CATALYTIC HYDROCRACKING AND HYDROGENATION OF AROMATIC COMPOUNDS IN TRICKLE BED REACTOR

By

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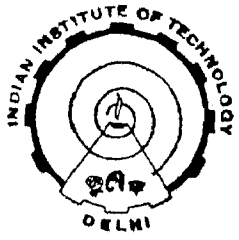
Thesis submitted to the
Indian Institute of Technology, Delhi
for the award of the Degree of

DOCTOR OF PHILOSOPHY



DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, DELHI

1987

CERTIFICATE

This is to certify that the thesis entitled **"CATALYTIC HYDROCRACKING AND HYDROGENATION OF AROMATIC COMPOUNDS IN TRICKLE BED REACTOR"** is being submitted by Mr. Sunil Dutt Sharma to Indian Institute of Technology, Delhi, for the award of Doctor of Philosophy. Mr. Sunil Dutt Sharma has worked under our guidance and has fulfilled the requirements for the submission of thesis which, to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for the award of any Degree or Diploma.

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Acknowledgements

The author wishes to express his sincere thanks and gratitude to Prof. M.K.Sarkar for his guidance, encouragement, and help throughout the course of this work. The author wishes thanks to Dr. K. Gadgil for her cooperation.

With great pleasure author wishes to record his sincere thanks to Indian Institute of Petroleum, Dehradun, for the characterization of the catalysts.

The author wishes to mention his special thanks to Prof. P.N. Sahgal and Dr. V.K. Shrivastawa for their invaluable suggestions in the thermodynamic calculations. Thanks to Dr. S.C. Dhingra for his help in the computation. Also wishes to thanks to Dr. B.K. Guha for time to time encouragement given by him.

The author appreciates the constant help and encouragement by faculty members and cooperation rendered by fellow research scholars specially Dr. Sudhir Garg and Mr. M.S. Lyal. Thanks to the staff members for their help during the fabrication.

Thanks are also due to Mr. K.K. Pathak for providing fabrication drawing for the reactor.

Finally author wishes to acknowledge Rajhans Commercial Agencies, Munirka for the typing of the thesis.

Date: 29-7-1987 *[Sunil Dutt Sharma]*

ABSTRACT

Cataly tic hydrocracking has assumed special significance for the production of lighter hydrocarbons from heavier petroleum recycle stock as well from other feedstocks such as coal derived liquids. The process has certain advantages in a petroleum refinery as compared to normal catalyic cracking such as production of more high grade saturated lighter hydrocarbons with much less amount of residues. For coal liquids, if a two stage coal liquifaction program is considered the heavy and highly aromatic mixture of liquid hydrocarbons produced in the first step would need extensive hydrogenation and hydrocracking in order to produce petroleum derived liquid fuel substitutes.

The proposed investigation on catalytic hydrocracking and hydrogenation of aromatic compounds had its origin in a coal liquifaction program of the department. Such a program had envisaged generation of a coal liquid equivalent to a light reduced tar produced through treatment of catalysed coal with steam and syngas under low temperature pyrolysis conditions. It was proposed that such coal liquids, containing aromatic and oxy-aromatic compounds would

require hydrotreatment for obtaining substitutes of petroleum derived fuels. In order to pursue such a program, a high pressure high temperature catalytic hydrocracking unit based on a co-current down flow Trickle Bed Reactor was installed in the laboratory and it was proposed to study various prepared and commercially available catalysts for hydrogenation and hydrocracking of simple aromatic and oxy-aromatic model compounds to evaluate various rate parameters in a trickle bed reactor.

Four catalysts ($NiO-WO_3$-pumice stone, $NiO-ZnO$ -pumice stone, $NiO-WO_3-SiO_2-Al_2O_3$, $NiO-MoO_3-SiO_2$), were prepared by impregnating metal oxides on various supports and one ($CoO-MoO_3-Al_2O_3$) was obtained commercially. Out of these five catalysts, $NiO-WO_3$-pumice stone was chosen for detailed study. Hydrotreating of phenol and benzene were carried out at a temperature range between 100 and 400°C and pressure between 70 and 125 atmospheres. Hydrocracking was observed only above 400°C below which hydrogenation reaction was predominant. Catalyst poisoning was appreciable at higher temperature particularly for phenol hydrotreating. A number of products such as cyclohexane, cyclohexanone, cyclohexanol, isohexane, hexane and traces of butane,

water etc. were observed during the hydrocracking of benzene and phenol. Furthermore hydrocracking began only after considerable amount of hydrogenation of aromatic rings. Assuming major influence of hydrogenation on hydrocracking and significant poisoning of the catalyst with phenol reactions, it was proposed to study benzene hydrogenation as a model for Trickle Bed Kinetics.

Assuming benzene hydrogenation to be reversible reaction equilibrium conversions were evaluated thermodynamically from available thermochemical data. Vapour-liquid equilibrium calculations were also performed. Non-ideality of the system was taken into account by considering fugacities.

Kinetics of hydrogenation of benzene were studied in the differentially packed bed reactor under trickle flow conditions. Differential reactor was chosen to minimise the effect of concentration and temperature gradients on the reaction. External and internal mass transfer effects were minimised by using appropriate particle size of the catalyst and flow rates. A series of runs were conducted varying pressures (25-120 atmospheres) and temperatures (120-450 $^{\circ}$C). Below the critical temperature

of benzene (290°C) reaction was considered to be predominantly in liquid phase whereas at higher temperatures (above 290°C), only vapour phase reaction was possible. Therefore interpretation of the data were done separately.

For liquid phase data (120-280°C) a reversible rate equation based on first order with respect to benzene, cyclohexane and dissolved hydrogen, was derived. Assuming that catalyst was completely wetted, rate constants at different temperatures were determined graphically. Arrhenius plot for the data showed a straight line only in the lower temperature region. Subsequently fraction of wetted surface of the catalyst (ratio of total holdup to the catalyst pore volume) were considered in the rate equation and an Arrhenius plot showed considerable improvement except near the critical temperature region. Further improvement was affected by considering liquid holdup only (substracting the vapour fraction of the total holdup), in the rate equation. This showed higher rate in the critical region than contributed by the liquid phase reaction alone. This was attributed to the vapour phase reaction on the dry surface not considered in the liquid phase rate equation. Further analysis was carried

out after evaluation of vapour phase kinetics.

For vapour phase reaction a reversible, rate equation based on first order with respect to benzene, hydrogen and cyclohexane was attempted to interpret the data. This was found to be unsatisfactory. A decrease in rate with the increase in temperature led to the testing of adsorption models on the data. A model based on the rate of benzene adsorption where molecularly adsorbed benzene and hydrogen reacted, was found to be suitable for interpretation of all vapour phase data (300-400 °C). Constants of the equation gave straight lines for their Arrhenius plots.

For evaluating the kinetics in the mixed phase region (200-240 °C) the wet and dry surface contributions to the reaction were desired. The deviation in the liquid phase Arrhenius plot was considered to be due to the change in liquid solid contacting efficiencies. A method was established to evaluate relative contacting efficiencies at different temperatures with reference to assumed unit contacting efficiency for a low temperature run.

These calculated values were compared with absolute values calculated by a method given in the literature, considering vapour and liquid phase reaction rates in this region. Trend of variation of both values with respect to temperature was found to be similar. With calculated contacting efficiencies a new Arrhenius plot, which yielded a good straight line, the liquid phase reaction rate was established. To prove the validity of liquid-vapour and mixed phase interpretations, theoritically calculated rates (for all other conditions from these equations considering constants for a single set of conditions) were compared with those observed experimentally. A good agreement between the two rates indicated the correctness of the interpretation of the data.

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