = 14.689 \text{ kmol/m}^3$

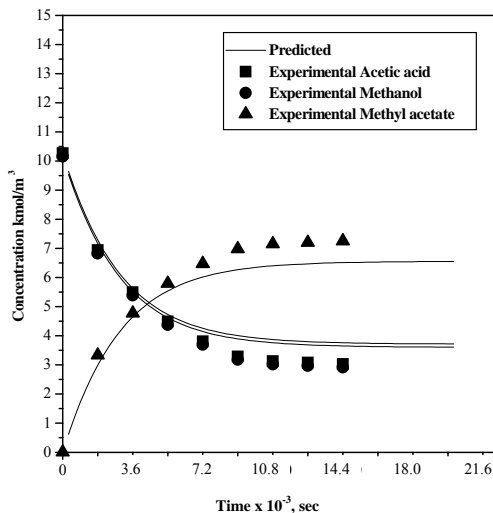
Fig. 2.18: Concentration-time profiles for various particle sizes at 328 K



Reaction Condition: $T = 308 \text{ K}$
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 10.25 \text{ kmol/m}^3$, $C_{B0} = 10.207 \text{ kmol/m}^3$

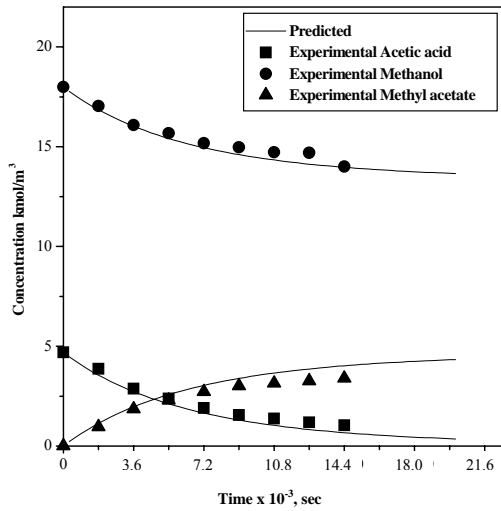


Reaction Condition: $T = 318 \text{ K}$
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 10.35 \text{ kmol/m}^3$, $C_{B0} = 10.02 \text{ kmol/m}^3$

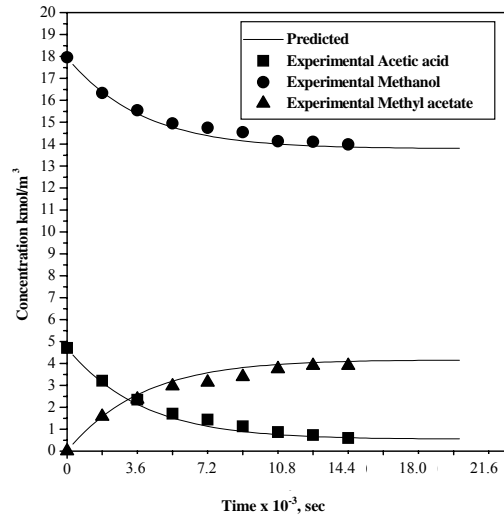


Reaction Condition: $T = 328 \text{ K}$, $w = 16.3 \text{ kg/m}^3$, $d_p = 1.0 \times 10^{-3} \text{ m}$
 $C_{A0} = 10.274 \text{ kmol/m}^3$, $C_{B0} = 10.163 \text{ kmol/m}^3$

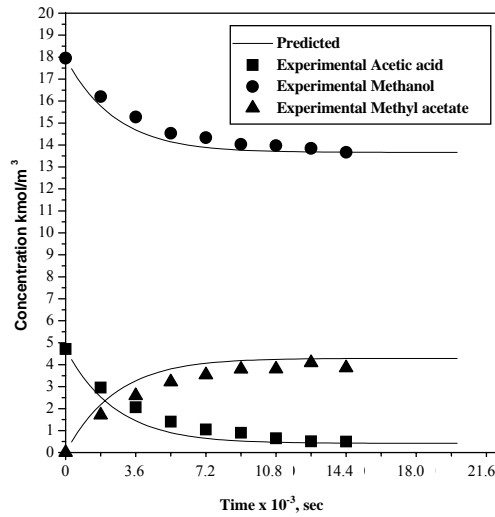
Fig. 2.19: Concentration-time profiles at various temperatures with acid-alcohol molar ratio of 1:1



Reaction Condition: $T = 308 \text{ K}$
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 4.69 \text{ kmol/m}^3$, $C_{B0} = 17.99 \text{ kmol/m}^3$

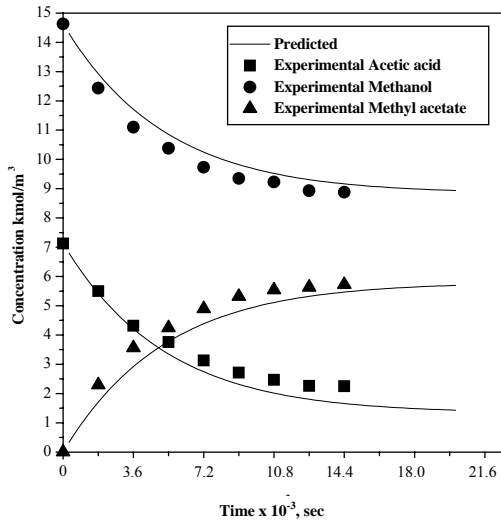


Reaction Condition: $T = 318 \text{ K}$
 $w = 16.3 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 4.707 \text{ kmol/m}^3$, $C_{B0} = 17.96 \text{ kmol/m}^3$



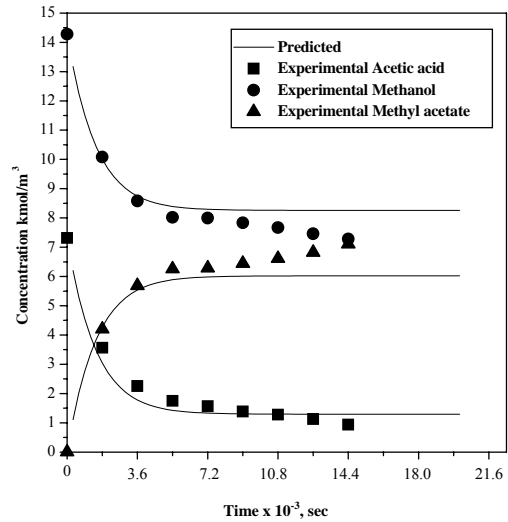
Reaction Condition: $T = 328 \text{ K}$, $w = 16.3 \text{ kg/m}^3$, $d_p = 1.0 \times 10^{-3} \text{ m}$
 $C_{A0} = 4.71 \text{ kmol/m}^3$, $C_{B0} = 17.95 \text{ kmol/m}^3$

Fig. 2.20: Concentration-time profiles at various temperatures with acid-alcohol molar ratio of 1:4



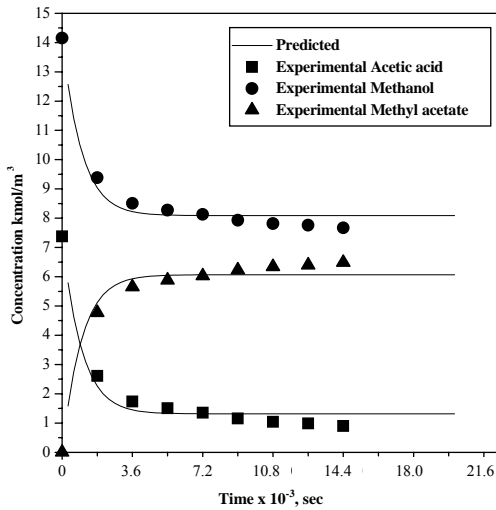
Reaction Condition:

$w = 8.14 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 7.127 \text{ kmol/m}^3$, $C_{B0} = 14.632 \text{ kmol/m}^3$



Reaction Condition:

$w = 32.8 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$, $C_{A0} = 7.315 \text{ kmol/m}^3$
 $C_{B0} = 14.27 \text{ kmol/m}^3$



Reaction Condition: $w = 48.82 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$
 $C_{A0} = 7.38 \text{ kmol/m}^3$, $C_{B0} = 14.155 \text{ kmol/m}^3$

Fig. 2.21: Concentration-time profiles at various catalyst loadings at 318 K

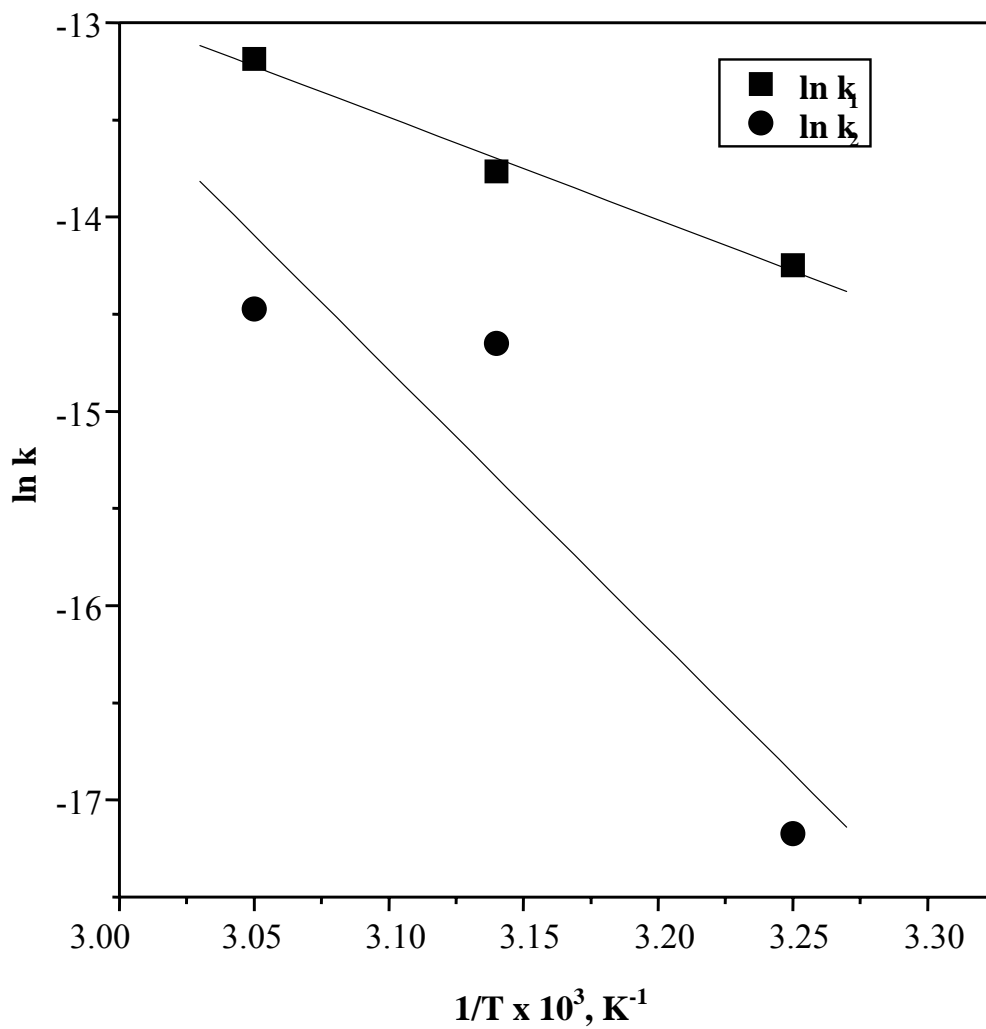


Fig. 2.22: Effect of temperature on heterogeneous catalyzed reaction rate constants

2.7 Conclusions

A detailed study on the ion exchange resin (Dowex 50W) catalyzed esterification of acetic acid with methanol in a batch slurry reactor was undertaken. Since, esterification can also take place in the homogeneous phase, the kinetics of homogeneous non-catalytic esterification was investigated separately to assess its contribution. The effect of temperature, methanol concentration, catalyst loading and particle size on the overall rate of reaction as well as concentration-time profiles were investigated. The initial rate data were mainly used to determine significance of mass transfer. While, liquid-solid mass transfer resistance was negligible, the intraparticle diffusion effects were significant for higher catalyst particle size ($d_p > 0.5$, mm). For interpretation of the kinetics, the observed concentration-time data were used and the rate parameters evaluated at each temperature using a batch reactor model. The activation energies for homogeneous forward and backward reactions were evaluated as 115.18 and 43.82 kJ/mol, and for the heterogeneous forward and backward reactions were evaluated as 38.69 and 46.27 kJ/mol. The experimental data agreed very well with model predictions for the entire range of conditions studied.

Notations

a_p	effective liquid-solid interfacial area per unit volume of slurry, m^2/m^3 .
C_1	concentrations of acetic acid, $kmol/m^3$
C_2	concentrations of methanol, $kmol/m^3$
C_3	concentrations of methyl acetate, $kmol/m^3$
C_4	concentration of water, $kmol/m^3$
C_{A0} ,	concentrations of acetic acid at $t = 0$, $kmol/m^3$
C_{B0} ,	concentrations of methanol at $t = 0$, $kmol/m^3$
C_i	concentration of i^{th} component, $kmol/m^3$
D_e	effective diffusivity, m^2/sec
D	molecular diffusivity, m^2/sec
d_l	impeller diameter, m
d_p	catalyst particle diameter, m
d_T	diameter of tank, m

e	energy supplied to the liquid
F_c	shape factor, assumed to be unity for spherical particles.
g	acceleration due to gravity, cm/s^2
k_1	rate constant for the heterogeneous forward reaction, $\text{m}^3/\text{kmol}\cdot\text{s}$. m^3/kg
k_2	rate constant for the heterogeneous backward reaction, $\text{m}^3/\text{kmol}\cdot\text{s}$. m^3/kg
k_3	rate constant for the homogeneous forward reaction, $\text{m}^3/\text{kmol}\cdot\text{s}$
k_4	rate constant for the homogeneous backward reaction, $\text{m}^3/\text{kmol}\cdot\text{s}$
k_s	liquid-solid mass transfer coefficient, m/s .
L	total height of the slurry, meter.
N_m	speed of agitation, Hz
r_1	forward reaction rate, $\text{kmol}/\text{m}^3\cdot\text{s}$
r_2	backward reaction rate, $\text{kmol}/\text{m}^3\cdot\text{s}$
r_{i0}	initial rate of reaction
r_i	rate of reaction at any time
r_A	initial rate, $\text{kmol}/\text{m}^3\cdot\text{sec}$
w	catalyst loading, kg/m^3

<i>Greek</i>	α_2	parameter defined in equation 2.15
	η_c	catalytic effectiveness factor
	ε_p	porosity of catalyst
	ϕ	Thiele modulus given in equation 2.34.
	μ_l	Viscosity of liquids, $\text{gm}/\text{cm}\cdot\text{s}$
	τ	tortuosity factor
	ρ_l	density of liquids, gm/cm^3
	ρ_p	density of catalyst, gm/cm^3
	ψ	correction factor for the presence of gas bubbles

2.8 References

Agreda V. H. and Partin L. R., *US* 4,435,595 (1984)

Agreda V. H., Partin L. R. and William H. H., *Chem. Eng. Prog.* 86(2), 40-46 (1990)

Bischoff K. B., *AIChEJ.*, 11, 351 (1965)

Calderbank P. H., *Trans. Inst. Chem. Eng.*, 36, 443 (1958)

Carrigan T. E. and Ferris W. R., *The Can. J. Chem. Eng.*, 47, (1969)

Helfferich F., "Ion Exchange", *McGraw-Hill*, New York, (1962)

Neumann R. and Sasson Y., *Ind. Eng. Chem. Process Des. Dev.*, 23, 654-659 (1994)

Popken T., Gotze L. and Gmehling J., *Chem. Eng. Sci.* 39, 2601-2611 (2000)

Ronnback R., Salmi T., Vuori A., Haario H., Lehtonen J., Sundqvist A. and Tirronen E., *Chem. Eng. Sci.*, 52(19), 3369-3381,(1997)

Ramchandran P. and Chaudhari R. V., "Three Phase Catalytic Reactors", *Garden branch science publishers*, New York, (1983)

Robels-Dutenhefner ; *J. Mol.Catal.*, A, 164, 39-47, (2000)

Sano Y., Yamaguchi N. and Adachi T., *J. Chem. Eng. Japan.*, 1, 255 (1974)

Satterfield C., "Mass transfer in Heterogeneous Catalysis", *MIT Press*, Cambridge (1970)

Wilke C. R. and Chang P., *AIChE J.*, 1, 264 (1955)

Xu Z.P. and Chuang K.T., *Can. J. Chem.Eng.*, 74, 493-500, (1996)

Xu Z.P. and Chuang K.T., *Chem. Eng. Sci.*, 52(17), 3011-3017,(1997)

Zewtering T. N., *Chem. Eng. Sci.*, 8, 244 (1958)

3.1 Introduction

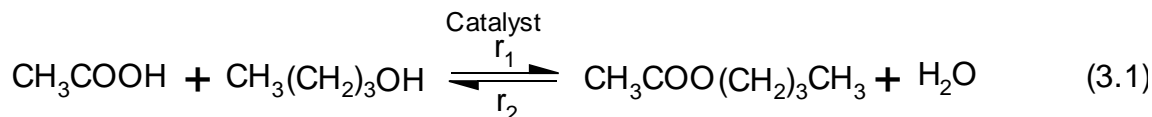
Butyl acetate is synthesized from acetic acid and butanol in the presence of an acid catalyst either homogeneous or heterogeneous. Like all other esterification reactions, this is also a reversible equilibrium driven one, which can be guided to completion by the azeotropic removal of one of the product components, mainly water. Butyl acetates are used primarily as solvents in the lacquer and enamel industries. It is used in coatings, where its solvent capacity and its low relative volatility make it useful for adjustment of evaporation rate and viscosity. It is particularly useful as a solvent or thinner for acrylic polymers, vinyl resins, as reaction medium for adhesives, as solvent for leather dressings, and a process solvent in various applications and in cosmetic formulations (Wilhelm (1999)).

A detailed literature review on this system is presented in Chapter-1. Literature survey shows that both homogeneous and heterogeneous catalysts have been used for this reaction. Leyes and Othmer (1945) reported studies on the kinetics of the reaction of butanol and acetic acid catalyzed by sulfuric acid, coupled with vapor-liquid equilibrium data for the design of a reactive distillation unit. Bianchi et. al. (2003) investigated the recovery of very low concentration of acetic acid (6 % w/w) by reacting it with n-butyl or 2-ethyl-1-hexyl alcohol in the presence of sulphuric acid as a homogeneous catalyst and Amberlist 200, Amberlist 15, Amberlist IR 120, Nafion NR50 and sulphated zirconia as heterogeneous catalysts. Gangadwala et. al. (2003) had reported the esterification of acetic acid with n-butanol in the presence of ion exchange resin Amberlyst-15 as a catalyst. They developed Eley-Rideal and Langmuir-Hinshelwood-Hougen-Watson models to represent and interpret the intrinsic kinetics of the reaction. The kinetics of homogeneous and ion exchange resin (IR-120) catalyzed esterification of acetic acid with butanol was studied by Altiokka and Citak (2003). The uncatalyzed reaction follows a simple second-order reversible reaction model. As reported, in the presence of resin catalyst, the activation energy reduced from 59.3 to 49 k J/mol.

From the literature survey it was observed that the reaction has been studied using various ion exchange resins or homogeneous catalysis by strong acids, however, detailed studies on intrinsic kinetics of the reaction are very limited. Also, kinetics of homogeneous-heterogeneous esterification has not been considered. Hence, the present

work was undertaken with the objective of studying the intrinsic kinetics of esterification of acetic acid with butanol. Theoretical models have been developed for overall rate of esterification incorporating mass transfer effects for the homogeneous-heterogeneous reaction.

The stoichiometric reaction involving esterification of acetic acid with butanol is given below:



Since, esterification reaction can also occur in the homogeneous phase (without catalyst), experimental studies on homogeneous reaction were carried out over temperature range of 343-363 K. The kinetics of homogeneous reaction was then used along with the heterogeneous reaction data to obtain the overall reaction kinetics. For the heterogeneous catalytic esterification reaction, the effect of various reaction parameters such as temperature, catalyst loading and reactant concentration on the concentration-time profile was also studied in a temperature range of 343-363 K. These data were used to develop the intrinsic kinetics of homogeneous and heterogeneous reactions. A rate model has been developed incorporating the effect of intraparticle diffusion for [1,1] order reversible reaction. The model predictions for different operating conditions are compared with experimental data.

3.2 Experimental

3.2.1 Materials

Butanol and acetic acid used in the study were A.R. grade (99.8%) and were obtained from S.D. Fine Chemicals, India. Purity was verified by gas chromatography, and were used without further purification.

3.2.2 Catalyst

The cation exchange resin Dowex 50 W (Dow Chemical Co.) used as the catalyst was procured from Vijay Chemicals, India. Before the use of the catalyst for experiments, the resin was pretreated using standard procedures described previously in Section 2.2.2

3.3 Analytical procedure

The analysis of the reactants and products of esterification reaction of acetic acid and butanol was carried out using gas chromatography. The gas chromatograph used for analysis was a Hewlett-Packard, model no. HP 5890. A FFAP column was used for separating the components from the reaction mixture. The conditions of Gas Chromatographic analysis were:

Column temperature:	80-200°C (Programmed at 20°C /min)
Injector temperature:	250°C
Detector (FID):	250°C
Carrier gas (He) flow:	35 ml/ min

This recorded the concentration change of all the species from time to time. It may be noted that one of the products formed in esterification of butanol is water, and since FID was used for analyzing the components, the analysis of water had not been possible to be carried out in this work.

3.4 Kinetics of esterification of acetic acid and butanol

3.4.1 Preliminary experiments

The experiments were carried out using the same procedure as described in Chapter-2 (Section 2.4.1) Some preliminary experiments were carried out to select a range of reaction conditions suitable for studying the reaction kinetics and establish the product distribution, material balance etc. The range of operating conditions under which the present study was carried out is given in Table 3.1

Table 3.1: Range of operating conditions

Reaction temperature, K	343, 353 and 363
Agitation speed, rpm	800 - 1200
Catalyst loading, kg/m ³	10.90, 21.81 and 32.72
Acetic acid: Butanol ratio	1:1, 1:2 and 1:4
Particle sizes, mm	0.327, 0.50 and 0.74

Initial experimental data on concentration-time profiles (Figs. 3.1-3.3) showed that the material balance of the reactants consumed and the products formed were consistent (>95%) at all stages of conversion according to the stoichiometry given by equation 3.1.

3.4.2 Kinetics of homogeneous reaction

For kinetic study of the homogeneous esterification reaction (without ion exchange resin catalyst) experiments were carried out at 343, 353 and 363 K with mole ratio of acetic acid and butanol as 1:1, 1:2 and 1:4 respectively, at agitation speed of 1000 rpm. In each experiment the variation of concentration of reactants and products were recorded as a function of time.

The following forms of rate equations were proposed.

$$r_1 = k_3 C_1 C_2 \quad (3.2)$$

$$r_2 = k_4 C_3 C_4 \quad (3.3)$$

Where, r_1 and r_2 are forward and backward reaction rates respectively, kmol/m³/s, and C_1 , C_2 , C_3 and C_4 are concentrations of acetic acid, butanol, butyl acetate and water respectively, kmol/m³.

In order to evaluate rate parameters in the kinetic model, the observed concentration-time data were simulated by a trial and error method. The simulation model for the batch reaction under isothermal conditions can be written as

$$\frac{dC_1}{dt} = r_2 - r_1 \quad (3.4)$$

$$\frac{dC_2}{dt} = r_2 - r_1 \quad (3.5)$$

The initial conditions are, at $t=0$; $C_1=C_{A0}$, $C_2=C_{B0}$ and $C_3, C_4=0$ (3.8)

(C_{A0} and C_{B0} are the initial concentrations of acetic acid and butanol)

An identical procedure, as described in Chapter-2 (Section 2.4.2) was followed, to

$$\frac{dC_3}{dt} = r_1 - r_2 \quad (3.6)$$

$$\frac{dC_4}{dt} = r_1 - r_2 \quad (3.7)$$

evaluate the kinetic parameters, by substitution of equations 3.5-3.8. These kinetic parameters were evaluated for standard experimental conditions (Acid: Alcohol 1:2) at 343, 353 and 363K, and are presented in Table 3.2.

Table 3.2: Homogeneous reaction rate constants

Temp, K	$k_3 \times 10^6, \text{m}^3/\text{kmol}/\text{sec}$	$k_4 \times 10^5, \text{m}^3/\text{kmol}/\text{sec}$
343	0.59	0.624
353	1.16	0.818
363	1.80	1.500

The model predictions for these experiments are shown in Fig. 3.1-3.3. It can be seen that the agreement for model prediction was very good. The average error was found to be $< 5\%$. These rate constants as determined were also used to predict the concentration time profiles for 1:1 and 1:4 mole ratio of acetic acid and butanol at 353K, and are presented in Fig. 3.4 and 3.5 respectively. Again the agreement was found to be very good. The effect of temperature on the homogeneous rate constants is shown in Fig. 3.6 as Arrhenius plots and the activation energies for homogeneous forward and backward reactions were evaluated as 57.82 and 43.82 kJ/mol respectively.

3.4.3 Kinetics of ion exchange resin catalyzed esterification

The overall rate of reaction (with catalyst) was studied using ion exchange resin as catalyst. The effect of different parameters such as catalyst loading, initial concentration of reactants, temperature and particle size was studied. In each experiment the

concentration of reactant and products were recorded as a function of time. A typical concentration-time profile at 353 K is shown in Fig. 3.11.

3.4.3.1 Analysis of initial rate data

The initial rates of the reaction were calculated from the concentration-time data, based on acetic acid consumption during the reaction, following the procedure described in section 2.4.3.1. The initial rate data for all the runs at different reaction conditions are presented in Table 3.3.

The effect of catalyst loading on the initial rate was found to be linear (Fig. 3.7). For this case also, this curve had a significant intercept at the y-axis, which can be attributed to the homogeneous rate of reaction. From this figure the homogeneous rate of reaction was evaluated to be 1.597×10^{-5} kmol/m³/s. This was in reasonable agreement with the actual experimental rate of the homogeneous reaction of 1.019×10^{-5} kmol/m³/s. The agitation speed also showed no influence on the initial rate in the range of 900-1200 rpm, This indicates that the external mass transfer resistance is negligible in this range.

The effect of butanol concentration on the initial rate of reaction showed that the initial rate decreases with increase in the concentration of butanol, as shown in Fig. 3.8. This is due to the fact that an increase in butanol concentration decreases the concentration of acetic acid, since the total volume of the reactants was kept constant (120 cm³, see also Section 2.4.3.1).

In order to study the effect of particle size, the resin was sieved to obtain average particle sizes of 0.327, 0.5 and 0.74 mm diameter. The effect of particle size on initial rate of reaction is shown in Fig. 3.9. It was observed that there is significant effect of particle size on initial rate of reaction indicating the presence of intra particle diffusion.

3.4.3.2 Analysis of mass transfer effects

Following the procedures described in Section 2.4.3.2, the initial rate data was used to analyze the significance of mass transfer effect. It was found that the liquid-solid mass transfer resistance was negligible, as indicated by the value of α_2 (Table 3.3).

However, the intraparticle diffusion resistance was significant under most of the operating conditions as evidenced by the value of Thiele parameter, ϕ_{exp} (Table 3.3). The relevant diffusion coefficients were evaluated using Wilke-Chang equation and are presented in Table 3.4. The effective diffusivity was evaluated using equation 2.20.

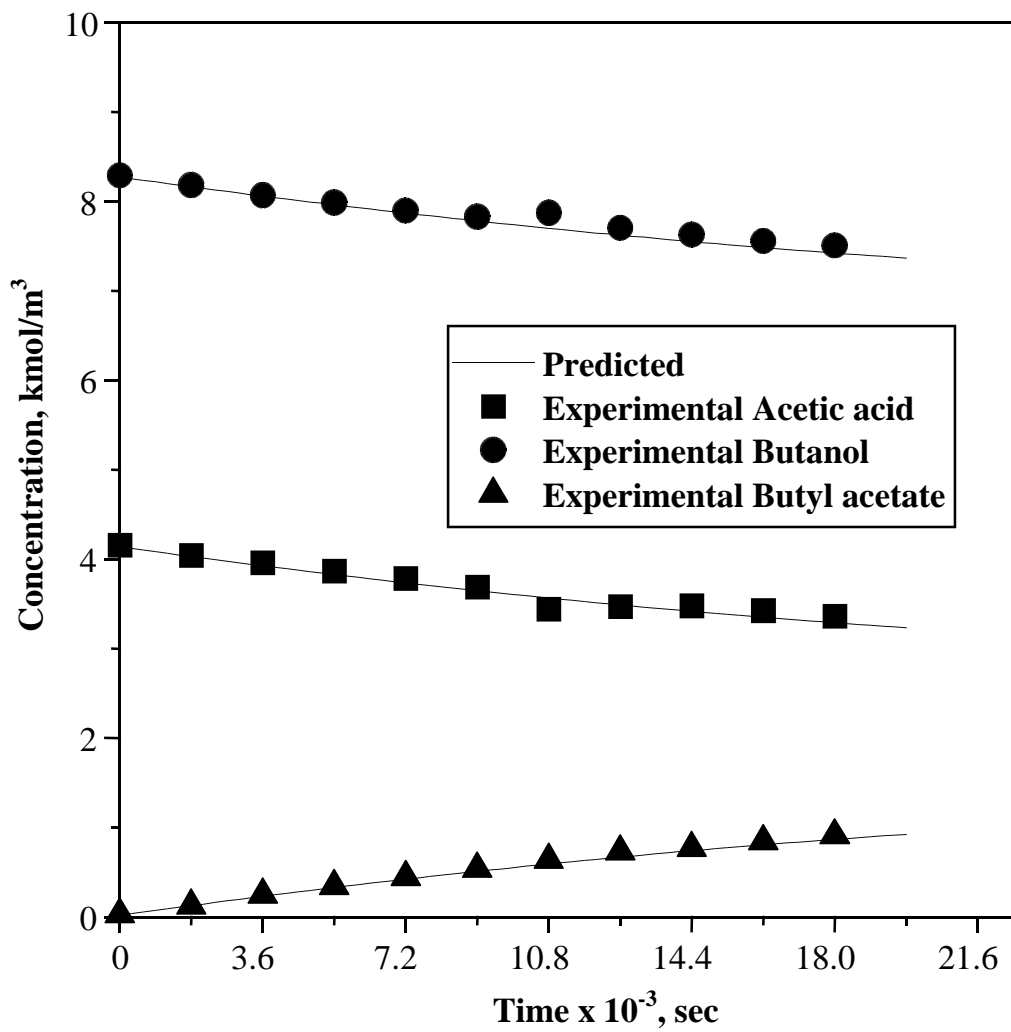


Fig. 3.1: Concentration-Time profile at 353 K
Reaction Conditions: $C_{A0} = 4.179 \text{ kmol/m}^3$, $C_{B0} = 8.279 \text{ kmol/m}^3$

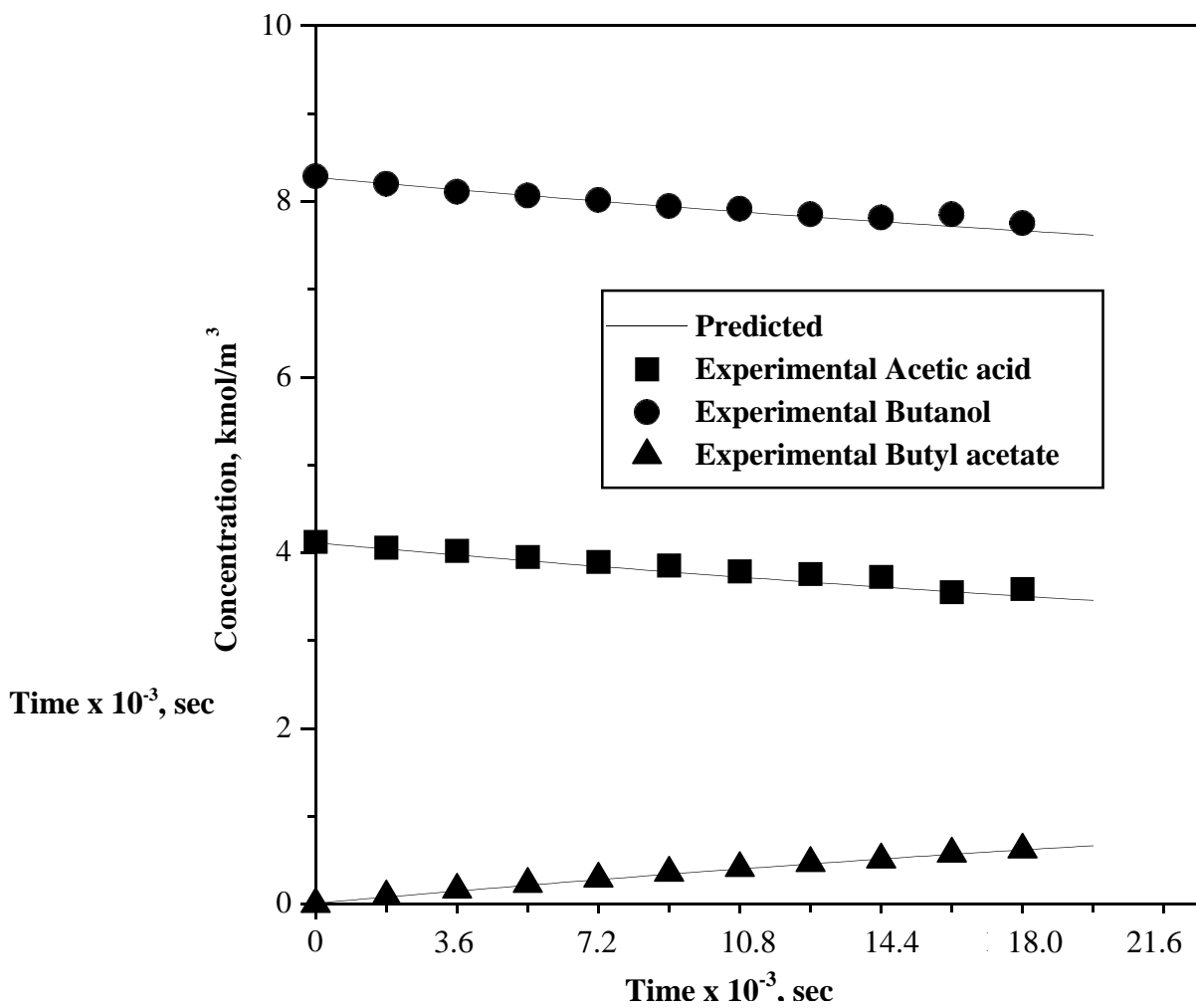


Fig. 3.2: Concentration-Time profile at 343 K
Reaction Conditions: $C_{A0} = 4.127 \text{ kmol/m}^3$, $C_{B0} = 8.286 \text{ kmol/m}^3$

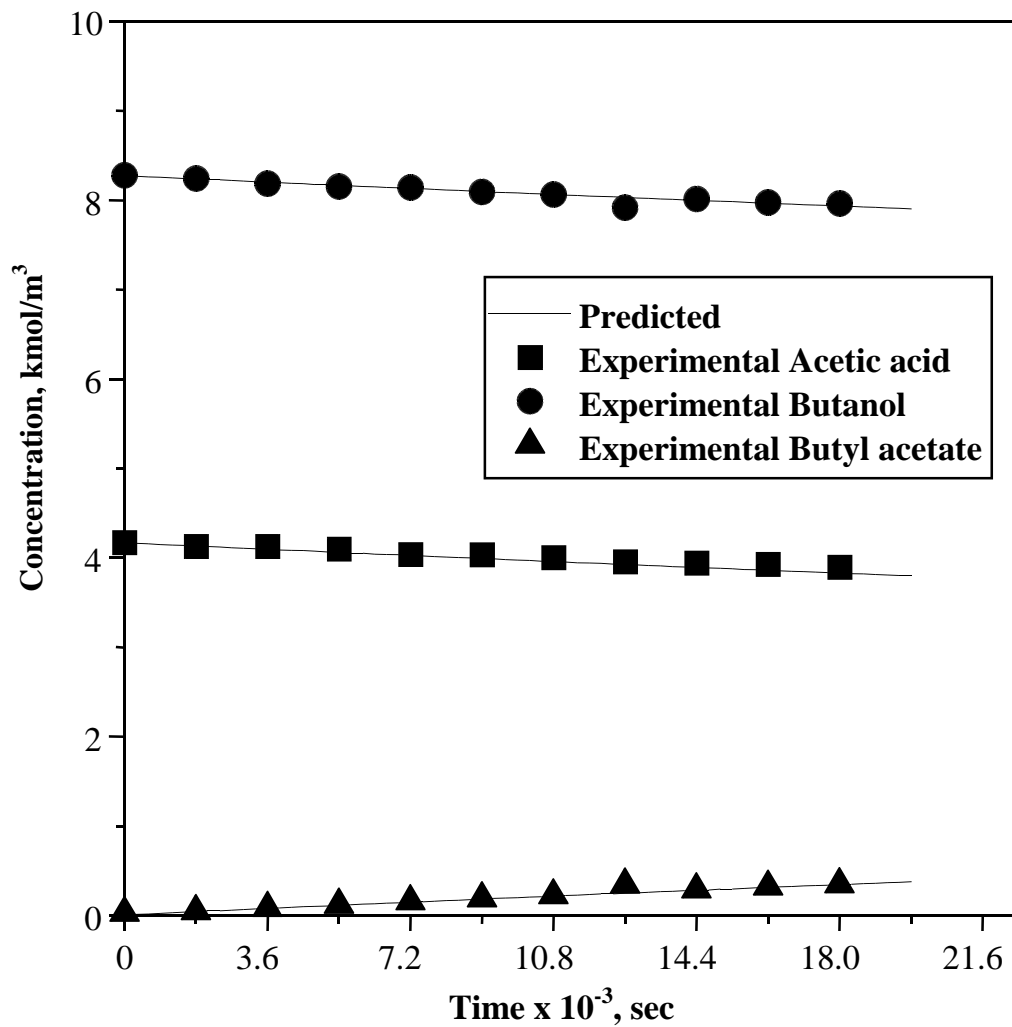


Fig. 3.3: Concentration-Time profile at 363 K
Reaction Conditions: $C_{A0} = 4.157 \text{ kmol/m}^3$, $C_{B0} = 8.292 \text{ kmol/m}^3$

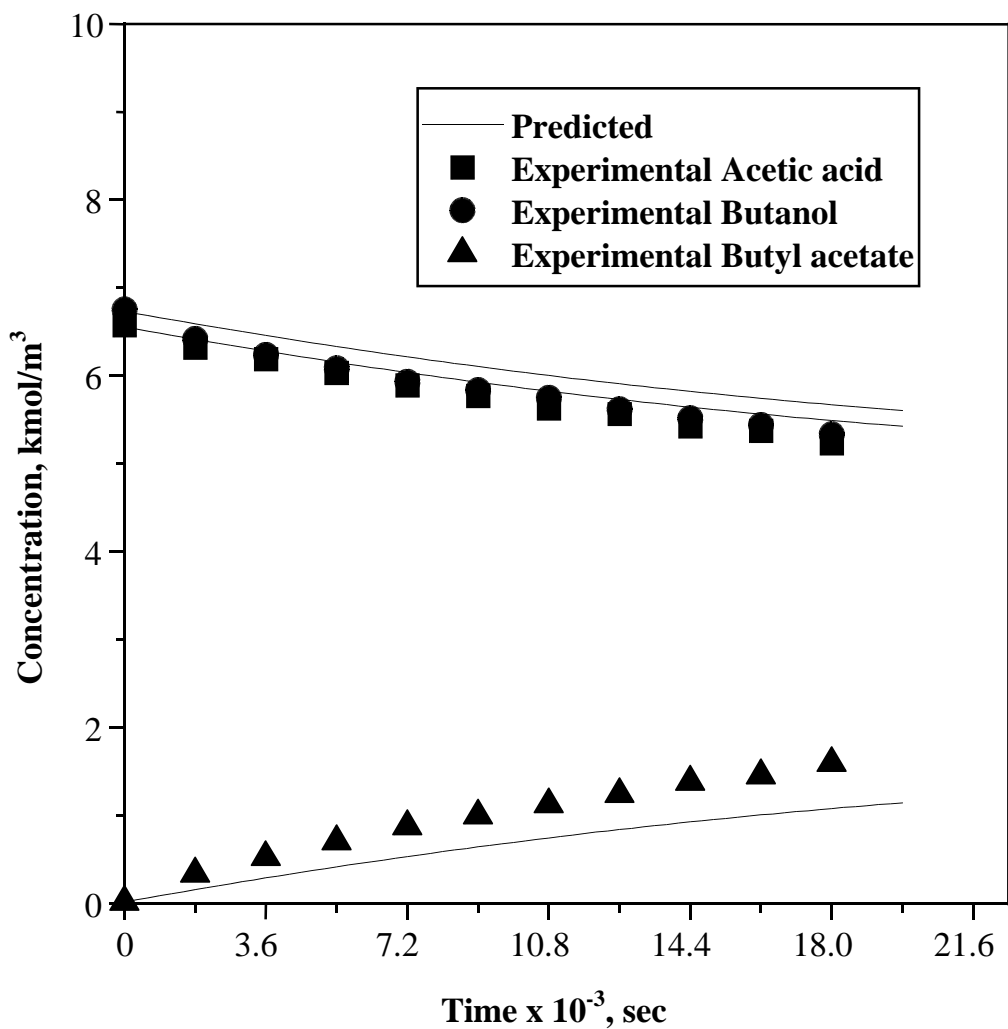


Fig. 3.4: Concentration-Time profile at 353 K
Reaction Conditions: $C_{A0} = 6.579 \text{ kmol/m}^3$, $C_{B0} = 6.758 \text{ kmol/m}^3$

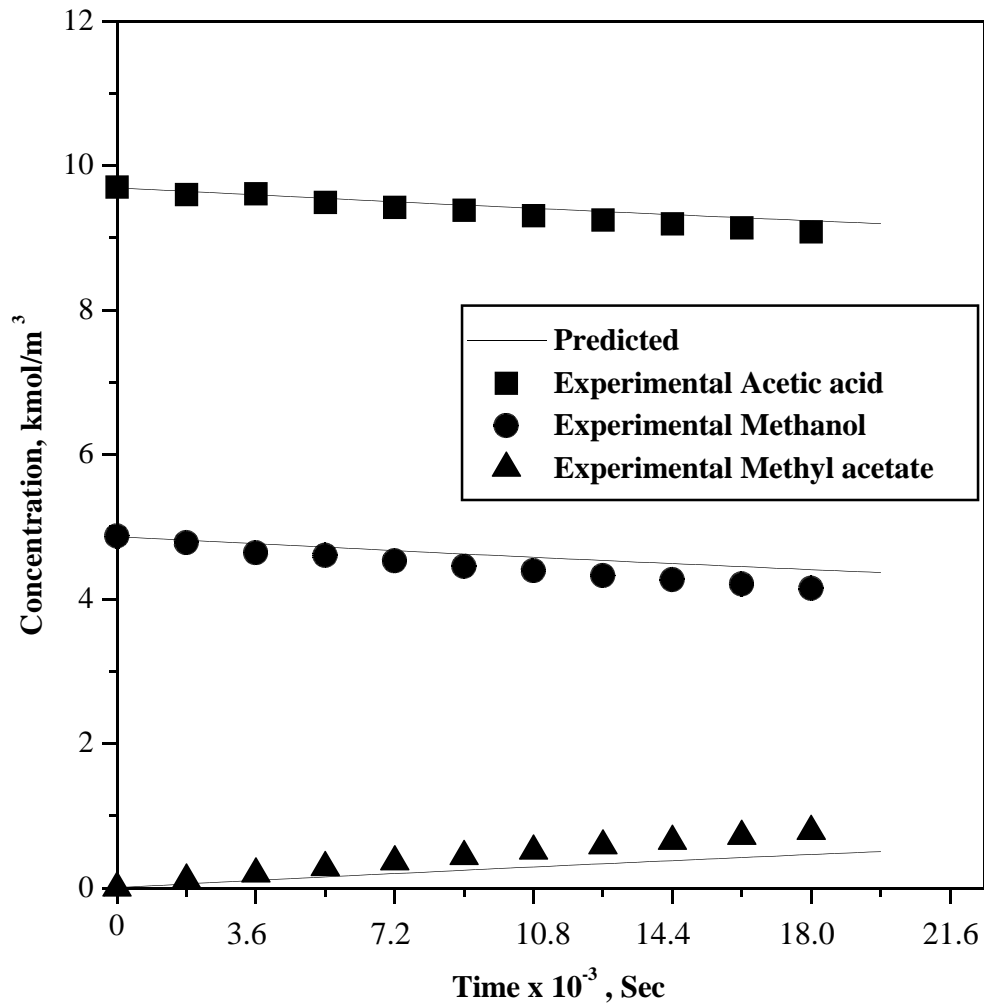


Fig. 3.5: Concentration Time Profile at 353K
Reaction Conditions: $C_{A0} = 9.718 \text{ kmol/m}^3$, $C_{B0} = 4.793 \text{ kmol/m}^3$

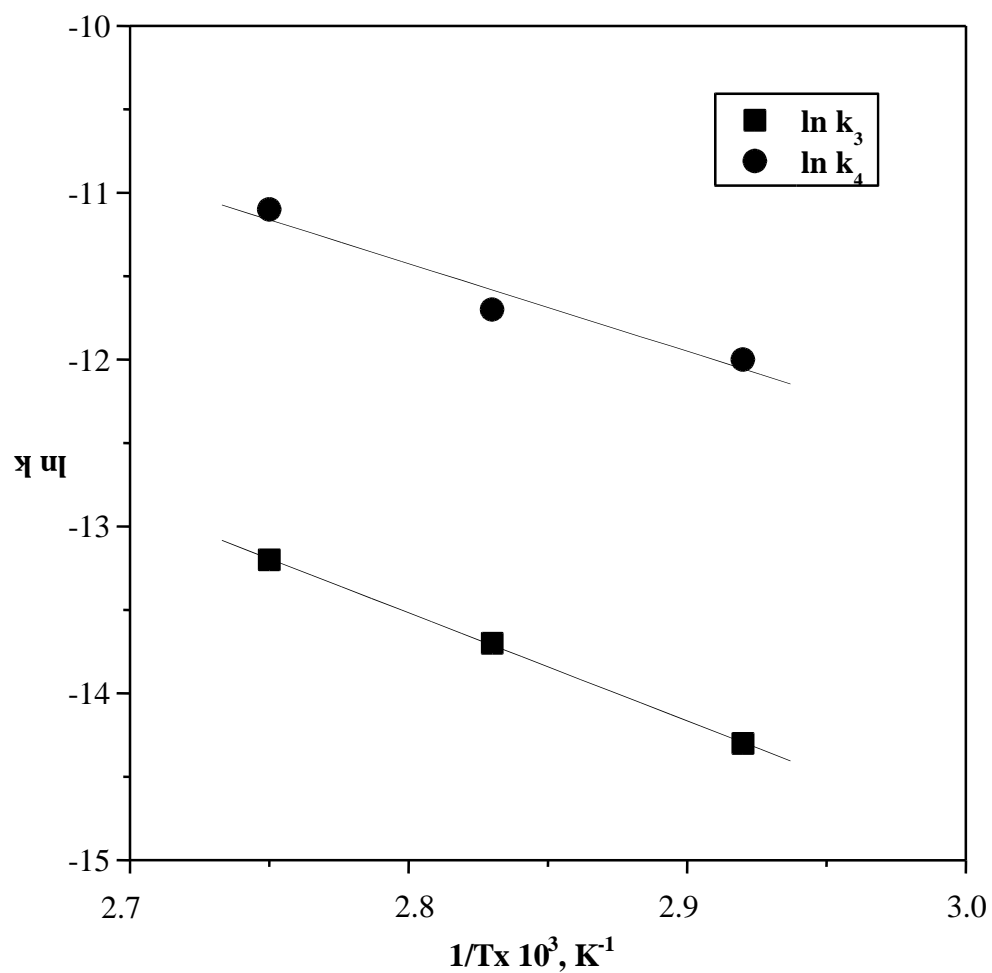


Fig. 3.6: Effect of temperature on rate constants of homogeneous esterification reaction

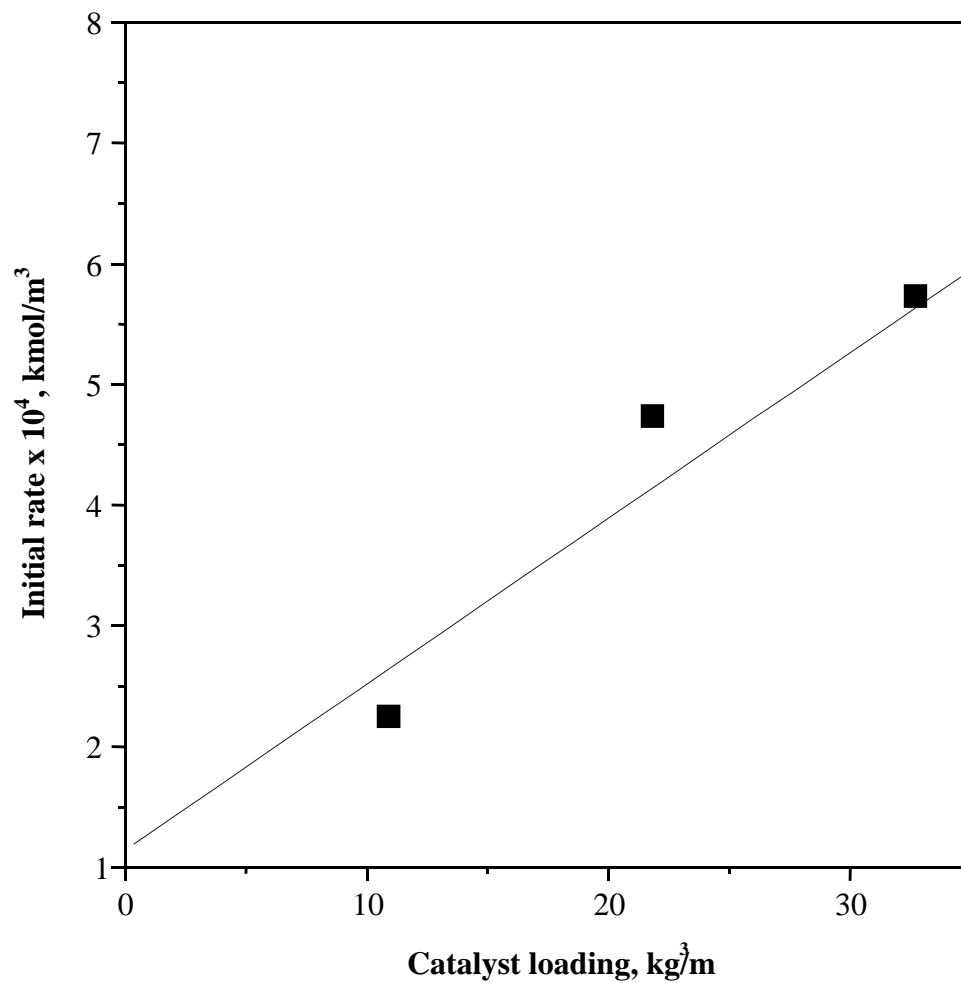


Fig. 3.7: Effect of catalyst loading on rate of reaction

Reaction Conditions: Temp = 353 K, Acetic acid-Butanol molar ratio = 1:2, $d_p = 4.58 \times 10^{-4}$ m.

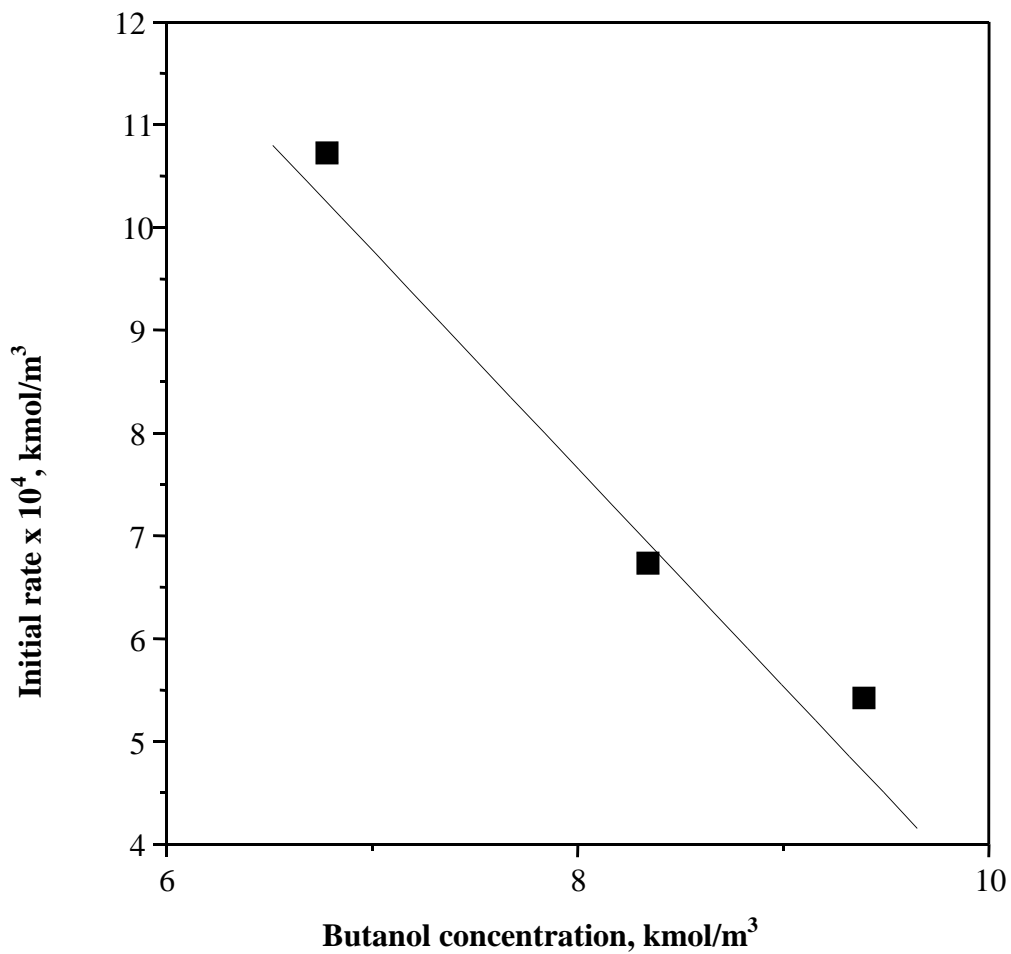


Fig. 3.8: Effect of butanol concentrations on rate of reaction

Reaction Condition: Temperature = 353 K, $d_p = 4.58 \times 10^{-4}$ m.

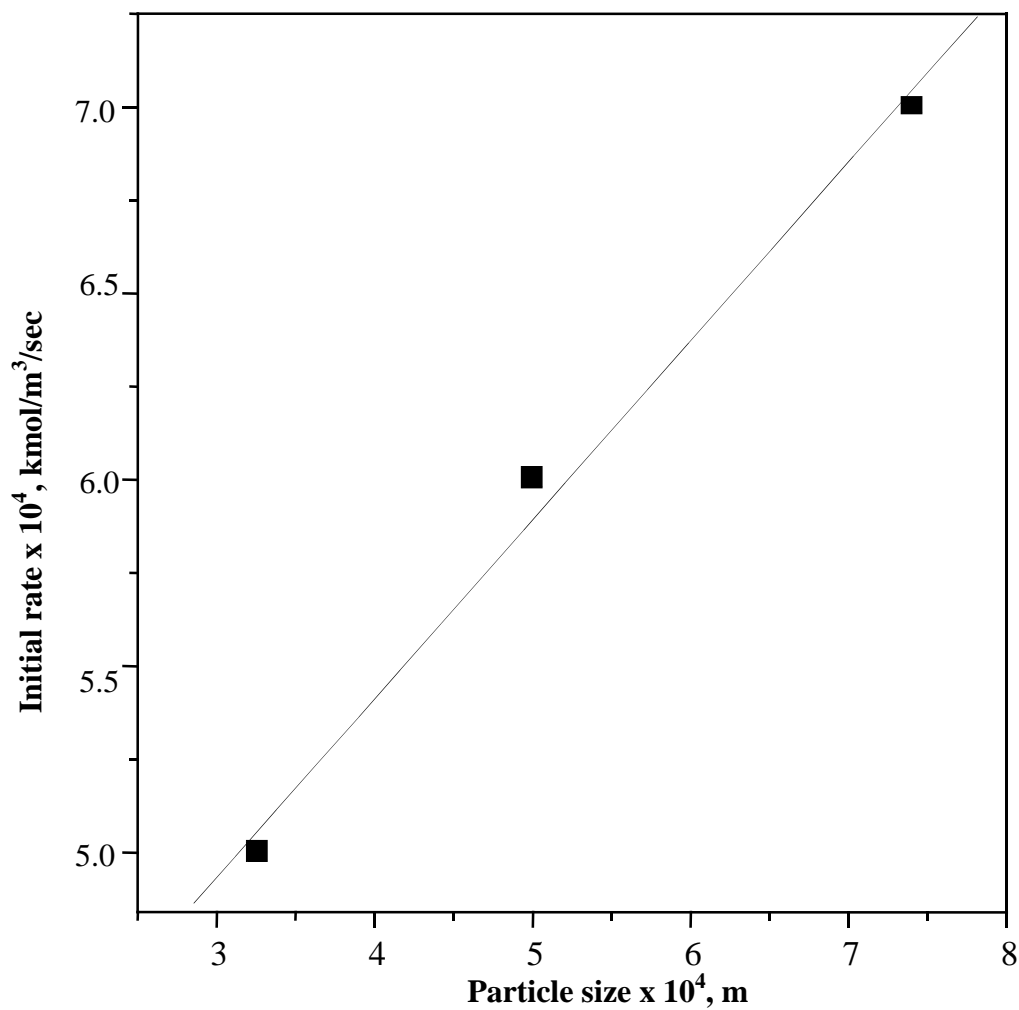


Fig. 3.9: Effect of particle size on rate of reaction

Reaction Conditions: Temp = 353K, Acetic acid-Butanol molar ratio = 1:2, $w = 21.81 \text{ kg/m}^3$

Table 3.3 Initial rate data for ion exchange resin catalyzed esterification of acetic acid with butanol

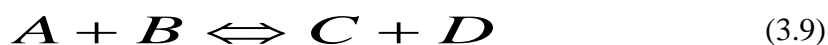
Temp. K	$d_p \times 10^3, m$	Catalyst loading, kg/m^3	Initial AcOH conc, $kmol/m^3$	Initial BuOH conc, $kmol/m^3$	Initial rate $\times 10^4$, $kmol/m^3/sec$	$\alpha_2 \times 10^5$	ϕ_{exp}
343	0.5	21.81	4.378	8.106	3.744	0.354	0.179
	0.74	21.81	4.146	8.299	2.438	0.360	0.242
353	0.5	21.81	4.144	8.341	5.735	0.572	0.250
	0.327	21.81	4.135	8.349	6.759	0.442	0.149
	0.74	21.81	4.088	8.343	5.233	0.783	0.398
	0.5	21.81	6.571	6.782	1.072	0.675	0.280
	0.5	21.81	2.385	9.391	5.426	0.941	0.348
	0.5	10.90	3.990	8.092	4.048	0.840	0.323
	0.5	32.72	4.034	8.057	6.346	0.447	0.209
363	0.5	21.81	4.3889	8.083	7.148	0.673	0.274
	0.74	21.81	4.030	8.192	8.045	1.222	0.413

Table 3.4 Diffusivity of acetic acid in butanol

Temperature K	Molecular Diffusivity $D \times 10^9, m^2/s$	Effective Diffusivity $D_e \times 10^{10}, m^2/s$
343	3.3685	7.0178
353	3.4779	7.2456
363	3.5872	7.4735

3.5 Reactor model

The esterification of butanol with acetic acid can be written as



Where A, B, C and D represent the concentration of Acetic acid, Butanol, Butyl acetate and Water. This system is identical the esterification of methanol with acetic acid. Hence the same model equations developed for the esterification of acetic acid with

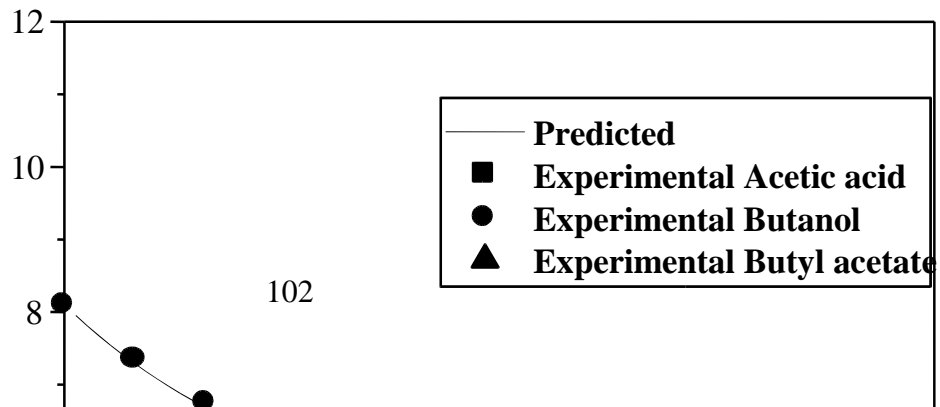
methanol can be used for the esterification of butanol with acetic acid also. Therefore, the Thiele modulus can be written as:

$$\Phi = \frac{R}{3} \left[\frac{\rho_p k_1 C_{2,1} \left(1 - k' \frac{C_{3,1} C_{4,1}}{C_{1,1} C_{2,1}} \right)}{D_e \left[\left(1 - \frac{D_{e1} C_{1,1}}{3 C_{2,1}} \right) + k' \left(\frac{D_{e1} C_{1,1}}{D_{e3} C_{2,1}} - \frac{2 D_{e1}^2 C_{1,1}}{3 D_{e3} D_{e4} C_{2,1}} - \frac{D_{e1} C_{3,1}}{D_{e4} C_{2,1}} - \frac{2 D_{e1} C_{4,1}}{D_{e3} C_{2,1}} - \frac{2 C_{3,1} C_{4,1}}{C_{1,1} C_{2,1}} \right) \right]} \right]^{-1/2} \quad (3.10)$$

3.6 Kinetic model for the heterogeneous reaction

In this case, the experiments were carried out using ion exchange resin catalyst in the same reactor, following the procedures described earlier (Section 2.2.4). For interpretation of the kinetics, several experiments were carried out in which observed concentration-time data were recorded over a range of condition given in Table 3.1. The concentration-time profile for standard experimental conditions (Acid: Alcohol 1:2, particle size 0.458 mm.) at 343, 353 and 363 K is shown in Figs. 3.10 to 3.12 respectively. The reaction rates will be the sum of homogeneous and heterogeneous reaction rates. The forward and backward reaction rates respectively are expressed as

$$r_4 = k_4 C_3 \cdot C_4 + \eta k_c k_2 C_3 \cdot C_4 \quad (3.12)$$



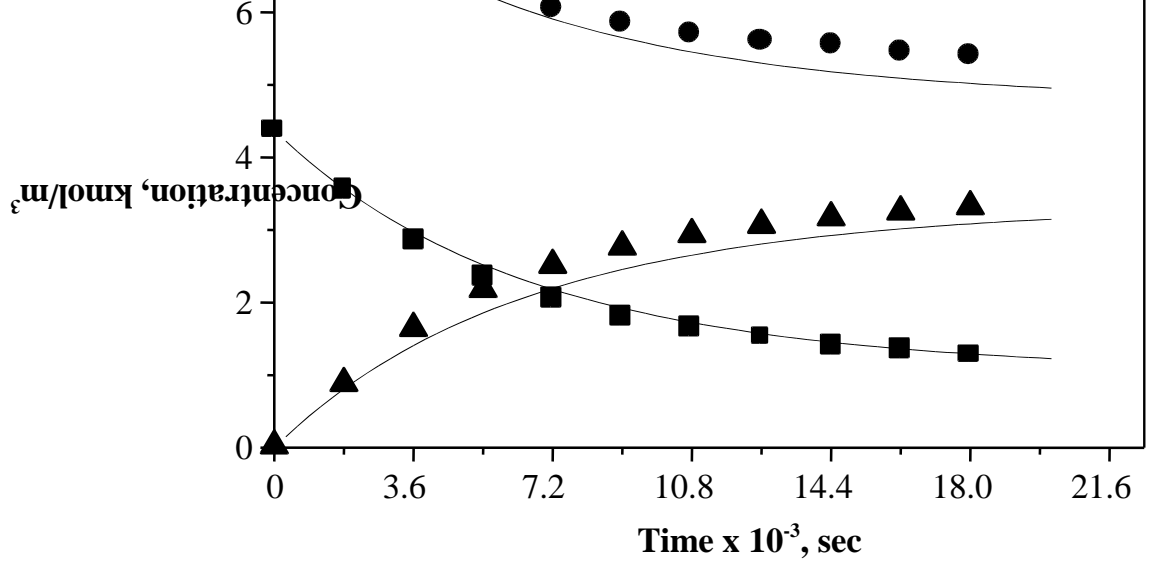
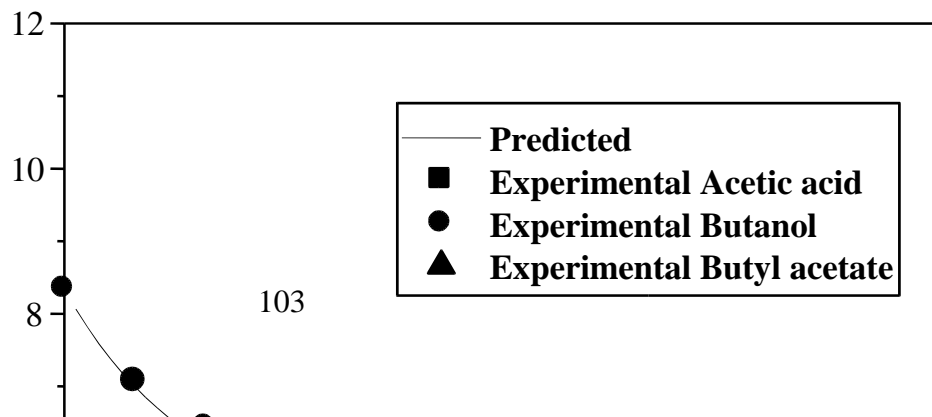


Fig. 3.10: Concentration-Time profile at 343 K

Reaction Conditions: $C_{A0} = 4.378 \text{ kmol/m}^3$, $C_{B0} = 8.106 \text{ kmol/m}^3$,
 $w = 21.81 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$.



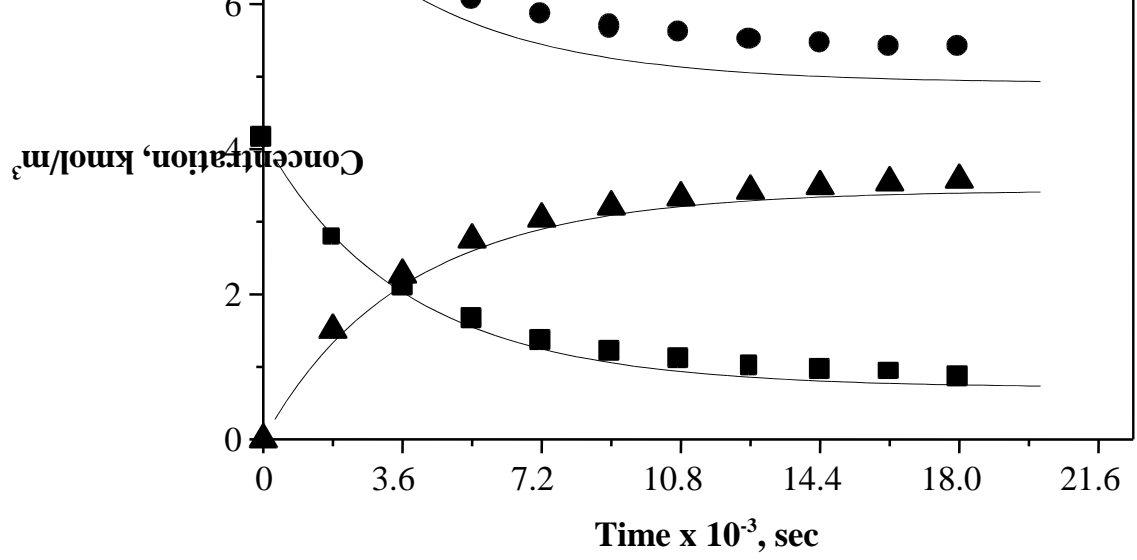
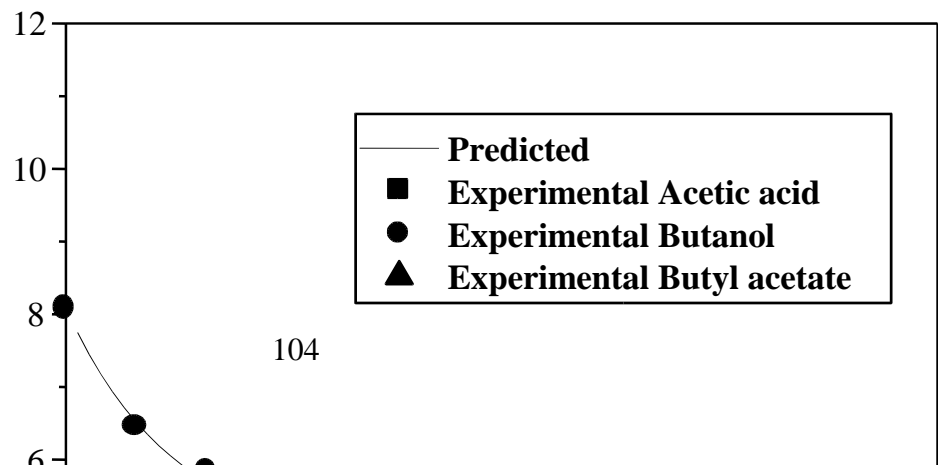


Fig. 3.11: Concentration-time profile at 353 K

Reaction Conditions: $C_{A0} = 4.144 \text{ kmol/m}^3$, $C_{B0} = 8.341 \text{ kmol/m}^3$,
 $w = 21.81 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$.



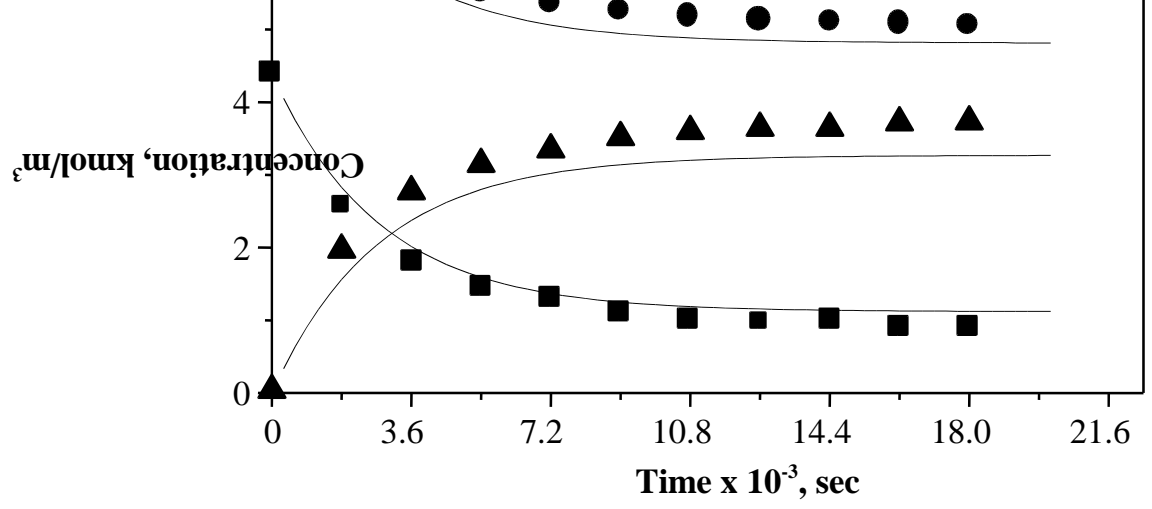


Fig. 3.12: Concentration time profile at 363 K
Reaction Conditions: $C_{A0} = 4.389 \text{ kmol/m}^3$, $C_{B0} = 8.083 \text{ kmol/m}^3$,
 $w = 21.81 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$.

Where, w is the weight of catalyst in kg/m^3 , η_c is the catalytic effectiveness factor;

$$\eta_c = \frac{1}{\phi} \left[\coth \left(3\phi - \frac{1}{3\phi} \right) \right] \quad (3.13)$$

and ϕ is the Thiele modulus given in equation 3.11

The batch reactor model at isothermal conditions for each species can be written as:

$$\frac{dC_1}{dt} = r_4 - r_3 \quad (3.14)$$

$$\frac{dC_2}{dt} = r_4 - r_3 \quad (3.15)$$

$$\frac{dC_3}{dt} = r_3 - r_4 \quad (3.16)$$

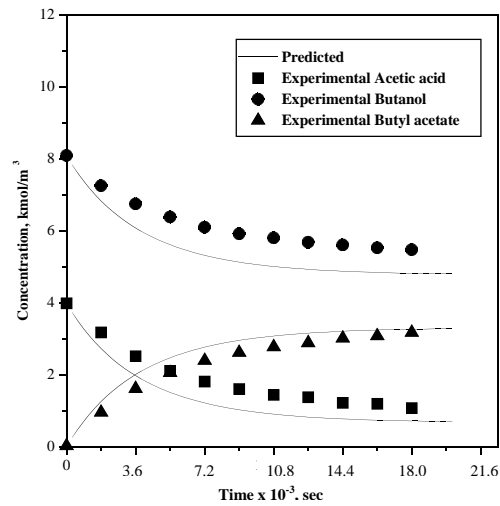
$$\frac{dC_4}{dt} = r_3 - r_4 \quad (3.17)$$

The initial conditions are,

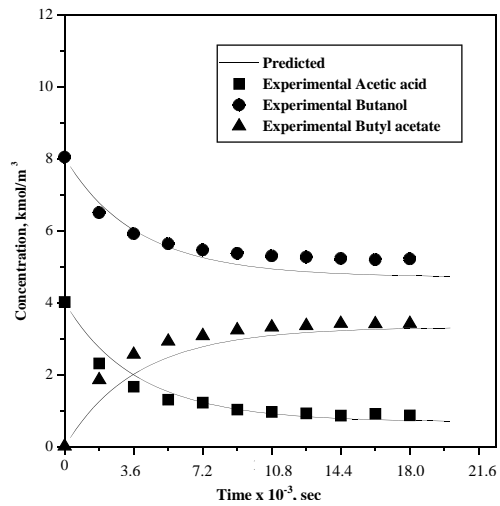
$$\text{at } t=0, C_1=C_{A0}, C_2=C_{B0} \text{ and } C_3, C_4=0 \quad (3.18)$$

Here, C_{A0} and C_{B0} are the initial concentrations of acetic acid and butanol in kmol/m^3

The rate parameters were evaluated, following the same approach described in Chapter 2. (Section 2.4.2) These are presented in Table 3.5. From Figs. 3.10 to 3.12, it is clearly observed that the model predictions and experimental observations are in good agreement for experiments at standard conditions. Using these parameters, the concentration-time profiles at different other operating conditions were also predicted. The effect of catalyst loading on the concentration-time profile is presented in Fig. 3.13. The model predictions for the effects of catalyst loading, initial concentration of reactants and particle size are shown in Figs. 3.14, 3.15 and 3.16 respectively. In all the cases the model predictions agreed well with the actual observations. The temperature dependence of the rate parameters k_1 and k_2 are shown in Fig. 3.17. From this, the value of activation

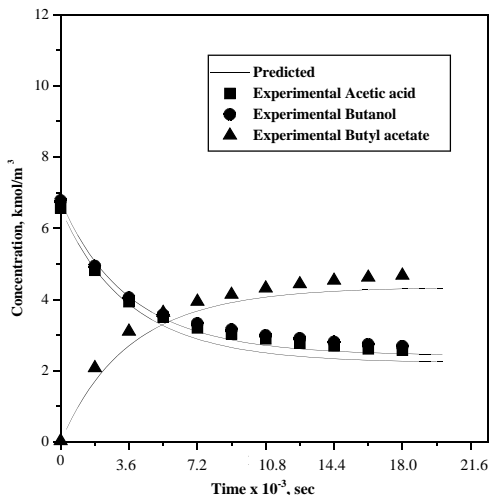


Reaction Conditions: $C_{A0} = 3.989 \text{ kmol/m}^3$,
 $C_{B0} = 8.092 \text{ kmol/m}^3$, $w = 10.9 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$.



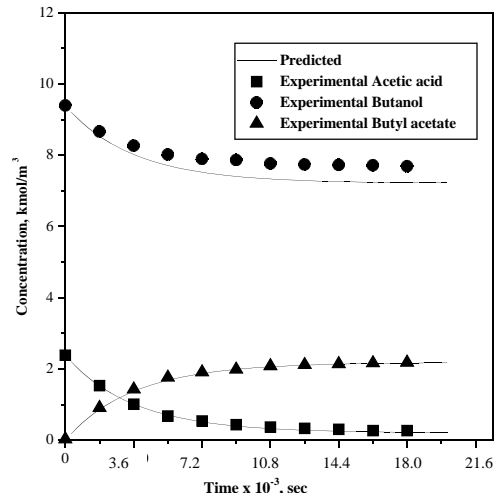
Reaction Conditions: $C_{A0} = 4.034 \text{ kmol/m}^3$,
 $C_{B0} = 8.057 \text{ kmol/m}^3$, $w = 32.72 \text{ kg/m}^3$, $d_p = 4.58 \times 10^{-4} \text{ m}$.

Fig. 3.13: Concentration-time profiles at various catalyst loadings at 353K



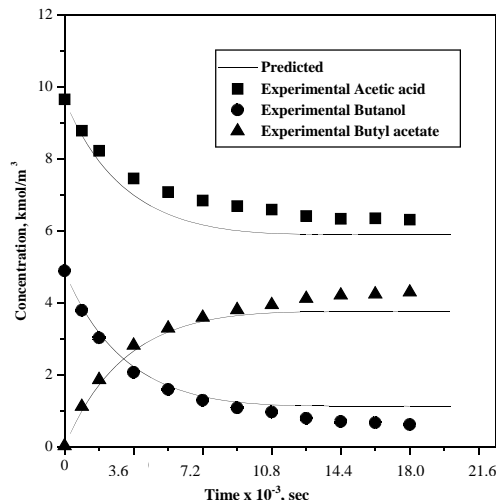
Reaction Conditions:

$C_{A0} = 6.571 \text{ kmol/m}^3$, $C_{B0} = 6.782 \text{ kmol/m}^3$,
 $w = 21.81 \text{ kg/m}^3$,
 $d_p = 4.588 \times 10^{-4} \text{ m}$.



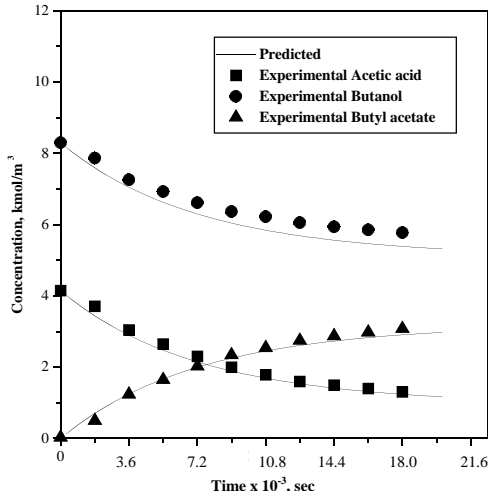
Reaction Conditions:

$C_{A0} = 2.385 \text{ kmol/m}^3$, $C_{B0} = 9.39 \text{ kmol/m}^3$,
 $w = 21.81 \text{ kg/m}^3$,
 $d_p = 4.58 \times 10^{-4} \text{ m}$.



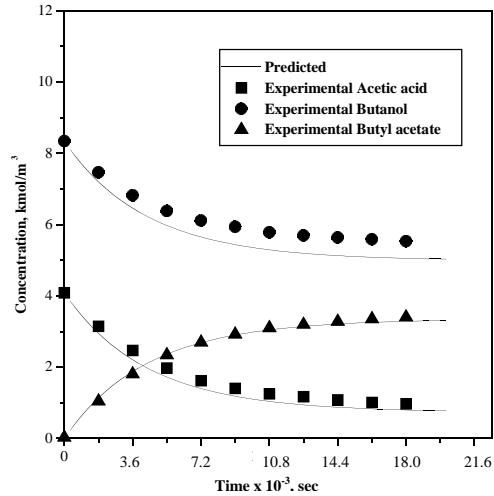
Reaction Conditions: $C_{A0} = 9.718 \text{ kmol/m}^3$, $C_{B0} = 4.793 \text{ kmol/m}^3$,
 $w = 21.81 \text{ kg/m}^3$, $d_p = 4.588 \times 10^{-4} \text{ m}$.

Fig. 3.14: Concentration-time profiles for various reactant concentrations at 353 K



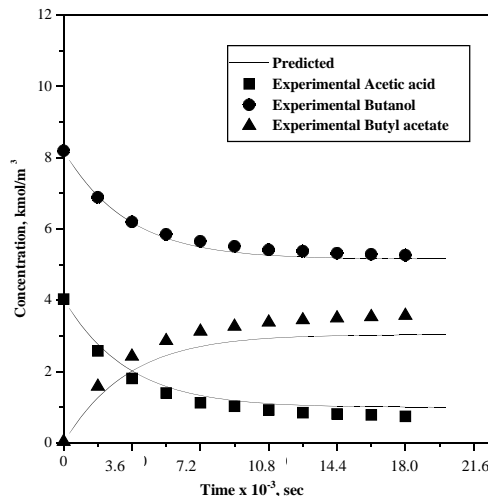
Reaction Conditions:

Temp = 343 K, $w = 21.81 \text{ kg/m}^3$
 $C_{A0} = 4.146 \text{ kmol/m}^3$, $C_{B0} = 8.298 \text{ kmol/m}^3$



Reaction Conditions:

T = 353 K, $w = 21.81 \text{ kg/m}^3$,
 $C_{A0} = 4.088 \text{ kmol/m}^3$, $C_{B0} = 8.343 \text{ kmol/m}^3$



Reaction Conditions: Temp = 363 K, $w = 21.81 \text{ kg/m}^3$,

$$C_{A0} = 4.03 \text{ kmol/m}^3, C_{B0} = 8.196 \text{ kmol/m}^3$$

Fig.3.15: Concentration-Time profile for temperatures at $d_p = 7.8 \times 10^{-4} \text{ m}$

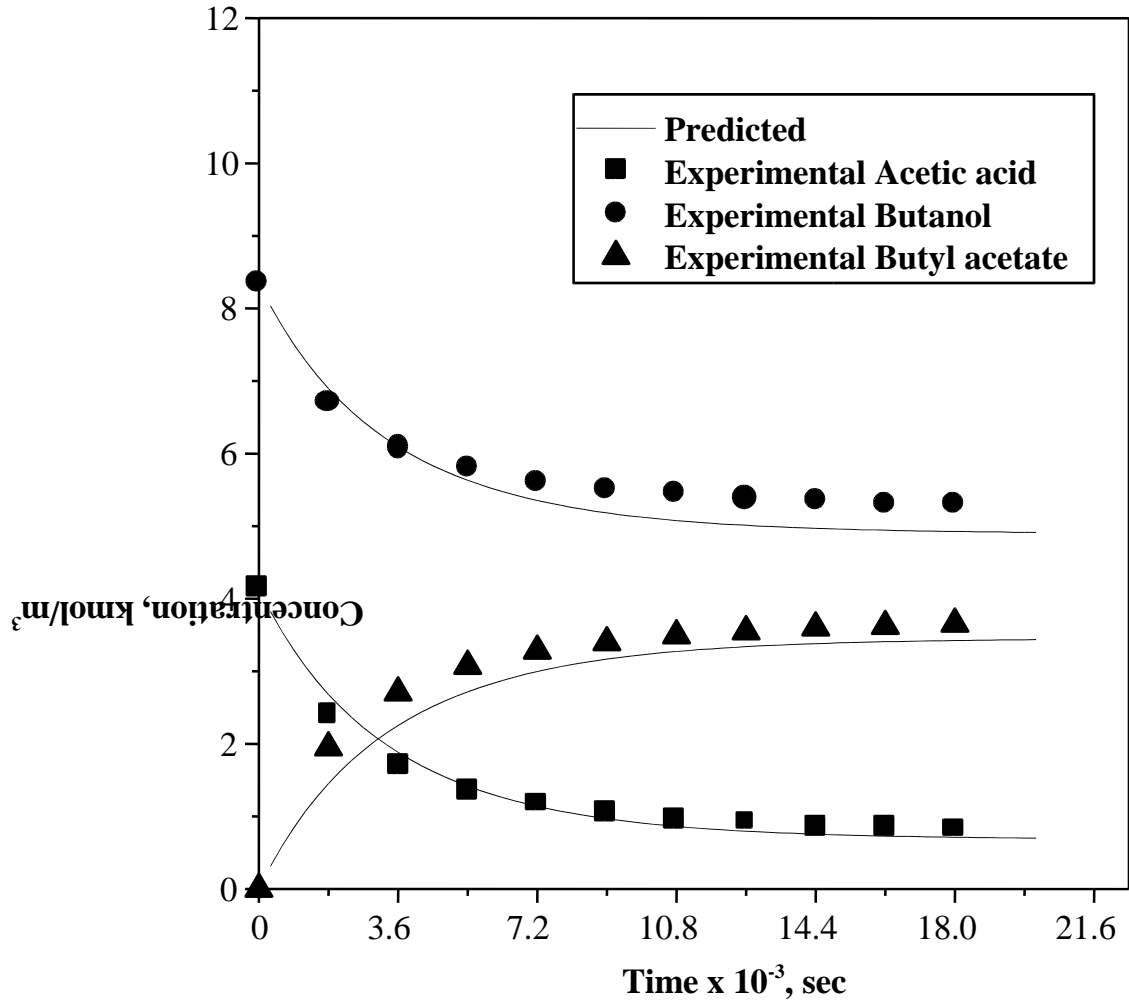


Fig. 3.16: Concentration time profile for lower particle sizes at 328 K

Reaction Condition: $C_{A0} = 4.135 \text{ kmol/m}^3, C_{B0} = 8.349 \text{ kmol/m}^3,$
 $w = 21.81 \text{ kg/m}^3, d_p = 3.75 \times 10^{-4} \text{ m}$

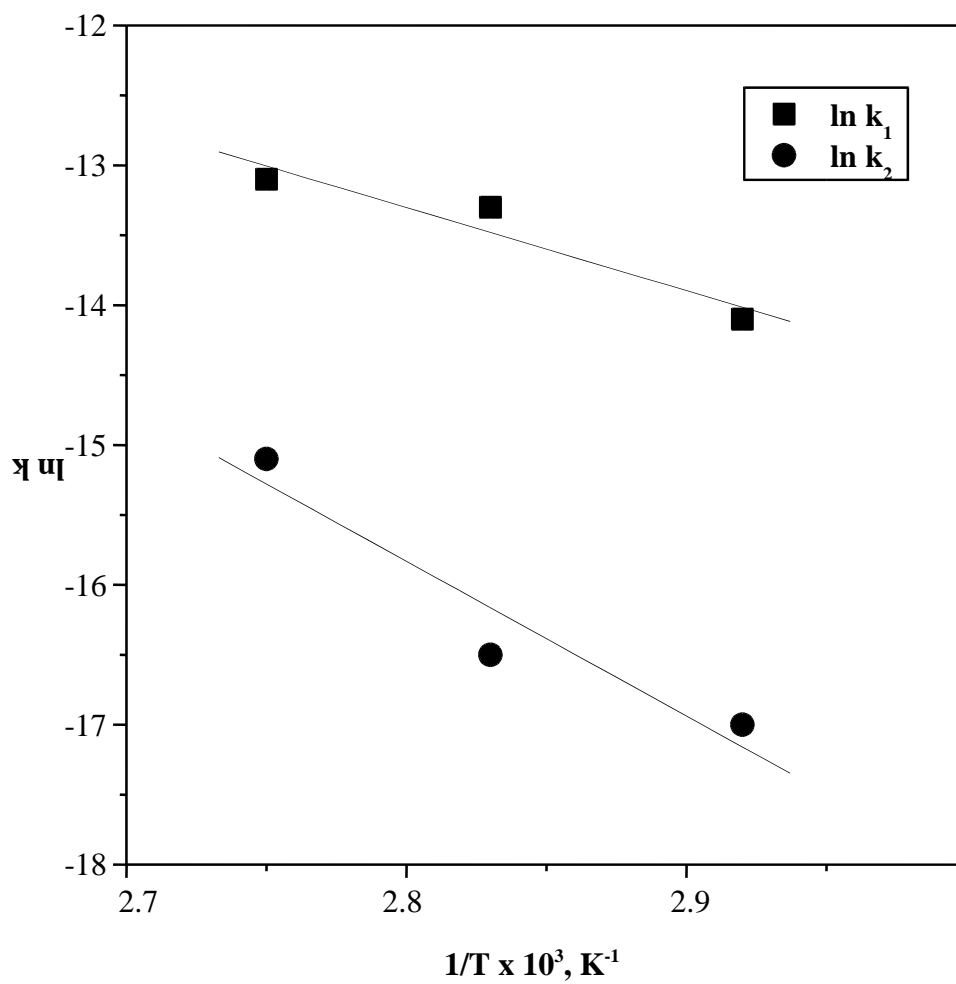


Fig. 3.17: Effect of temperature on heterogeneous reaction rate constants

3.0

energy for the forward and reverse heterogeneous reactions was evaluated as 49.42 and 91.95 kJ/mol. respectively.

Table 3.5: Heterogeneous reaction rate constants

Temp, K	$k_1 \times 10^5, \text{m}^3/\text{kmol}/\text{sec}$	$k_2 \times 10^7, \text{m}^3/\text{kmol}/\text{sec}$
343	0.0746	0.428
353	0.16	0.71
363	1.50	2.67

3.7 Conclusions

The esterification of acetic acid with butanol in a batch slurry reactor was studied in details. The kinetics of homogeneous non-catalytic esterification was investigated separately to understand its contribution in the overall heterogeneous catalyzed esterification reaction. The effect of reaction parameters such as temperature, butanol concentration, and catalyst loading and particle size were investigated thoroughly. For interpretation of the kinetics, the observed concentration-time data were used and the rate parameters evaluated at each temperature using a batch reactor model. The activation energies for homogeneous forward and backward reactions were evaluated as 57.82 and 43.82 kJ/mol and for heterogeneous forward and backward reactions were evaluated as 49.42 and 91.95 kJ/mol respectively.

Notations

- a_p effective liquid-solid interfacial area per unit volume of slurry, m^2/m^3 .
- C_1 concentrations of acetic acid, kmol/m^3
- C_2 concentrations of butanol, kmol/m^3
- C_3 concentrations of butyl acetate, kmol/m^3
- C_4 concentration of water, kmol/m^3
- C_{A0} concentrations of acetic acid at $t = 0$, kmol/m^3
- C_{B0} concentrations of butanol at $t = 0$, kmol/m^3
- C_i concentration of i^{th} component, kmol/m^3
- D_e effective diffusivity, m^2/sec

D	molecular diffusivity, m ² /sec
k ₁	rate constant for the heterogeneous forward reaction, m ³ /kmol/s. m ³ /kg
k ₂	rate constant for the heterogeneous backward reaction, m ³ /kmol/s. m ³ /kg
k ₃	rate constant for the homogeneous forward reaction, m ³ /kmol/s
k ₄	rate constant for the homogeneous backward reaction, m ³ /kmol/s
k _s	liquid-solid mass transfer coefficient, m/s.
r ₁	forward reaction rate, kmol/m ³ /s
r ₂	backward reaction rate, kmol/m ³ /s
r _A	initial rate (kmol/m ³ /sec.)
w	catalyst loading , kg/m ³ .

Greek

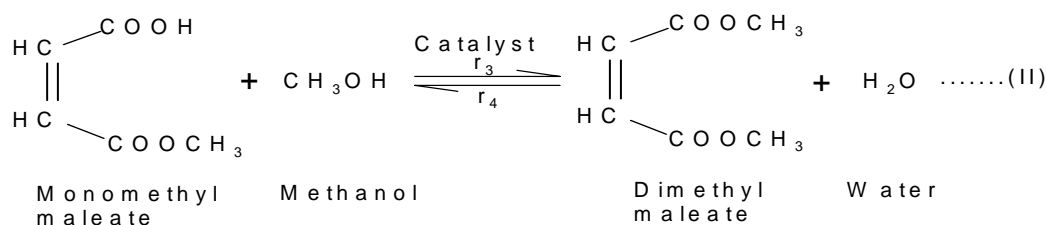
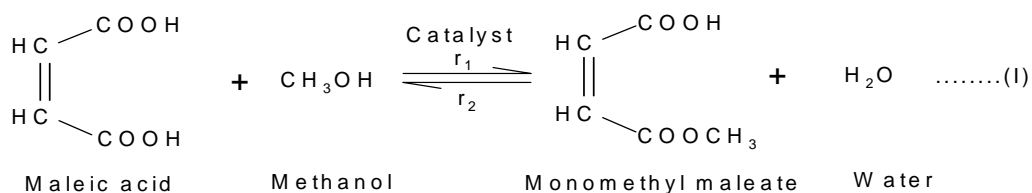
α ₂	parameter defined in equation 2.15
η _c	catalytic effectiveness factor
ε _p	porosity of catalyst
φ	Thiele modulus given in equation 2.34.
μ _l	Viscosity of liquids, gm/cm/s
τ	tortuosity factor
ρ _l	density of liquids, gm/cm ³
ρ _p	density of catalyst, gm/cm ³

3.8 References

- Altiokka M. R., *Appl. Catal. A: General*, 239, 141-148 (2003)
- Bianchi C.L., Ragaini V., Pirola C. and Carvoli G., *Appl.Catal B:Environ*, 40, 93, (2003)
- Gangadwala J., Mankar S. and Mahajani S., *Ind. Eng. Chem. Res.*, 42, 2146-2155 (2003)
- Leyes C. E. and Othmer D. F., *Ind. and Eng. Chem.*, 36- 37, 968-977 (1945)
- Venimadhavan G., Malone M. F., and Doherty M. F., *Ind. Eng. Chem. Res.*, 38, 714 (1999)
- Wilhelm R., *Ullman's Encyclopedia of Industrial Chemistry*, A9, 5th Ed (1999).

4.1 Introduction

Esterification of maleic acid with methanol in presence of an acid catalyst gives dimethyl maleate as a major product. This is an example of a multistep reaction where, the first reaction involves the formation of a monoester, monomethyl maleate (MMM) that further reacts with methanol to form the di-ester, dimethyl-maleate (DMM). The stoichiometric reactions involving esterification of maleic acid with methanol are described below:



Maleate esters such as dimethyl maleate, diethyl maleate and dibutyl maleate are extensively used in the production of latex emulsion polymers, thermoplastic and thermosetting plastics. Dimethyl maleate has found use in applications where improvement in hardness and toughness of polymer films are desired. This includes, in particular, the improvement of anti-blocking properties of copolymers of vinyl acetate with dimethyl maleate. It is also used as an internal modifier to increase the glass transition temperature of styrene or vinyl chloride polymer. The intermediate in esterification of maleic acid with methanol, monomethyl maleate provides plastizing effect, as well as promotion of improved polymer adhesion due to the carboxylic group. It can be copolymerized with a variety of vinyl and acrylic monomers to provide coatings with improved stiffness and adhesion and reduced tackiness or tendency to block. Monoesters of maleates are used to provide carboxylic acid functionality in emulsions and water-soluble polymers.

Though there are studies reported on the esterification of maleic anhydride and maleic acid with ethanol (Chawla and Hussain (1982); Rode et. al. (1996); Yadav

(2002), there are no significant reports on the esterification of maleic acid with methanol. In the esterification of a dicarboxylic acid with an alcohol the contribution of uncatalyzed reaction where carboxylic acid itself acts as catalyst, is prominent and cannot to be routinely ignored. Hence, it is necessary to study reaction kinetics of homogeneous and heterogeneous catalyzed esterification. The aim of this work was to study the intrinsic kinetics of the esterification of maleic acid with methanol in a batch slurry reactor, using ion-exchange resin (Dowex 50W) as catalyst.

The kinetics of homogeneous esterification was investigated separately at different temperatures. The kinetics of homogeneous reaction was then used to obtain the rates of heterogeneous reactions in the presence of ion exchange catalyst. For the heterogeneous catalytic esterification reaction, the effect of temperature, catalyst concentration, and maleic acid concentration on the initial rate of reaction was also studied. A rate model has been developed using the concentration time data obtained in a batch slurry reactor. Based on the kinetic models the concentration profiles were also predicted using a batch reactor model for different operating conditions and compared with experimental data.

4.2 Experimental

4.2.1 Materials

The reactant methanol and maleic acid used was A.R. grade (99.8%) and were obtained from S.D. Fine Chemicals, India. Purity was determined by gas chromatography. The chemicals were used without further purification. The same catalyst Dowex 50W (Dow Chemical Co.) was used for the present work. The specifications and the pretreatment procedure have been already described in Chapter 2 (Section 2.2.2).

4.2.2 Reactor Setup

The same reactor setup described in Chapter-2 was used for this study also (sec.2.2.3). A schematic diagram of the experimental setup is shown in Fig. 2.1. It consisted of a glass reactor of 10 cm i. d. and 16 cm height. An outer jacket was provided in the reactor through which water at constant temperature could be circulated. The temperature in the jacket was maintained within $\pm 0.1^{\circ}\text{C}$ using a thermostat. A glass stirrer with four blades, turbine type impeller (1cm in width), was

used for agitation. The agitation speed could be varied using a constant speed regulator.

4.2.3 Experimental procedure

In all the experiments, a known amount of methanol was charged to the reactor and heated to the desired temperature. When the temperature remained constant, the required amount of maleic acid was added under constant stirring. It was observed that the maleic acid dissolved in methanol in a relatively short time because of the presence of excess methanol in all the experiments. The temperature fall as a result of this addition was not significant and the temperature equilibrium was reached very soon. A sample was removed for analysis. This was taken as the starting point of the homogeneous (uncatalyzed) reaction. For the catalytic reaction, after dissolution of maleic acid and attaining the desired temperature, a known quantity of ion exchange resin was added to the reactor. The moment of resin addition was taken as the starting time of reaction. Samples were withdrawn at regular time intervals for analysis. The volume of sample withdrawn from the reactor during a run was negligible compared with the total volume of the system. The total volume of reactants was 200 cm³ in all the experiments.

4.3 Analysis

The analysis of reactants and products were carried out using a Hewlett-Packard (model no. HP 5890) gas chromatograph instrument. HP-1 (phenyl methyl siloxane as stationary phase) capillary column (diameter: 30 μm, film thickness: 0.25 μm, length: 30 m) was used for quantitative analysis of the reactant and products. The conditions of GC analysis were:

Column temperature: 100-200°C (Programmed at 20°C /min)

Injector temperature: 250°C

Detector (FID): 250°C

Carrier gas (He) flow: 35 ml/min

By this analysis, the concentration change of all the species with time was recorded. The concentrations of maleic acid, methanol and dimethyl maleate were determined by external standard method using a calibration curve. Since, pure monomethyl maleate was not available to be used as an external standard, the following procedure

was used to evaluate a response factor for monomethyl maleate. A reaction was taken in a 50 ml round bottom flask with ion exchange resin catalyst. A large excess of methanol was used in this reaction. The initial concentrations of reactants, maleic acid and methanol were determined. Reaction was run for complete conversion of MMM. Samples were withdrawn after every hour. After completion of the reaction, at each stage maleic acid conversion and dimethyl maleate formation was estimated. Then from maleic acid conversion and dimethyl maleate formation the stoichiometric concentration of monomethyl maleate was calculated. The chromatographic peak area vs. stoichiometric concentration of monomethyl maleate showed a linear response. This response factor was used for further calculations of monomethyl maleate concentrations. It may be mentioned here that it was not possible to obtain pure monomethyl maleate. As soon as the reactants and products were heated for distillation, it was observed monomethyl maleate was converted back to maleic acid, which separated out in the distillation flask.

4.4 Kinetics of Esterification

4.4.1 Preliminary Experiments

Some preliminary experiments were carried out to select a suitable range of reaction conditions for kinetic study and to establish the product distribution, material balance etc. Notably, the concentration of maleic acid in methanol is limited by its solubility in the solvent, and is reported as 41% at 295.5 K (Schlessinger G. G., 1970). The maximum molar ratio of maleic acid to methanol was calculated as 1:2.5. Hence, all the experiments were carried out above a molar ratio of 1:4 of maleic acid to methanol. The operating range of reaction for the present study is given in Table 4.1. Typical concentration-time profiles are shown in Figs. 4.1-4.3 for 308, 318 and 328 K respectively. The experimental data on concentration-time profiles showed that the material balance of maleic acid converted and esters formed matched > 98%, at all stages of conversion according to the stoichiometry given by equations (I) and (II).

Table 4.1: Range of operating conditions

Reaction temperature, K	308, 318 and 328
Agitation speed, rpm	1000
Catalyst loading, kg/m ³	38.5, 57.75 and 77.00
Maleic acid: methanol molar ratio	1:4 and 1:6
Particle size, mm	0.300, 0.458 and 0.74

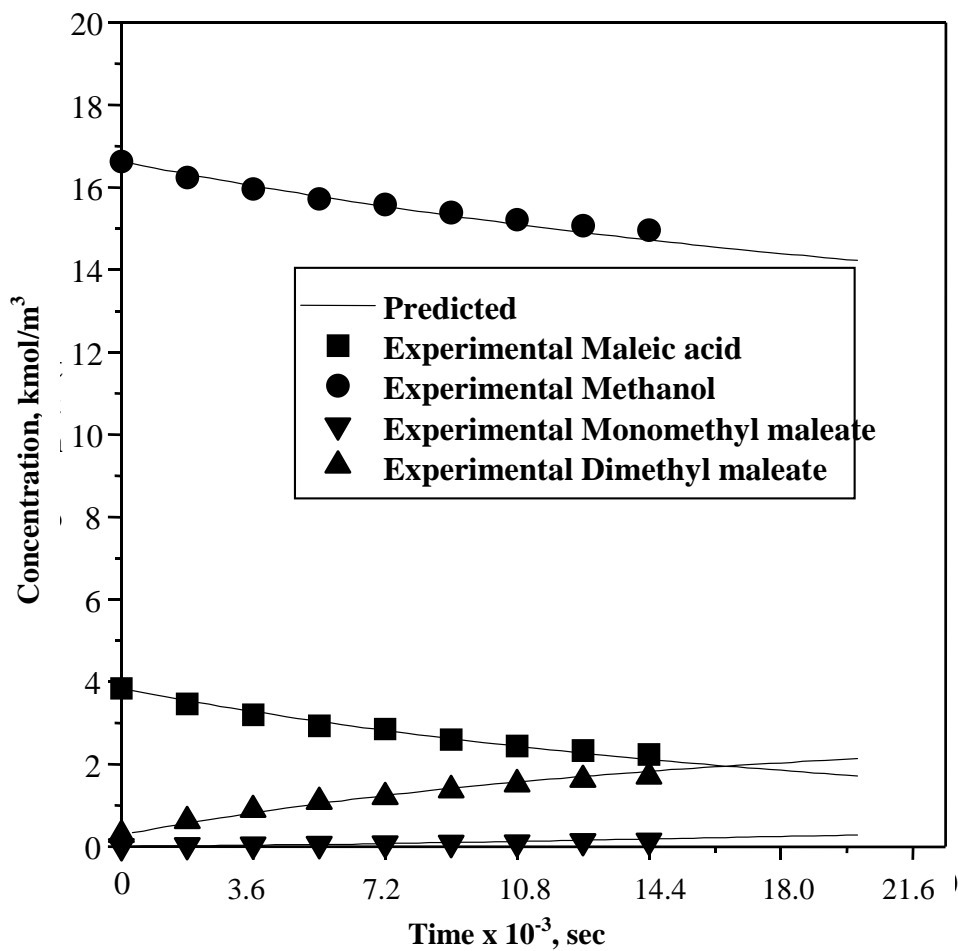


Fig. 4.1: Concentration-time profile at 308 K

Reaction Conditions: $C_{A0} = 4.122 \text{ kmol/m}^3$, $C_{B0} = 16.911 \text{ kmol/m}^3$

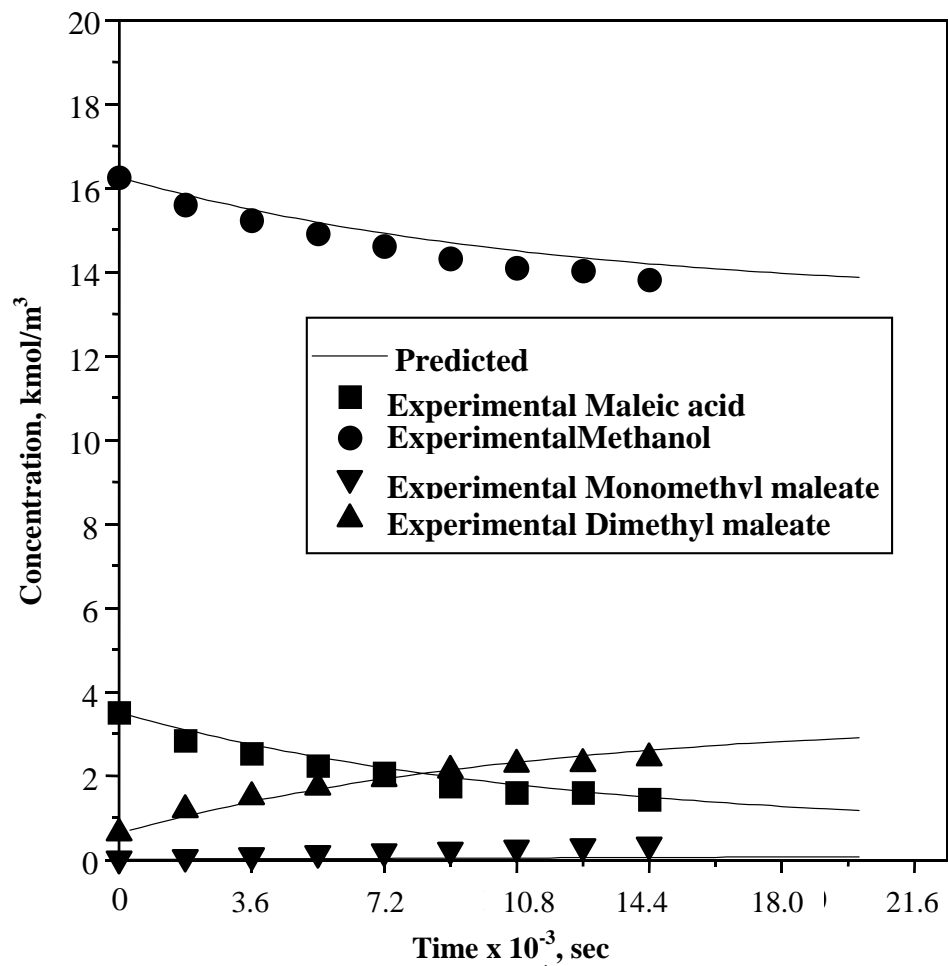


Fig. 4.2: Concentration-time profile at 318 K
Reaction Conditions: $C_{A0} = 4.152 \text{ kmol/m}^3$, $C_{B0} = 16.58 \text{ kmol/m}^3$

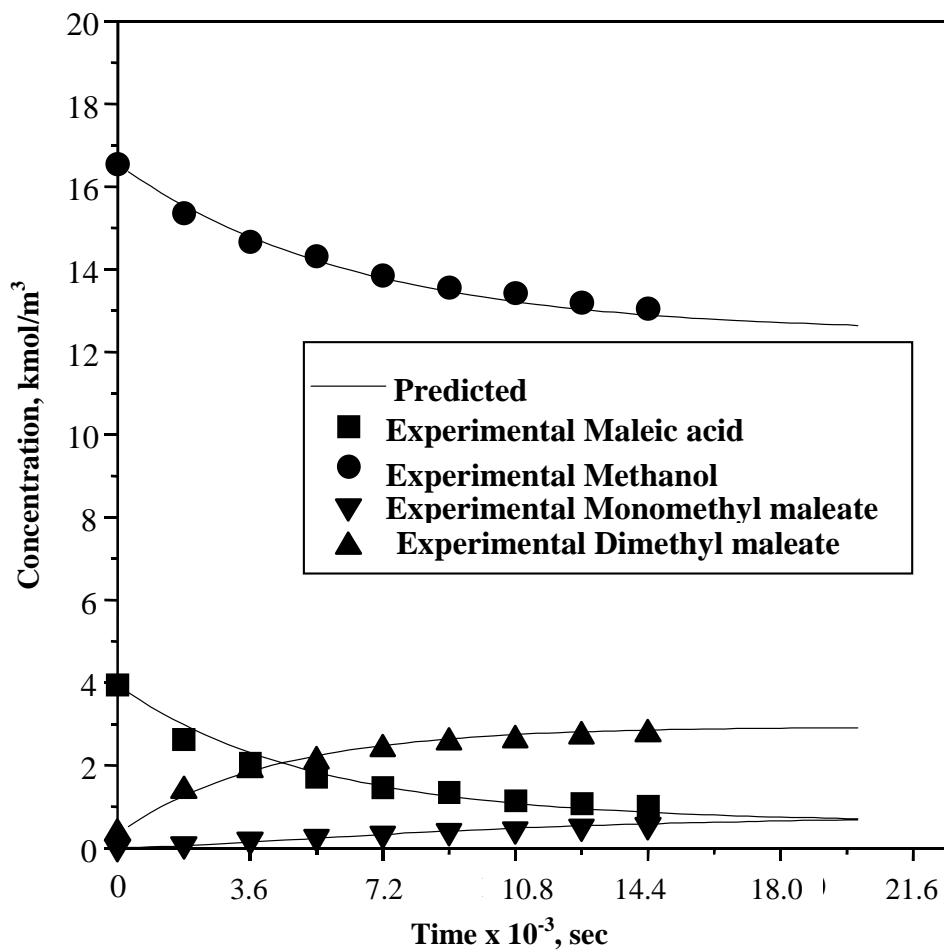


Fig. 4.3: Concentration-time profile at 328 K
Reaction Conditions: $C_{A0} = 4.296 \text{ kmol/m}^3$, $C_{B0} = 16.731 \text{ kmol/m}^3$

4.4.2 Kinetics of homogeneous reaction

In order to study the kinetics of homogeneous esterification reaction, several experiments were carried out at different concentrations of maleic acid and methanol over a temperature range of 308-328 K. The results are presented in Figs. 4.1- 4.6 for different reactant concentrations. One interesting observation was that the homogeneous reaction rate was very significant for this system. This is due to the strong catalytic effect of the maleic acid. The homogeneous rate of reaction can be represented as:

$$r_1 = k_1 C_1 \cdot C_2 \quad (4.1)$$

$$r_2 = k_2 C_4 \cdot C_5 \quad (4.2)$$

$$r_3 = k_3 C_4 \cdot C_2 \quad (4.3)$$

$$r_4 = k_4 C_3 \cdot C_5 \quad (4.4)$$

Where, r_1 and r_2 represent forward and backward reaction rates for step-I (kmol/m³/s); r_3 and r_4 represent forward and backward reaction rates for step-II (kmol/m³/s); C_1, C_2, C_3, C_4, C_5 are concentrations of maleic acid, methanol, monomethyl maleate, dimethyl maleate and water respectively (kmol/m³). The rate constants k_1 to k_4 in the kinetic model for the homogeneous reaction were evaluated by simulating the observed concentration-time data. The simulation model for the batch reactor under isothermal conditions can be written as:

$$\frac{dC_1}{dt} = r_2 - r_1 \quad (4.5)$$

$$\frac{dC_2}{dt} = (r_2 - r_1) + (r_4 - r_3) \quad (4.6)$$

$$\frac{dC_3}{dt} = r_3 - r_4 \quad (4.7)$$

$$\frac{dC_4}{dt} = (r_1 - r_2) + (r_4 - r_3) \quad (4.8)$$

$$\frac{dC_5}{dt} = (r_1 - r_2) + (r_3 - r_4) \quad (4.9)$$

The initial conditions are,

$$\text{at } t=0; C_1=C_{A0}, C_2=C_{B0} \text{ and } C_3, C_4 \text{ and } C_5=0 \quad (4.10)$$

where, C_{A0} and C_{B0} are the initial concentrations of maleic acid and methanol respectively.

A nonlinear regression analysis was used to obtain the best-fit values of the kinetic parameters. For this purpose, an optimization program based on Marquart's method combined with a Runge-Kutta method was used to solve the above set of equations 4.5-4.10. The kinetic parameters were evaluated for standard experimental conditions (Acid: Alcohol 1:4) at 308, 318 and 328K respectively, as presented in Table 4.2.

Table 4.2: Homogeneous reaction rate constants

Temp, K	$k_1 \times 10^5$, m ³ /kmol/s	$k_2 \times 10^4$, m ³ /kmol/s	$k_3 \times 10^4$, m ³ /kmol/s	$k_4 \times 10^5$, m ³ /kmol/s
308	0.405	1.239	1.084	1.067
318	0.853	5.946	1.783	1.935
328	1.489	9.581	3.101	3.661

A comparison of model predictions with experimental data is shown in Figs. 4.1-4.3. It can be seen that the model prediction was found to be in good agreement with the experimental data. The average error was found to be < 5%. These rate constants were also used to predict the concentration time profiles at 1:6 molar ratio of acetic acid and methanol at 308, 318 and 328K, as shown in Figs. 4.4-4.6 respectively. For these experiments also, the agreement was found to be very good. The effect of temperature on the rate constants is shown in Fig. 4.7, in form of Arrhenius plots and the activation energies for homogeneous forward and backward reactions were evaluated as 53.89, 85.18 and 43.34, 50.89 kJ/mol respectively. The activation energies indicate that the uncatalyzed reaction was prominent.

4.4.3 Kinetics of ion exchange resin catalyzed esterification reaction

The overall rate of reaction (with catalyst) was studied using ion exchange resin as a catalyst following the procedure described in section 4.2.3. The effect of different parameters such as catalyst loading, initial concentration of reactants, temperature and particle size was studied. In each experiment, the concentrations of reactants and products were recorded as functions of time. A typical concentration-

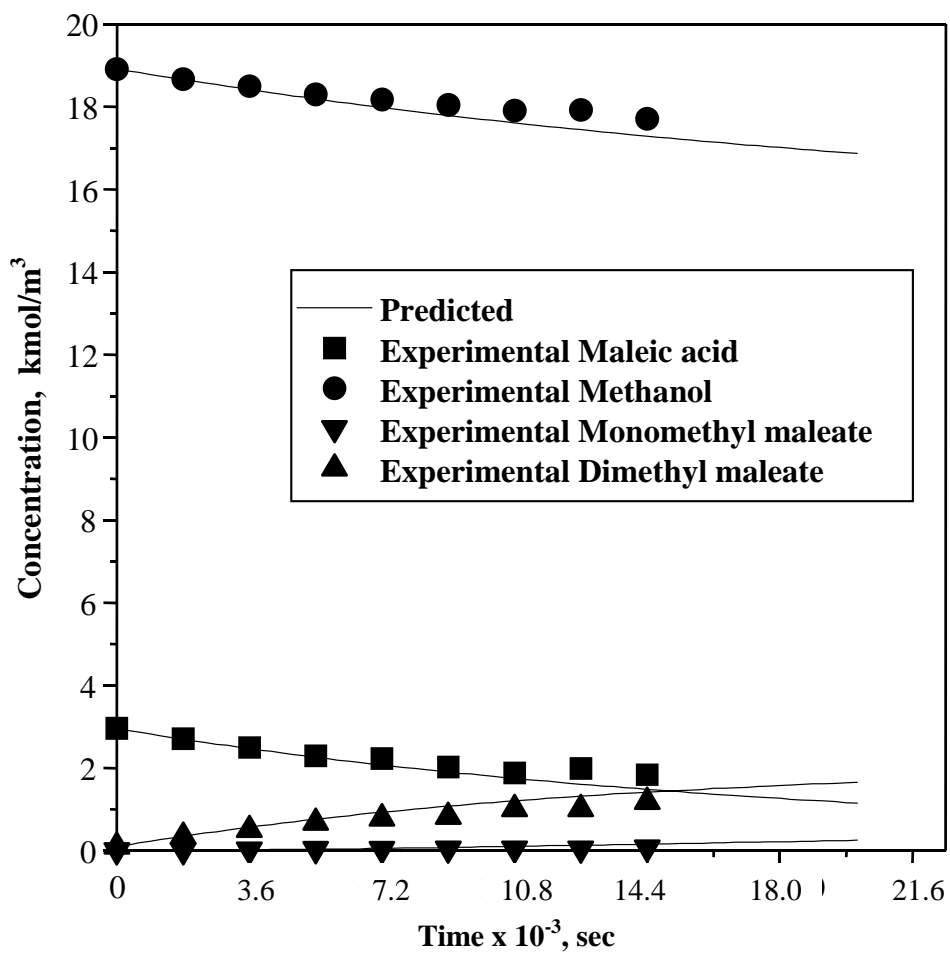


Fig. 4.4: Concentration-time profile at 308 K, for Maleic acid-Methanol molar ratio of 1:6
Reaction Conditions: $C_{A0} = 3.049 \text{ kmol/m}^3$, $C_{B0} = 18.961 \text{ kmol/m}^3$

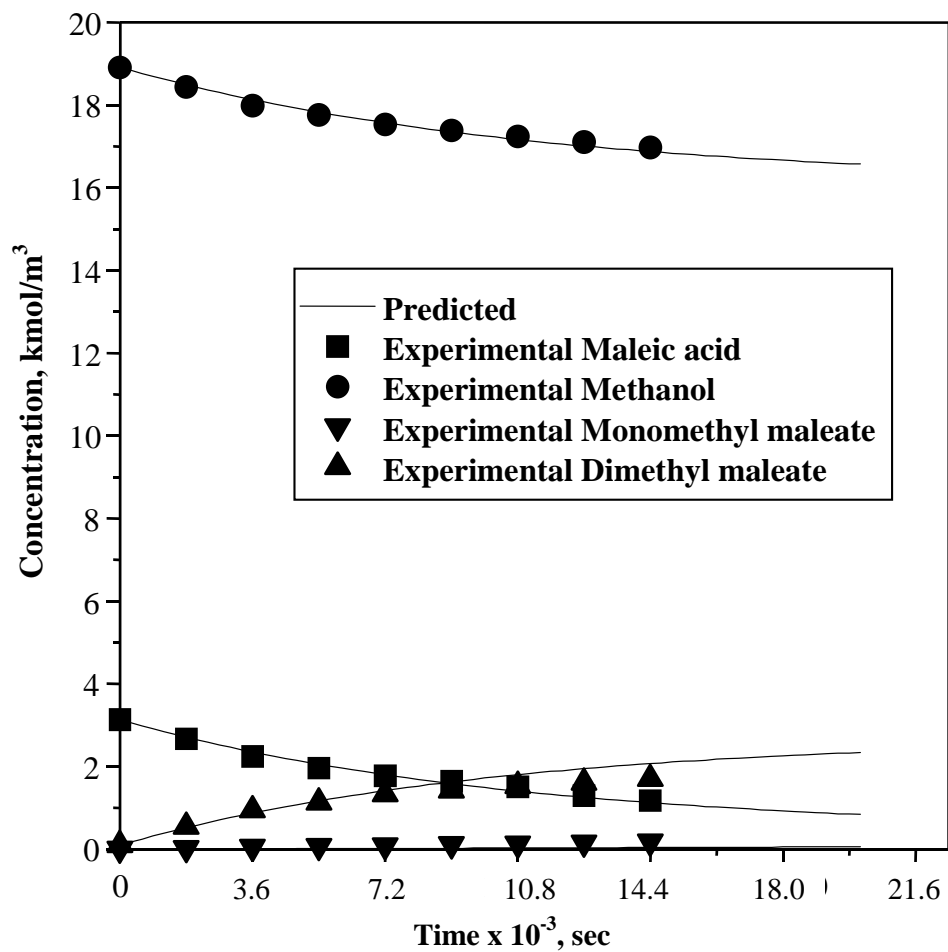


Fig. 4.5: Concentration-time profile at 318 K, for Maleic acid-Methanol molar ratio of 1:6
Reaction Conditions: $C_{A0} = 3.224 \text{ kmol/m}^3$, $C_{B0} = 18.961 \text{ kmol/m}^3$

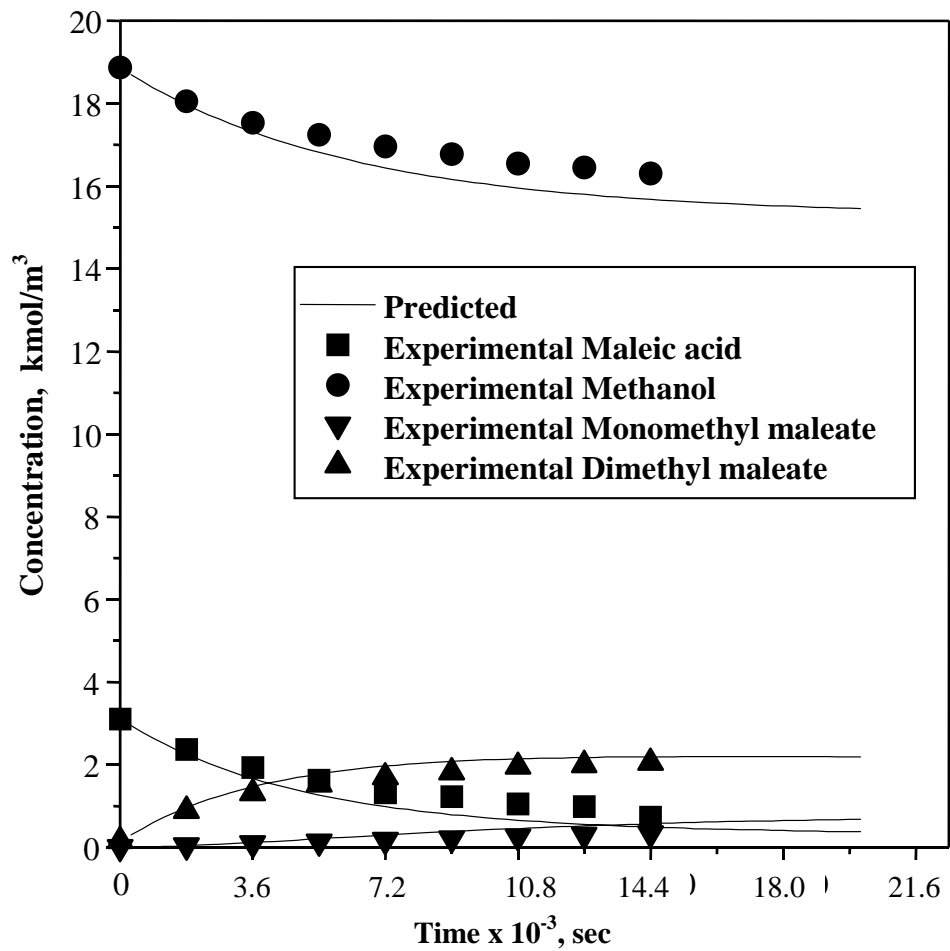


Fig. 4.6: Concentration-time profile at 328 K, for Maleic acid-Methanol molar ratio of 1:6

Reaction Conditions: $C_{A0} = 3.256 \text{ kmol/m}^3$, $C_{B0} = 18.936 \text{ kmol/m}^3$

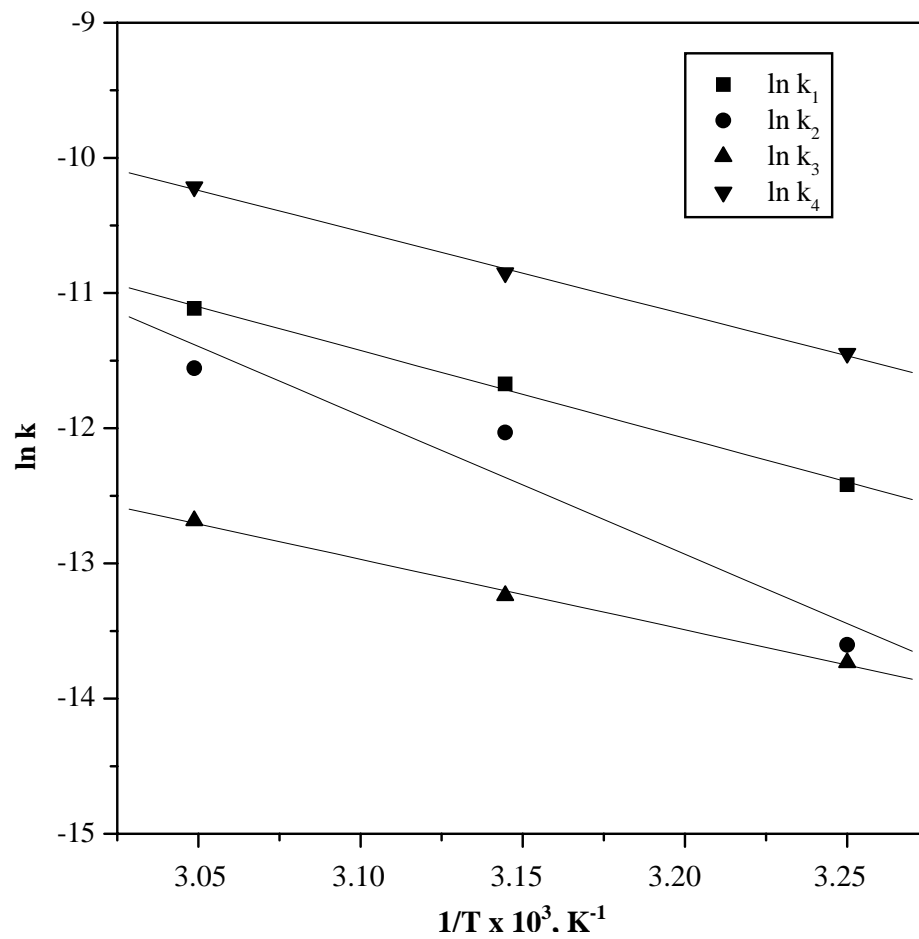


Fig. 4.7: Effect of temperature on homogeneous reaction rate constants

time profile at 308 K is shown in Fig. 4.10 for the ion exchange resin catalyzed esterification of maleic acid.

It is interesting to note that the concentration-time profiles under identical reaction conditions for the homogeneous and the heterogeneous reactions were almost similar (Figs. 4.2 and 4.11). The major difference was that for the ion exchanged resin catalyzed reaction, the amount of dimethyl maleate formed was significant compared to that in the homogeneous reaction.

4.4.3.1 Analysis of initial rate data

Initial rate data were used to understand the effect of different operating parameters such as temperature, reactant concentration, catalyst loading and particle size as well as the significance of mass transfer effects. Initial rates were calculated from concentration-time data of maleic acid in a similar way as described in Section 2.4.3.1 and are presented in Table 4.3.

The effect of catalyst loading on the initial rate was studied at 318 K. The results are presented in Fig. 4.8, which shows that there is no significant effect of catalyst loading on the initial rate of reaction. This may be due to the fact that the homogeneous reaction is predominant here and hence the effect is not seen clearly.

The effect of particle size on initial rate of reaction is shown in Fig 4.9. It can be seen that the initial rate was found to be independent of particle size below 0.5×10^{-3} m, indicating the absence of intraparticle diffusion effects. For the kinetic study all the experiments were conducted using an average particle size of 0.458 mm.

4.4.3.2 Analysis of mass transfer effects

The initial rate data were also analyzed to check the significance of liquid-solid and intraparticle mass transfer effects under the conditions used in this work. For this purpose factors α_2 and ϕ_{exp} were evaluated as described earlier (Section 2.4.3.2) and are presented in Table 4.3.

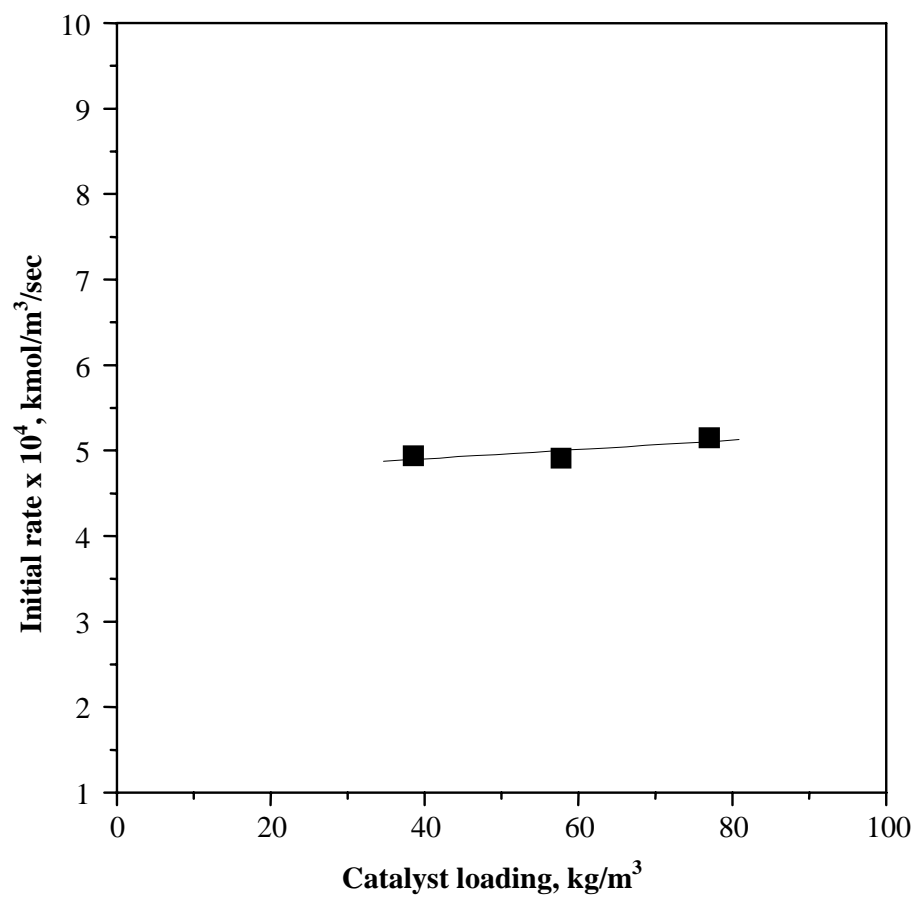


Fig. 4.8: Effect of catalyst loading on rate of reaction
Reaction Condition: Temp = 318 K, Maleic acid-MeOH molar ratio = 1:4, $d_p = 4.58 \times 10^{-4}$ m

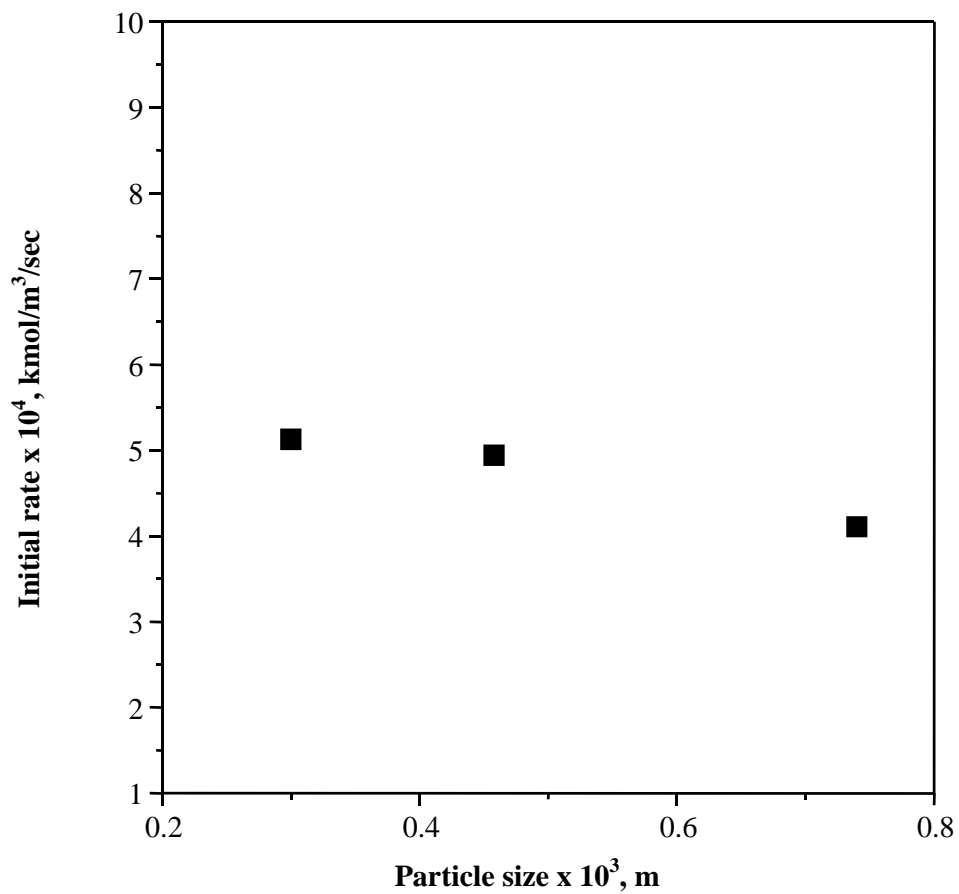


Fig. 4.9: Effect of particle size on rate of reaction

Reaction Condition: Temp = 318 K, Maleic acid-MeOH molar ratio = 1:4, w = 16.3 kg/m³

Table 4.3: Initial rata data for ion exchange resin catalyzed esterification of maleic acid with methanol

Temp. K	d _p , mm	Catalyst loading, kg/m ³	Initial Maleic acid conc., kmol/m ³	Initial MeOH conc., kmol/m ³	Initial rate × 10 ⁴ , kmol/ m ³ /sec	α ₂ × 10 ⁵	φ _{exp}
308	0.458	38.5	4.185	16.733	1.96	2.090	0.152
	0.458	38.5	3.049	18.958	2.06	3.016	0.182
318	0.458	38.5	4.681	16.537	4.94	4.711	0.224
	0.458	38.5	3.093	18.946	3.47	5.007	0.231
	0.458	57.75	4.161	16.788	4.91	3.512	0.193
	0.458	77.0	4.090	16.762	5.15	2.810	0.173
	0.300	38.5	4.127	16.734	5.13	3.634	0.159
	0.740	38.5	4.155	16.778	4.11	6.749	0.331
328	0.458	38.5	4.5735	16.714	4.91	4.792	0.222
	0.458	38.5	3.2268	18.932	4.55	6.294	0.255

Table 4.4: Diffusivity of maleic acid in methanol

Temperature, K	Molecular Diffusivity D × 10 ⁹ , m ² /s	Effective Diffusivity D _e × 10 ¹⁰ , m ² /s
308	2.222	4.633
318	2.295	4.780
328	2.367	4.931

The α₂ values were in a range 1 × 10⁻⁵ to 8 × 10⁻⁵ indicating the absence of liquid-solid mass transfer resistance, for the range of operating conditions used in this work. The values of φ_{exp} varied within 0.1 to 0.3, indicating that the intraparticle diffusion is likely to be significant under certain experimental conditions. The values of diffusivity and effective diffusivity of maleic acid - methanol system, using Wilke-Chang equation (1955), are presented in Table 4.4. To study the intrinsic kinetics of heterogeneous reaction, a smaller particle size (0.46 μm) of the ion exchange resin was used where the intraparticle diffusion resistances were negligible.

4.5 Kinetic model for the heterogeneous reaction

In this case the experiments were carried out using ion exchange resin catalyst in the same reactor. For interpretation of the kinetics, several experiments were carried out in which concentration-time data were observed over a range of conditions given in Table 4.1. The concentration-time profiles for typical sets of experimental conditions (Acid: Alcohol = 1:4, particle size 0.458 mm.) are shown in Figs. 4.10 - 4.12, for 308, 318 and 328 K respectively. The overall reaction rate is the sum of homogeneous and heterogeneous reaction rates and can be represented as:

$$r_5 = k_1 C_1 \cdot C_2 + w k_5 C_1 \cdot C_2 \quad (4.11)$$

$$r_6 = k_2 C_4 \cdot C_5 + w k_6 C_4 \cdot C_5 \quad (4.12)$$

$$r_7 = k_3 C_4 \cdot C_2 + w k_7 C_4 \cdot C_2 \quad (4.13)$$

$$r_8 = k_4 C_3 \cdot C_5 + w k_8 C_3 \cdot C_5 \quad (4.14)$$

Where, w is the weight of catalyst in kg/m^3 ; r_5 and r_6 represent overall forward and backward reaction rates for step-I; r_7 and r_8 represent overall forward and backward reaction rates for step-II; C_1, C_2, C_3, C_4, C_5 are concentrations of Maleic acid, Methanol, Mono-methyl maleate, Di-methyl maleate and water respectively, (kmol/m^3). The batch reactor model at isothermal conditions can be written as,

$$\frac{dC_1}{dt} = r_6 - r_5 \quad (4.15)$$

$$\frac{dC_2}{dt} = (r_6 - r_5) + (r_8 - r_7) \quad (4.16)$$

$$\frac{dC_3}{dt} = r_7 - r_8 \quad (4.17)$$

$$\frac{dC_4}{dt} = (r_5 - r_6) + (r_8 - r_7) \quad (4.18)$$

$$\frac{dC_5}{dt} = (r_5 - r_6) + (r_7 - r_8) \quad (4.19)$$

The initial conditions are,

$$\text{at } t = 0; C_1 = C_{A0}, C_2 = C_{B0} \text{ and } C_3, C_4 \text{ and } C_5 = 0 \quad (4.20)$$

where, C_{A0} and C_{B0} are the initial concentrations of maleic acid and methanol respectively.

The rate constants k_5 to k_8 for the heterogeneous reactions were evaluated by simulation of the experimental data on concentration-time, using the batch reactor model at different temperatures. The approach followed to evaluate the kinetic parameters for the overall rate of reaction was the same as described in (Section 2.2.5). A nonlinear regression analysis combined with a Runge-Kutta method was used to solve the equations 4.15 to 4.20 to obtain the best-fit values of the parameters. Only the parameters k_5 to k_8 in equations 4.11 - 4.14 were optimized. The homogeneous rate constants k_1 to k_4 were not optimized and the values already determined were used (Table 4.2). This exercise was repeated for the concentration-time profiles at other temperatures. The optimized values of the heterogeneous reaction rate constants are presented in Table 4.5. Figs. 4.13 to 4.15 show comparison of model prediction with experiments, which indicated that the agreement between the model predictions and experimental observations are excellent.

Using these parameters, the concentration-time profiles at different operating conditions were also predicted. For example the effect of catalyst loading on the concentration-time profile is presented in Fig. 4.16, while the model predictions for the effect of particle size are shown in Fig. 4.17. In all these cases the model predictions were found to agree well with the experimental observations. The temperature dependence of the rate parameters k_5 to k_8 is shown in Fig. 4.18. From these Arrhenius plots the values of activation energies for the forward and reverse heterogeneous reactions were evaluated as 38.5, 28.894 and 72.1, 46.03 kJ/mol respectively.

Table 4.5: Heterogeneous reaction rate constants

Temp, K	$k_5 \times 10^7,$	$k_6 \times 10^6,$	$k_7 \times 10^7,$	$k_8 \times 10^6,$
	$\text{m}^3/\text{kmol}/\text{sec}.$	$\text{m}^3/\text{kmol}/\text{sec}.$	$\text{m}^3/\text{kmol}/\text{sec}.$	$\text{m}^3/\text{kmol}/\text{sec}.$
	m^3/kg	m^3/kg	m^3/kg	m^3/kg
308	0.920	0.702	0.501	2.011
318	1.625	1.051	1.519	4.126
328	2.310	1.410	2.910	6.101

4.6 Selectivity behavior of monomethyl maleate

In a series/ parallel reaction system such as esterification of maleic acid, it is useful to study the selectivity pattern of the intermediate product (monomethyl maleate) as a function of different operating parameters. For the present work, the selectivity of monomethyl maleate was calculated at different conversion levels of maleic acid. In Figs. 4.19-4.21, the selectivity of monomethyl maleate obtained as a function of maleic acid conversion is presented for different reaction conditions. Some specific observations on selectivity behavior are summarized below.

Homogeneous reaction:

- At all temperatures the selectivity of MMM decreased with increase in conversion of maleic acid, however, the decrease was only marginal. The selectivity decreased from about 98 % to about 68 % when conversion increased from 10% to 80 % (see Fig. 4.19)
- At higher mole ratio (1: 6), the selectivity off MMM was marginally higher at higher temperatures at all levels of conversion. However, at a lower molar ratio (1:4), the selectivity decreased at higher temperatures, though the variations observed were not very significant.

Heterogeneous reaction:

- For heterogeneous reaction, the selectivity of MMM as a function of reactant concentration (molar ratio) was similar to that observed for the homogeneous reaction (Fig. 4.20).
- The variation of the selectivity of MMM as a function of catalyst loading was negligible for a given set of reaction conditions at all conversion levels (Fig. 4.21).
- Compared to the homogeneous reaction, the selectivity of MMM in heterogeneous reaction was lower. This showed that the use of catalyst increases the conversion of monomethyl maleate to dimethyl maleate.

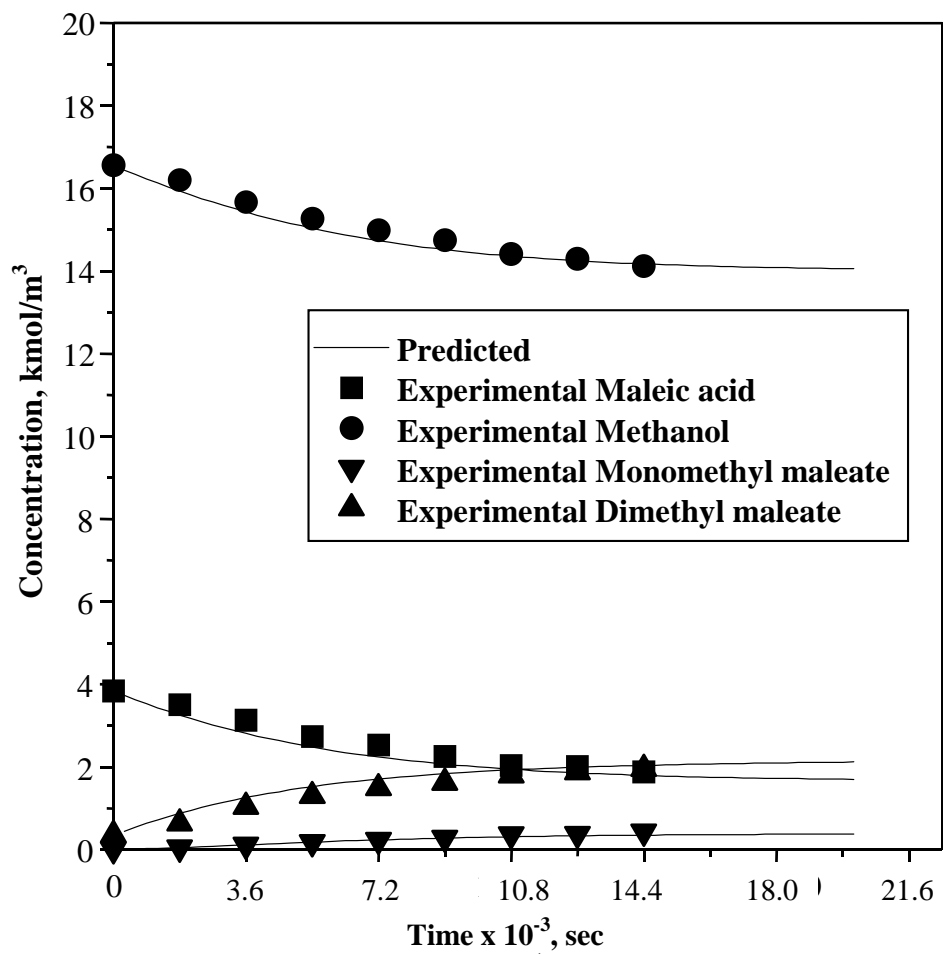


Fig. 4.10: Concentration-Time profile at 308 K
Reaction Conditions: $C_{A0} = 4.185 \text{ kmol/m}^3$, $C_{B0} = 16.733 \text{ kmol/m}^3$,
 $w = 38.5 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$

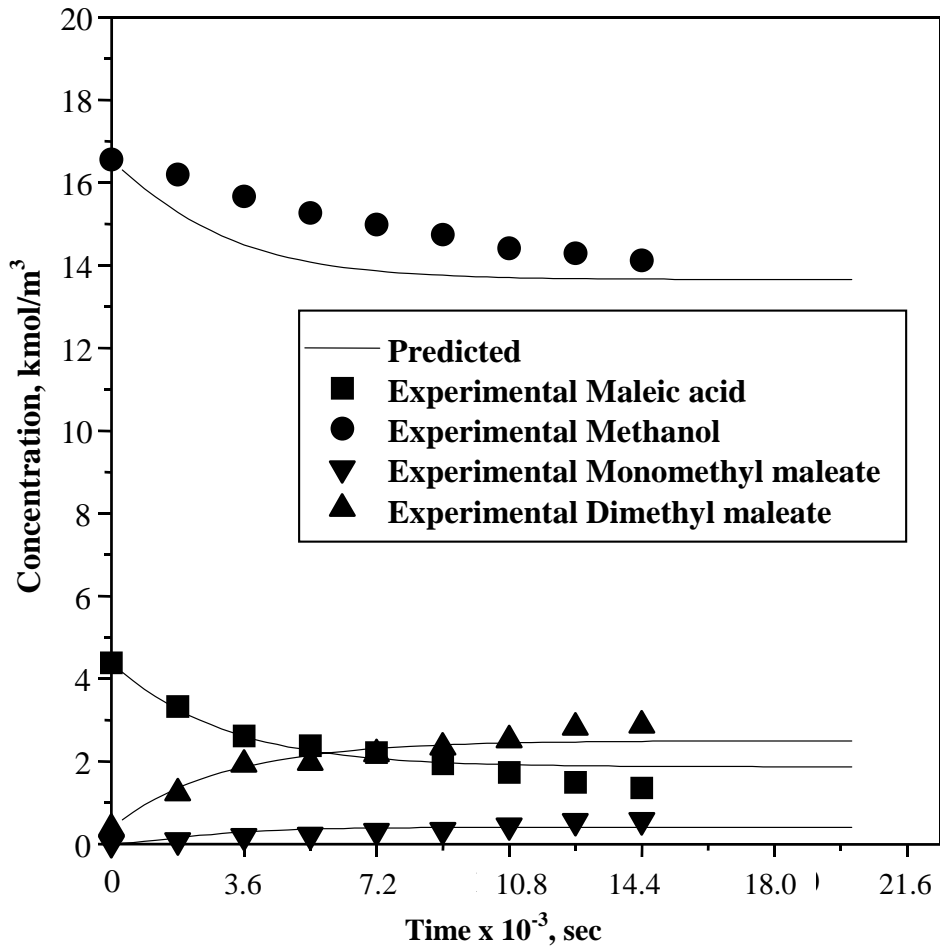


Fig. 4.11: Concentration-Time Profile at 318 K

Reaction Conditions: $C_{A0} = 4.681 \text{ kmol/m}^3$, $C_{B0} = 16.537 \text{ kmol/m}^3$,
 $w = 38.5 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$

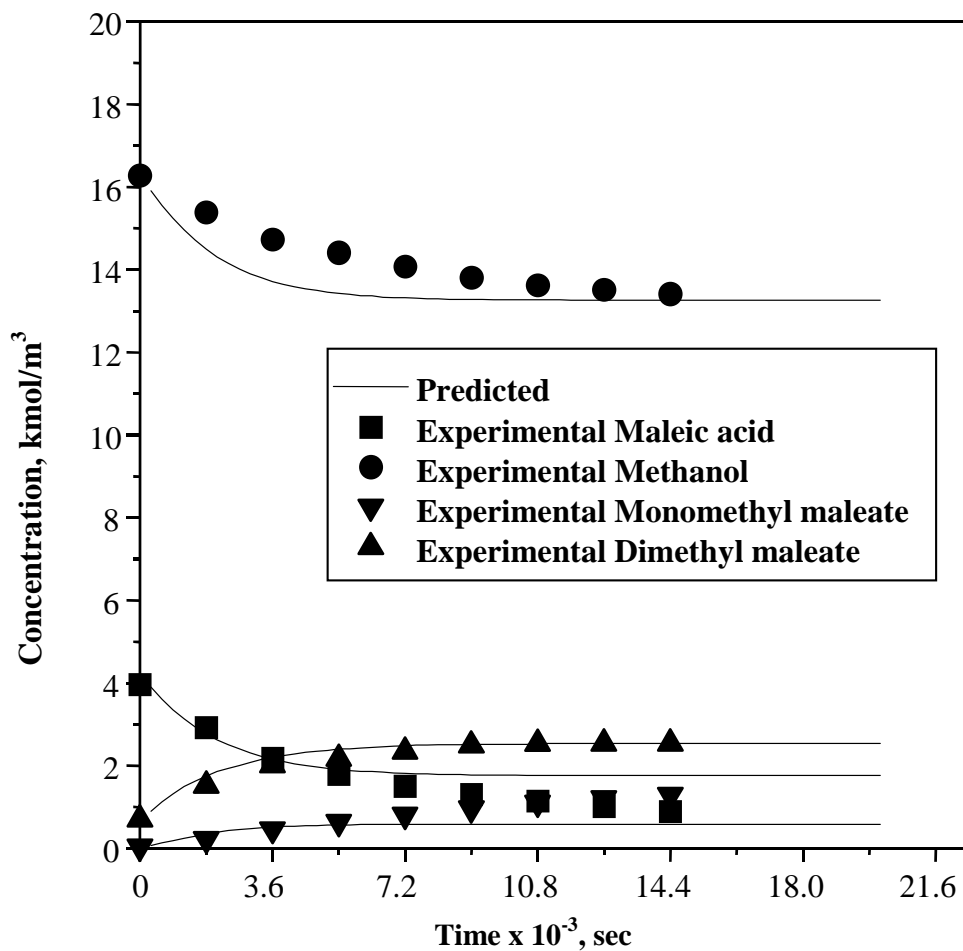


Fig. 4.12: Concentration-Time profile at 328K

Reaction Conditions: $C_{A0} = 4.573 \text{ kmol/m}^3$, $C_{B0} = 16.714 \text{ kmol/m}^3$,
 $w = 38.5 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$

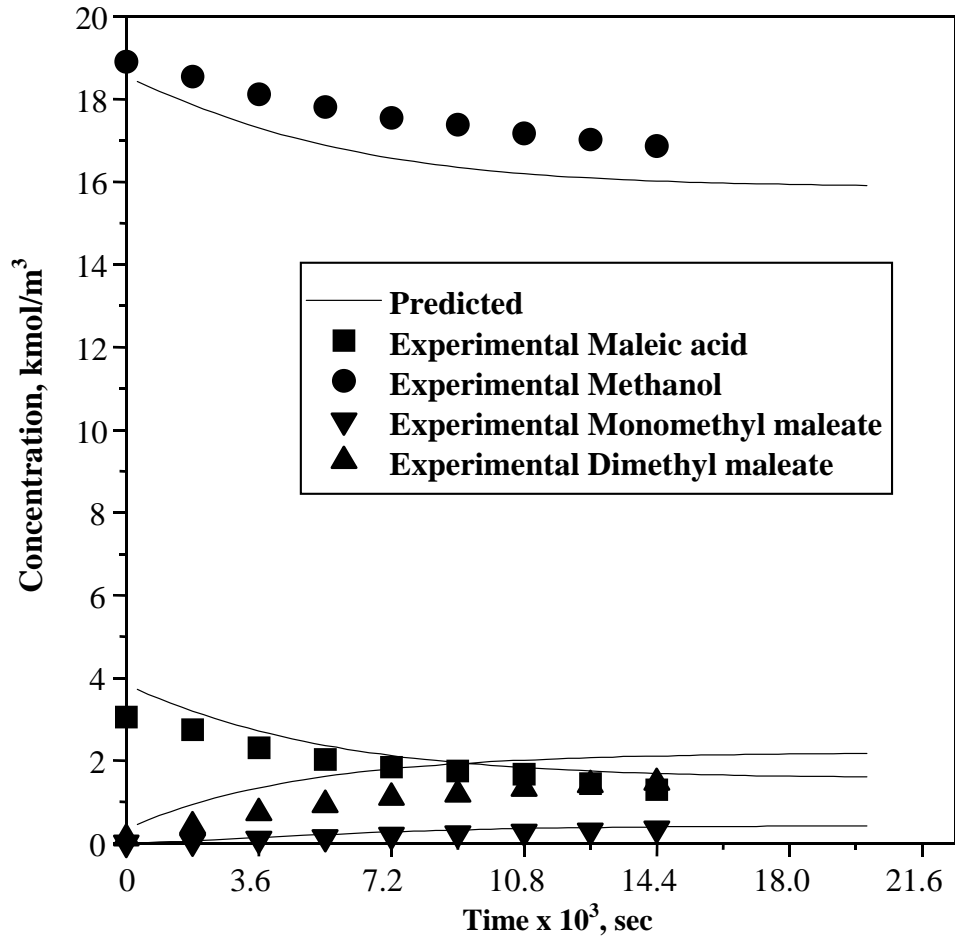


Fig. 4.13: Concentration-Time profile at 308 K for Maleic acid-Methanol molar ratio of 1:6

Reaction Conditions: $C_{A0} = 3.049 \text{ kmol/m}^3$, $C_{B0} = 18.958 \text{ kmol/m}^3$,
 $w = 38.5 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$

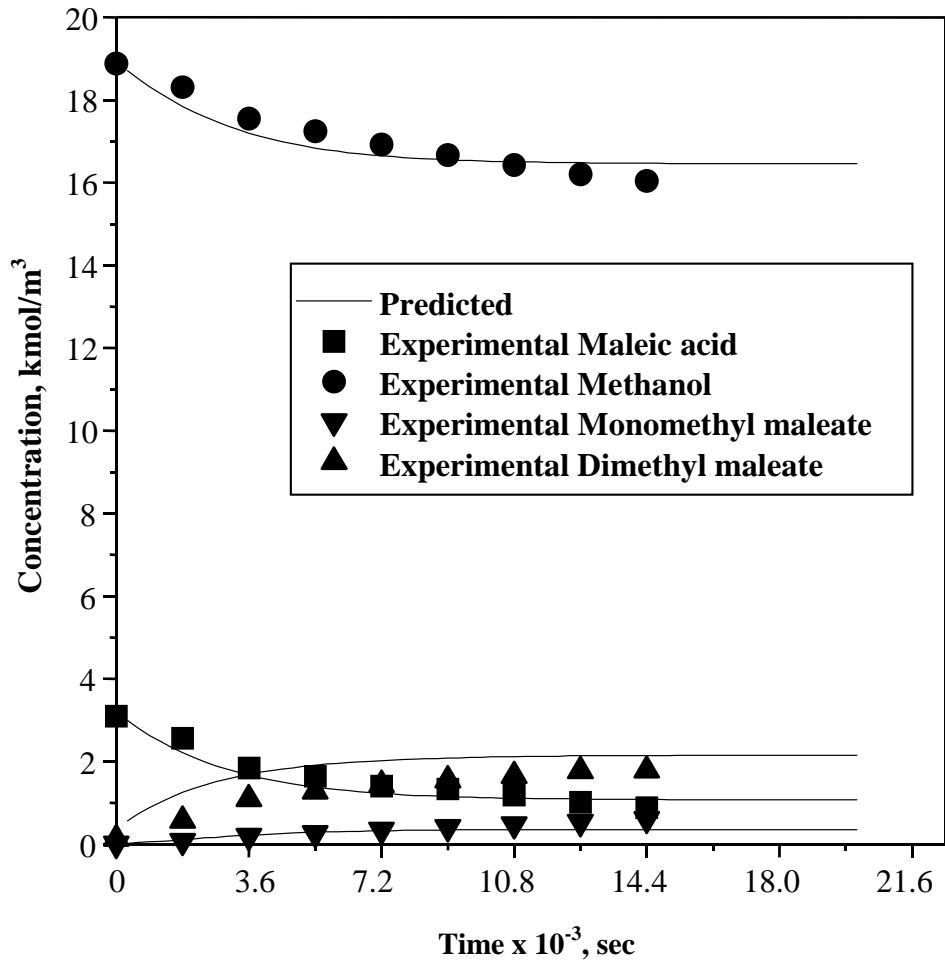


Fig. 4.14: Concentration-Time profile at 318 K, for Maleic acid-Methanol molar ratio of 1:6

Reaction Conditions: $C_{A0} = 3.093 \text{ kmol/m}^3$, $C_{B0} = 18.946 \text{ kmol/m}^3$, $w = 38.5 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$

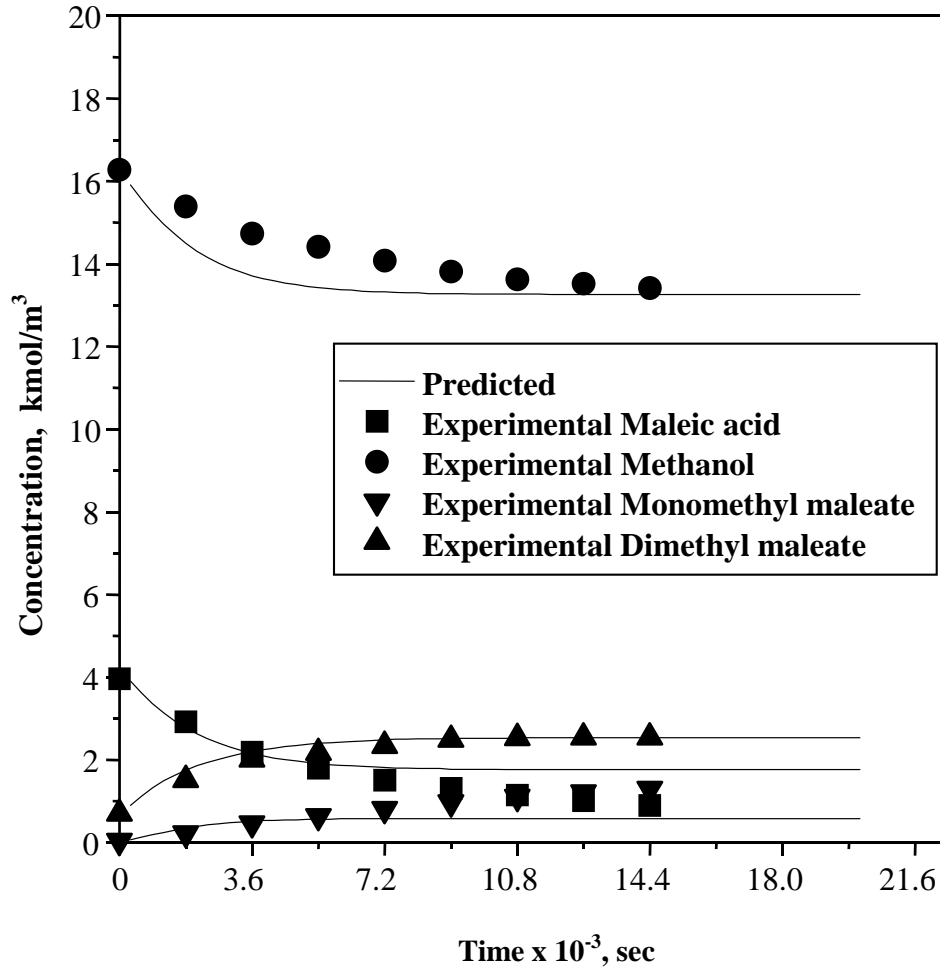
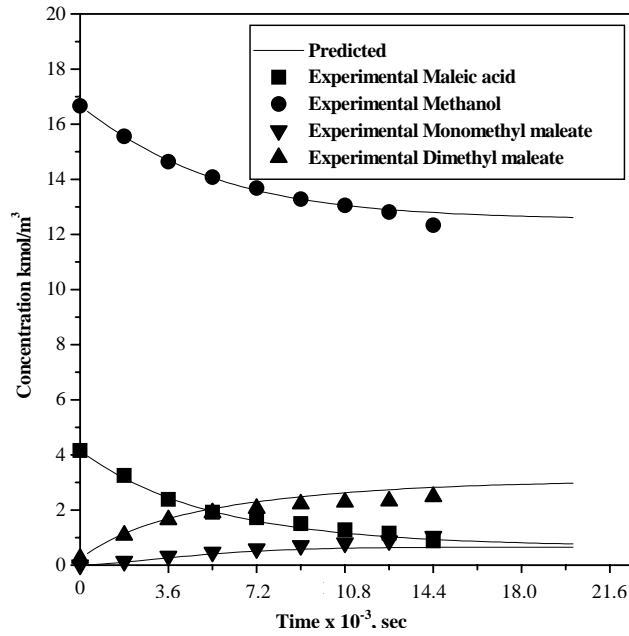
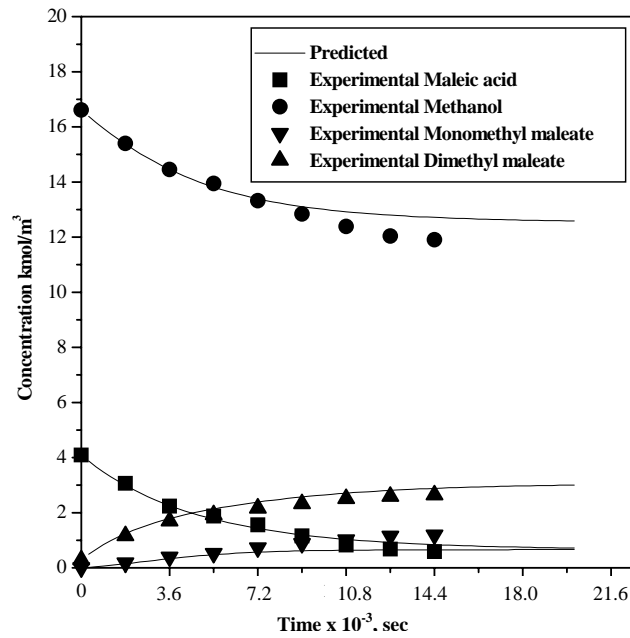


Fig. 4.15: Concentration-Time Profile at 328 K, for Maleic acid-Methanol molar ratio of 1:6

Reaction Conditions: $C_{A0} = 3.227 \text{ kmol/m}^3$, $C_{B0} = 18.932 \text{ kmol/m}^3$,
 $w = 38.5 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$

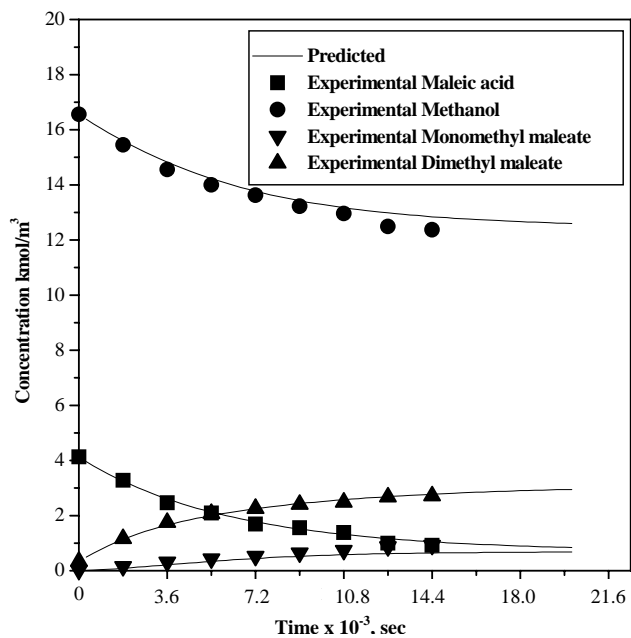


Reaction Conditions: $w = 57.75 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$,
 $C_{A0} = 4.161 \text{ kmol/m}^3$, $C_{B0} = 16.788 \text{ kmol/m}^3$

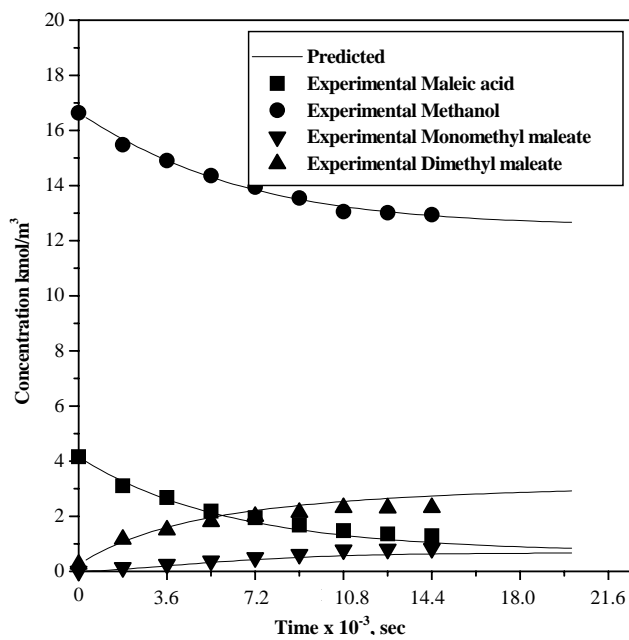


Reaction Conditions: $w = 77.0 \text{ kg/m}^3$, $d_p = 5 \times 10^{-4} \text{ m}$,
 $C_{A0} = 4.09 \text{ kmol/m}^3$, $C_{B0} = 16.762 \text{ kmol/m}^3$

Fig. 4.16: Concentration-time profile for catalyst loading at 318 K for Maleic acid : Methanol of 1:4



Reaction Conditions: $w = 38.5 \text{ kg/m}^3$, $d_p = 3 \times 10^{-4} \text{ m}$,
 $C_{A0} = 4.155 \text{ kmol/m}^3$, $C_{B0} = 16.778 \text{ kmol/m}^3$



Reaction Conditions: $w = 38.5 \text{ kg/m}^3$, $d_p = 7.5 \times 10^{-4} \text{ m}$,
 $C_{A0} = 4.155 \text{ kmol/m}^3$, $C_{B0} = 16.778 \text{ kmol/m}^3$

Fig. 4.17: Concentration-time profile for particle sizes at 318 K for Maleic acid:Methanol of 1:4

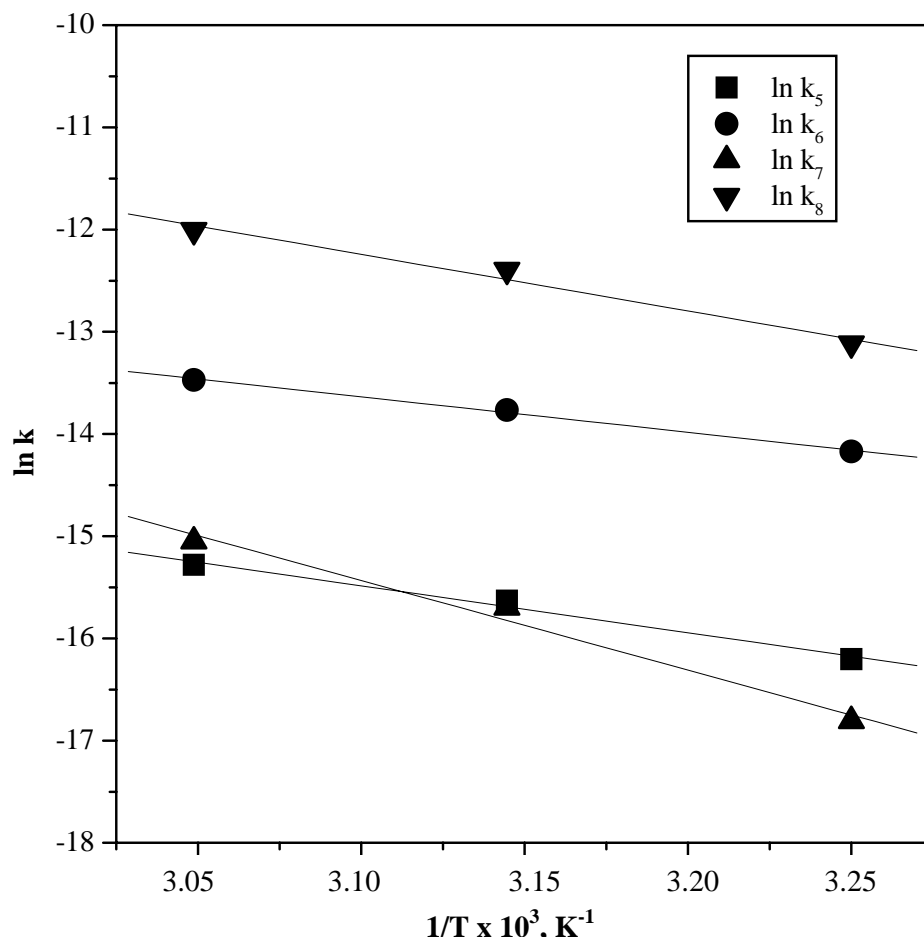
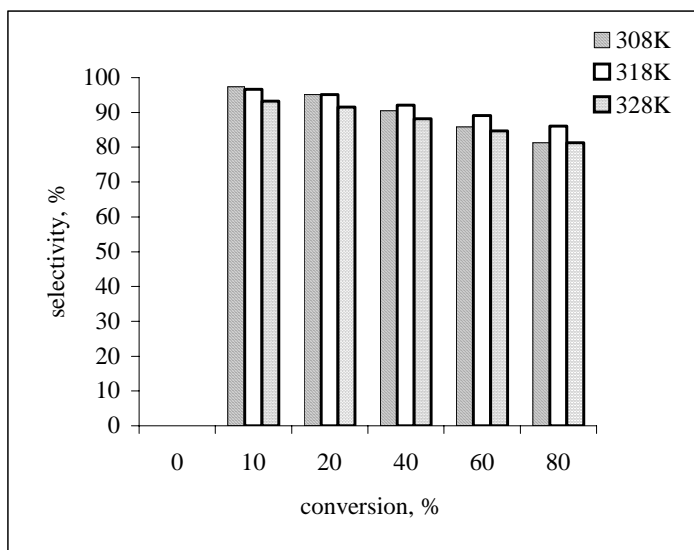
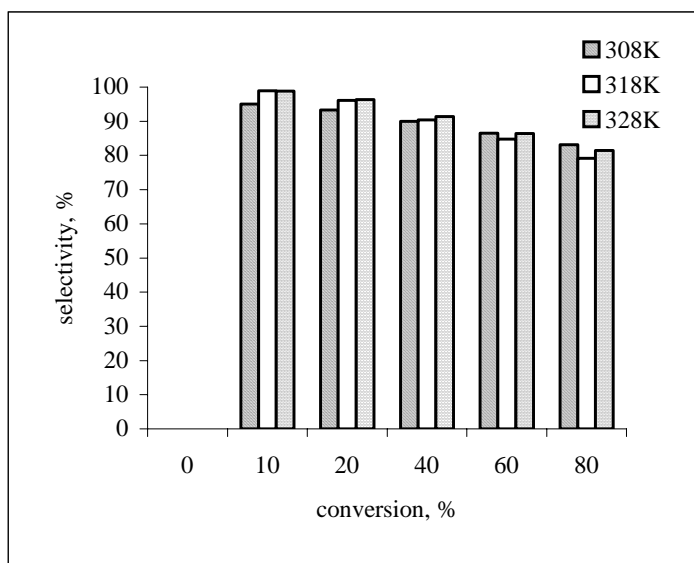


Fig. 4.18: Effect of temperature on heterogeneous rate constants



(A)

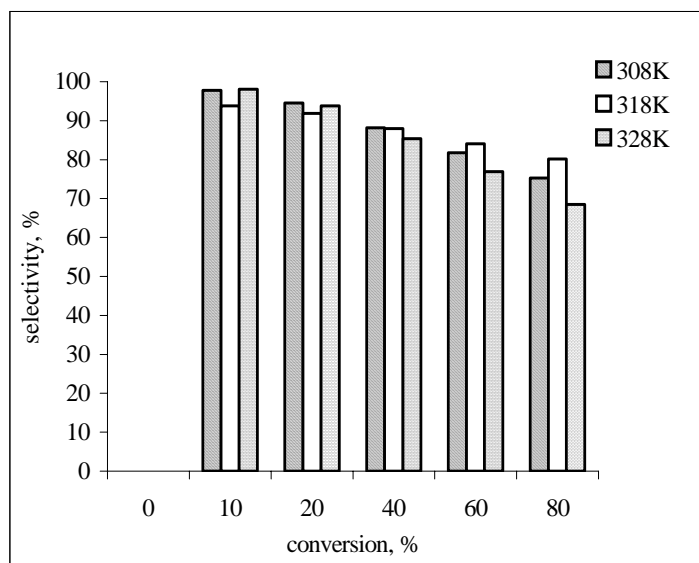


(B)

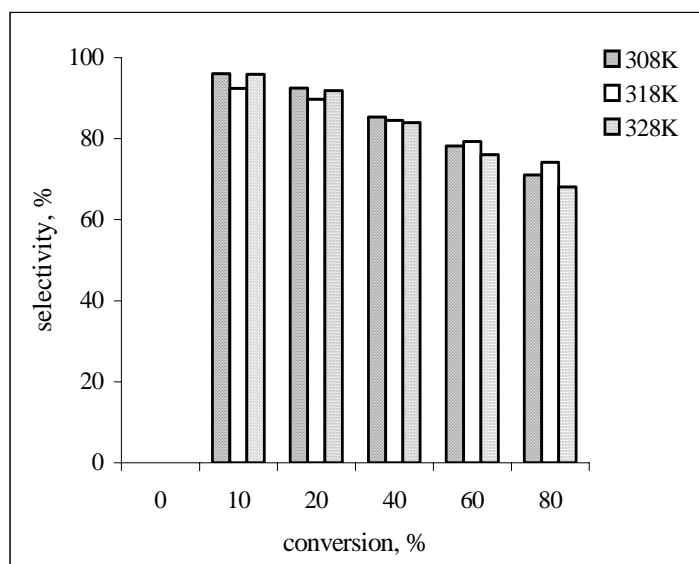
Fig. 4.19: Selectivity behavior of monomethyl maleate in homogeneous reactions

(A) Maleic acid: Methanol = 1:4

(B) Maleic acid : Methanol = 1:6



(A)



(B)

Fig. 4.20: Selectivity behavior of monomethyl maleate in heterogeneous reactions

(A) Maleic acid: Methanol = 1:4

(B) Maleic acid : Methanol = 1:6

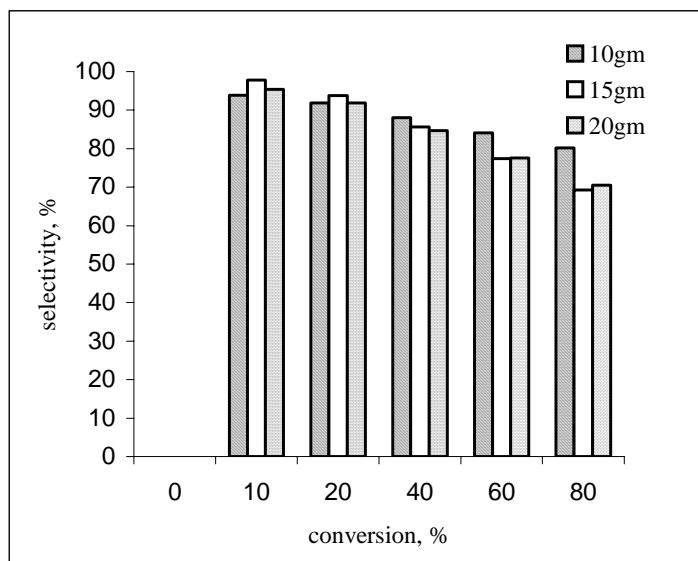


Fig. 4.21: Selectivity behavior of monomethyl maleate at different catalyst loading

Reactions condition: Maleic acid: Methanol = 1:4

Temperature = 318 K

4.7 Conclusions

The esterification of maleic acid with methanol in a batch slurry reactor was investigated. The kinetics of homogeneous esterification was investigated separately to assess its contribution. For the heterogeneous catalytic reaction, the ion exchange resin with a smaller particle size (0.46 μm) was used where the intraparticle diffusion resistances were negligible. One interesting observation was that the homogeneous reaction rate was significantly higher for this system compared to the esterification of monoacids discussed in Chapters 2 and 3. This is due to the catalytic effect of the maleic acid. The effects of temperature, methanol concentration, catalyst loading and particle size were investigated to evaluate the intraparticle diffusive resistance. For interpretation of the kinetics, the observed concentration-time data were used and the rate parameters were evaluated at each temperature using a batch reactor model. The activation energies for homogeneous forward and backward reactions were evaluated as 53.89, 85.18 and 43.34, 50.89 kJ/mol respectively. For heterogeneous forward and backward reactions these were evaluated as 38.5, 28.894 and 72.1, 46.03 kJ/mol respectively.

Notations

a_p	effective liquid-solid interfacial area per unit volume of slurry, m^2/m^3
C_1	concentrations of maleic acid, kmol/m^3
C_2	concentrations of methanol, kmol/m^3
C_3	concentrations of monomethyl maleate, kmol/m^3
C_4	concentration of water, kmol/m^3
C_5	concentrations of dimethyl maleate, kmol/m^3
C_{A0}	concentrations of maleic acid at $t = 0$, kmol/m^3
C_{B0}	concentrations of methanol at $t = 0$, kmol/m^3
C_i	concentration of i^{th} component, kmol/m^3
D_e	effective diffusivity, m^2/sec
D	molecular diffusivity, m^2/sec
k_1, k_2	rate constants for homogeneous forward reactions, $\text{m}^3/\text{kmol}/\text{sec}$
k_3, k_4	rate constants for homogeneous backward reactions, $\text{m}^3/\text{kmol}/\text{sec}$
k_5, k_6	rate constants for heterogeneous forward reactions, $\text{m}^3/\text{kmol}/\text{sec} \cdot \text{m}^3/\text{kg}$

k_7, k_8	rate constants for heterogeneous backward reactions, $\text{m}^3/\text{kmol}/\text{sec} \cdot \text{m}^3/\text{kg}$
k_s	liquid-solid mass transfer coefficient, m/s
r_1	forward reaction rate for equation (i), $\text{kmol}/\text{m}^3/\text{s}$
r_2	backward reaction rate for equation (i), $\text{kmol}/\text{m}^3/\text{s}$
r_3	forward reaction rate for equation (ii), $\text{kmol}/\text{m}^3/\text{s}$
r_4	backward reaction rate for equation (ii), $\text{kmol}/\text{m}^3/\text{s}$
r_{i0}	initial rate of reaction, $\text{kmol}/\text{m}^3/\text{s}$
r_i	rate of reaction at any time, $\text{kmol}/\text{m}^3/\text{s}$
r_A	initial rate, $\text{kmol}/\text{m}^3/\text{sec}$
w	catalyst loading, kg/m^3

Greek

α_2	parameter defined in equation 2.15
ρ_l	density of liquids, kg/m^3
ρ_p	density of catalyst, kg/m^3

4.8 References

- Chawla H. S. and Hussan Zahed S., *Ind. J. Tech.*, 20, 22, (1982)
- Huang T., Wan J. and Tsai L.i, *J. Chin. Chem. Soc.*, 14(2-3), 72, (1967)
- Rode C. V., Chaudhari S.T., Jaganathan R., Chaudhari R.V. and Mali S., *Procs. ICACHE-96*, Eds. Varma, Y. B. G., Rao. D., Balkrishnan A.R. and Ananth M.S., Allied Publishers, India (1996)
- Schlessinger G. G., *Handbook of chemistry and physics*, Chemical Rubber Co., 1970
- Yadav G. D. and Thathagar M. B., *Reactive and Functional Polymers*, 52, 99 (2002)

5.1 Introduction

Trickle-bed reactors, wherein gas and liquid reactants are contacted in a co-current down flow mode in the presence of heterogeneous catalysts, are used in a large number of industrial chemical processes. Being a multiphase catalytic reactor with complex hydrodynamics and mass transfer characteristics, the development of a generalized model for predicting the performance of such reactors is still a difficult task. However, due to its direct relevance to industrial-scale processes, several important aspects with respect to the influence of external and intraparticle mass transfer effects, partial wetting of catalyst particles and heat effects have been studied previously (Satterfield and Way (1972); Hanika et. al., (1975,1977,1981); Herskowitz and Mosseri (1983)). The previous work has mainly addressed the question of catalyst effectiveness under isothermal conditions and for simple kinetics. It is well known that most of the industrially important reactions represent complex reaction kinetics and very often multistep reactions. Very few attempts have been made on experimental verification of trickle-bed reactor models for multistep catalytic reactions in the previous work.

The analysis of mass transfer effects in a trickle-bed reactor has been extensively studied and the relevant literature on this subject has been reviewed by Satterfield (1975), Herskowitz and Smith (1983), Ramchandran and Chaudhari (1983), Mills and Dudukovic (1984), Gianetto and Specchia (1992) and Rajashekharan et. al. (1998). Several models have been proposed to describe the influence of partial external wetting of catalyst particles (Ramchandran and Smith (1979); Herskowitz et. al., (1979); Tan and Smith, (1980); Mills and Dudukovic (1980); Goto et. al., (1981)). From the practical point of view it is important to incorporate the complexities of hydrodynamics and mass transfer steps coupled with a catalytic reaction in a model for the entire reactor under integral conditions. Several reports on modeling of trickle-bed reactors have been published with the aim of understanding the overall reactor performance and comparison of the predictions with experimental data (Goto and Smith (1975); Levec and Smith (1976); Herskowitz (1985)). The aim of this work was to investigate esterification of mono and dibasic acids in a trickle bed reactor as an example of a reversible reaction with wide ranging industrial applications. The relevant literature pertaining to esterification in a fixed bed reactor has been discussed in Chapter 1 and some important studies are highlighted below.

Saletan and White (1952) obtained quantitative-reaction-rate data on the formation of ethyl acetate from ethanol and acetic acid in a fixed bed of cation exchange resin catalyst. The complex interaction of diffusion and reaction kinetics within the resin that determines the overall esterification rate has been resolved mathematically. The rate expression finally obtained includes a multiplier function that gives the volumetric efficiency of the resin catalyst. This volumetric efficiency is shown to be a function of temperature and resin-bead size exclusively. Hanika et. al. (2003) studied synthesis of alkylacetates in a multi-functional trickle bed reactor. They studied the esterification of acetic acid with butanol using strong acid ion exchange resin catalyst as a model system. The influence of temperature and concentration of reaction components on the reaction rate was investigated. The conversion of alkyl carboxylic acids could be shifted beyond its equilibrium value by combining the esterification and simultaneous separation of water in a reactor system. They found that if the esterification reaction is operated at a temperature above the boiling point of the azeotropic mixture formed during the reaction, the evaporation process shifts the conversion to a higher level value compared to the equilibrium conversion without application of a molar excess of one of the reaction components in the feed.

There are only a few reports on trickle bed reactor modeling for esterification reactions incorporating various complexities such as liquid-solid mass transfer resistance, intraparticle diffusion resistance and partial wetting. Hence, it was thought important to develop a predictive model for trickle bed reactor for esterification and undertake a detailed study on the experimental verification of a trickle-bed reactor model. For the purpose of experimental verification, the following two reaction systems were investigated using Dowex 50W ion exchange resin catalyst:

- (a) Esterification of acetic acid with methanol and butanol and
- (b) Esterification of maleic acid with methanol

The experimental data have been compared with the model predictions for different sets of conditions in which liquid velocity, molar ratio of reactants and temperature were varied.

5.2 Experimental

5.2.1 Materials

The reactants methanol, butanol, acetic acid and maleic acid used were of A.R. grade (99.8%) and obtained from S.D. Fine Chemicals, India. Purity was determined by gas chromatography. The chemicals were used without further purification

5.2.2 Catalyst

The cation exchange resin Dowex 50W (Dow Chemical Co.) used as the catalyst was procured from Vijay chemicals, India. Before using in the experiments, the resin was pretreated using a standard procedure described in Chapter-2 (Section 2.2.2). Specifications of this catalyst are given in Table 5.1.

Table 5.1: Catalyst specifications

Catalyst	Dowex 50W resin (Macroporous Cross-linked DVB)
Particle diameter, m	0.5×10^{-3}
Density of catalyst, kg/m ³	1370
Tortousity factor	2.4
Porosity of catalyst	0.5

5.2.3 Reactor

The experiments were carried out in a trickle bed glass reactor, the schematic diagram of which is shown in Fig. 5.1. Other details of the reactor are given in Table 5.2.

Table 5.2: Reactor details

Reactor length, m	30×10^{-2}
Catalyst packing length, m	8×10^{-2}
Reactor inner diameter, m	2.5×10^{-2}
Bed voidage	0.7

The catalyst was packed at the bottom of the reactor using a plug of glass wool as the catalyst support. The reactor was provided with an outer jacket through which water at a constant temperature could be circulated. The temperature in the jacket was maintained within $\pm 0.1^\circ\text{C}$ using a thermostat. The reactor was provided with three thermocouples axially placed along the reactor length. The reactant feed from storage, consisting of graduated glass vessel, was introduced at the top of the reactor using a metering pump. The glass vessel was kept on a weighing balance, which allowed measurement of the liquid flow rate precisely. The reactor outlet was connected to a condenser to cool the product coming out of the reactor. The product stream flow rate in the exit was also recorded.

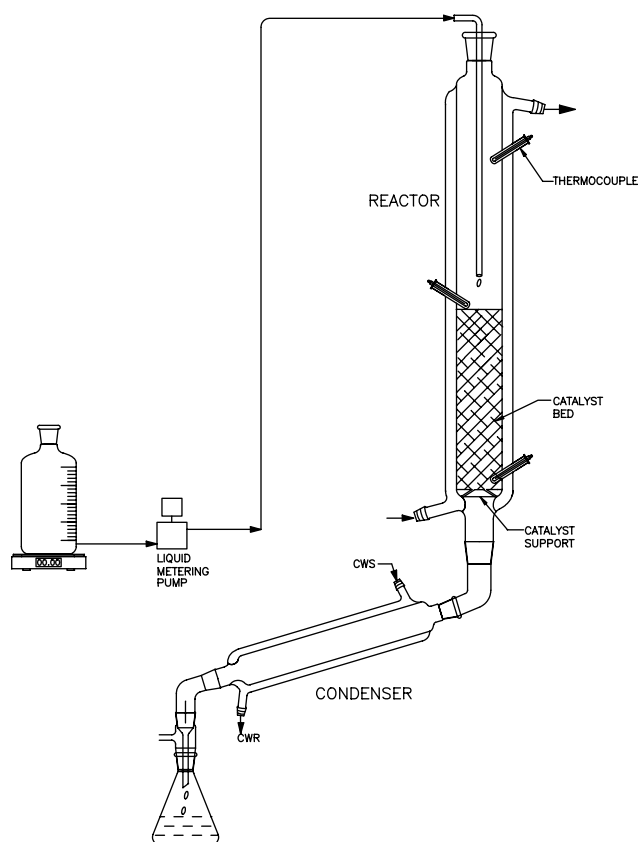


Fig: 5.1 Experimental setup for trickle bed reactor

5.2.4 Experimental procedure

In a typical experiment, ion exchanged resin catalyst (2×10^{-2} kg) was charged to the reactor. Then the temperature of the reactor was set to a desired value by circulating water at constant temperature from the thermostat. Once the temperature inside the reactor was stable the liquid flow was started after adjusting the required flow rate. The temperature was monitored at three positions inside the reactor: (1) liquid feed inlet (2) top of the catalyst bed and (3) bottom of the catalyst bed. It was found that the temperature recorded at the top and bottom of the catalyst bed were nearly the same, indicating that the liquid feed attained temperature equilibrium by the time it reached the top of the catalyst bed. The product stream was cooled in the condenser and was collected in a product receiver. Experiments were carried out at different inlet conditions and steady state performance of the reactor was observed by analysis of reactants and products in the exit streams. The range of operating conditions for which the present study was carried out is given in Table 5.3. Liquid samples (product stream) were analyzed by gas chromatographic technique using procedures described in Chapters 2, 3 and 4 (Sections 2.3, 3.3 and 4.3).

Table 5.3: Range of operating conditions

Inlet concentration of acetic acid, kmol/m ³	4-12
Inlet concentration of maleic acid, kmol/m ³	1-4
Inlet concentration of methanol, kmol/m ³	5-18
Inlet concentration of butanol, kmol/m ³	5-12
Liquid flow rate, m/s	$2-14 \times 10^{-5}$
Temperature, K	308-363

5.3 Trickle Bed Reactor Model

5.3.1 Reactor model for esterification of acetic acid with methanol/ butanol

For the purpose of developing a trickle-bed reactor model for esterification reactions the approach used by Rajshekharam et. al. (1998) was used. They have

developed a model for a gas–liquid-solid reaction system incorporating the effect of partial wetting of the catalyst pellets. However, for the present case, since, the gas phase is not present in esterification reaction, the effect of partial wetting will be significant only if liquid-solid mass transfer limitation is important. The following assumptions were made in the development of the model: (a) liquid is in plug flow, (b) liquid phase reactants are non-volatile, (c) the liquid-solid mass transfer resistances are considered for all the components. (d) the catalyst is wetted completely internally due to capillary forces, (e) the intrinsic kinetic equations, described in chapters 2, 3 and 4 for the esterification of acetic acid with methanol, acetic acid with butanol and maleic acid with methanol respectively were used to analyze the performance of the trickle bed reactor.

The reaction scheme for a first order reversible esterification reaction can be written as,



Where, A is acetic acid, B is methanol or butanol, C is methyl or butyl acetate and D is water. The forward rate of reaction is given as:

$$r_1 = \varepsilon_1 k_3 A_1 B_1 + \eta_c \rho_p (1-\varepsilon_B) k_1 A_s B_s \quad (5.2)$$

The backward rate of reaction is given as:

$$r_2 = k_4 \varepsilon_1 C_1 D_1 + \eta_c \rho_p (1-\varepsilon_B) k_2 C_s D_s \quad (5.3)$$

Where, η_c is overall catalytic effectiveness factor. The overall catalytic effectiveness factor for a spherical catalyst particle can be expressed as:

$$\eta_c = \frac{1}{\phi} \left[\coth \left(3\phi - \frac{1}{3\phi} \right) \right] \quad (5.4)$$

Where, ϕ is the Thiele modulus. Following the procedure described in Chapter-2 (see Section 2.3) it was evaluated as:

$$\Phi = \frac{R}{3} \left[\frac{\rho_p k_1 B_s \left(1 - k' \frac{C_s D_s}{A_s B_s} \right)^2}{D_e \left\{ \left(1 - \frac{D_A A_s}{3 D_B B_s} \right) + k' \left(\frac{D_A A_s}{D_C B_s} - \frac{2 D_A^2 A_s}{3 D_C D_D B_s} - \frac{D_A C_s}{D_D B_s} \right) \right\}} \right]^{-1/2} \quad (5.5)$$

In the presence of liquid-solid mass transfer resistance, we also have the following equations in dimensionless form:

$$(a_l - a_s) = \alpha_A \eta_c (a_s b_s - k'_2 c_s d_s) \quad (5.6)$$

$$(b_l - b_s) = \alpha'_C \eta_c (a_s b_s - k'_2 c_s d_s) \quad (5.7)$$

$$(c_l - c_s) = \alpha_B \eta_c (k'_2 c_s d_s - a_s b_s) \quad (5.8)$$

$$(d_l - d_s) = \alpha'_D \eta_c (k'_2 c_s d_s - a_s b_s) \quad (5.9)$$

The dimensionless parameters are given in Table 5.4. The mass balance equations for species A, B, C and D in the trickle bed reactor are then given by the following equations:

$$\frac{-u_L dA_l}{dx} = \begin{matrix} \varepsilon_l k_3 A_l B_l + \eta_c \rho_p (1 - \varepsilon_B) k_1 A_s B_s \\ - \varepsilon_l k_4 C_l D_l - \eta_c \rho_p (1 - \varepsilon_B) k_2 C_s D_s \end{matrix} \quad (5.10)$$

$$\frac{-u_L dC_l}{dx} = \begin{matrix} \varepsilon_l k_4 C_l D_l + \eta_c \rho_p (1 - \varepsilon_B) k_2 C_s D_s \\ - \varepsilon_l k_3 A_l B_l - \eta_c \rho_p (1 - \varepsilon_B) k_1 A_s B_s \end{matrix} \quad (5.12)$$

$$\frac{-u_L dB_l}{dx} = \begin{matrix} \varepsilon_l k_3 A_l B_l + \eta_c \rho_p (1 - \varepsilon_B) k_1 A_s B_s \\ - \varepsilon_l k_4 C_l D_l - \eta_c \rho_p (1 - \varepsilon_B) k_2 C_s D_s \end{matrix} \quad (5.11)$$

$$\frac{-u_L dD_l}{dx} = \begin{matrix} \varepsilon_l k_4 C_l D_l + \eta_c \rho_p (1 - \varepsilon_B) k_2 C_s D_s \\ - \varepsilon_l k_3 A_l B_l - \eta_c \rho_p (1 - \varepsilon_B) k_1 A_s B_s \end{matrix} \quad (5.13)$$

Where, u_L is the superficial liquid velocity, m/s and x the axial distance along with the axis of the catalyst bed. The above equations in dimensionless form are:

$$\frac{-da_l}{dz} = \varepsilon_l \beta_2 (a_l b_l - k'_4 c_l d_l) + \eta_c \beta_1 (a_s b_s - k'_2 c_s d_s) \quad (5.14)$$

$$\frac{-db_l}{dz} = \varepsilon_l \beta_2 (a_l b_l - k'_4 c_l d_l) + \eta_c \beta_1 (a_s b_s - k'_2 c_s d_s) \quad (5.15)$$

$$\frac{-dc_l}{dz} = \varepsilon_l \beta_2 (k'_4 c_l d_l - a_l b_l) + \eta_c \beta_1 (k'_2 c_s d_s - a_s b_s) \quad (5.16)$$

$$\frac{-dd_l}{dz} = \varepsilon_l \beta_2 (k'_4 c_l d_l - a_l b_l) + \eta_c \beta_1 (k'_2 c_s d_s - a_s b_s) \quad (5.17)$$

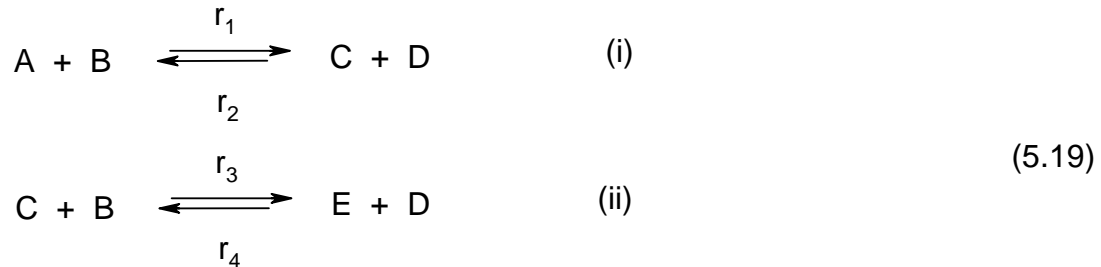
Where, z is the dimensionless reactor length defined as x/L and ε_B the bed porosity. The initial conditions are:

$$\text{At } z = 0, a_l = 1, b_l = B_{l0}/A_{l0}, c_l = d_l = 0 \quad (5.18)$$

The above set of equations 5.14-5.18 can be used to predict the performance of the trickle bed reactor for both esterification of acetic acid with methanol and butanol.

5.3.2 Reactor model for esterification of maleic acid

The reaction scheme for esterification of maleic acid with methanol is given as,



Where, A, B, C, D and E represent maleic acid, methanol, monomethyl maleate, water and dimethyl maleate respectively.

For the present case the following model assumptions were made:

- (a) liquid is in plug flow
- (b) isothermal reaction condition
- (c) liquid-solid mass transfer resistance is negligible
- (d) intraparticle diffusional resistance is not significant

The forward and backward rate of reaction (i) can be written as:

$$r_1 = \varepsilon_1 k_1 A_1 B_1 + \rho_p(1-\varepsilon_B) k_5 A_1 B_1 \quad (5.20)$$

$$r_2 = \varepsilon_1 k_2 C_1 D_1 + \rho_p(1-\varepsilon_B) k_6 C_1 D_1 \quad (5.21)$$

The forward and backward rate of reaction (ii) can be written as:

$$r_3 = \varepsilon_1 k_3 C_1 B_1 + \rho_p(1-\varepsilon_B) k_7 C_1 B_1 \quad (5.22)$$

$$r_4 = \varepsilon_1 k_4 E_1 D_1 + \rho_p(1-\varepsilon_B) k_8 E_1 D_1 \quad (5.23)$$

Overall rate of reaction for species A, B, C, D and E can be written as:

$$r_A = (\varepsilon_1 k_2 C_1 D_1 + \rho_p(1-\varepsilon_B) k_6 C_1 D_1) - (\varepsilon_1 k_1 A_1 B_1 + \rho_p(1-\varepsilon_B) k_5 A_1 B_1) \quad (5.24)$$

$$r_B = \left[(\varepsilon_1 k_2 C_1 D_1 + \rho_p(1-\varepsilon_B) k_6 C_1 D_1) - (\varepsilon_1 k_1 A_1 B_1 + \rho_p(1-\varepsilon_B) k_5 A_1 B_1) \right. \\ \left. - (\varepsilon_1 k_3 C_1 B_1 + \rho_p(1-\varepsilon_B) k_7 C_1 B_1) + (\varepsilon_1 k_4 E_1 D_1 + \rho_p(1-\varepsilon_B) k_8 E_1 D_1) \right] \quad (5.25)$$

$$r_C = \left[(\varepsilon_1 k_2 C_1 D_1 + \rho_p(1-\varepsilon_B) k_6 C_1 D_1) - (\varepsilon_1 k_1 A_1 B_1 + \rho_p(1-\varepsilon_B) k_5 A_1 B_1) \right. \\ \left. - (\varepsilon_1 k_3 C_1 B_1 + \rho_p(1-\varepsilon_B) k_7 C_1 B_1) + (\varepsilon_1 k_4 E_1 D_1 + \rho_p(1-\varepsilon_B) k_8 E_1 D_1) \right] \quad (5.26)$$

$$r_D = \left[(\varepsilon_1 k_2 C_1 D_1 + \rho_p(1-\varepsilon_B) k_6 C_1 D_1) - (\varepsilon_1 k_1 A_1 B_1 + \rho_p(1-\varepsilon_B) k_5 A_1 B_1) \right. \\ \left. + (\varepsilon_1 k_3 C_1 B_1 + \rho_p(1-\varepsilon_B) k_7 C_1 B_1) - (\varepsilon_1 k_4 E_1 D_1 + \rho_p(1-\varepsilon_B) k_8 E_1 D_1) \right] \quad (5.27)$$

$$r_E = (\varepsilon_1 k_4 E_1 D_1 + \rho_p (1 - \varepsilon_B) k_8 E_1 D_1) - (\varepsilon_1 k_3 C_1 B_1 + \rho_p (1 - \varepsilon_B) k_7 C_1 B_1) \quad (5.28)$$

The mass balance equations for species A, B, C, D and E in the trickle bed reactor in a dimensionless form (Table 5.4) can be written as:

$$\frac{-da_l}{dz} = \left[\varepsilon_1 \beta_3 (a_l b_l - k'_6 c_l d_l) + \beta_4 (a_l b_l - k'_2 c_l d_l) \right] \quad (5.29)$$

$$\frac{-db_l}{dz} = \left[\varepsilon_1 \beta_3 (k'_6 c_l d_l - a_l b_l - k'_4 c_l b_l + k'_5 c_l d_l) + \beta_4 (k'_2 c_l d_l - a_l b_l - k'_3 c_l b_l + k'_4 c_l d_l) \right] \quad (5.30)$$

$$\frac{-dc_l}{dz} = \left[\varepsilon_1 \beta_3 (a_l b_l - k'_6 c_l d_l - k'_4 c_l b_l + k'_5 c_l d_l) + \beta_4 (a_l b_l - k'_2 c_l d_l - k'_3 c_l b_l + k'_4 c_l d_l) \right] \quad (5.31)$$

$$\frac{-dd_l}{dz} = \left[\varepsilon_1 \beta_3 (a_l b_l - k'_6 c_l d_l + k'_4 c_l b_l - k'_5 c_l d_l) + \beta_4 (a_l b_l - k'_2 c_l d_l + k'_3 c_l b_l - k'_4 c_l d_l) \right] \quad (5.32)$$

$$\frac{-de_l}{dz} = \left[\varepsilon_1 \beta_3 (k'_4 c_l b_l - k'_8 c_l d_l) + \beta_4 (k'_3 c_l b_l - k'_4 c_l d_l) \right] \quad (5.33)$$

The initial conditions are

$$\text{at } z = 0, a_l = 1, b_l = B_{10}/A_{10}, c_l = d_l = 0 \quad (5.34)$$

5.4 Method of solution

5.4.1 Esterification of acetic acid with methanol and butanol

The exit concentration of liquid phase reactant can be calculated by solving the set of ordinary differential equations 5.14-5.18 along with the corresponding initial conditions. For this Runge-Kutta method was used. It may be noted that the exit concentrations are a function of unknown surface concentrations a_s , b_s , c_s , and d_s . These

four unknown concentrations and these were evaluated by solving the simultaneous equations 5.6-5.9, using IMSL subroutine (IMSL (1994)).

Table 5.4: Dimensionless parameters used in the model

$a_1 = \frac{A_1}{A_{10}}$	$b_1 = \frac{B_1}{A_{10}}$	$c_1 = \frac{C_1}{A_{10}}$
$d_1 = \frac{D_1}{A_{10}}$	$e_1 = \frac{E_1}{A_{10}}$	
$a_s = \frac{A_s}{A_{10}}$	$b_s = \frac{B_s}{A_{10}}$	$c_s = \frac{C_s}{A_{10}}$
$d_s = \frac{D_s}{A_{10}}$	$e_s = \frac{E_s}{A_{10}}$	
$\beta_1 = \frac{k_1 \rho_p (1-\varepsilon_B) A_{10} L}{u_L}$	$\beta_2 = \frac{k_3 A_{10} L}{u_L}$	
$\beta_3 = \frac{k_5 \rho_p (1-\varepsilon_B) A_{10} L}{u_L}$	$\beta_4 = \frac{k_1 A_{10} L}{u_L}$	
$\alpha_a = \frac{\rho_p (1-\varepsilon_B) k_1 A_{10}}{(k_s a_p)_A}$	$\alpha_b = \frac{\rho_p (1-\varepsilon_B) k_3 A_{10}}{(k_s a_p)_B}$	
$\alpha_c = \frac{\rho_p (1-\varepsilon_B) k_3 A_{10}}{(k_s a_p)_C}$	$\alpha_d = \frac{\rho_p (1-\varepsilon_B) k_3 A_{10}}{(k_s a_p)_D}$	

5.4.2 Esterification of maleic acid with methanol

The method of solution is relatively simple for maleic acid esterification. To evaluate the exit concentration of maleic acid, methanol, monomethyl maleate, dimethyl maleate and water, the set of ordinary differential equations 5.29-5.34 were solved using Runge-Kutta method. The above models allow prediction of the concentration of reactants and products along the length of reactor. Thus at any given length of the reactor the fractional conversion of the acid can be calculated as

$$X_A = 1 - a_L \quad (5.34)$$

When calculations are performed for $z = 1$, we get the conversion of acid at the exit of the reactor.

5.5 Results and discussion

In order to understand the performance of the trickle bed reactor for esterification reactions, experimental data were obtained under steady state conditions for the following reaction systems:

- a) Esterification of acetic acid with ethanol and butanol
- b) Esterification of maleic acid with ethanol

In these experiments, the concentrations of reactants and products at the exit of the reactor were observed under steady state conditions for different liquid velocities and molar ratio of reactants in a temperature range of 298 – 363 K. Typical results are shown in Fig. 5.1 for acetic acid-methanol system. For acetic acid with butanol and maleic acid with methanol esterification the results are shown in Fig 5.2 and 5.3 respectively. From these data the conversion of acid as a function of liquid velocity was also evaluated for all the systems. For example, the acetic acid conversion obtained for esterification with methanol is presented in Fig. 5.4 and 5.5 for 318 and 328 K respectively.

5.5.1 Comparison with experimental data

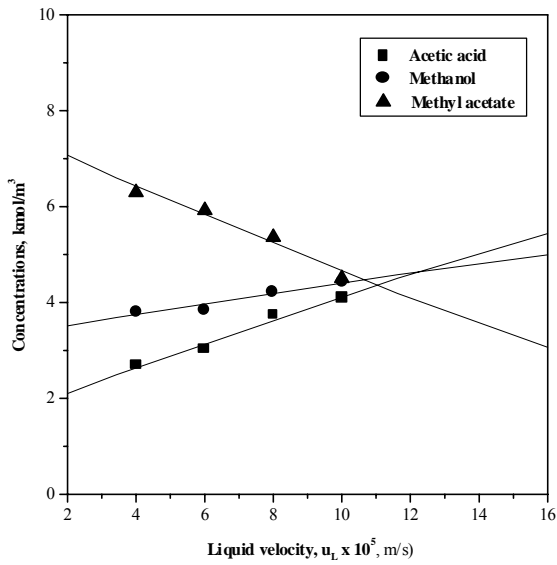
The model equations were solved for predicting the acetic acid conversion using appropriate kinetics for acetic acid –ethanol, acetic acid-butanol and maleic acid ethanol systems reported in Chapters 2, 3 and 4. Other parameters required for model predictions are summarized in Table 5.3.

To validate the model, experiments were conducted in the trickle bed reactor at different flow rates of liquids, temperature and different reactant concentrations. In each experiment the concentration of reactants and product coming out of the reactor were analyzed. Steady state was assumed to be reached, when the analysis of two consecutive samples was the same.

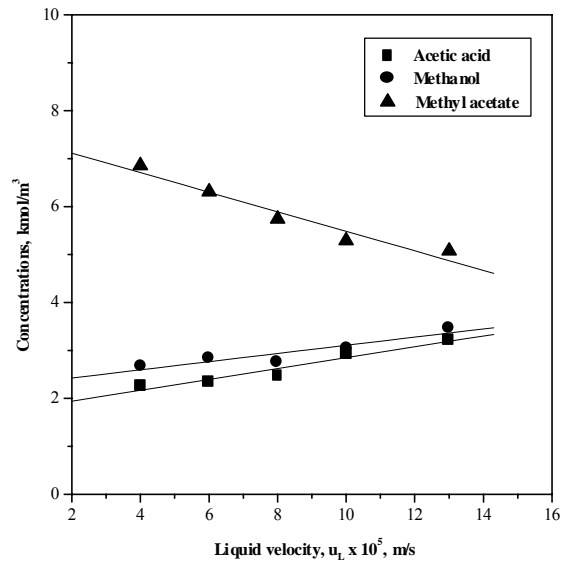
For example, the experimental data obtained at a given temperature was simulated using the model by adjusting liquid holdup in the model. The liquid holdup thus calculated for different velocities were used to predict experimental data at other reaction conditions. The experimental results obtained are summarized below:

1. The conversion of acetic acid obtained for acetic acid with methanol esterification is shown in Fig. 5.6 for different liquid velocities and mole ratios. As expected the conversion falls with increase in velocity. The agreement with model predictions and experimental data for different reactant concentration was very good.
2. For esterification of acetic acid with butanol, the results are shown in Fig. 5.7 and 5.8 for different temperature and different reactant concentrations respectively. For acetic acid-butanol esterification also, the model prediction was very good compared with experimental results.
3. For esterification maleic acid with methanol the results are presented in Fig. 5.9 for different temperatures. The model predictions of the experimental data were found to be satisfactory.

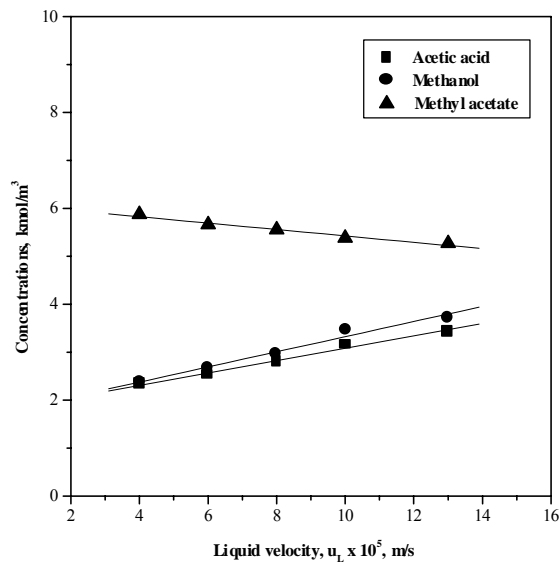
It may be noted that the liquid holdup was adjusted between 0.4-0.5 to have a good agreement with experimental data. The liquid holdup calculated from literature correlation (Sato et. al., (1973)) was in the range of 0.6-0.8. The disagreement may be due to the fact that the correlation was not proposed for ion exchange resin catalysts.



Temp : 308 K



Temp : 318 K



Temp : 328 K

Fig. 5.1: Exit concentrations for esterification of acetic acid with methanol at different temperatures

Reaction conditions: Acetic acid: Methanol = 1:2, $d_p = 4.58 \times 10^{-4}$ m

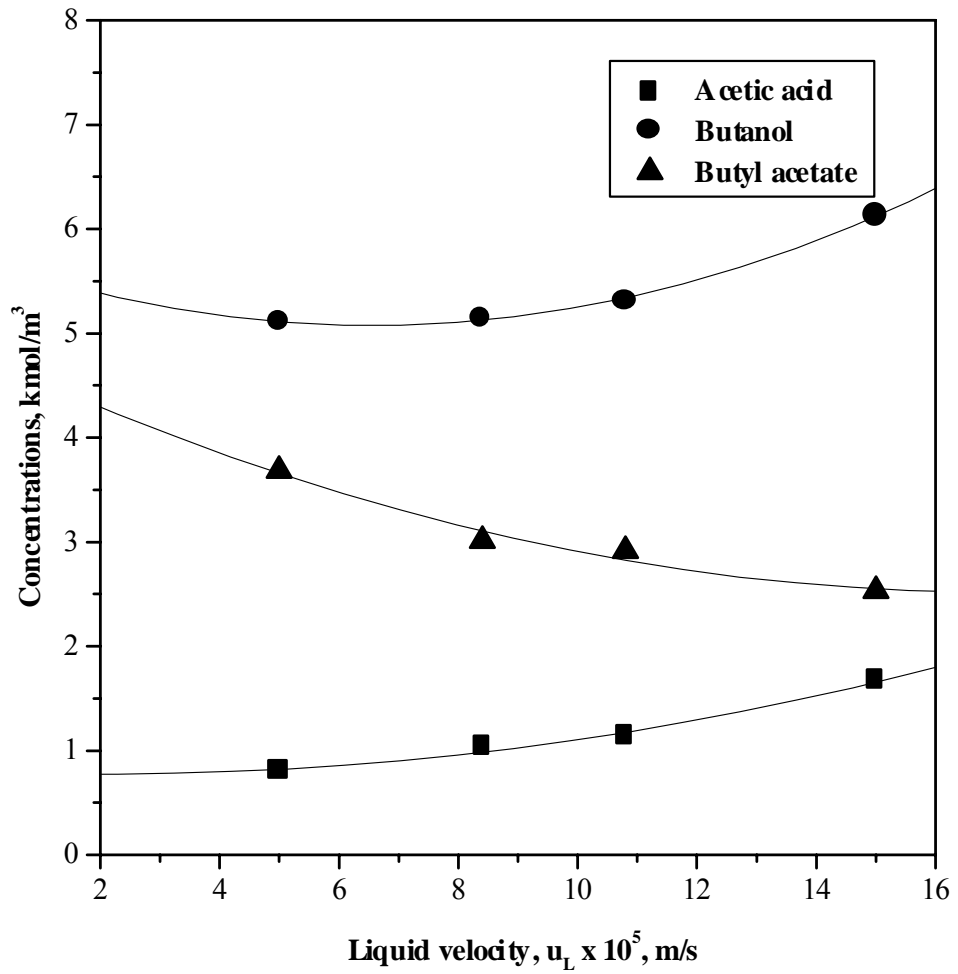


Fig. 5.2: Exit concentrations for esterification of acetic acid with butanol at 353 K

Reaction conditions: Acetic acid : Methanol=1:2, $d_p = 4.58 \times 10^{-4}$ m

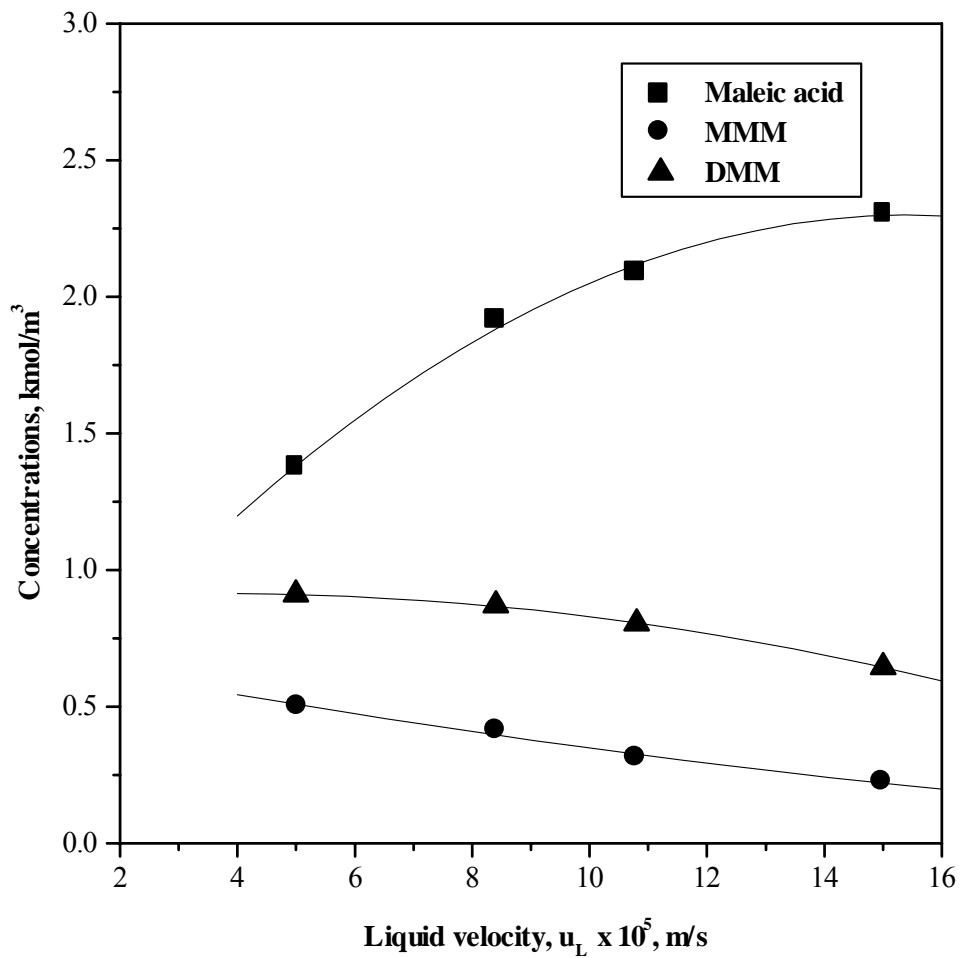


Fig. 5.3: Exit concentrations for esterification of maleic acid with methanol at 318 K
Reaction conditions: Acetic acid:Methanol = 1:2; $d_p = 4.58 \times 10^{-4}$ m

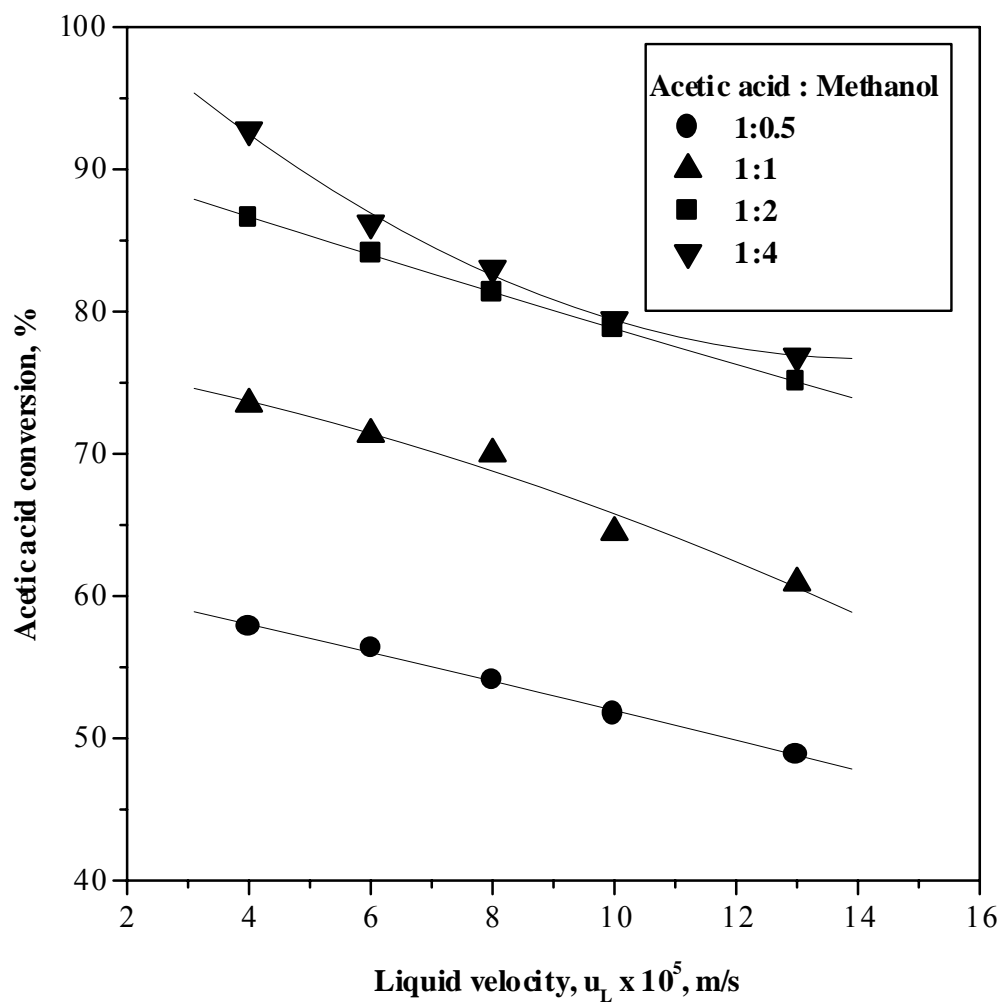


Fig. 5.4: Conversion of acetic acid for esterification with methanol for different reactant concentrations at 318 K

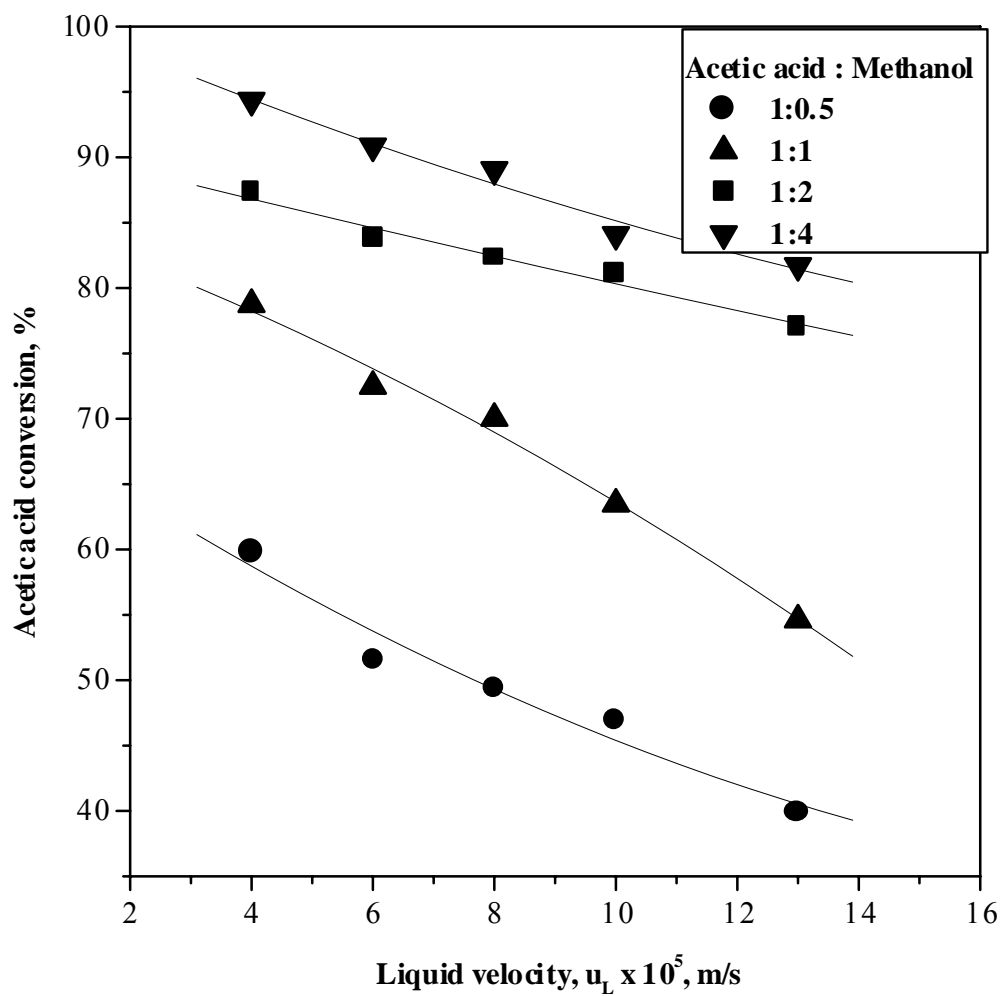


Fig. 5.5: Conversion of acetic acid for esterification with methanol for different reactant concentrations at 328 K

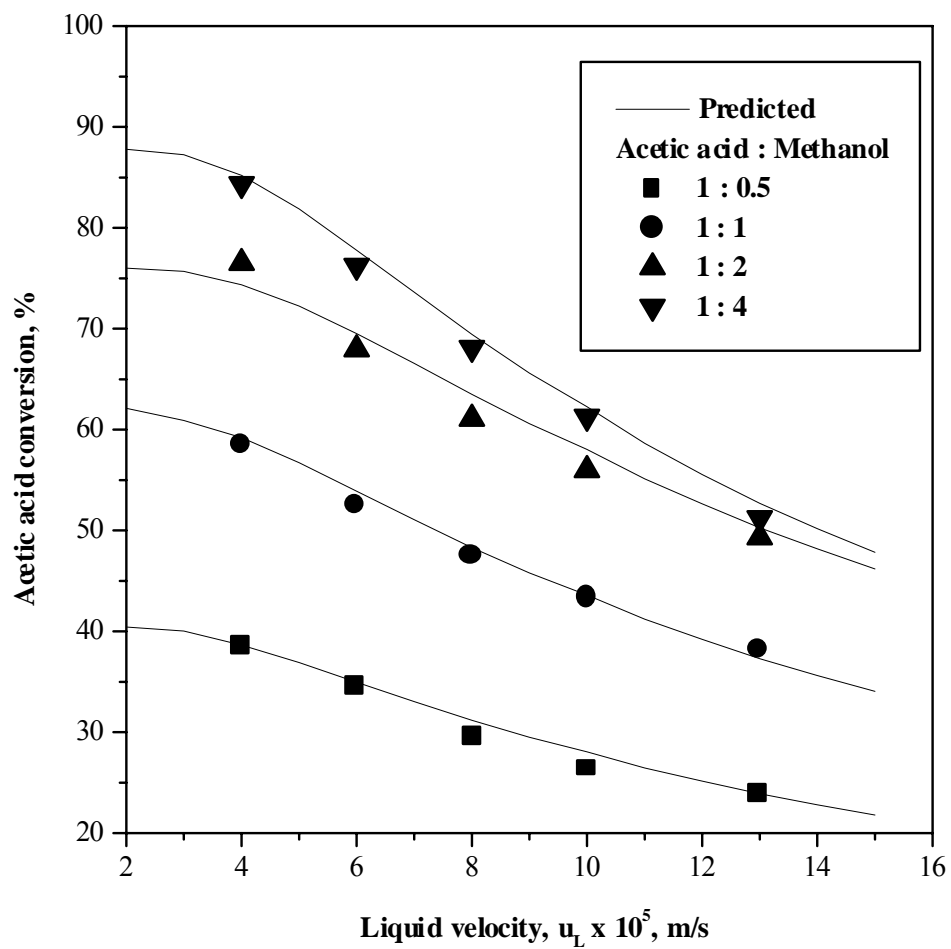


Fig. 5.6: Conversion of acetic acid for esterification with methanol for different reactant concentrations at 308 K

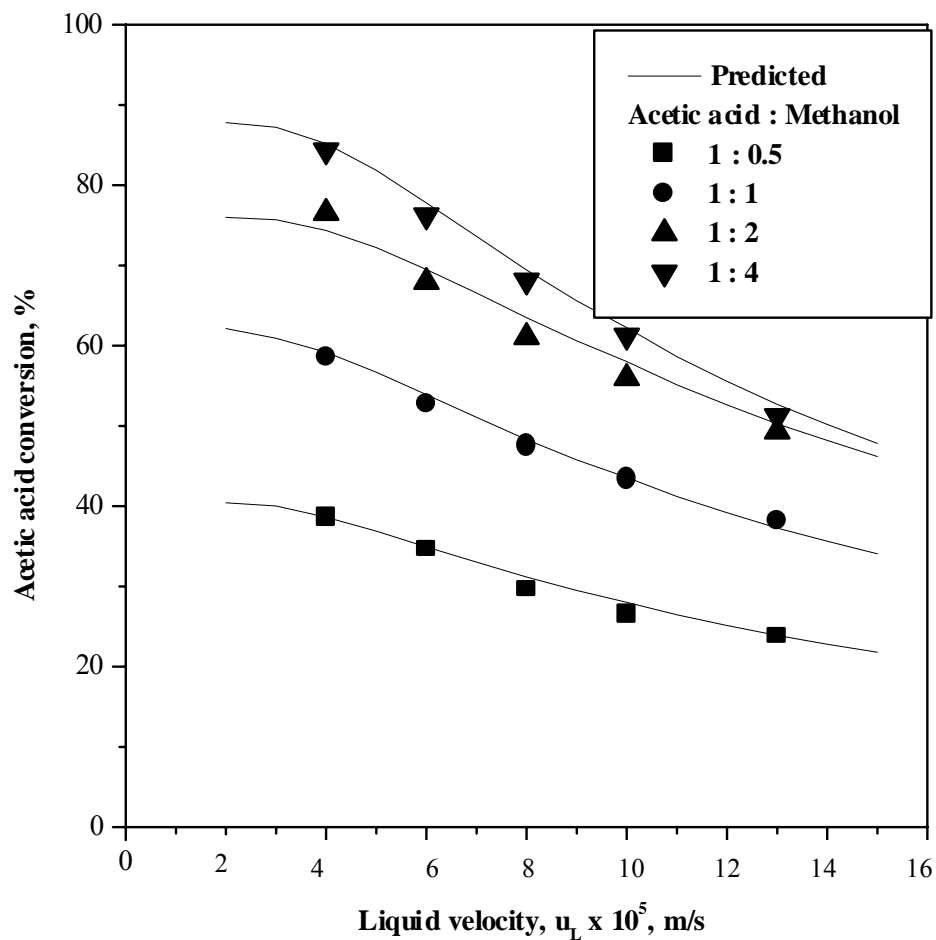


Fig. 5.7: Conversion of acetic acid for esterification with butanol for different reactant concentration at 353 K

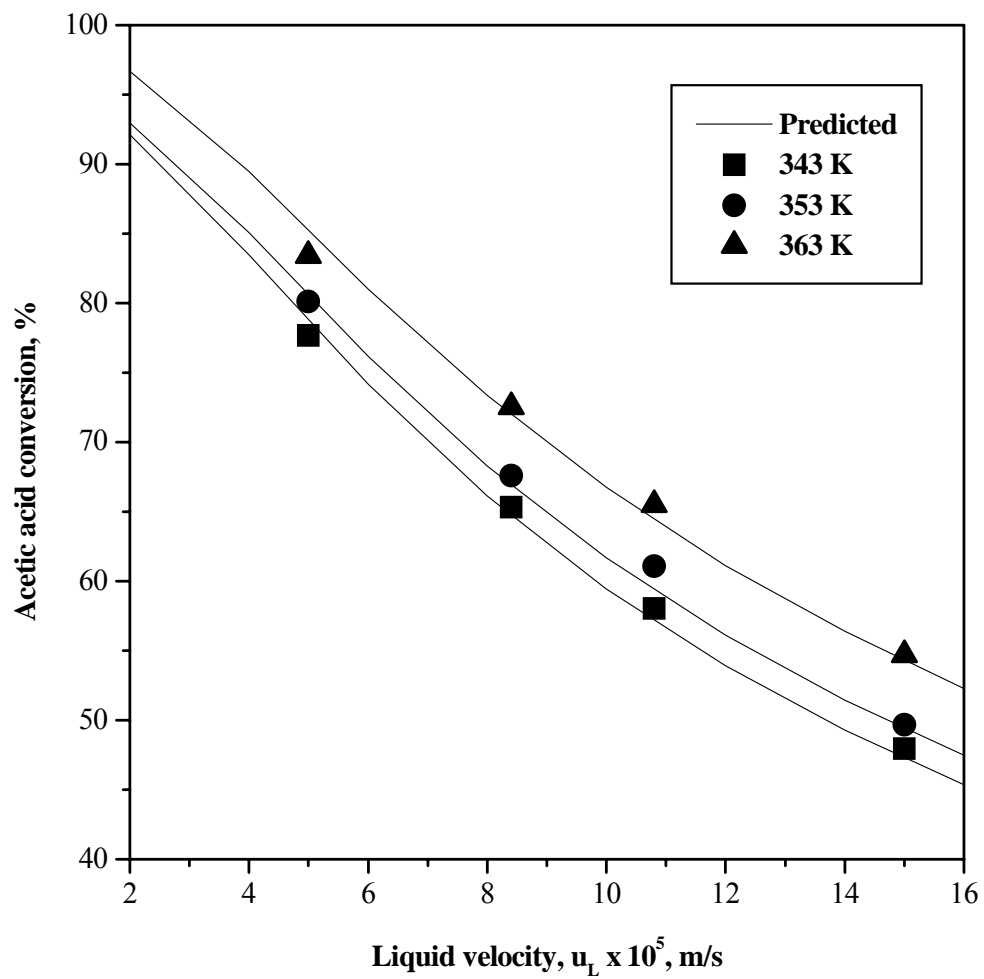


Fig. 5.8: Conversion of acetic acid for esterification with butanol for different temperature

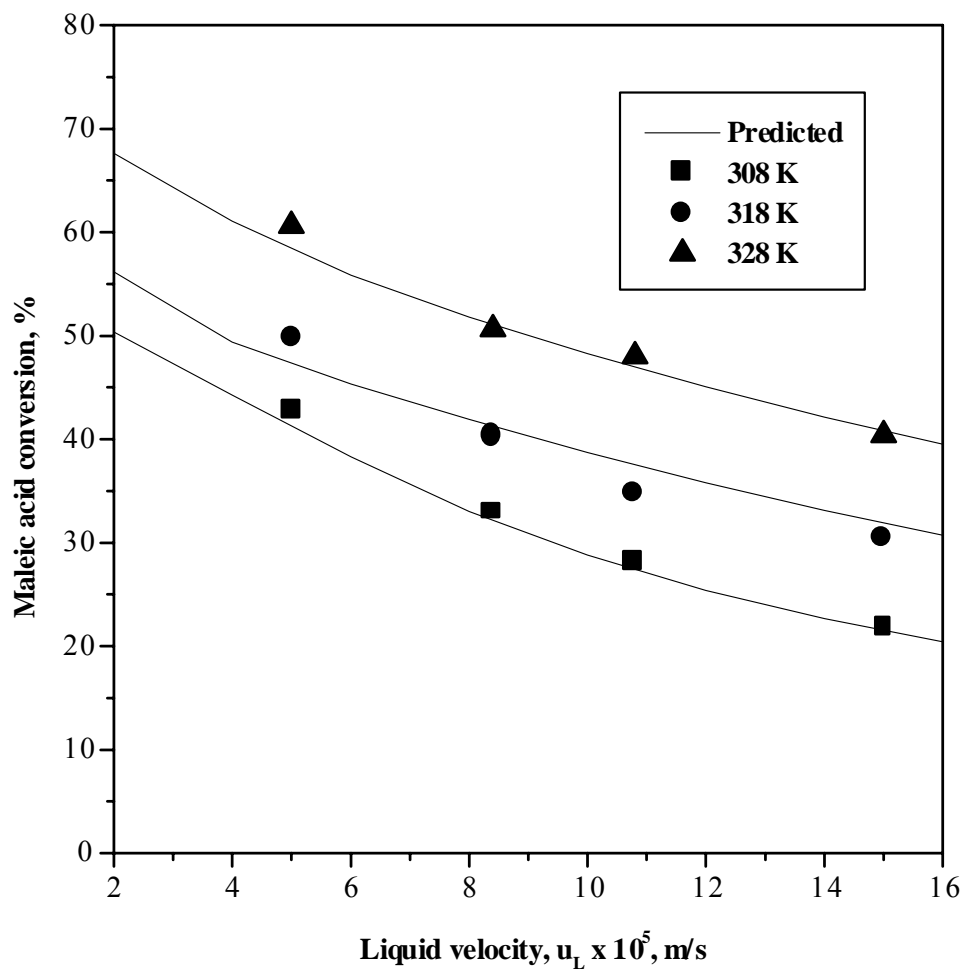


Fig. 5.9: Conversion of maleic acid for esterification with methanol at different temperature

Table 5.5 Summary of various correlations used in this work

Parameter	Correlation	Reference
Liquid-solid mass transfer	$\frac{k_l a_B}{D_M} = 6 \left(\frac{\rho_l U_l}{u_l} \right)^{0.24} \left(\frac{u_l}{\rho_l D_M} \right)^{0.5}$	Goto and Smith (1975)
Molecular diffusivity	$D_M = \frac{7.4 \times 10^{-8} x T x (x M_w)^{0.5}}{\mu_L \nu_M^{0.6}}$	Wilky and Chang (1955)
Liquid plug flow	$\frac{L}{d_p} > \left(\frac{20 n D_e}{U_l d_p} \right) \left(\frac{B_{li}}{B_{lout}} \right)$	Mears (1971)
Total liquid holdup	$\frac{\varepsilon_l}{\varepsilon_B} = 0.185 (a_t)^{1.3} X_A^{0.22}$	Sato et al (1973)

5.6 Conclusions

An experimental study on esterification of acetic acid with methanol, acetic acid with butanol and maleic acid with methanol was carried out in trickle bed reactor using ion exchange resin as catalyst. The first two reactions are simple first order reversible reaction system, while the esterification of maleic acid represents a complex multistep reaction. For acetic acid esterification reactions a model has been developed taking into consideration the liquid-solid mass transfer resistances. For maleic acid esterification system a simple homogeneous model has been developed. Experimental data for all the three system were obtained over wide range of operating conditions and compared with model prediction. The kinetic parameters required to be used in the model were experimentally determined taking into account both homogeneous and heterogeneous reactions. Mass transfer parameters and diffusion coefficients were calculated from literature correlations. The agreement between the model prediction and experimental data was very good.

Notations

A_l	concentration of acid in liquid phase, kmol/m^3
A_g	concentration of acid on catalyst surface, kmol/m^3
A_{l0}	inlet concentration of species A, kmol/m^3
B_{l0}	inlet concentration of species B, kmol/m^3
a_w	catalyst area wetted, kmol/m^3
B_l	concentration of methanol/butanol in liquid phase, kmol/m^3
B_g	concentration of methanol/butanol on catalyst surface, kmol/m^3
C_l	concentration of methyl/butyl ester and MMM in liquid phase, kmol/m^3
C_g	concentration of methyl/butyl ester and MMM on catalyst surface, kmol/m^3
D_l	concentration of water in liquid phase, kmol/m^3
D_g	concentration of water on catalyst surface, kmol/m^3
E_l	concentration of DMM in liquid phase, kmol/m^3
E_g	concentration of DMM on catalyst surface, kmol/m^3
d_p	particle diameter, m

d_T	reactor diameter, m
f_d	fraction of catalyst wetted by the dynamic liquid
f_g	fraction of catalyst wetted by the stagnant liquid
k_1 to k_4	homogeneous reaction rate constants, $m^3/kmol/s$
k_5 to k_8	heterogeneous reaction rate constants, $m^3/kmol/s$. m^3/kg
k'_2	k_2 / k_1
k'_3	k_3 / k_1
k'_4	k_4 / k_1
k'_6	k_6 / k_5
k'_7	k_7 / k_5
k'_8	k_7 / k_5
r_1 to r_4	reaction rate for individual esterification steps, $kmol/m^3/s$
u_L	liquid velocity, m/s
w	weight of the catalyst, kg/m^3

5.7 References

- Gianetto A. and Specchia V., *Chem. Engng Sci.*, *41*, 3197 (1992)
- Goto S., Lakota A. and Levec J, *Chem. Engng Sci.*, *36*, 157 (1981)
- Goto S. and Smith J. M., *A.I.Ch.E.J.*, *21*, 706 (1971)
- Hanika J., Sporka V., Ruzicka V. and Pistek R., *Chem. Engng Sci.*, *2*, 19 (1975)
- Hanika J., Sporka V., Ruzicka V. and Pistek R., *Chem. Engng Sci.*, *32*, 525 (1977)
- Hanika J., Vosecky V., and Ruzicka V, *Chem. Engng. J.*, *21*, 108 (1981)
- Hanika Jiri, Kolena Jiri, Kucharova Magdalen, Havlickova Karla, *Tatranske Matliare, Slovak Republic*, *30* (2003)
- Hanika Jiri, Kucharova Magdalena, Kolena Jiri and Smejkal Quido, *Catalysis Today* *79-80*, 83 (2003))
- Herskowitz M., *Chem. Engg. Sci.*, *40*, 1309 (1985)
- Herskowitz M., Carbonell R. G. and Smith J. M., *A.I.Ch.E.J.*, *25*, 272 (1979)
- Herskowitz M., and Smith J. M., *A.I.Ch.E.J.*, *29*, 1 (1983)
- Herskowitz M., and Mosseri S., *Ind. Engg. Chem. Fundam.*, *22*, 4 (1983)
- Levec J. and Smith J. M., *A.I.Ch.E.J.*, *22*, 159 (1976)

Mears D. E., *Ind. Engng Chem. Proc. Des. Develop*, 10, 541 (1971)

Mills P. L. and Dudukvoc M. P., *Chem. Engg. Sci.*, 35, 2267 (1980)

Mills P. L. and Dudukvoc M. P., *Chemical and Catalytic Reactor Modeling*, eds P.L. Mills and M.P. Dudukvoc, 37, ACS (1984)

Ramchandran P.A. and Chaudhary R.V. "Three Phase Catalytic Reactor", Gardon and Breach, New York, USA (1983)

Ramchandran P.A and Smith J. M., *A.I.Ch.E.J.*, 25, 538 (1979)

Saletan David I. and White Robert R., *A.I.Ch.E. Symposium Series No. 4*, 48, 59 (1952)

Sato Y., Hirotsu T., Takajashi F. and Toda M., *J. Chem. Engng Japan.*, 6, 147 (1973)

Satterfield C. N. and Way P. F. *A.I.Ch.E.J.*, 18, 305 (1972)

Tan C. S. and Smith J. M., *Chem. Engg. Sci.*, 35, 1601 (1980)

Wilke C. R. and Chang P., *A.I.Ch.E.J.*, 1, 264 (1955)