

KINETICS OF THERMAL CRACKING OF LIQUID
HYDROCARBONS AND THEIR MIXTURES

BY

BHALENDU K. DESAI
DEPARTMENT OF CHEMICAL ENGINEERING

SUBMITTED
IN FULFILMENT OF REQUIREMENTS OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

TO THE
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
JULY 1978

ACKNOWLEDGEMENT

The author wishes to express his sincere thanks and gratitude to Professors M.K.Sarkar and P.N.Sangal for their encouragement, guidance and help throughout the course of this work.

The author appreciates the constant help and encouragement by faculty members and cooperation rendered by the fellow research scholars and staff members.

Thanks are also due to Dr. Deepak Kunzru of IIT Kanpur for his active help.

The financial support provided by Council of Scientific and Industrial Research, New Delhi in the initial stages of work is also gratefully acknowledged.

Delhi

July, 1978

B. K. Desai.
(B.K.Desai)

ABSTRACT

The interaction of cyclic hydrocarbons, such as: cyclohexane and benzene on the thermal cracking of a straight chain hydrocarbon, such as hexane was studied experimentally. Detailed kinetics experimentation on thermal cracking of hexane, cyclohexane, hexane-cyclohexane mixtures, hexane-benzene mixtures, cyclohexane-benzene mixture and hexane-cyclohexane-benzene mixtures were carried out in a pulsed microreactor system. A specially designed stainless steel microreactor was packed with quartz particles and heated in an electric radiation furnace. The reactor was operated between 630°C and 800°C with residence times varying between 0.5 and 0.9 second with conversions ranging from 5% to 95%. The products were analysed on a temperature programmed Pye 104 chromatograph with flame ionization detector using 5 percent squalane on alumina column.

On kinetic analysis it was found that the cracking of hexane and its mixtures with other cyclic compounds fitted first order reaction rates. Over the range of experimental conditions studied, the activation energies for thermal cracking of hexane and cyclohexane were 55780 and 57530 cal/gm.mole respectively. The distribution of cracking products from hexane and cyclohexane was studied. The Rice-Kossiakoff theory, the Woinsky model, the Gavalas

model and the models proposed by Murata and Saito for the prediction of product distribution in thermal cracking has been reviewed. The rice theory and the models proposed by Murata and Saito were applied to thermal cracking of hexane in present investigation.

The kinetic data for cyclohexane obtained from pulse technique in present study compared well with the data compiled from literature by Fabuss et al.

It has been experimentally shown that there was significant interaction when hexane was copolymerized with cyclohexane and benzene. It was observed that cyclohexane in quantities between 5 and 50 percent by volume in mixture caused appreciable rise in the activation energy of hexane; presence of benzene from 5 to 25 percent by volume was found to decrease activation energy of hexane. Presence of hexane upto 25 percent in hexane-cyclohexane-mixture did not cause much change in the activation energy of cyclohexane. 50 percent hexane in the mixture with cyclohexane slightly lowered the activation energy of cyclohexane. 20% benzene in cyclohexane decreased the activation energy of cyclohexane. In the ternary mixture of hexane, cyclohexane and benzene the effects of cyclohexane and benzene on hexane were almost balanced and the

activation energy of hexane was almost identical to that of pure hexane. The predicted values of activation energy of hexane in ternary mixtures, on the basis of binary mixture data matched quite closely with experimental values of activation energy whereas the predicted values of conversions on the basis of binary mixture data were 5 to 16 percent less than the experimental values of conversion of hexane in ternary mixtures. The predicted conversions were more close to experimental conversions when amounts of cyclic compounds in general and aromatics in particular were less in the mixture.

The selectivity of products decreased in binary mixtures of hexane and cyclohexane and in ternary mixtures of hexane, cyclohexane and benzene as compared to pure component cracking. The selectivity of products decreased considerably in the binary mixtures of hexane and benzene when selectivity was calculated on the basis of hundred moles of feed cracked but the selectivity of methane, ethylene and propylene increased when moles products formed were calculated on the basis of 100 moles of hexane cracked in the mixture.

The severity factor, $t \cdot T^{0.06}$ was used to correlate the product yields obtained in the cracking of pure hydrocarbons and their mixtures studied in the present investigation.

CONTENTS

	<u>Page No.</u>
Acknowledgement	... i
Abstract	... ii-iv
List of Figures	...ix - xii
List of Tables	... xiii - xiv
Nomenclature	... xv
Chapter-1 INTRODUCTION	... 1
Chapter-2 LITERATURE SURVEY	... 7
2.1 Thermal Cracking of n-hexane	... 9
2.2 Thermal cracking of Cyclohexane	...14
2.3 Thermal cracking of Hydrocarbon Mixtures	...17
2.3.1 Thermal Cracking of Gaseous Hydrocarbon Mixtures	...17
2.3.2 Thermal cracking of Liquid Hydrocarbon Mixtures	...22
Chapter-3 EXPERIMENTAL	...27
3.1 Experimental set-up	...30
3.1.1 Reactor Assembly	...31
3.2 Chromatographic Analysis	...33
3.3 Experimental Procedure	...35
3.4 Kinetic Analysis of Experimental data	...36

Chapter-4	RESULTS AND DISCUSSION	... 39
4.1	Cracking of Pure Hexane	... 39
4.1.1	Kinetics of Thermal Cracking of Hexane	... 39
4.1.2	Product Distribution	... 42
4.1.3	Review of Theoretical Models for Prediction of Product Distribution from Thermal Cracking of Hydrocarbons	46
4.1.3.1	Theory of Rice and Kossiakoff	... 46
4.1.3.2	Murata and Saito Models	... 48
4.1.3.3	Winsky Model	... 49
4.1.3.4	Gavalas Model	... 50
4.1.4	Comparison of Experimental Data on Hexane Cracking with Rice Theory and Murata and Saito Models	... 51
4.1.4.1	Experimental Data versus Theory of Rice	... 51
4.1.4.2	Experimental Data versus Murata and Saito Model	... 54
4.1.5	Qualitative Explanation of the Products Formed	... 56
4.2	Cracking of Pure Cyclohexane	... 59
4.2.1	Kinetics of Thermal Cracking of Cyclohexane	... 59
4.2.2	Comparison of the Pulse Micro-Reactor Kinetics of Present Study with the Kinetics Data from Literature	... 61

4.2.3	Product Distribution	... 63
4.2.4	Discussion of Results	... 65
4.3	Thermal cracking of Hydro- carbon Mixtures	... 67
4.3.1	Thermal Cracking of Hexane- Cyclohexane Mixtures	... 68
4.3.1.1	Kinetics of Thermal Cracking .. of Hexane-Cyclohexane Mix- tures	68
4.3.1.2	Product Distribution	... 72
4.3.1.3	Discussion of Results	... 76
4.3.2	Thermal Cracking of Hexane-Benzene Mixtures	... 77
4.3.2.1	Kinetics of Cracking	... 78
4.3.2.2	Product Distribution	... 80
4.3.2.3	Discussion of Results	... 85
4.3.3	Thermal Cracking of Cyclo- hexane-Benzene Mixture	... 87
4.3.3.1	Kinetics of Cracking	... 87
4.3.3.2	Product Distribution	... 88
4.3.4	Thermal Cracking of Ternary Mixtures containing Hexane, Cyclohexane and Benzene	... 88
4.3.4.1	Kinetics of Cracking of Ternary Mixtures	... 89
4.3.4.2	Product Distribution	... 89
4.3.4.3	Discussion of Results	... 94
4.4	Correlation of Data with Severity Factor	...100

Chapter-5	CONCLUSIONS	... 103
	BIBLIOGRAPHY	... 107
Appendix-A	Theoretical Approach as suggested by Blanton, Evers and Merrill for the Analysis of Pulsed Reactor Data	... 121
Appendix-B	Sample Calculations	... 124
Appendix-C	Calculation of Product Distri- bution for Hexane Cracking from Rice Theory	... 126
Appendix-D	The Decomposition Scheme for Hexane as given by Frey and Hepp	... 129
Appendix-E	Experimental Data	... 132
	About the Author	... 148