

KINETICS OF HYDROCARBON COMBUSTION IN A PACKED BED

by

SURAJ B. RANA

Chemical Engineering Department

Submitted

in fulfilment of the requirements of the degree of
Doctor of Philosophy

to the

Indian Institute of Technology, Delhi

October, 1976

ACKNOWLEDGEMENTS

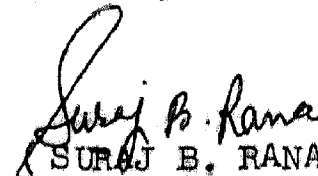
The author is extremely grateful for the guidance and valuable suggestions given to him by Professor M.K. Sarkar, Department of Chemical Engineering, I.I.T. Delhi, during the course of completion of this thesis.

The UNESCO research fellowship in 1973-74, provided the author with an opportunity to come in contact with Professor H. Imai, Laboratory of Engineering Materials, Tokyo Institute of Technology, Tokyo, where most of the experiments were carried out. The facilities and the guidance rendered by Professor Imai at different stages of experimental program are highly appreciated. The financial support given by Kureha Chemical Industries Co., Ltd., (Japan) is also gratefully acknowledged.

Thanks are also due to Dr. L.D. Ahuja, Department of Chemistry, for useful discussions and to Dr. R.G. Gupta, Computer Centre, for his help during the computational work.

Delhi

Oct., 1976.


(SURAJ B. RANA)

ABSTRACT

An extensive survey of the literature available on surface/catalytic combustion of hydrocarbons was made.

Kinetics studies were conducted on combustion of propane with air/oxygen, over NiO-Al₂O₃ catalyst in an iso-thermal flow reactor system using steady-state as well as pulse techniques. Experimental data was obtained at atmospheric pressure and in the temperature range of 300-800°C. On kinetic analysis, order of the reaction was observed to change from zero at lower temperatures to one at higher temperatures. The study revealed that the homogeneous gas phase combustion in the void of the packed bed was also taking place simultaneously though its effect could be considered negligible at lower temperatures. Surface contribution in case of heterogeneous reaction was observed to decrease with the increase in temperature. The reaction was found to conform to the rate equations, $r_H = A_0 \exp(-E/RT)$ at lower temperatures (300-450°C), and $r_H = A_1 \exp(-E/RT)p_H$ at higher temperatures (650-800°C). In the temperature range 450-650°C, the following rate equation fitted the data well.

$$r_H = \frac{k p_H}{1 - K_H p_H}$$

From comparison of the steady-state and the pulsed data it was concluded that reliable rate expressions could be evaluated at higher temperatures using the pulse technique. However, at lower temperatures with a porous catalyst, the reaction approached zero-order and adsorption of reactants played an important role, therefore, steady-state technique would be more suitable.

CONTENTS

	<u>Page</u>
List of figures	
Nomenclature	
<u>CHAPTER</u>	
I INTRODUCTION	1-5
II LITERATURE SURVEY	6-14
III EXPERIMENTAL SET-UP	15-21
3.1 Experimental Apparatus	15
3.1.1 Steady-State System	15
3.1.2 Pulsed-System	18
3.2 Catalyst	20
IV EXPERIMENTAL RESULTS	22-45
4.1 Mass Transfer Effects	22
4.1.1 External Heat and Mass Transfer Effects	22
4.1.2 Internal Diffusion	23
4.2 Effects of Various Factors Like Cracking, and Non-Catalytic and Catalytic Combustion	24
4.3 Effects of Temperature and Space Velocity on Conversion	25
4.4 Effects of Partial Pressure of Reactants	26
4.5 Reaction Rate Parameters	26
4.5.1 Steady-State System	26
4.5.2 Pulsed-System	38
4.6 Comparison of Steady-State and Pulsed Systems	42

<u>CHAPTER</u>		<u>Page</u>
V	REACTION MECHANISM AND REACTION SCHEME	46-69
	5.1 Reaction Mechanism	46
	5.1.1 Langmuir-Hinshelwood Mechanism	48
	5.1.2 Ideal Mechanism	49
	5.1.3 Redox Mechanism	51
	5.1.4 Empirical Models	53
	5.2 Comparison of Various Models	57
	5.3 Reaction Scheme	62
VI	SUMMARY AND CONCLUSIONS	70-73
	BIBLIOGRAPHY	
	APPENDICES	
	Appendix-A	
	A-1 Properties of Catalyst	
	Appendix-B	
	B-1 Determination of Resistances due to Heat and Mass Heat Transfer	
	B-2 Determination of Reynold's Number	
	B-3 Theoretical Approach as suggested by Merrill and Co-workers for the Analysis of Pulsed Reactor Data	
	B-4 Langmuir Theory	
	B-5 Hougen-Watson Rate Equations	
	B-6 Application of Hougen-Watson Rate Equations to Integral Data as Suggested by Barnard and Mitchell	
	Appendix-C	
	List of Tables	
	C-1 Steady-State Data	
	C-2 Pulsed System Data	