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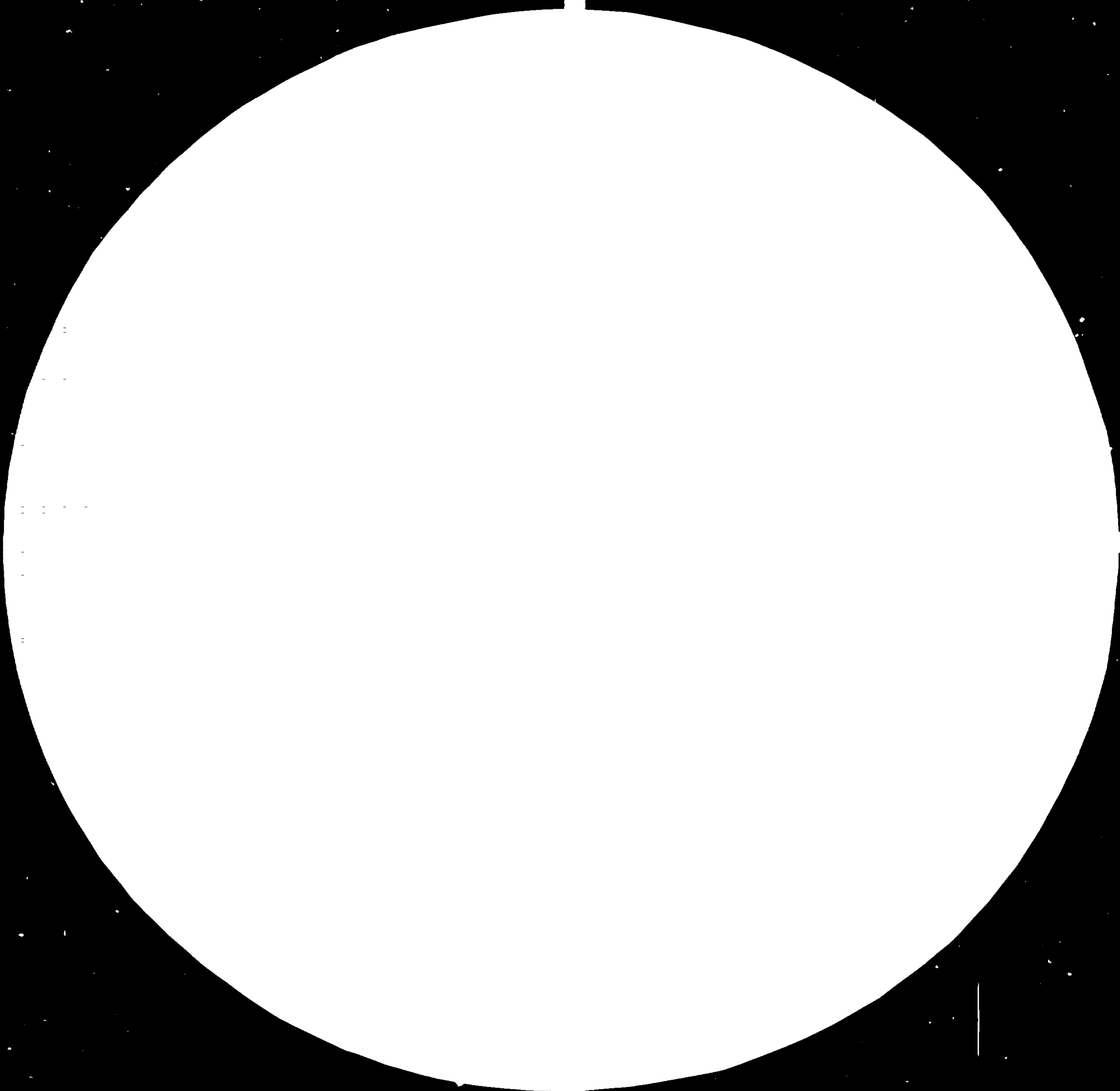

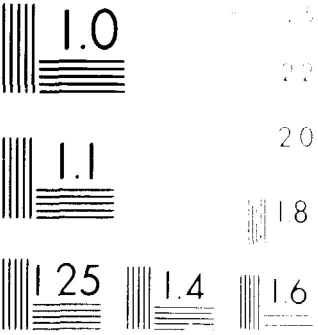
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24 May 1982
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MODERNIZATION OF ENGINEERING DESIGN
AND
CONSULTANCY SERVICES, PYROLYSIS PROCESS DESIGN.

DP/IND/78/054

INDIA.

Terminal report *

Prepared for the Government of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of R.W. King, expert, Pyrolysis Process Design

United Nations Industrial Development Organization
Vienna

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V.82-26535

SUBJECT

Note: The modern chemical nomenclature, ethene, ethyne, propene, have been used exclusively in this report even where the older nomenclature ethylene, ocetylene, propylene, were used in my reports written in India and referred to here.

I - SUMMARY

1. EIL have gone a long way in the last five years to develop an ethene furnace design capability, due largely to the capable technical leadership of Dr. D.N. Rihani.

2. Whilst they have developed a complete computer model for ethane-propane cracking based on the published molecular mechanisms and rate constants of Professor Froment, its yield predictions appear to be in considerable error. It also fails to show the trends in yields of individual hydrocarbons anticipated with rising temperature when conversions and mass velocity are kept constant.

3. EIL have as yet no order to design a commercial cracker, but an order to design a small prototype unit for India Petrochemicals Ltd (IPCL) at Baroda is expected imminently.

4. There is a real need for EIL to improve their existing cracking model or to make or acquire a better one. Dr. Moll, the ethene cracker specialist from Holland, whom EIL wish to retain for the second half of this assignment, appears to be in a better position to supply this service than the undersigned.

5. The proposed experimental bench scale cracking set up at Baroda has been reviewed and a number of suggestions made for its improvement.

6. A programme for the experimental investigation of coking in cracking tubes has been suggested. This has as its objective the catalytic removal of coke on the point of deposition through the water gas reaction with the steam diluent used in cracking.

7. Following discussions outside the scope of this programme with Indian industrialists concerned with the use of fermentation alcohol as a chemical raw material, it is recommended that UNIDO support an international seminar in India on the manufacture of chemicals from fermentation ethanol as soon as this can conveniently be arranged.

II - INTRODUCTION

8. I was first approached directly by Dr. D.N. Rihani of Engineers India Ltd by letter of May 6, 1981 to enquire whether I could assist EIL for a period of 4 months under a UNDP funded project in the area of pyrolysis process design. Having been actively involved on a full time basis in this field several years ago, and having kept broadly in touch with recent developments, I informed Dr. Rihani of my experience in this field and expressed my readiness to accept. I informed UNIDO, Vienna, of this approach and in due course was offered a four month assignment with EIL by UNIDO as the first half of an 8 month 'split mission'.

9. I was briefed by Mr. Keleti in Vienna on December 15/16, 1981 and reached New Delhi on December 17, where I was met by a UNIDO car, taken in hand by Mr. Sat Pal of the UNDP office in New Delhi and introduced to the various UNDP/UNIDO functionaries there.

10. On December 18 I first met Mr. R.S. Grover, Manager of Engineering Technology and Development, EIL in their office at 4 Sansad Marg, New Delhi (where I was to spend most of my working time in India), and Mr. J.R. Prasher, EIL, welding expert and assistant to Mr. Grover. Mr. Prasher acts as liaison officer between EIL and visiting experts. I then met Dr. D.N. Rihani of EIL's R & D department who has been responsible inter alia for developing EIL's process know-how in the field of ethene pyrolysis over a number of years, Dr. Mukhopadhyay, head of EIL's R & D department, Mr. B.R. Choudhury, head of EIL's process department (since seconded to a post with the World Bank in Saudi Arabia), and Messrs. Veeranna and Dongaonkar, two graduate engineers working for Dr. Rihani.

11. I met my two UNIDO colleagues, Dr. Alfredo Margola, Environmental Engineer, with whom I was to share an office, and Dr. Rustam Aleiv, Petroleum Engineer.

12. Dr. Rihani, who plays a key part in the development of process know-how for the design of ethene pyrolysis furnaces, took a Ph.D. in chemical engineering under Professor Froment of Ghent University, Belgium, working in the field of pyrolysis reaction kinetics. Before joining EIL he was mainly involved in teaching.

13. EIL have a first class library of books and periodicals on chemical engineering and fundamental aspects of the petrochemical industry, and have produced their own comprehensive bibliographies and reviews of published work on hydrocarbon pyrolysis for ethene production.

14. EIL have developed as a working tool a computer model for the simulation of ethene cracking furnaces using ethane-propane feedstocks, based on the rate constants for a molecular mechanism proposed by Professor Froment and his collaborators.

15. EIL work in close liaison with IPCL (India Petrochemicals Ltd) at Baroda, acting as engineering consultants and contractors to them and deriving some operating data and experience from them.

16. In practical terms, EIL's main present function in the field of ethene pyrolysis appears to be to assist IPCL in de-bottlenecking existing ethene plants at Baroda and in negotiating with international contractors (Stone and Webster, Lummus, Technip and others) for the design, construction and commissioning of a new ethene plant at Maharastra which is planned for about 1988 and which will be based on ethane, propane and possibly butane derived from associated (and/or natural) gas from the Bombay High field.

17. EIL's next objective in this field is to design and build ethene pyrolysis plants (which form the basis of the petrochemical industry) for use by IPCL and other operating companies in India, in competition with international contractors. They have prepared outline designs and have some prospect of designing and building a prototype ethane-propane cracker for IPCL at Baroda.

18. In the course of developing know-how in technologies in which it has no design experience (such as ethene production) EIL's R & D department also plays the role of process designer, acting in direct liaison with the other departments involved, i.e. furnace design and heat transfer, materials of construction, mechanical engineering, instrument engineering, piping, civil and electrical engineering, etc.

19. Dr. Rihani's team has a first class theoretical background although the tools they are using need improvement and updating. They are rather lacking at present in practical experience.

III - Work Programme

20. The following work programme, based on a draft prepared by Dr. Rihani, with some modifications which I introduced, was agreed and accepted by both parties.

(i) Review of the cracking model and correlation and comment on computed yields and other outputs with computer imputs (feedstock composition, coil design, pressure, temperatures and other variables).

(ii) Review of the procedure for predicting coke lay-down in furnaces (i.e. in cracking tubes).

(iii) Development of simplifying kinetic and thermodynamic parameters incorporating cracking temperatures, pressure and contact time to aid correlation of cracking yield patterns with cracking conditions.

(iv) Review of the experimental set-up at IPCL, Baroda.

(v) Formulation of proposal to investigate coking mechanism.

21. In addition to this formal programme, I became involved in the following related activities:

* Review of a proposal by EIL for the design of a cracker using ethane-propane feed from the Bombay High field.
* Preparation and delivery of a lecture at IPCL, Baroda, on 'Safety in Ethene Plants'.
* Review of an EIL report on models and published data on naphtha cracking. (Note the model reviewed in item (i) of my work programme was for cracking ethane and propane only).
* A preliminary design suggestion for a cylindrical cracking furnace with multi-start helical coils, in place of the present rectangular furnaces now in general use.
* Consideration of the pros and cons of high alloy drawn and centrifugally cast cracking tubes.

22. I also became briefly involved in information gathering in connection with a further UNDP/UNESCO project,in Brazil,in which I have been asked to participate, 'The Manufacture of Chemicals from Fermentation Ethanol'. I met several Indians with special knowledge of this subject, including Mr. Purushottam, M. Kavadia, chairman of the Indian Chemical Manufacturers Association and vice President of the All India Alcohol based Industries Development Association. In view of the interest in this subject both to India and other developing countries, I would suggest to UNIDO that an international symposium on the subject might be held in India as soon as possible.

IV - THE GAS PYROLYSIS COMPUTER MODEL AND ITS IMPORTANCE TO EIL

23. The importance of the computer model to EIL for the process design of ethane-propane crackers and the downstream gas separation and ethene and propene utilization units can scarcely be exaggerated. A reliable model will not only give the yields of hydrogen, methane,

ethyne, ethene, ethane, propadiene, propyne, propene, propane and C_4 and heavier hydrocarbons for any ethane-propane feed mixture under a range of different design variants and cracking conditions. It should also enable the most economic combination of tube diameters and materials to be selected and enable tube metal temperatures to be calculated both along the length of the tube and through the course of a run as a coke layer builds up on the inside wall of the tube. It should enable the choice of cracking variables to be optimised for a range of feed compositions and product mixes, and enable the required flexibility in the design of the downstream units to be established. These are only a few of its uses.

24. Whilst the model developed by EIL attempts to do all these things, its absolute accuracy as well as its response to changes in cracking conditions are recognised by EIL to be inadequate and in need of improvement. This is very difficult and laborious and also requires a good deal of high class operating data from commercial plants of different design to check and correlate the predictions of the model against real performance. The computer model used by EIL is probably two generations behind those currently in use by international contractors. Whilst I was ultimately able, after developing certain thermodynamic criteria, to review the EIL model, point out some of its deficiencies, and suggest how these be remedied, I was in no position to offer EIL an improved set of reaction mechanisms and rate constants on which a better model could be based.

25. In consequence, I must endorse EIL's decision to call in Dr. A. Moll a Dutch specialist in the design of pyrolysis furnaces for the second 4 month part of this split mission. Dr. Moll has apparently an improved model to offer to EIL which can probably be adapted to use by their own Roboton computer. This was made in East Germany and is roughly equivalent to the IBM 360 computer.

V - OUTLINE OF WORK CARRIED OUT AND VISIT TO IPCL, BARODA

26. As will be apparent from III, my working time apart from a three day visit to Baroda, was largely spent in studying EIL reports, and memoranda, published papers, data and contractors' proposals in EIL's possession, reviewing EIL's reports and proposals in writing and formulating certain proposals of my own. Most of my outputs were in writing, with supporting calculations and graphs. Most, but not all, of my reports were discussed with Dr. Rihani and other engineers, usually in a draft stage before they were finalised.

27. My time during my four month assignment was thus very fully occupied, so much so that this terminal report could not be written during my stay in India but is being written now after its completion.

28. Copies of all reports made by me under the agreed work programme were sent to UNIDO, Vienna, and filed in the UNIDO office, New Delhi, besides being given to EIL and in some cases IPCL, Baroda. No reports have been sent to UNIDO covering my other activities mentioned under III(21). My outputs from these other activities were sometimes typed, sometimes hand written notes, and sometimes oral.

29. By prior agreement with UNIDO and EIL, I took one week's unpaid leave during my mission (during which I visited India Explosives Ltd fertilizer factory at Kanpur by invitation of its general manager, Mr. Ajit Chakrabarty, an old friend). To make up for this, I extended my stay in India for one week beyond the normal completion date of my mission.

30. I visited IPCL, Baroda, from Thursday, 18 February to Saturday, 20 February inclusive with my wife, travelling by night train from Delhi. We were hospitably accommodated there in the IPCL 'Experts' Guest House, where we met two other UNIDO experts who were assigned to Baroda, one a French-Canadian expert on maintenance and rotating equipment who has since died in India.

31. I first met Dr. I.S. Bhardwaj, head of the research centre at Baroda, Dr. J.S. Arnand, senior research officer and Dr. K.N. Ponnani, research officer in charge of the pilot plant section, and spent most of Thursday visiting the research centre and pilot plant.

32. On Friday morning I visited the works and was introduced to a number of senior staff and spent my time between the safety department and the ethene cracker (based on naphtha feed, with one furnace for recycle ethane). On Friday afternoon I gave a talk to about 20 engineers on safety in ethene plants, which was well received.

33. On Saturday morning I had further discussions with Dr. Ponnani on the incomplete bench scale cracker, a joint venture between EIL and IPCL. The unit as designed appeared to me to be unworkable. I made a number of suggestions for its improvement, which have subsequently been incorporated in a report (Section VI, c).

VI - HIGHLIGHTS OF MAIN REPORTS PREPARED DURING MISSION

34. I prepared five main reports during my mission in the following order:

A. "Development of Kinetic and Thermodynamic Parameters for Correlation of Cracking Conditions and Yield Patterns in Ethene Production" (item (iii) of programme).

B. "Proposal for Experimental Investigation of Coking in Ethene Pyrolysis Tubes." (Item (v) of programme).

C. "Review of Experimental Bench Scale Cracker Set-up at IPCL, Baroda). (Item (iv) of programme).

D. "Equilibrium Approach in Tubular Crackers for Ethene Production" (Refers to item (iii) of programme).

E. "Review of Gas Cracking Model and Review of Procedure for Predicting Coke Lay Down in Furnaces". (Items (i) and (ii) of programme).

35. Items (i) and (ii) of my work programme were treated last and covered in a single report. There were two reasons for this:

(i) I wanted some computer runs carried out to test certain aspects of the computer model, but these could not be carried out until the end of March due to staff shortages and transfers.

(ii) Before reviewing the cracking model and coke lay-down procedure, I needed to develop certain criteria and standards against which its outputs could be compared and its performance assessed. There were three possible bases for such comparison:

* published data
* thermodynamic considerations
* past personal experience.

Much of the published data on which EIL had relied for evaluating their model turned out to be incomplete, of low quality (i.e. showing a great deal of 'scatter') and derived from small scale laboratory experiments which seldom match the results obtained on commercial plants.

36. I did, however, spend a good deal of time in developing the 'Equilibrium Approach' (Report D), based on thermodynamic data published in API project 44, which I had found very useful when engaged several years ago in experimental cracking studies at Shell Chemicals, Carrington. This method which was used in a limited way and discussed in 1959 by Shutt, a pioneer in the process design of ethene crackers, as a means of correlating results, seems to have been largely neglected by most later researchers in this field.

37. Since the trends revealed by the 'Equilibrium Approach' were entirely in line with my personal experience, I felt some justification in using them as a basis for comparing the yield trends shown by the computer model.

38. Report A. "Development of Kinetic and Thermodynamic Parameters for Correlation of Cracking Conditions and Yield Patterns in Ethene Production."

This summarises the theoretical conclusions I had reached several years ago after extensive cracking studies on a pilot plant scale on the effect of cracking conditions on yield patterns. Since there are at least five important and independent variables in cracking conditions and three others of somewhat lesser importance, the mental task of correlating these directly against cracking yields is almost impossible. I had however found that as a first approximation, the five main variables could be combined to give two contrasting parameters which could be quantified and which together defined the yield pattern from any hydrocarbon feedstock. These are:

(i) a kinetic parameter, a function of the contact time and cracking temperature, which governs the depth of cracking and the general distribution of C_1, C_2, C_3, C_4 and heavier hydrocarbons in the cracked product.

(ii) A thermodynamic parameter, a function of the cracking temperature and hydrocarbon partial pressure, which governs the degree of unsaturation of the C_2, C_3 and C_4 fractions, i.e. the ratio of acetylenes:olefins:paraffins in each fraction.

39. Report B. "Proposal for Experimental Coking in Ethene Pyrolysis Tubes"

A four part programme is proposed which differs from most published coking studies. Its aim is to discover a selective catalyst which can be incorporated into the material of the cracking tubes which will catalyse the rate of coke gasification during cracking by steam diluent through the water gas reaction without at the same time increasing the rate of coke deposition.

Whilst the chances of success may not be high, the jackpot would be considerable. The incidental knowledge acquired through this research should be at least as valuable as that acquired through most published coking studies.

40. Report C. "Review of Bench Scale Cracker Set-Up at IPCL, Baroda."

This proposed set-up at Baroda was neither complete nor operational when I visited Barodaand discussed it with Dr. Ponnani, who will be responsible for it. My report makes a number of criticisms and proposals for modification of the design, which I fear will not be successful as it stands. The most important proposal which has wider significance than this unit is that bench scale and small pilot plant units of all types be designed and constructed by a special design and workshop team created solely for this purpose, and not by engineers whose main function is the design of large scale commercial units. The main reason is that the problems of bench scale and small pilot plant units are usually totally different from those of large industrial units, and require a different approach on the part of designers. As an example, the heat losses from a bench scale cracker will represent a much ligher proportion of the total heat imput than for a commercial cracker and require much closer integration and compaction of all parts subjected to high temperatures.

41. Report D. "Equilibrium Approach in Tubular Crackers for Ethene Production."

This is a further development of Report A. Its basic thesis may be stated as follows:

"All hydrocarbons are unstable at the temperatures employed in ethene crackers and eventually decompose to hydrogen and carbon at prolonged contact times. Nevertheless, if we consider a number of dehydrogenation reactions represented by:

$$C_mH_{2n} \rightleftharpoons C_mH_{2n-2} + H_2$$

and substitute the concentrations found at the outlet of the cracking reactor in the expression:

$$K' = \frac{(C_mH_{2n-2})(H_2)}{(C_mH_{2n})}$$

we find that for a given cracking reactor and feedstock:

$$K' = fK$$

where K' is the 'pseudo equilibrium constant',

K is the true equilibrium constant calculated from published free energy data (API project 44), and

f is the equilibrium approach factor.

f is always less than unity and is either constant or varies systematically over a small range with temperature for each dehydrogenation reaction considered, in spite of large changes in the values of K' and K." This thesis was tested against the best published data reviewed by EIL for naphtha cracking, for the following dehydrogenation reactions:

Ethane - ethene
Propane-propene
Ethene - ethyne
Propene-propyne + propadiene
Total n-butenes - 1:3 butadiene

The thesis was found to be generally valid, and may thus be used to check the quality or consistency of experimental data from a series of runs using the same feedstock and cracking unit. It can also be used to assist in the correlation of yield patterns under various cracking conditions.

In an app endix to this report the partial pressures (which are vanishingly small) of the main cracked products which would be in equilibrium with carbon and hydrogen over the usual range of temperatures used in ethene cracking are calculated and plotted against temperature. Some partial pressures increase with temperature whereas others decrease. The results are in keeping with the thesis that"the yields of hydrocarbons whose equilibrium partial pressures increase with temperature do themselves increase with temperature at the expense of those whose equilibrium partial pressures decrease with rising temperatures." If this generalization can be accepted, it affords a criterion for assessing the validity of predictions made by the computer model on the influence of temperature on the relative yields of various hydrocarbons at constant conversions or depth of cracking. From my own direct experience and from the published results which I have been able to study, I have found this to be valid.

42. Report E. "Review of Gas Cracking Model and Review of Procedure for Predicting Coke Lay Down in Furances."

The heat transfer and pressure drop expressions used in the model are assumed to be correct and only the molecular cracking mechanisms and rate constants proposed by Froment and Sundaram are examined. The model is treated as an empirical one, since the true mechanism is undoubtedly by free radicals rather than by molecular reactions. Nonetheless, it is believed that a molecular mechanism when used in conjunction with appropriate rate constants (collision frequencies and activation energies) should be capable of giving yield predictions in close agreement with actual cracking results.

The reactions used by Froment for the molecular mechanism are examined. One at least, the production of ethyne by demethanation of propene is shown to be less in agreement with results than the more obvious dehydrogenation of ethene. The three main reactions used by Froment are accepted but doubts arise on the validity of several others.

Some test runs were carried out on the computer model in March and April 1982 at my suggestion to investigate the changes predicted by a rise in temperature on the yields of a number of compounds, when the conversion and other main variables were kept constant. The results were generally in conflict with the thesis put forward in my Report D, and in some cases were quite obviously incorrect. These implied deficiencies in the model could be attributed to the use of incorrect activation energies in the model.

The incorrectness of the yield patterns predicted by the model for the EIL design of a commercial ethane-propane cracker had previously been recognised by Dr. Rihani who had been obliged to apply a number of corrections, in some cases over 100%, to its predicted yields which were quite out of line with those given by international contractors.

To conclude, EIL are in urgent need of a better model which gives better agreement with actual yields under a variety of conditions. They are also in need of better yield and operating data on a commercial scale against which to check the validity of their model's predictions. Most of the published data against which their model has been tested are from bench scale cracking units and are either very incomplete or of doubtful quality or both. In any case, the degree of scatter in the experimental results and the degree of discrepancy between them and the predictions of the model are far too high.

The coking mechanism used in conjunction with the cracking model is one posposed in a Ph.D. thesis by Sundaram at Ghent University. It treats propene as the only coke precursor. This model has been criticised by later workers, particularly Goossens, Dente and Ranzi. Whilst I believe a model such as that proposed by Sundaram may still have some empirical value I think it will give too rapid coking rates for propane cracking and too low coking rates for ethane cracking. I believe a model based on both propene and ethene as precursors is more likely to be capable of matching actual coking rates.

The model has the virtue of taking the temperature of the gas-coke boundary into account, as well as the average gas temperature, but it takes no account of the laminar film thickness adjacent to the coke boundary or the Reynolds number in the gas which determines it. Unfortunately EIL lack the practical data needed to check the predictions of any coking model against plant performance.

VII- RECOMMENDATIONS

43. Collection of Plant Data on Ethane-Propane Cracking

To provide a firm design basis, EIL are in need of reliable data on cracking yields, feedstock compositions and design and operating conditions for commercial ethane-propane cracking. A special effort will be needed to collect such data,involving the assistance of 'friendly operators' such as IPCL.

44. Validation and Correlation of Data used as Check Points for Computer Models.

Data used as check points for computer models should be taken predominantly from industrial scale crackers.

Such data should first be screened for (a) completeness, particularly in product analysis, (b) mass balance and particularly carbon and hydrogen balance over cracker feed and product streams (this is already done by EIL), and (c) consistency in the approach to the various possible dehydrogenation equilibria (see my Report D, section VI).

Data which does not pass such screening should be rejected and not used as computer model check points.

45. Improved Computer Model

EIL are in serious need of a more accurate, reliable and sensitive computer model for ethane-propane cracking. Whilst it is possible to buy the results obtained from a reputable and up-to-date model such as SPYRO, the model itself, or the mechanism on which it is based are not for sale or transfer.

It is understood that Dr. A. Moll can provide EIL with the mechanistic basis for a better model and if so his services should be retained by EIL.

46. The research programme on coking in ethene cracker tubes put forward in my report B (section VI) should be followed up.

47. The suggestions put forward in my Report C on the bench scale cracker at Baroda should be followed up.

48. Though outside the scope of the present programme, it is recommended that UNIDO/UNDP take up and support a suggestion made to me by Mr. Kavadia, Vice President of the All India Alcohol Based Industries Development Association, that an international symposium on the manufacture of chemicals from fermentation alcohol be held in India as soon as it can be organised.