ALKYLATION OF PHENOLS USING IONIC LIQUID CATALYSTS

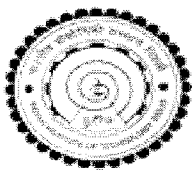
by

P. Elavarasan

Department of Chemical Engineering

Submitted
in fulfillment of the requirement for the award of degree of
Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

NEW DELHI- INDIA

JANUARY 2011

CERTIFICATE

This is to certify that the report titled "**Alkylation of phenols using ionic liquid catalysts**" is a bonafide record of the project work carried out by **P. Elavarasan** (2007CHZ8214) under my supervision and guidance, in fulfillment of the requirements for the award of the degree of **Doctor of Philosophy.** Further, to the best of my knowledge this has not been submitted to any other University or Institute for the award of any Degree or Diploma.

Date : 7/1/2011

Dr Sreedevi Upadhyayula
Department of Chemical Engineering
IIT Delhi

ACKNOWLEDGEMENTS

Many peoples have accompanied me during this adventure and provided their support and encouragement. First and foremost I would like to thank my supervisor **Dr Sreedevi Upadhyayula** who provided me guidance, knowledge, insight and direction for my research work. It is hard to describe the immeasurable impact she has on my career and professional development. It has been a great pleasure discussing my ideas with her and receiving her encouragement and excellent advice at every step of the way, often-long distance and always a promptly right on the point. I owe her so much.

I thank my research committee members **Prof. A.N. Bhaskarwar, Prof. A Ramanan, Dr K.K. Pant** and **Dr V.V. Krishnan** for their invaluable suggestions and directions especially during my research work.

Special thanks to the authorities of Annamalai University and **Prof. T Viruthagiri** HOD Department of Chemical Engineering, Annamalai University, permitting me through AICTE-QIP (Ph D) and their constant support and encouragement to the entire project. I thank my colleagues **S. Rengadurai, Dr S. Dhansekaran** and **Dr K. Manikandan** for their encouragement and support through my research work.

I would like to thank **Mr. Kondamudi Kishore** who has shared the same work place with me, helped from the joining to complete my thesis work. Special thanks to Mr **K. Rajkumar** who always helped me in characterizing the materials and shared knowledge for my research work from the very beginning. I also thank **Dr. Senthil kumar** and Mr. **Nagarajan** for their help to analysis NMR, FT-IR and characterization techniques with me during my experimental work.

I would like to thank my lab mates **B. Pradeep kumar** and **Ashish Nayak** for their help to experimental work. I also thank my friends **Varagunapandian, Sathish** and **Sathish kumar** who have helped me during my research work.

Finally and most importantly with the blessings from my father Mr **J. Pandian** and mother Mrs **Rani**. I thank my family members, brother **Dr P. Dhinakaran**, **Shankaripriya**, nephew **Dharanidaran**, sister **Indumathi Elangovan,** niece **Deepti** and **Megha**. I hereby express my hearty & sincere thanks to all whoever supported me either directly or indirectly in completion of my research work successfully.

P. Elavarasan

P. Elavarasan

ABSTRACT

Alkylation of aromatics is of immense importance to the chemical and petrochemical industry. Alkylation processes were traditionally conducted using Friedel-Crafts catalysts. In recent years these are being replaced by more economical, energy saving and environmentally benign catalysts. Also, the use of alcohols as alkylating agents is being researched the world over due to the inherent problems of transportation, handling and unavailability of alkenes. The present work is focused on investigating the alkylation reaction of phenol and *p*-cresol with *tert*-butyl alcohol to produce 2, 4-*tert*-di-butylphenol (2, 4-DTBP) and 2-*tert*-butyl-*p*-cresol (TBC), 2,6-di-*tert*-butyl-*p*-cresol (DTBC) respectively. An attempt is made to develop novel Bronsted acidic ionic liquid catalyst system that could be used efficiently in this reaction.

The ionic liquids and supported ionic liquid catalyst were prepared in the laboratory and characterized using NMR, TG-DTA, SEM and FTIR. A statistical design of experiments was used to predict the effect of various process variables on the phenols conversion and desired product selectivities. Experimental kinetic investigations were conducted in a batch autoclave and the optimum temperature, reaction time, reactant mole ratio and reactant to catalyst ratio are reported. The catalysts were found to be completely recoverable and recyclable.

A reaction mechanism was proposed based on the product distribution obtained from experimental investigations. Semi-empirical computations were used to model this reaction system and further assess the reaction pathway and mechanism. Based on the proposed reaction mechanism, kinetic models were developed and the kinetic parameters were estimated using non-linear Marquadt's routine.

Key words: alkylation, *tert*-butylation, phenol, *p*-cresol, 2, 4-*tert*-di-butylphenol, 2-*tert*-butyl-*p*-cresol, 2,6-di-*tert*-butyl-*p*-cresol, ionic liquid, supported ionic liquid, kinetics.

CONTENTS