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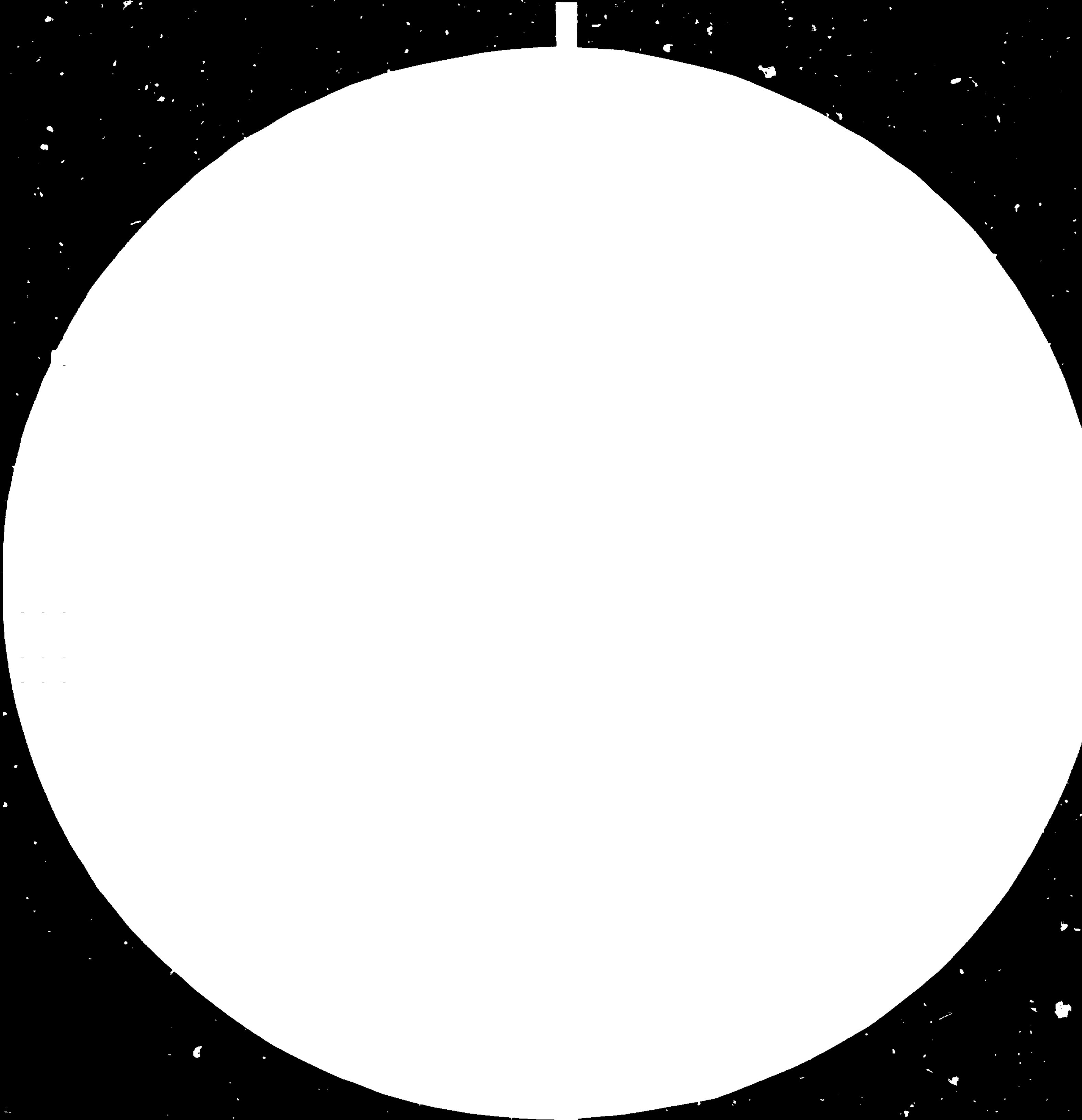

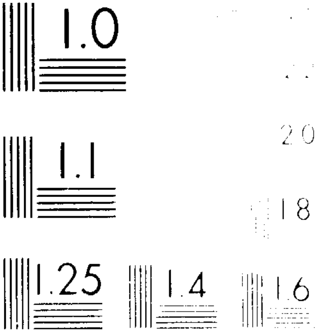
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BEIJING RESEARCH INSTITUTE OF CHEMICAL INDUSTRY

MINISTRY OF CHEMICAL INDUSTRY

BEIJING, CHINA

FINAL REPORT

submitted

by

DR. ROBERT L. LAURENCE

Post: DP/CPR/80/009/11-01/32.1H

Mission Duration: 26 July to 20 September 1982

FINAL REPORT

TO

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION

Mission
to
Beijing Research Institute of Chemical Industry
Ministry of Chemical Industry
Beijing, China

Reference: UNIDO Job Description DP/CPR/80/009/11-01/32.1H

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Mission Duration: 26 July to 20 September 1982

ABSTRACT

The purpose of this mission was to aid in the development of a Chemical Engineering group at the Beijing Research Institute of Chemical Industry. The two major tasks were consulting and lecturing on the analysis, design and control of polymerization reactors. A course on polymerization reaction engineering was given over a five week period. Afternoon discussions were held with several Chemical Engineering groups dealing with current and future problems in reactor engineering. These meetings were broadened to include participation of other groups within the Institute also having interests in polymer reactors.

Planning discussions were held with Polymer Reactor group personnel to assess their programs, determine their needs, and to propose a viable structure for the unit and its activities.

Robert L. Laurence
15 September 1982

INTRODUCTION

The Beijing Research Institute of Chemical Industry is a large research and development complex whose task it has been since its inception in 1958 to offer support to the chemical industry of the People's Republic of China. The focus has been on reactive processing of chemical substances and those engineering tasks which facilitate processing. Their approach, it appears, has been along the lines of classical industrial chemistry, i.e., doing enough bench scale chemistry to afford some confidence in process feasibility, following a largely Edisonian approach to process scale-up, having recourse to extensive use of workshop or pilot plant facilities.

Recognition that this pattern might not lead to consistent incorporation of current and developing engineering practice led to the establishment of a Chemical Engineering Division. An important and growing aspect of this division's activities is the support and development of polymerization processes.

The particular purpose of this mission was to aid in the development of a Polymer Reaction Engineering group within the Chemical Engineering Division through a series of lectures and discussions on the design and scale-up of polymerization processes. This report describes in detail these activities and presents an assessment of the program and recommendations for its continued development.

LECTURING ACTIVITIES

An important component of this mission was the presentation of a series of 75 hours of lectures on " Polymerization Reaction Engineering", covering virtually all facets of reaction engineering for polymerizing systems. A detailed outline is presented in Appendix A. The first two weeks dealt with an extensive discussion of the kinetics of homo- and co-polymerization, with particular emphasis on batch systems. The third week's lectures covered ideal continuous reactors, the effects of macro- and micro-mixing, and the analysis of tubular polymerization reactors. During the fourth week were discussed the heat and mass transfer problems attendant to polymerization. In pariculer, emphasis was placed on the diffusion problems in polymerizing systems. Also discussed were the dynamics, control, and optimization of polymerization reactors.

The final week consisted of a detailed discussion of current technology for the polymerization of styrene and alpha-olefins, paying particular attention to the structure-property relations.

These lectures were ably interpreted by Lu Tian-Xiong, an engineer at the Institute. Six chapters of a manuscript were left with the Polymer Reaction Engineering group. In addition, several hundred pages of notes were also left, offerring some techinical base upon which to establish their program.

The emphasis in these lectures was to present a balanced view of polymer reaction engineering, showing the need and utility of analysis, a thorough understanding of polymer structure-property relations, and those practical considerations leading to sound reactor design.

CONSULTING ACTIVITIES

Discussions were held daily throughout the mission with several groups having an interest in polymerization. Several sessions were held with each group, focussing each time on a particular problem. The discussions were of three types. The first were usually expository, describing the particular programs and problems; the second dealt with the bench scale development work and scale-up problems prior to transfer to the workshop; the last dealt with the scale-up problems from pilot to commercial scale.

The content of these discussions is summarized topically, lumping all three types into one, and presenting these by subject area.

The expository discussions covered all the programs at the Institute with some relevance to the activities of the Chemical Engineering Division. These included the Reaction Engineering group, the Fluidization group, the Distillation group, the Thermodynamics group, and, of course, the Polymer Reactor Engineering group. These along with an extensive tour of the facilities and shops afforded a good perspective of the existing programs.

An extended discussion was held with Mr. Zhao and the Polymer Reactor Engineering group detailing the particular programs. It was these programs which formed the basic for the technical discussions reported and summarized below. These included poly(Propylene), Ethylene-Vinyl Acetate co-polymer, Ethylene-Propylene terpolymer, and impact poly(Styrene).

In addition, several discussions were held with Mr. Zhao on the current and future programs of his group, paying attention to the personnel and equipment needs required for the operation of a productive Polymer Reactor Engineering group. These discussions and the findings are also summarized below.

Technical Discussions of Poly(propylene)

The many discussions of propylene and its polymerization were held with members of the Polymer Reactor Engineering group as well as with the pilot plant and chemistry personnel. The particular process for propylene polymerization currently under study is a slurry phase process using a Mitsui type catalyst, e.g., $TiCl_3$, alkyl Al, & $MgCl_2$, with a liquid propylene feed into an autoclave charged with hexane as a diluent. The catalyst activity is very high, comparable with the more active catalysts used commercially in the West. The problems facing both the pilot plant and reactor engineering groups are the scale-up questions which arise in going from bench to pilot to commercial scale.

In the course of the discussion, it was demonstrated that the bench scale experiments sufficed to provide the requisite kinetic data for scale-up. The physical system is particularly amenable to modelling, thereby reducing the need for expensive and redundant experiments in the pilot plant. Studies done in the U.S.A. and in Italy show that the monomer concentration in the diluent and throughout the polymerizing particle is constant. One can model, therefore, the polymerization using a chain growth mechanism with transfer and some first order termination. Prediction of the polymer chain length distribution is difficult since the breadth of the distribution is governed by the distribution of activation energies of the active catalyst centers.

It was pointed out that a continuous well-stirred reactor is of necessity segregated when the product polymer is precipitated from the diluent-monomer mixture. However, the polymerization reaction is first order in active polymer and the resulting distribution should show no appreciable effects of segregation. In order to do an effective scale-up, it was agreed that the deactivation of the catalyst had to be taken into account. Usual bench scale experiments do not concern themselves with deactivation questions. It was recommended that particular attention be paid to these deactivation questions, since the residence time distribution in a CSTR will result in a larger fraction of the polymer in the vessel being inactive. Although it will not have serious consequences with regard to the polymer chain length distribution, it will result in a considerable yield loss, predictable with reasonable deactivation data.

Technical Discussions on Ethylene-Vinyl Acetate Copolymer

The copolymerization of ethylene with vinyl acetate is a heterophase free radical chain growth process. The reaction is carried out in a semi-batch process where t-butanol, water, and vinyl acetate are charged to the reactor. The initiator is azo-bis-isobutyronitrile. The ethylene is added continuously over the course of the polymerization. The reactivity ratios for the system are unity.

The essential questions asked in the course of the discussions related to scale-up. An estimate of the heat transfer rate indicated that the pilot plant reactor is operating near the performance limits of the jacket, i.e., for heat transfer. There are two options open, to provide additional heat transfer area with external heat exchangers, or to slow the rate of polymerization. Either solution has problems. An external heat exchanger is not feasible, given the high viscosity of the reacting medium. Additional water added to the system might make the use of a reflux condenser feasible. Control of the rate of polymerization can be effected through temperature, pressure and composition control, e.g. continual addition of vinyl acetate during the course of the polymerization.

The complexity of this system lies in the phase equilibrium and not in the kinetics, One program essential would be the determination of ethylene solubility in the course of the polymerization. This being known, one can then proceed to find optimal temperature and pressure histories which would maximize productivity and minimize the copolymer composition distribution. This is, of course, a 5 component three phase system, giving 4 degrees of freedom e.g., pressure, temperature, and two compositions which can be set independently. This suggests that there may be an optimal charge to the reactor as well as an optimal pressure-temperature history.

Technical Discussions on Ethylene-Propylene Terpolymers

Ethylene-Propylene terpolymer is produced by coordination catalysis using a Vanadium oxychloride/Al alkyl chloride catalyst. Norbornene is the termonomer, a non-conjugated diene. The pilot plant reactor is a 50 liter continuous stirred tank reactor. The solvent is hexane. Solids levels in the reactor are approximately 8 percent by weight with an ethylene/propylene ratio of 0.4. The reactivity ratios for the system are $r_1 = 10$ and $r_2 = 0.03$. The investigators wanted to know how to go about an optimization of the process. There are, of course, two types of optimization: steady state and dynamic. The application of different procedures are required by the different objectives posed. The objective here was to find the best reactor configuration and operating conditions, a steady state optimization.

This system operates at a high viscosity and therefore might change in performance with an increase in solids level. For example, the reactivity ratios are a function of the state of the system and could vary with conversion or viscosity of the reacting medium. It was suggested that the reactivity ratios be studied as a function of conversion on the bench scale.

In the pilot scale system , it appears that water removal from monomer is difficult. The molecular sieve material used in the process may not have been regenerated properly. It should not be difficult to evaluate and properly size the drying system.

It was asserted that there is a gel that forms as a result of the polymerization. From my perspective, what appears to be a gel is probably copolymer of high ethylene composition. The problem of monomer drift had been ignored, so that a measurement of copolymer cmposition using NMR could establish whether this insoluble material is markedly different in composition from the soluble fraction. If so, then some means must be developed to control the monomer drift which may occur as a result of segregation in the reactor. Some changes in operating conditions can reduce segregation, e.g., mixing conditions, or operation at lower concentrations, reducing the solution viscosity sufficiently to allow improved micromixing.

Miscellaneous Activities

During the seven weeks spent at the Institute in Beijing, there were several visits made to other research, production, and teaching facilities in or near Beijing and in Tianjin.

One chemical complex was visited, the Yan Shan Chemical complex near the Yan Shan Mts. approximately 40 kms. from Beijing. This was an impressive collection of production and research facilities using current technologies to produce a number of petrochemicals and polymers.

I was hosted at the Institute of Chemistry of the Academia Sinica by Dr. Qian RenYuan. The extensive programs at the Institute appeared equally as process and application focussed as the programs at the Beijing Research Institute of Chemical Industry. The facilities were not significantly better, although the rheological equipment already available or on order are of good quality.

At the request of Prof. Stephen Lenk, a UNIDO expert visiting an Institute of the Ministry of Light Industry, I presented 3 hours of lectures on polymer science and engineering programs in the United States, discussing the focus and nature of the research and teaching programs.

Near the end of my stay in Beijing, I was invited to the Beijing Institute of Chemical Technology to view its polymer engineering and science facilities.A brief visit was also made to the Chemical Engineering Department at the University of Tianjin where I presented a review of our program activities.

Discussions on the Polymer Reactor Group

A number of discussions were held with Mr. Zhao WenBin and members of his group to assess current programs, plans for the group, possible structure, and interactions and cooperation with related chemistry and pilot plant groups.

A program and a group structure was suggested, as well as recommendations for equipment which should be made available to this group through other divisions and groups in the Institute.

Mr. Zhao's group numbers currently 10 people, all directed to the support of programs already under study at the Institute. The objective of the group has yet to be clearly defined. There seems to be a paranoid interest in scale-up without a sufficiently sound perception of the needs of a polymerization process. There is no consistent methodology to be followed by the group in attacking new problems. Most of this can be cured by some simple change in the responsibilities, definition of the objectives, and the development of skills within the group that provide it with independence and versatility. This is addressed in the subsequent discussion of the plans and needs of this program.

Program Recommendations-Polymer Reactor Engineering

Professor Alvin H. Weiss spelled out quite clearly in his report covering his mission in 1981 the role of all the groups in a Chemical Engineering program, the particular directions that the Division at the Beijing Research Institute of Chemical Industry, in his perception, has taken, and his particular biases for the future directions of the program. The objective of this mission is somewhat different. The essential task was, as I said above, was to offer technical help and training to personnel concerned with polymerization and to aid in the structuring of a polymer reactor group. This particular set of recommendations deals with this latter aspect of my mission.

The nature of polymer reaction engineering is interdisciplinary. As such, a program in this area needs personnel with appropriate training and experience in Chemical Engineering, Polymer Science, and Physical Chemistry. The problems in polymer reactors require an awareness to problems conditioned by exposure to reaction kinetics, reactor modelling, fluid mechanics, thermodynamics, polymer characterization, and pilot scale experience. With this in mind, there are several recommendations which should be made about the structure and goals of a polymerization reactor group and its needs.

A polymer reactor group in this Institute has to be of assistance to other divisions and groups within the Institute as well as to the chemical industry in the People's Republic of China. This assistance must assume several forms: Process and Reactor Development, Exploratory Research, Process Engineering, and Technical Service. To be of utility in all of these areas, the group cannot be aligned in its current fashion, responsible for projects currently under investigation at the Institute.

The Polymer Reactor group in this Institute must have a technical base on which to build its service activities. The Fluidization group, for example, has a long history of generic research in the applications and technology of fluidization of fine particulate systems. This provides this group with a unique expertise on which to base its other activities. Within the Polymer Reactor group, there should be developed independent research programs whose goal would be to develop a technology base in reactor engineering suitable to apply to other aspects of the Institute's program.

Independent research programs on polymer reactor should be initiated in four particular areas. The first is in the modelling and design of copolymerization reactors. Two of the problems currently under investigation by the group deal with with copolymerization, ethylene-vinyl acetate coplymerization and the production of ethylene-propylene terpolymer. Future programs will in all likelihood involve copolymerizing systems. Multiphase polymerization reactors represent a significant fraction of the reactor types currently used at the Institute. Both propylene and the vinyl acetate-ethylene systems are heterophase systems and present unique design and operational problems, e.g., mass transfer of monomerto the system, phase equilibria, particle size distribution , etc. A research program seeking to understand the idiosyncracies of multiphase polymerization reactors would be an important contribution to the activities of the Institute. The third area, which might well be shared with other groups in the Institute,is the control and optimization of polymerization reactors. There are a class of problems which are archetypical of many polymerization systems. The methodology one must use remains the same although the particular kinetics and physical situation may change. These aspects should also be considered. Currently no work at the Institute deals with Reaction Injection Molding. Understanding of the molding process requires knowledge of fluid mechanics and reaction kinetics and the subject area ,of growing importance in the United States and Japan, should be included among programs at the Institute.

Once a technical base is established with its own research program, the personnel can be assigned to those problems which require their particular skills. Personnel within the group could and should be loaned to other groups or divisions so that they can participate in all aspects of process development, to a chemistry group where they can aid in the development of basic data for process scale-up, to a pilot plant group where they can help in the development of the experimental program in the pilot plant.

Experimental capabilities should exist within the group for the research programs, but it is more important that facilities exist within the Institute which would be accessible to the staff of the Polymer Reactor group. The accessibility is important, physical location and responsibility are irrelevant.

These equipment requirements are:

1) Polymer Characterization
   Rheological properties
   --Viscometers-- to measure intrinsic viscosities
   --Melt Indexer- to measure apparent viscosity
   --Mechanical Spectrometer-- to measure viscosity and normal stresses as a function of shear rate

Molecular Weights

--Membrane Osmometer- to measure M_n

--Light Scattering-- to measure M_w

--Gel Permeation Chromatographs- to measure molecular weight distributions. At least two should be available to operate at low and high temperatures for olefins and other polymers. Each should have multiple detectors in order to characterize copolymers and branched polymers effectively.

2) Polymerization Reactor System-- a general purpose system useful in the measurement of fundamental kinetic data. The scale should be bench scale with reactor volumes up to one liter. This system should have pumps, temperature measurement and control, as well as in-line composition and molecular weight measurement, e.g., refractive index and viscosity. The system, if possible should be interfaced with a dedicated microprocessor for control, data acquisition, and evaluation. Mr. Tang in his report earlier this year made a similar recommendation.

3) Physical and Transport Properties

The experimental capabilities should exist to develop the data necessary to scale-up heat and mass transfer processes that occur during and after polymerization. There should be means of determining solvent, diluent, or monomer diffusion from the polymer. These could be classical sorption techniques or Inverse Gas Chromatography. Autoclaves should be instrumented to simulate the reactor in order to evaluate heat transfer and mixing phenomena, e.g., as an aid in agitator selection.

I have tried to stress that the essential need for a Polymer Reactor group is a fundamental outlook with which the practical problems can be attacked efficiently. It will be the responsibility of the group leader to set the tone, to show that such a tack can provide marked improvement in productivity.

CONCLUSIONS

The major activities during my stay at the Beijing Research Institute of Chemical Industry were teaching and consulting on programs in Polymer Reaction Engineering. The course that I taught was the most inclusive that I have ever assembled on the problems in polymer reactor engineering. The group of over thirty people who sat through the entire course now form a base from which the ideas and methodology that I described will be used in the programs at the Institute. It was stressed throughout the lectures that a sound understanding of polymer science is important for rational design and operation of polymer reactor systems.

The technical discussions sought to answer the specific problems which face a rresearch or pilot plant group. The fashion in which I sought to answer these questions was to ask the group to address the cause of the problem and not its consequences. For example, the problem of gel formation during a co-polymerization may not be gel at all, but the formation of an insoluble fraction of the co-polymer as a result of monomer drift. The several sessions suggest that these meetings were well received.

The several discussions on the role and program of a polymer reactor group led to the set of recommendations presented in this report. This proposed program was discussed at length with Mr. Zhao WenBin.

Finally, I concur with the observations of both Dr. Weiss and Mr. Tang that the program of the Chemical Engineering Division appears to be on the way to meeting the goals of the UNIDO project.

Acknowledgment

I would like to thank Mr. Lu Tian-Xiong for his able interpretation of my lectures and of the technical discussions. Without his yeoman work, none of this woulf have been possible, nor would any of the discussions had any hope of being effectively received. Many individuals at the Institute deserve my evrlasting thanks for their welcomed reception and considerate help which they unselfishly tendered during my stay.

APPENDIX A

Polymer Reactor Engineering
a Course by Robert L. Laurence

Beijing Institute of Chemical Industry
He Ping Li, Beijing, China

5 August to 8 September 1982

Week 1 - Introduction to Reaction Engineering of Polymerizing Systems
- -Overview & Definitions
- -Aspects of Polymer Characterization
- -Polymerization Methods
- -Examples of Industrial Processes

-Mathematical Modelling Techniques
- -Methodology
- -Outline of Techniques
- -Transform Methods
- -Statistical Methods
- -Population Balances

Week 2 - Step Growth Polymerization
- -Statistical and Deterministic Analysis
- -Simple Step Growth
- -Effect of Chain Stoppers
- -Effect of Stoichiometry
- -Rversible Step Growth

- Chain Growth Polymerization
- -Radical Chain Growth
- -Complexities

Week 3 - Chain Growth Polymerization (cont'd)
- Ionic Chain Growth Processes
- Coordination Polymerization

- Copolymerization
- -Mayo equation
- -Composition and Sequence Distribution

- Continuous Polymerization Reactors
- -Macromixing
- -Micromixing
- -Experimental Observations

Week4 - Heat & Mass Transfer in Polymer Reactors
- -Thermal Effects in Tubular & Well-stirred Reactors
- -Mass Transfer & Devolatilization
- -Diffusion in Polymers
- -Continuous Polyesterification

- Dynamics & Optimization
- -Reactor Dynamics
- -Optimization Problems
  - Temperature Control & Policy Improvement
  - Reactor Turnaround

-Practical Problems in the Design and Optimization of Free Radical Chain Growth Polymers

Appendix A (cont'd)

Week 5

- Technology of Styrenic Polymers
  - Properties and Reactor Variables
  - Batch Processes-Bulk
    -Suspension
  - Continuous Processes
  - Controlling Runaway Reactions
- Technology of Olefin Polymers
  - Applications and Manufacturing
  - Chemistry of Polymerization
  - Commercial Processes for Poly(ethylene)
    - High Density
    - Low Density
  - Property-Structure Data for Poly(ethylene)
  - Models for High Pressure Poly(ethylene) for Poly(propylene)
- Directions for Current & Future Research and Development