

COMBUSTION OF LIQUEFIED PETROLEUM GAS  
IN A PACKED BED

by

ASHWANI KUMAR

Chemical Engineering Department

submitted

in fulfilment of the requirements of the degree of

Doctor of Philosophy

to the

Indian Institute of Technology, Delhi

1979

CERTIFICATE

This is to certify that thesis entitled 'COMBUSTION OF LIQUEFIED PETROLEUM GAS' being submitted by Mr. Ashwani Kumar to Indian Institute of Technology, Delhi, for the award of degree of DOCTOR OF PHILOSOPHY, is a record of bonafide research work carried out by him. Mr. Ashwani Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or in full to any other university or institute for the award of any degree or diploma.

(M.K. Sarkar)

### ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Professor M.K. Sarkar for his encouragement, guidance and help during the course of this work. Thanks are due to Dr. M.S. Murthy for his active help.

The author appreciates the constant help and encouragement by Dr. S.B. Rana, P. Haribabu, other fellow research workers and staff members.

Thanks are due to Miss. S. Nanda of Chemistry Department and Dr. Ramaswamy of I.I.P. Dehradun, for their help in determining the BET surface areas of catalysts.

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

(Ashwani Kumar)

## ABSTRACT

The literature on the kinetics of catalytic combustion of  $C_2-C_4$  hydrocarbons and their mixtures, specially at higher temperatures, is limited. Apart from the low temperature combustion for air-pollution control, catalytic combustion of hydrocarbons for high temperature applications in furnaces etc. remains to be fully exploited. In an earlier investigation combustion of propane in presence of nickel oxide-alumina catalyst was studied in a temperature range  $300-800^{\circ}C$ . The reaction mechanism could be well explained between  $300-450^{\circ}C$  by a zero order reaction, and above  $650^{\circ}C$  by two parallel first order reactions. However, combustion in the middle temperature range of  $450-600^{\circ}C$  could not be properly explained. The present work was undertaken to investigate the combustion of hydrocarbons in this temperature range.

The present study on liquefied petroleum gas combustion was conducted using an isothermal packed bed plugflow micro-reactor (stainless steel) under steady state conditions. The catalysts employed were (i) copper oxide impregnated over silica gel ( $425-650^{\circ}C$ ) and (ii) alumina ( $450-700^{\circ}C$ ). Analyses of reactants and products were done by gas chromatography. The effects of temperature, time factor and particle size on conversion were investigated for both the catalysts. On kinetic analysis the order of the hydrocarbon disappearance :

reaction was found to be unity with respect to hydrocarbon concentration (on carbon basis) for both the catalysts.

Assuming there were no internal diffusion effects present in copper oxide impregnated catalyst, the results could be explained satisfactorily. The Arrhenius plots of hydrocarbon disappearance and carbon dioxide formation were found to fall almost on the same line at lower temperatures indicating that hydrocarbon disappearance yielded carbon dioxide as the only carbon containing combustion product in this region. Beyond the temperature of  $550^{\circ}\text{C}$  unsaturates were forming and a break in the Arrhenius plot of hydrocarbon disappearance appeared. The rate equation for unsaturate formation was evaluated by assuming that the hydrocarbon disappearance beyond  $550^{\circ}\text{C}$  was taking place via two parallel reactions giving carbon dioxide and unsaturates. The activation energies of both the parallel reactions were found to be in close agreement with the reported values in literature.

In case of alumina catalyst, presence of internal diffusion was indicated by a decrease in the slope of the Arrhenius plot with increase of temperature. The values of effectiveness factors calculated from the experimental data on carbon dioxide formation, assuming that at the lowest temperatures the reaction was diffusion free, were comparable to those calculated by using a theoretical method. The diffusion corrected Arrhenius

plots were similar to copper oxide impregnated silica gel catalyst except at lowest temperatures where the Arrhenius plots of hydrocarbon disappearance and carbon dioxide formation did not match satisfactorily. Results beyond 550°C could be explained on the basis of two parallel reactions for hydrocarbon disappearance viz. formation of carbon dioxide and formation of unsaturates.

==

## CONTENTS

<u>Chapter</u>		<u>Page</u>
	Abstract ..	1-3
	List of figures ..	4-6
	List of tables ..	7-8
	Nomenclature ..	9-11
1	INTRODUCTION ..	12-15
2	LITERATURE SURVEY ..	16-24
3	EXPERIMENTAL ..	25-39
	3.1 Experimental set-up ..	27
	3.1.1 Reactor assembly ..	28
	3.2 Catalyst preparation and characterization ..	30
	3.2.1 Preparation ..	30
	3.2.2 Characterization ..	31
	3.3 Analytical technique ..	31
	3.4 Experimental procedure ..	33
	3.5 Range of experimental variables ..	35
	3.6 Methods of calculations ..	35
	3.7 Reproducibility of data ..	39

CONTENTS (Contd.)

<u>Chapter</u>		<u>Page</u>
4	EXPERIMENTAL RESULTS AND ANALYSIS ..	40-74
4.1	Results of preliminary experiments ..	40
4.1.1	Identification of reaction products ..	40
4.1.2	Experimentation on combustion run on fused alumina ..	41
4.1.3	External mass transfer effects ..	41
4.2	Effects of various factors on conversion ..	42
4.2.1	Heat transfer effects ..	42
4.2.2	Effect of temperature on conversion ..	47
4.2.3	Effect of time factor on conversion ..	48
4.2.4	Effect of particle size on conversion ..	48
4.3	Kinetic analysis of results on copper oxide impregnated silica gel catalyst ..	52
4.4	Kinetic analysis of results on alumina catalyst ..	57
4.4.1	Theoretical method for calculating diffusion effects ..	62
4.4.2	Diffusion free kinetic analysis for alumina catalyst ..	69
5	SUMMARY AND CONCLUSIONS ..	75-82

CONTENTS (Contd.)

<u>Chapter</u>		<u>Page</u>
APPENDICES	..	83-119
Appendix-A	SPECIFICATIONS AND OPERATING CONDITIONS FOR CHROMATOGRAPHIC COLUMNS	.. 83
Appendix-B	EXPERIMENTALLY OBSERVED CONVERSIONS	.. 84-87
Appendix-C	EFFECT OF TIME FACTORS ON CONVERSIONS	.. 88-101
Appendix-D	CALCULATIONS FOR HEAT TRANSFER EFFECTS	.. 102-105
Appendix-E	CALCULATIONS FOR THEORETICAL.. EFFECTIVENESS FACTORS	106-110
Appendix-F	A KINETIC ANALYSIS THROUGH CONSECUTIVE REACTION	.. 111-119
BIBLIOGRAPHY	..	.. 120-132

====