STUDIES OF REFORMING REACTIONS WITH CATALYST DEACTIVATION IN TUBULAR REACTORS

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By
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CERTIFICATE

Certified that the thesis entitled "STUDIES OF REFORMING REACTIONS WITH CATALYST DEACTIVATION IN TUBULAR REACTORS" which is being submitted by Sri MUKESH CHANDRA BANSAL, Lecturer in Chemical Engineering, in fulfilment of the requirements for the award of DOCTOR OF PHILOSOPHY in Chemical Engineering of the University of Roorkee, Roorkee, is a record of candidate's own work carried out by him under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree.

This is further certified that the candidate has worked for a period of nearly eight years, as a part time student, for preparing this thesis.

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ABSTRACT

Dehydrogenation of cyclohexane to benzene under conditions of catalyst deactivation was investigated in an integral reactor under quasi-isothermal conditions and at atmospheric pressure. Commercial platinum-on-alumina reforming catalyst (Sinclair-Baker RD-150) was used for investigation. The operating variables and their range studied are : mole-ratio of hydrogen to cyclohexane (0.94 to 4.8), reaction temperature (310-435°C) and liquid-hourly-space-velocity (1.28 to 4.77). Reaction product consisted of mainly benzene with some hydrocracked gases. Gas chromatographic analysis of liquid product samples using Carbonax-4000 on Celite column indicated benzene as the only reaction product.

Experimental set-up consisted of a feeding section for cyclohexane and hydrogen, vaporizer and preheater section, a reactor section and a liquid product collection section. The flow rate of exit gases was recorded with time. The pressure drop in the reactor increased with time due to coke formation and care was taken to keep the flow rates of the reactants constant by compensating for the increase in pressure drop. The catalyst bed was diluted with glass beads, to maintain it near isothermal using suitable dilution criterion.

The kinetic model used in the analysis consists of the following reactions:

Dehydrogenation : $C_6H_{12} \xrightarrow{k_1} C_6H_6 + 3H_2$

Hydrocracking: $C_6H_{12} \xrightarrow{k_2}$ hydrocracked products

Deactivation: $C_6H_{12} \xrightarrow{k_d}$ catalyst poisons (coke)

The material balance calculations were carried out considering equilibrium at the exit of condenser and material balance checked well for most of the samples in all the sets for both the cyclohexane and hydrogen feeds. The conversion of cyclohexane into hydrocracked products was calculated from the material balance of cyclohexane using time average feed rate. It is assumed that the loss of cyclohexane due to the deactivation reaction is negligible.

The kinetic data for undeactivated catalyst was obtained by extrapolation of experimental conversion data under deactiving catalyst condition to initial conditions and the same was analysed by assuming first order irreversible kinetics and plug flow behaviour. These assumptions result in the following conversion - space velocity relationship, for initial rate data :

$$X_A + \left[\frac{1 + \frac{(1+\nu)\,(1+K)}{3-K}}{1 + K} \right] \ln\left(1 - (1 + K)X_A\right) = - \frac{k_1' \, Co \, (1+K)}{3-K} \cdot \frac{W}{F} \qquad (1)$$

Under experimental conditions the external heat- and mass-transfer and internal heat-transfer resistances were found to be negligible but the intrapellet mass-transfer resistance was found to be significant. The values of effectiveness factor for the desired dehydrogenation reaction varied between 0.12 and 0.77, and for the dehydrocracking reaction it varied between 0.60 to 0.93. With the help of equation 1 and experimental conversion data the apparent rate constants k_1' and k_2' were determined. The values of effectiveness factors were estimated from the plot of η versus $\phi^2\eta$, where:

$$\eta = \frac{1}{\phi} \left[\frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right] \qquad (2)$$

$$\phi = \left(\frac{V'}{S_e} \right) \sqrt{\frac{k \, \rho_p}{D_e}} \qquad (3)$$

and $$\phi^2 \eta = \left(\frac{V'}{Se} \right)^2 \quad \frac{k' \rho_p}{D_e} \qquad (4)$$

It is to be noted that $\phi^2 \eta$ can be calculated from the experimental data directly. Knowing the values of k_1', k_2', η_1 and η_2, and the intrinsic rate constants k_1 and k_2 were calculated. The intrinsic rate constants k_1 and k_2 were observed to depend only on temperature which confirmed the validity of first order irreversible kinetics for dehydrogenation and hydrocracking of cyclohexane. The values of activation energy and pre-exponential factor were calculated from the regression analysis of ln k versus 1/T values for each rate constant, to give

$$k_1 = \exp \left(31.57 - \frac{27,300}{RT} \right) \quad \frac{cm^3}{(hr.)(g\ catalyst)} \qquad (4)$$

$$k_2 = \exp \left(18.97 - \frac{15,150}{RT} \right) \quad \frac{cm^3}{(hr.)(g\ catalyst)} \qquad (5)$$

The correlation coefficients for dehydrogenation and hydrocracking rate constants are 0.992 and 0.902 respectively, and indicate good fit of data on Arrhenius plots.

It is safe to assume that coke formation on catalyst results in a loss of catalyst activity for only dehydrogenation reaction involving platinum sites and not for hydrocracking reactions. Thus, the rates of dehydrogenation and hydrocracking reactions with catalyst deactivation, are given by :

$$\bar{r}_1 = k_1 \ \eta_1 \ a \ C_A \qquad (6)$$

$$\bar{r}_2 = k_2 \eta_2 \ C_A \qquad (7)$$

The rate of change of activity with time is considered to depend on m^{th} power of activity and n^{th} power of concentration ratio of cyclohexane to hydrogen as given below :

$$- r_d = - \frac{da}{dt} = k_d a^m (C_A/C_H)^n \qquad (8)$$

In equation (6) and (7) undeactivated catalyst effectiveness factors are used and any change in dehydrogenation activity due to the coke formation is accounted by activity factor a. Non-linear equations 6 to 8 were solved simultaneously for $n = 1$ and assumed values of k_d and m, to calculate cyclohexane and benzene mole-fraction at reactor exit, for different times-on-stream using fourth - order Runge-Kutta method on IBM 370/145, UNIVAC 1100 or DEC 2050 computers. The optimal values of k_d and m were found for each set by minimizing the variance between calculated and experimental values of benzene mole fraction at the reactor exit for different times -on-stream. The values of k_d and m were optimized to within ± 5 and $\pm$ 2 percent respectively. The values of m and k_d are in the range of 1.11 to 3.11, and 0.41 to 4.53 $(hr)^{-1}$ respectively. For the solution of differential equations 40 bed increments and 5 minutes time interval was chosen after careful error analysis. The 40 bed increments (bed increment of the order of pellet diameter) gave a computation accuracy of better than 0.05 percent, and 5 minutes time interval resulted in a computation accuracy of better than 0.12 percent, in exit conversion values at the end of five hours time-on-stream. Activity and conversion profiles were calculated for all the sets along the length of the bed for different times-on-stream using optimal values of m and k_d, and the intrinsic reaction rate constants k_1 and k_2 .

A total of 19 sets were analyzed for deactivation parameters. The deactivation rate constant was found to vary only with temperature. The values of activation energy and pre-exponential factor for catalyst deactivation rate constant were found from the linear regression of ln k_d versus 1/T values, to give -

$$k_d = \exp\left(9.475 - \frac{12,260}{RT}\right) \quad (hr)^{-1} \qquad (9)$$

The value of correlation coefficient, 0.872, for the above equation indicates a good fit of data.

A second order polynomial was used to correlate m with Thiele parameter ϕ_1 (based on k_1) and the constants obtained by regression analysis are as given below:

$$m = 0.9502 + 0.2623\,\phi_1 - 0.005806\,\phi_1^2 \qquad (10)$$

For a given set of operating conditions equations 2,3,4,5,9 and 10 were used to calculate the intrinsic dehydrogenation and hydrocracking rate constants, deactivation rate constant, Thiele parameters, effectiveness factors and m, and these values were then used to calculate the conversion and activity profiles along the catalyst bed for different times-on-stream by simultaneous solution of equations 6 to 8 for all the sets. The proposed model gave a good fit with experimental data as is evident from the absolute percentage error variance between the experimental and predicted values of conversion which is 5.5 for benzene and 4.7 for cyclohexane considering all the experimental points.

The values of m in the range of 1 to 3 indicate pore-mouth poisoning and confirms simultaneous deactivation.

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(M. C. Bansal)

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NOMENCLATURE

a	dehydrogenation activity of catalyst at any time t , considering activity a = 1 at t = 0	
A	cyclohexane , specie A concentration	
B	benzene, intermediate or product concentration	
C	hydrocracked gases, concentration	
C_A, C_H	concentration of cyclohexane and hydrogen respectively	
C_b	bulk concentration	
C_o	concentration (p_t/R_gT)	
C_p	heat capacity	
C_P	poison concentration	
d	order of deactivation with respect to species concentration	
d_p	particle or pellet diameter	
d_t	reactor diameter	
D_{AB}	bulk diffusivity of components A and B,	Cm^2/sec
D_e	effective diffusivity,	$\frac{cm^3 \text{ of gas}}{Sec. cm \text{ of catalyst}}$
D_K	Kundsen diffusivity,	$\frac{cm^3 \text{ of gas}}{Sec. cm \text{ of catalyst}}$
E	activation energy	
F	Molar feed (or flow) rate,	gmol/hr
G	mass velocity,	$g/hr. cm^2$

ΔH_A	heat of reaction	
j_D	Colburn mass transfer factor	
k	intrinsic reaction rate constant,	$\frac{\text{cm}^3 \text{ of gas}}{\text{hr. gm of cat.}}$
k_d	deactivation rate constant,	hr^{-1}
k_e	axial thermal conductivity	
$k_m a$	mass transfer coefficient	$\frac{\text{cm}^3 \text{ of gas}}{\text{hr.gm of catalyst}}$
k'	apparent or effective rate constant under experimental conditions for undeactivated catalyst	$(k' = k\,\eta)$
K	ratio of hydrocracking to dehydrogenation apparant rate constants	
L	reactor length	
LHSV	liquid hourly space velocity = volumetric flow rate per hour/volume of catalyst	
m	order of deactivation with respect to activity	
MR	mole ratio of hydrogen to cyclohexane in the feed	
n	order of deactivation with respect to ratio (C_A/C_H) in deactivation rate equation	
P	atmospheric pressure, mm of Hg , Poison concentration	
P_t	total pressure, mm of Hg	
r^-_o	global rate for dehydrogenation reaction at reactor inlet	

$\bar{r}$	global rate of reaction ,	$\frac{\text{gmole}}{\text{hr. g of cat}}$
r_A	reaction rate	
r_d	deactivation reaction rate	
r_p	global reaction rate for the pellet	
R	radius of the pellet or particle	
R_e	Reynold's number	
R_g	gas constant	
S	number of active sites	
S_e	external surface area of pellet,	cm^2
S_g	total surface area of catalyst ,	m^2/g
T	temperature of the reactor ,	^oK
T_b	bulk gas temperature	
TEMP	temperature of the reactor,	^oC
T_s	surface temperature	
V'	volume of catalyst pellet ,	cm^3
W	weight of catalyst in the reactor,	g
X	fractional conversion	
X_A	fraction of cyclohexane feed remained unconverted	
X_B, X_c	fraction of cyclohexane feed converted into benzene and hydrocracked gases	

Subscript

1 and 2,dehydrogenation and hydrocracking reactions respectively

Greek letters

α	fraction of poisoned catalyst sites at any time t
β_m	dimensionless maximum temperature rise
γ	mole ratio of hydrogen to cyclohexane in the feed
φ	Thiele parameter
φ_p	Thiele parameter for poison precursor
φ_r	Thiele parameter for reactants
η	internal effectiveness factor
ρ	density of fluid at operating conditions, g/cm^3
ρ_p	density of catalyst pellet

CHAPTER - 1

INTRODUCTION

1.1 CATALYTIC REFORMING

Catalytic reforming of naphtha (gasoline boiling range) over a bifunctional catalyst is carried out to obtain high octane gasoline or aromatics as end product. Hydrogen and lighter hydrocarbons (C_1 - C_4) are also obtained as side products. High octane gasoline is needed for efficient performance of high compression ratio engines without knocking. Aromatics are essential and valuable feed stock for petrochemical industry.

Reforming of naphtha results in restructuring the available classes of hydrocarbons (paraffins, naphthenes and aromatics), without changing the number of carbon atoms in the molecule. Though some hydrocracking also takes place resulting in lower hydrocarbons essentially paraffins.

The feed have three classes of hydrocarbons, whereas in each class large number of chemical structures are possible, so, the feed is a complex mixture of series of hydrocarbons. As the desired end products are aromatics, the desired reactions which increase the octane number of the reformate, are:

(1) Dehydrogenation of naphthenes
(2) Dehydrocyclization of parafinns
(3) Isomerization of paraffins
(4) Olefins saturation
(5) Dehydroisomerization of C_5 ring naphthenes

Undesirable simultaneous reaction are :

(1) Hydrocracking of paraffins and naphthenes
(2) Dealkylation of side chains of naphthenes and aromatics.

Studies of reaction mechanism (7,16,33,46,63,64) have shown that olefins are intermediates, but under reforming conditions only trace can exist. Dehydrogenation reactions are rapid and highly endothermic, and contribute maximum toward high aromatic concentration. High temperature, low pressure, low space velocity and low hydrogen/hydrocarbon mole ratio favours the reaction. Dehydrocyclization is also endothermic but slow in nature. It is also favoured under the same operational conditions as the aromatization of naphthenes. Isomerization reactions are fairly rapid with insignificant heat effects at high temperature, low pressure and low space velocity. Condensation and polymerization are also reported and these reactions result in heavier compounds and coke.

The most desirable conversion is of naphthenes and paraffins into aromatics for the gain in the octane number of the product. Isomerization is of limited value as the equilibrium concentration of highly branched paraffins fall rapidly at high temperatures. Hydrocracking of paraffins eventhough increases octane number by reducing paraffin content in C_5^+ reformate, but is not considered desirable due to the loss of valuable product.

Considering the importance of dehydrogenation of naphthenes in reforming, dehydrogenation of cyclohexane has been chosen as a model reaction for the present study. The conversion of cyclohexane (to benzene) over platinum-on-alumina catalyst is essentially complete at approximately 300°C and at atmospheric pressure. In cyclohexane dehydrogenation intermediate species are not reported (3) and this indicates that six hydrogen atoms from cyclohexane are removed simultaneously. The absence of the intermediate dehydrogenation products in the case of cyclohexane is also evident from the observation of the relevant thermodynamic data which shows that only trace concentrations of the intermediate dehydrogenation products are possible at equilibrium at 300°C (80).

1.2 DEACTIVATION OF CATALYSIS :

Most of the catalyst systems of both practical and theoretical interests are based on catalysts whose activity is not constant with time-on-stream (9,10) and loose their activity during progress of reaction. This very complicated phenomena is made even more confusing by the wide variety of deactivation phenomena and the lack of systematic investigation in this field. Catalyst deactivation can be defined as a phenomena which lowers the overall rate of a catalytic reaction below the value which can be obtained with a fresh catalyst and uncontaminated reagents. In order to place the subsequent theoretical treatment in proper perspective with relation to the entire field of catalyst deactivation, an attempt is made to categorize the various deactivation phenomena encountered in practice. In general, deactivation encompasses three subclasses of behaviour called poisoning, fouling and sintering (15).

POISONING: - Poisoning is chemisorption of reactants, products, or impurities (singly or in combination) found in the reactor feed, which occupy catalyst sites otherwise available for catalysis. Chemisorption of poisoning agents may be reversible or irreversible. In the first case, elimination of the poison precursor from the feed restores catalyst vitality. If the reversibly poisoning specie is a reactant, its elimination is meaningless, if it is a product, a remedy might consist in a low-conversion, high-recycle reactor net work with product removal in the recycle loop. Poisoning, in so far as it is a chemisorptive event, constitutes chemical deactivation.

FOULING: - Fouling is caused by species in the fluid phase being physically deposited upon the surface, thereby covering or blocking sites otherwise available to catalysis. Fouling can also be a result of surface reactions yielding products that foul the surface, for example, coke produced during cracking of hydrocarbons. Catalyst can be 'regenerated' by burning the coke under controlled conditions.

SINTERING AND PHASE TRANSFORMATIONS :

As a consequence of local high temperature and in some instances the existence of the oxidizing and reducing atmosphere, the catalyst per se and/or its supports suffer a reduction in specific surface area or the chemical nature of the catalytic agent is so altered as to render it catalytically ineffective.

In general it can be suggested that poisoning and fouling rates may depend upon reactant and/or product concentrations, while sintering and phase transformations may be assumed to be independent of fluid phase composition for a given oxidizing or reducing atmosphere.

The term catalyst activity is used in the literature both comparing various catalysts for a given process and for comparing the various states of the same catalyst. The changes in the catalyst activity as a function of time is of prime importance in the study of catalyst deactivation. The most frequently used quantitative description of catalyst activity is given by Szepe and Levenspiel (79). They have discussed the relative merits and demerits of each definition and indicated that, from theoretical point of view, the definition based on rate is most satisfactory, For given operating and catalyst conditions, the measure of activity based on reaction rate is independent of the conversion level and contacting pattern and it also allows for spatial variations of activity. As the activity is defined with reference to fresh catalyst with no impurity in the feed, for catalysts with high initial rates of deactivation, reaction rates for fresh catalysts can be obtained only by extrapolating the experimental data points as reported by Blanding (9) for the catalystic cracking of gas oil on natural clay.

1.3 AIMS AND OBJECTIVES OF THE PRESENT STUDY :

Considering the importance of dehydrogenation of naphthenes and the deactivation of catalyst during reforming, it was decided to study the cyclohexane dehydrogenation reaction at atmospheric pressure under suitable conditions of space velocity, temperature and cyclohexane to hydrogen mole ratio. The reaction conditions chosen in the present investigation were close to those used in commercial reforming process except for the use of atmospheric pressure instead of high pressure so as to increase the catalyst deactivation rate.

In most of the heterogeneous catalytic reactions, the presence of external and internal heat and mass transfer limitations often disguise the intrinsic kinetic constants. Thus, the external and internal, heat and mass transport resistances are carefully estimated to ascertain their effects on global reaction rates of dehydrogenation and hydrocracking reactions with catalyst deactivation. The kinetics of the main and deactivation reactions are developed and an attempt is made to develop equations for global rates for dehydrogenation and hydrocracking reactions and catalyst deactivation. The kinetic and deactivation rate constants are evaluated for the proposed kinetic model using experimental data. Intrinsic rate constants for dehydrogenation and hydrocracking reactions are estimated from initial rate data and deactivation rate constants are estimated by minimizing the variance between experimental conversion data and that predicted by solving the non-linear simultaneous equations using IBM 370/145, DEC 2050 and UNIVAC 1100 computer systems.

CHAPTER - 2

LITERATURE REVIEW

2.1 CATALYTIC REFORMING :

Until about 1940 the octane number of straight run naphtha was improved by thermal reforming causing cracking of low octane number paraffins producing high octane number olefins. But the advent of catalytic reforming in 1940 made thermal reforming obsolete. Initially molybdena or chromia catalysts supported on activated alumina were used in fixed bed reformer units but they were discarded soon due to rapid loss of activity due to catalyst fouling. Around 1950, fluidized beds were used but discarded after explosion during regeneration. Introduction of platinum-on-alumina catalyst by Universal Oil Products for reforming in 1950 made thermal reforming and molybdena or chromia based reforming processes completely obsolete by about 1955.

A typical catalytic reforming process has three or more fixed beds packed with platinum-on-alumina catalyst, with intermediate heaters. Since dehydrogenation reactions are highly endothermic and cause a rapid decrease in temperature in adiabatic reformers, it is necessary to use intermediate heaters between the catalyst beds to maintain reaction temperature in a desired temperature range.

The range of process variables used in commercial reforming process is given below:

Temperature	450 - 550°C
Liquid-hourly-space-velocity	2 - 5 $\frac{\text{vol. of liquid feed}}{\text{(hr.)(vol. of Catalyst)}}$
Pressure	475 - 575 psig
Hydrogen to oil-ratio (mole basis)	3 - 10
Water content	less than 10 ppm

High temperature, low pressure, low space velocity and low hydrogen to hydrocarbon mole-ratio favours the yield of aromatics in dehydrogenation reactions. Hydrocracking reactions are exothermic in nature and are relatively slow. Hydrocracking yield increases at high temperature, high pressure and low space velocity.

To understand the behaviour of reforming reactions, we must understand the reaction kinetics and the influence of heat effects. A qualitative summary of the rate behaviour of the important reaction classes catalyzed by a modern bi-functional catalyst is given in Table 2.1, with statements of the heat effects. This information largely determines what is needed for the reactor design. Naphthene and paraffin dehydrogenation reactions are so rapid that they are essentially in equilibrium. Similarly, the equilibrium of n-paraffins and isoparaffins is usually closely approached. In contrast, the rates of cyclization and hydrocracking are typically low and greatly influence the overall performance of the reformer process.

Table 2.1 Rate Behaviour and Heat Effects of Important Reforming Reactions (47)

Reaction type	Relative type	Effect of increase in total pressure	Heat effect
Hydrocracking	slowest	increase rate	quite exothermic
Dehydro-cyclization	slow	none to small decrease in rate	endothermic
Isomerization of paraffins	rapid	decrease rate	mildly exothermic
Naphthene isomerization	rapid	decrease rate	mildly exothermic
Paraffin dehydrogenation	quite rapid	decrease conversion	endothermic
Naphthene dehydrogenation	very rapid	decrease conversion	very endothermic

Hydrogen partial pressure is an important variable since it strongly affects the conversion to aromatics and the rate of hydrocracking. Since reforming reactions which produce hydrogen, especially aromatization, predominate over those which consume hydrogen, the process is a net hydrogen producer.

Many literature references are available on general reforming processes, but only few investigations are reported on detailed kinetic study specially under conditions of catalyst deactivation. Since present investigation pertains basically to dehydrogenation of cyclohexane on platinum-on-alumina catalyst under conditions of catalyst deactivation, only relevant literature is reviewed briefly in the following sections.

2.2 NAPHTHENE DEHYDROGENATION WITH SPECIAL REFERENCE TO CYCLOHEXANE DEHYDROGENATION

2.2.1 Kinetics and Mechanism:

Haensel and Donaldson (30) working with Universal Oil Products carried out investigations for Platforming by using various pure hydrocarbons. They had carried out investigations using n-heptane, n-pentane, cumene and methylcyclohexane. With methylcyclohexane, its conversion to toluene is essentially complete quantitatively and was found close to that calculated by equilibrium data at the temperature of operation.

Hinemann et al (39) also carried out studies with pure hydrocarbons for Houdriforming process. Dehydrogenation of napthenes to aromatics was the main reaction of interest and this was investigated by using cyclohexane and methylcyclohexane as reactants. In cyclohexane dehydrogenation at 950°F, 300 psig pressure, 3 LHSV and hydrogen to cyclohexane mole ratio of 4.91. Five percent benzene was formed on volume of feed basis, which was close to equilibrium value under these conditions. With methylcyclohexane also near equilibrium yields were found during dehydrogenation.

In methylcyclopentane dehydroisomerisation reaction at 300 psig pressure, hydrogen to methylcyclopentane ratio of 4, 950°F temperature and 2LHSV, near equilibrium yield is reported. They have reported that with increase in temperature and decrease in LHSV the yield of aromatics is increased.

Mills et al. (63) have analysed the data as obtained by Heinemann et al (39) for the reaction mechanism. They have also compared the effect of catalyst type and hydrocarbon structure and their results are given in Table 2.2. In each of the experiments the total product was more than 90 percent by weight of the charge. Reforming reactions which occur readily for C_6 hydrocarbons are shown in Fig. 2.1. for a dual function catalyst. Methyl cyclopentane can be converted to benzene only on a dual function catalyst, after dehydrogenation on dehydrogenation site to methylcyclopentene, the adsorbed molecule must move to an isomerisation site, form cyclohexene and then return to a site of the first type before dehydrogenating to benzene. The large yield of benzene from cyclohexane compared with those from cyclohexene shows that once cyclohexane is adsorbed on a dehydrogenation site it goes all the way to benzene, whereas cyclohexene can also isomerize on an acidic site to give methylcyclopentane.

Haensel and Berger (32) have reported the energy of activation for the dehydrogenation of cyclohexane and methylcyclopentane into benzene as 18,100 and 32,800 calories per mole, respectively from an unpublished data (7).

Smith (78) had carried out reforming studies using a commercial reformer naphtha feed on 0.6 percent platinum-on-alumina (1/16 in.extrudate) catalyst, the complex feed mixture and product stream was simplified by considering four model reactions :

Table-2.2 : Effect of Catalyst Type and Hydrocarbon Structure on Product:

(950°F, 300 psig, LHSV=3 , H_2/Hydrocarbon mole ratio = 4)

		Vol. % of Liquid Product		
		CATALYST		
Charge	Product	Isomerization	Dehydrogenation	Dual Function
Cyclohexane	Aromatics	2	52	92
	Olefin	0	1	2
	Naphthene	98	2	1.5
	Paraffin	0	5	4.5
	C_6/C_5 ring ratio[a]	> 50 to 1	>25 to 1	1 to 4
Methyl-cyclopentane	Aromatics	3	7	49
	Olefin	0	4	2
	Naphthene	95	80	23
	Paraffin	2	9	26
	C_6/C_5 ring ratio[a]	Traces of cyclohexane	Traces of Cyclohexane	1 to 4
Cyclohexene	Aromatics	8	92	83
	Olefin	86	3	2
	Naphthene	5	0	11
	Paraffin	7	5	4
	C_6/C_5 ring ratio[a]	Approx 1 to 10	> 50 to 1	Approx. 1 to 4
Methyl-cyclopentene	Aromatics	7	16	48
	Olefin	74	2-3	1
	Naphthene	19	48-70	13
	Paraffin	0	34-11	38
	C_6/C_5 ring ratio[a]	1 to 14	< 1 to 50	< 1 to 25

[a] in naphthene and olefin product

Naphthenes $\rightleftharpoons$ aromatics + 3 H_2 (2.1)

Paraffins $\rightleftharpoons$ naphthenes + H_2 (2.2)

Hydrocracking of paraffins (2.3)

Hydrocracking of naphthenes (2.4)

The C_1 through C_5 fractions produced by hydrocracking were observed experimentally to occur in approximately equal molar portions. Extensive experimental reforming runs using naphthas yielded the following equilibrium constants for naphthenes being converted to aromatics:

$$K_{p_1} = \frac{P_A P_H^3}{P_N} = \exp\left(46.15 - \frac{46,045}{T}\right) \text{atm}^3 \qquad (2.5)$$

where T = °F, P_A, P_N and P_H are the partial pressures in atm. of aromatics, naphthenes, and hydrogen, respectively. For the dehydrogenation reaction, Eq. 2.1, the empirical rate equation and constant are as given below:

Naphthenes to Aromatic -

$$(-\bar{r}_1) = \bar{k}_{p_1} \left(P_N - \frac{P_A P_H^3}{K_{p_1}}\right) \frac{\text{moles naphthene converted to aromatics}}{(\text{hr})\ (\text{lb.cat.})} \qquad (2.6)$$

where

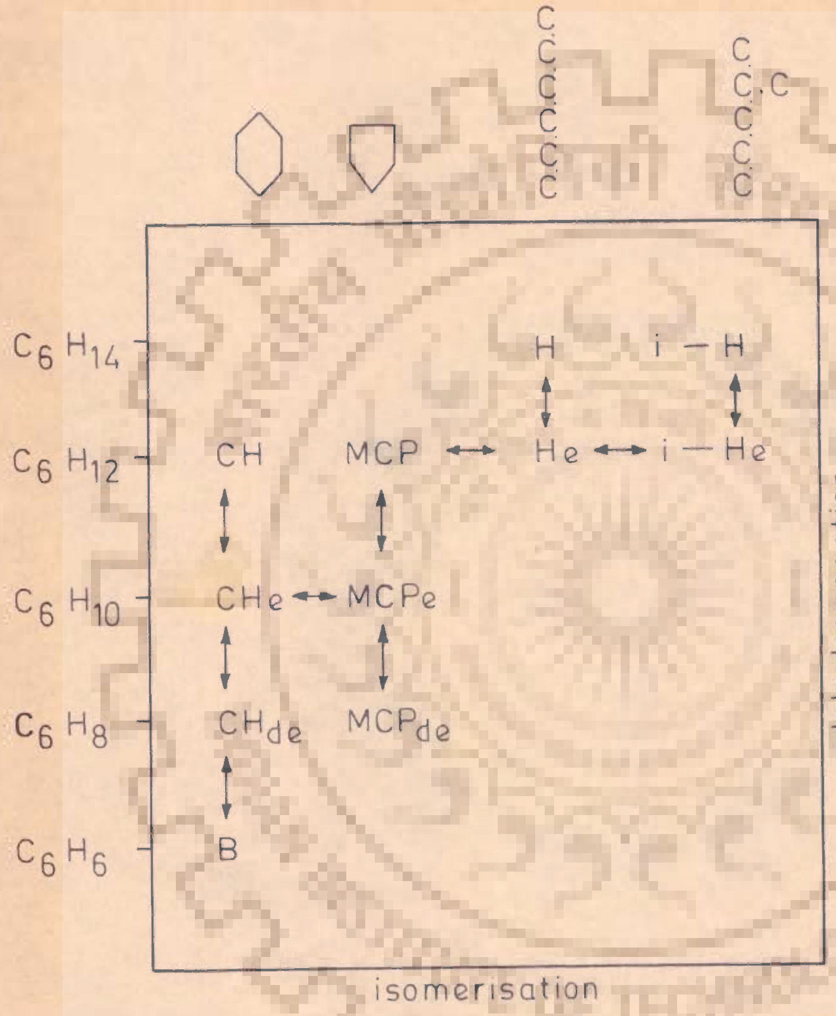
$$\bar{k}_{p_1} = \exp\left(23.31 - \frac{34,750}{T}\right) \frac{\text{moles}}{(\text{hr})\ (\text{lb.cat.})(\text{atm})} \qquad (2.7)$$

Barnett et al (6) studied the dehydrogenation of cyclohexane to benzene by carrying out experiments at 200 psig on platinum-on-alumina catalyst and concluded that (i) internal diffusion influence is exhibited by 1/8" x 1/8" pellets above 700°F, (ii) activation energy for the intrinsic catalytic reaction was found to be 41.6 kcal/gmole and with reaction controlled by internal diffusion on apparent activation energy of onehalf of this value was obtained, and (iii) the reaction follows essentially first order kinetics at low conversions. For a mole ratio of hydrogen-to-cyclohexane as 4, using first order irreversible kinetics for cyclohexane dehydrogenation reaction only and assuming plug flow, they calculated apparent rate constant by

$$k = \frac{F}{W} \left(- 1.6 \ln (1 - x) - 0.6 x\right) \qquad (2.8)$$

where F/W is space velocity and x is the fraction cyclohexane converted into benzene. If internal diffusion effects are considered absent then the above equation will give intrinsic reaction rate constant. The best fit to the data was obtained by them by using Knudsen diffusion coefficient with a tortuosity factor of one-eighth to describe the diffusion in the catalyst pores. Experiments carried out at low temperature with -30 to +40 mesh catalyst fines indicated that the effectiveness factor for the pelletted catalyst was unity for runs below 700^{o}F.

In order to ascertain the findings of Heinemann et al about the path really followed by C_6 hydrocarbons on dual function catalyst, Fig.2.1, Haensel, Donaldson and Riedl (33) carried out investigations in bench scale Platforming units using platinum-on-alumina halogen catalyst for methylcyclopentane processing and a platinum-on-alumina catalyst for cyclohexane processing. They also observed that as the LHSV is increased from 10 to 120, the product distribution for feed containing methylcyclopentane and benzene, based on methylcyclopentane reacted, shifts markedly in the direction of methylcyclopentane at the expense of benzene and other products Their findings also confirmed that the sequence followed is as shown in Fig. 2.1 and that cyclohexene shall form if cyclohexane is converted into benzene. Using 50 mole percent cyclohexane and 50 mole percent benzene feed they again found that Fig. 2.1 truly shows the reaction sequence. They also investigated the effect of poisons in the feed and have found



CH	Cyclohexane
CHe	Cyclohexene
H	Hexane
He	Hexene
MCP	Methylcyclopentane
MCPe	Methylcyclopentene
CH_{de}	Cyclohexadiene
B	Benzene
MCP_{de}	Methylcyclopentadiene

FIG. 2.1 REFORMING C_6 HYDROCARBONS WITH DUAL FUNCTION CATALYST.

that sulfur acts as poison to platinum sites and nitrogen to acidic sites.

Khoobiar et al. (46) had studied the mechanism of cyclohexane dehydrogenation with platinum-on-alumina commercial reforming catalyst in a diluted bed with alumina particles at 435-480°C temperature, 250-500 psig pressure, 2-6 hydrogen to hydrocarbon mole ratio and 1-800 W/hr/w space velocity range. They had shown that the rate of heat and mass transfer are not controlling, and stated that reaction starts on the catalyst surface and is propagated elsewhere, possibly at the surface of added diluent. Their data were later analysed by Chambers and Boudart (16) and found that the calculations of Khoobiar for mass transfer were inaccurate and the reaction rates were severely affected by diffusional resistances.

Minachev et al. (64) studied the mechanism of conversion of cyclohexane to benzene with catalyst poisoning due to sulfur compounds in feed. They observed that an equilibrium is achieved between the sulfurous compound in gas phase and that on the surface, and cyclohexane conversion to benzene is adversely effected. However, when sulfur compounds are removed from cyclohexane feed, the original activity of the catalyst was regained after sometime and conversion to benzene was increased. They did not get cyclohexene as intermediate product, as reported by Haenesel et al. (33). They have also reported that cyclohexane converts into benzene to a greater extent with platinum catalyst and into methylcyclopentane with palladium catalyst.

Graham et al. (28) also carried out the experimental runs for the catalytic dehydrogenation of cyclohexane in a fixed bed flow reactor with very small catalyst concentrations in the bed. They used 1/8" x 1/8" (cylinder) catalyst of 90 m^2/g surface area over a temperature range of 400° to 500°C and a pressure range of 21 to 420 atm. with hydrogen-to-cyclohexane ratio 3 to 6 at modified Reynold's numbers of 20 to 65. They analysed the data on the assumption of complete external mass transfer control with reaction in equilibrium at the catalyst surface. They have reported an activation energy of 57 to 59 kcal/gmole. Surprisingly, they have also reported catalyst pellet (intrapellet) effectiveness factor from 0.025 to 0.068 and used these extremely low values to justify their assumptions.

Henningsen and Bundgaard-Nielson (40) carried out reforming studies on C_8 hydrocarbons and have reported the reaction rate constants for hydrogen partial pressure of 30 atm, hydrogen to hydrocarbon ratio of approximately 7 and at a temperature of 500°C for various reforming reactions based on the available literature, experience and experiments. The dehydrogenation reaction is first order in naphthene (alkyl cyclohexane) concentration and the rate constant is given by

$$k = \exp\left(20.4 - \frac{30,000}{RT} \right) \tag{2.9}$$

Lester (51) has carried out aromatization of trimethyl pentane and trimethylcyclopentane over K_2O-Cr_2O_3. Al_2O_3 and nonacidic Pt-on-alumina catalysts at 400 - 500°C in microreactor gaschromatographic apparatus. The catalyst loading was 0.5 cc contained in a 1-inch length block located at the injection port. The reactants were injected in the hydrogen carrier gas and products were analysed. The operation was at atmospheric pressure. They have reported that by using nonacidic Pt-on-alumina catalyst the dehydrogenation and hydrogenation activity of the catalyst remains essentially same while it looses its isomerisation activity. He has reported product distribution and claimed that cyclopentane is supposed to play an important role for aromatization on non-acidic platinum-on-alumina catalyst.

Christoffel, Vierrah and Fetting (17) have studied the dehydrocyclisation of methylcyclopentane, the isomerisation and dehydrogenation of cyclohexane and the hydrogenation of benzene in an integral reactor using a Ca-Y -zeolite covered with 0.5 weight percent platinum as catalyst. They performed experiments in the temperature range 350 - 530°C, pressure range 10 - 40 atm and space velocities of 0.5 to 5.0 lit.feed/hr. kg cat, and have predicted the activation energy for the reaction system,

$$\text{Cyclohexane} \begin{array}{l} \rightleftarrows \text{Benzene and Hydrogen} \\ \rightleftarrows \text{Methylcyclopentane} \end{array}$$

as 41.5 kcal/gmole based on cyclohexane conversion. For platinum-on-zeolite catalyst the conversion of cyclohexane to methyl cyclopentane always exceeded that to benzene. The reason is that the behaviour of Ca-Y -zeolite catalyst is nonacidic and alkyl cyclopentane is an important reaction product on such catalysts as already reported by Lester (51).

Haro et al. (35) have studied the role of paladium in dehydrogenation of cyclohexane over Pt - Pd/Al_2O_3 catalysts, by carrying reactions at 160 - 200°C under atmospheric pressure (580 torr). The conversion was kept less than 1 percent to avoid mass and heat transfer limitations. The mole ratio of hydrogen to cyclohexane was 1.8, and nitrogen was used as a diluent to keep cyclohexane nearly 8.5 percent on volume basis. Gas chromatographic analysis indicated only benzene and hydrogen as reaction product and no cyclohexene and cyclohexadiene was detected in the analysis. They have concluded that the total rate of conversion of cyclohexane decreases as palladium is added to platinum on co-impregnated catalysts.

Literature references for dehydrogenation studies under catalyst deactivation conditions using platinum reforming catalysts are discussed in detail in section 2.4.

2.2.2 Thermodynamics :

Thermodynamic data for typical reforming reactions at 500°C are given in Table 2.3.

Table 2.3 Thermodynamic data for typical reforming reactions (76)

Reaction	K_p [a] at 500°C, Pi in atm.	ΔH_r, kcal/mol. of hydrocarbon
Cyclohexane $\rightleftharpoons$ benzene + $3H_2$	6×10^5	52.8
Methylcyclopentane $\rightleftharpoons$ cyclohexane	0.086	-3.8
n - Hexane $\rightleftharpoons$ benzene + $4H_2$	0.78×10^5	63.6
n - Hexane $\rightleftharpoons$ 2-methylpentane	1.1	-1.4
n - Hexane $\rightleftharpoons$ 1-hexene + H_2	0.037	31.0

[a] For the reaction $(HC)_1 \rightleftharpoons (HC)_2 + n\,H_2$

the equilibrium constant is defined as :

$$k_p = \frac{P_{(HC)_2}\, P_H^n}{P_{(HC)_1}}$$

At equilibrium, cyclohexanes are essentially completely converted into aromatics at low hydrogen partial pressures, and cyclopentanes are favoured over cyclohexanes. At equilibrium only very small concentrations of olefins can exist with paraffins. The major reforming reactions are endothermic. The equilibrium between cyclohexane, benzene, and hydrogen as a function of temperature and pressure are illustrated in Fig. 2.2, which shows how operating temperature and pressure affect equilibrium conversion to aromatics. Under typical operating conditions, temperature ranges from 455° to 510°C and pressure ranges from 6.5 to 50 atm, only partial conversion to aromatics is achievable. Consequently, recent practice has been to operate at temperatures in the upper end of this

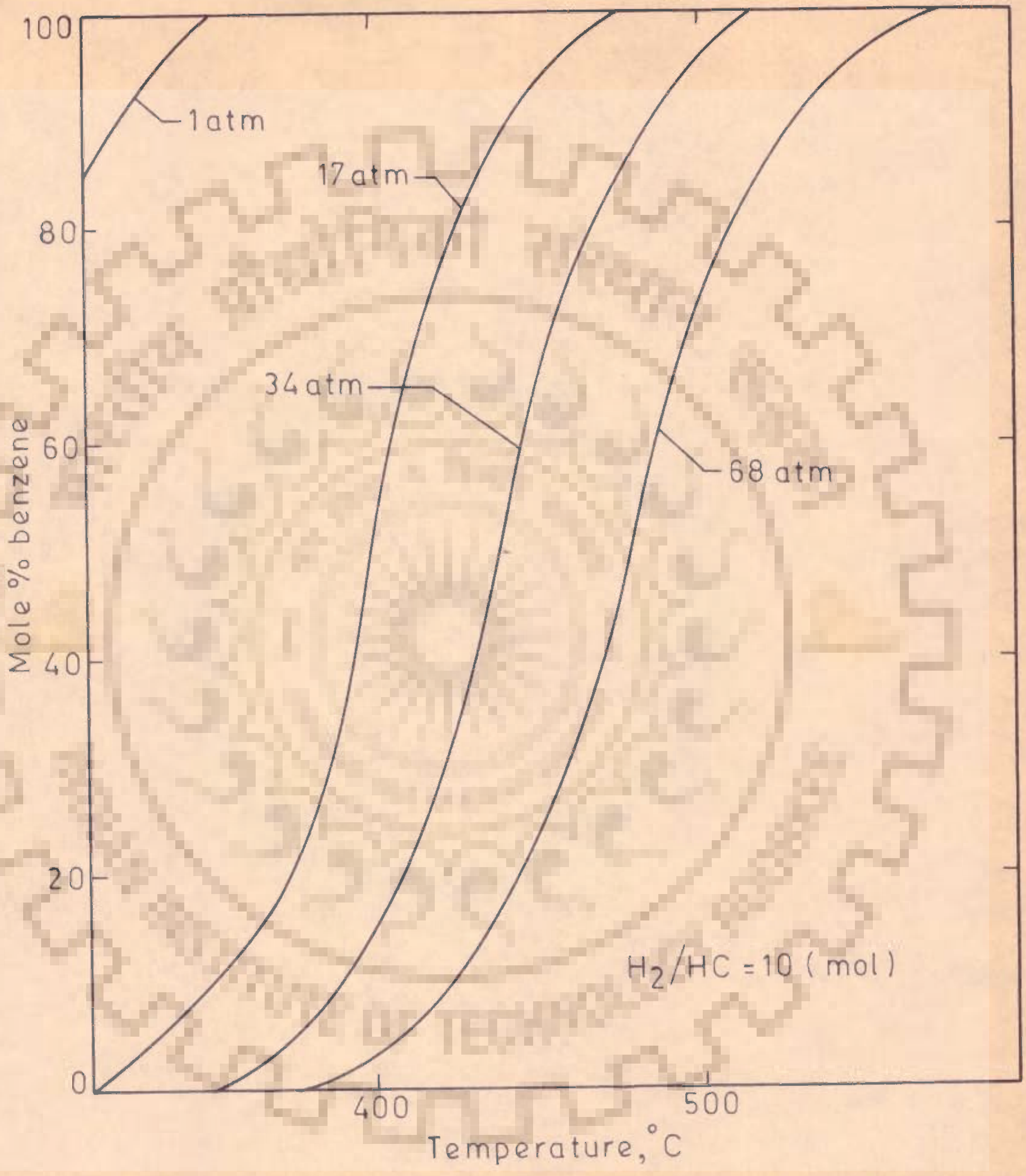


FIG. 2.2 Equilibrium distributions of cyclohexane, benzene and hydrogen.

range and to use pressures as low as 10 atm (19). At these conditions there is almost complete conversion of naphthenes into aromatics at equilibrium, but catalyst may deactivate rapidly.

2.2.3 Reforming Catalysts :

A number of catalytic reforming processes are in use depending upon the licenses using platinum-on-alumina catalysts. Besides these reforming processes on mono-metallic catalysts, bimetallic (Pt-Re) or indeed polymetallic (noble metal containing trimetallic alloys) dispersed clusters are recently being developed. The metal provides the hydrogenation - dehydrogenation activity, and the promoted acidic alumina provides the isomerization activity. The hydrogenation - dehydrogenation activity of the supported metal and the isomerization activity of the alumina are much greater than the respective activities of the early - generation metal oxides (27).

With long use, the alumina base loses some surface area and activity. But more important is the formation of platinum crystallite aggregate which decreases the affective Pt surface area for hydrogenation - dehydrogenation function. The latter change is usually the fastest, resulting in a change in the dehydrogenating to acidic activity ratio. This leads to more cracking and a decline in gasoline yield, with an increase in gas yield. The more severe the operating conditions, the greater the tendency for the Pt crystallites to aggregate. Pt aggregation is also related to Pt concentration. Low pressure reforming can be carried out with catalysts containing relatively low Pt concentration (e.g. 0.3 to 0.4 percent) and yet the conditions can be regarded as severe (81).

The growth of Pt crystallites can be inhibited by adding rhenium to the catalyst, which forms a stable alloy with Pt on the catalyst surface. The advantage of using bimetallic or multimetallic catalysts is that, the length of period between regenerations can be extended greatly, the severity can be increased to produce a further improved antiknock quality product, or the pressure can be reduced into the low pressure reforming range (15 atm or less) to get the benefits of low pressure operation while retaining the 6-9 months between regeneration. Mahoney (55) has carried out experiments using bimetallic Pt-Re on alumina catalyst for n-heptane dehydrocyclisation and compared the results with that obtained with monometallic Pt-on-alumina catalyst under similar deactivating catalyst operating conditions in a gradientless reactor system. He has reported that deactivation rates are significantly less when the promoter Re is added to the catalyst composition. The hypotheses that the metallic promoter affects only the dehydrocyclization deactivation rate and not initial activity is substantiated by this work.

2.3 HYDROCRACKING OF NAPHTHENES

Hydrocracking reactions are slowest among all the reforming reactions as indicated in Table 2.1. The major characteristics of the hydrocracking, are that (1) all cracked species are saturated, (2) the process involves bifunctional catalysis, and (3) catalyst deactivation is much less rapid than in catalytic cracking. Saturated paraffins predominate among the cracked products because the olefins formed are hydrogenated on the metal component.

Smith (78) has reported that during hydrocracking of naphthenes C_1 through C_5 fractions are produced approximately in equal molar proportions. Thus in general it can be written as :

$$C_n H_{2n} + \frac{n}{3} H_2 \rightarrow \frac{n}{15} C_1 + \frac{n}{15} C_2 + \frac{n}{15} C_3 + \frac{n}{15} C_4 + \frac{n}{15} C_5 \tag{2.10}$$

For hydrocracking of naphthenes, the rate equation and constant are as given below:

$$(-r)_h = k_h \frac{P_N}{P} \quad \frac{\text{moles naphthenes converted by hydrocracking}}{(\text{hr.})\ (\text{lb of catalyst})} \tag{2.11}$$

and

$$k_h = \exp\left(42.47 - \frac{62,300}{T}\right) \quad \frac{\text{moles}}{(\text{hr.})\ (\text{lb of cat})} \tag{2.12}$$

where T = $^{\circ}$F, P_N and P are the partial pressure of naphthenes and total pressure, respectively.

Henningsen and Bundgaard-Nielson (40) gave the following values of rate constants for conversion of alkyl cyclohexane to paraffins and isoparaffins, and their subsequent conversion to hydrocracked products :

$$\text{Alkylcyclohexane} \rightarrow \text{n-paraffin} : k = \exp\left(24.2 - \frac{45,000}{RT}\right) \tag{2.13}$$

$$\text{Alkylcyclohexane} \rightarrow \text{i-paraffin} : k = \exp\left(24.2 - \frac{45,000}{RT}\right) \tag{2.14}$$

$$\text{n-Paraffins} \rightarrow \text{hydrocracked} : k = \exp\left(30.5 - \frac{55,000}{RT}\right) \tag{2.15}$$

$$\text{i-Paraffins} \rightarrow \text{hydrocracked} : k = \exp\left(30.5 - \frac{55,000}{RT}\right) \tag{2.16}$$

Mahoney (55) carried out studies of hydrocracking reaction with dehydrocyclisation of n-heptane reaction and has indicated that the hydrocracking reaction rate constant does not change with time in deactivating catalyst systems. This indicates that change in catalyst activity will not affect the hydrocracking rate. He has reported the value of hydrocracking rate constant as 0.205 $\frac{\text{gmole}}{(\text{hr.})\ (\text{g.catalyst})}$, probably at 600°F.

Lambrecht et al. (49) in their study on isomerisation of n-pentane have used hydrocracking reactions in their kinetic model but could not determine hydrocracking rate parameters accurately. They felt that hydrocracking can hardly be considered as a single reaction and therefore, simple reaction rate expression may hardly be adequate.

Studies of Mahoney and Lambrecht et al. are discussed in more detail in next section.

2.4 DEACTIVATION REACTION KINETICS WITH SPECIAL REFERENCE TO REFORMING REACTIONS

Wheeler (88) was the first to account for the diffusional limitations in deactivation reactions. He observed that if the rate of poison deposition is low relative to its transport rate, then catalytic sites are poisoned uniformly with time. But if poison deposition is rapid relative to its transport rate, then poison will deposit preferentially on the pore mouth initially and grow inward with time in the form of shell progressive model (SPM) of gas solid reaction. He termed these limiting types of poisoning as uniform and pore mouth poisoning.

For uniform poisoning, using the rate of principal reaction as

$$r_p = k\,\eta\,(1-\alpha)A \qquad (2.17)$$

where α is the fraction of catalytic sites which are poisoned, A is the concentration of component A and η is the effectiveness factor. Realising that for low and high values of Thiele parameter ϕ, $\eta = 1$ and $\eta = 1/\phi$ respectively, Wheeler obtained the ratio F of poison-affected rates to unpoisoned rates for the two cases, as,

$$\text{For } \eta = 1;\ F = \frac{k(1-\alpha)A}{k\ A} = 1-\alpha$$

$$\text{and, for } \eta \ll 1;\ F = \sqrt{1-\alpha} \qquad (2.18)$$

For pore mouth poisoning, the shell progressive model postulates the creation of a region of total poisoning at the pore mouth and an unpoisoned interior region $(1 - \alpha)$. Using first order reaction in a spherical pellet with the rate equation as -

$$r_p = D_e 4\pi r^2 \frac{dA}{dr} \tag{2.19}$$

Wheeler obtained the ratio F as

$$F = \frac{1}{\frac{1}{(1-\alpha)} + \frac{3n\,\phi^2 \left(1 - (1-\alpha)^{1/3}\right)}{(1-\alpha)^{1/3}}} \tag{2.20}$$

The plots of F-versus - α indicate that for a given amount of imposed poison, pore mouth deposition proves to be more detrimental than the uniform poisoning.

Masamune and Smith (56) analysed the simultaneous, consecutive and independent deactivation schemes by solving the governing differential equations and comparing them with pseudo-steady-state shell progressive model. They presented the results of the deactivating catalysts in terms of an effectiveness factor which is a function of both the Thiele modulus and time-on-stream. They concluded that for consecutive and independent deactivation, the pellet of lowest intraphase resistance yields the highest activity-time profile, while for simultaneous deactivation, a pellet exhibiting an intermediate level of intraphase resistance gives the highest activity, particularly at long process times.

Carberry and Goring (14) analysed the deactivation process in terms of gas-solid noncatalytic reaction under conditions where the shell progressive model is applicable. The application of this model to coking, poisoning, and deactivation was encouraged because catalyst decay in petroleum processing have been correlated in terms of Voorhies (84) equation, which states that the extent of poisoning, coking or fouling, α , is related to time-on-stream, t by -

$$\alpha = k\sqrt{t} \qquad (2.21)$$

Szepe and Levenspiel (79) have reviewed the various available deactivation-time-on-stream relationships such, as, exponential, hyperbolic and power-law decay. Use of these relationships in determining rate coefficients and orders from experimental data has been discussed by Carberry (15).

Levenspiel (52) assumed d^{th} order catalytic reaction and m^{th} order activity decline, and was pioneer to suggest for decoupling of deactivation reaction equation from the main reaction equation.

The catalyzed reaction rate used by him is :

$$-r_p = \frac{dA}{d\theta} = k\, A^d a \qquad (2.22)$$

where $$a = \frac{\text{rate at any time, } t}{\text{rate at time, } t = 0} \qquad (2.23)$$

Then a is activity of the catalyst, which is equal to unity at time, t = 0 and declines with time. The kinetic model of activity decline is presumed as :

$$r_d = \frac{da}{dt} = k_d \; (A,\, B,\, P)^n \; a^m \qquad (2.24)$$

where

A - reactant concentration

B - product concentration

P - poison concentration

n,m - empirical order of deactivation with respect to species concentrations and activity , respectively

t - time-on-stream

θ - contact time

He analysed several possible networks for main and deactivation reactions as given below :

1. Simultaneous deactivation : $$\begin{tikzcd} & B \\ A \arrow[ur] \arrow[dr] & \\ & P \end{tikzcd}$$ $r_p = k(A)^n a^m$
   $r_d = k_d(A)^n a^m$

2. Consecutive deactivation : $A \longrightarrow B \longrightarrow P$

   $r_p = k A^d a \qquad r_d = k_d B^n a^m$

3. Parallel deactivation : $A \rightarrow B \qquad r_p = k A^d a$

   $P \rightarrow P \qquad r_d = k_d P^n a^m$

4. Independent deactivation : $A \longrightarrow B \qquad r_p = k A^d a$

   S-sites $\rightarrow$ (S-s) sites $r_d = k_d \; a^d$

5. Simultaneous-consecutive deactivation :

$$\begin{tikzcd} A \arrow[r, "1"] \arrow[dr, "2"'] & B \arrow[r, "3"] & P \\ & P & \end{tikzcd}$$

$$r_p = (k_1 + k_2)A^d a$$

$$r_d = k_d (A+B)^n a^m$$

However, case 5 is equivalent to independent deactivation since A + B is a constant for fixed feed compositions.

Lambrecht, Nussey and Froment (47) have carried out investigation on the fouling of a platinum-reforming catalyst used for the isomerization of n-pentane and considered the following reaction scheme :

$$\begin{aligned} \text{n - pentane} \; &\rightleftarrows \; \text{i-pentane} \\ &\longrightarrow \; \text{hydrocracked products} \\ &\longrightarrow \; \text{carbonaceous deposits} \qquad (2.25) \end{aligned}$$

Under isothermal conditions and assuming constant density and number of moles, and negligible loss of n-pentane to coke formation, they obtained continuity equations for n-pentane and hydrocracked products :

$$\text{n-Pentane} : \frac{\partial y_A}{\partial t} + \frac{\partial y_A}{\partial z} = - \frac{\rho_B \ \Omega \ dp}{F_t} r_A \tag{2.26}$$

$$\text{Hydrocracked products} : \frac{\partial y_H}{\partial t} + \frac{\partial y_H}{\partial z} = \frac{\rho_B \ \Omega \ dp}{F_t} r_H \tag{2.27}$$

and carbon deposition rate on the catalyst at any point in the bed :

$$\frac{\partial c}{\partial t} = \frac{\epsilon \ \Omega \ dp \ P_t}{F_t} r_C \tag{2.28}$$

$$\text{where} \quad Z = \frac{Z'}{dp} , \quad t = \frac{F_t \ R \ T}{\epsilon \ \Omega \ dp \ P_t} t' \tag{2.29}$$

The total rate of n-pentane disappearance r_A was defined as :

$$r_A = \frac{K_I \ (y_A - y_B/K)}{y_w + K_B \ y_B} + K_H \left(\frac{y_A}{y_W}\right)^{n_1} + K_c \left(\frac{y_A}{y_W}\right)^{n_2} \tag{2.30}$$

In order to account for deactivation, they defined the following fouling functions :

$$K_I = K_I^0 \ \phi_1$$

$$K_H = K_H^0 \ \phi_2$$

$$K_C = K_C^0 \ \phi_3$$

These simultaneous non linear equations were solved by assuming $\phi_1 = \phi_2 = \phi_3 = \phi$, and an exponential function -

$$\phi = \exp \ (- \alpha \ C^n) \tag{2.31}$$

to relate ϕ with C.

Differential and integral methods of analysis of data were separately applied for parameter estimation under fouling conditions, by minimization of an objective function with suitable weighting functions. The activation energies for isomerization and hydrocracking reactions are reported as 30,100 and 35,500 calories per gmole respectively and corresponding frequency factors are 19.1 ± 8.4 and 19.3. They also

Nomenclature for Lambrecht, Nussey and Froment (47)

C	Coke content , (g coke / g.cat)
d_p	particle diameter (cm)
F_t	total feed rate (mol /hr)
K	Isomerization equilibrium constant
K_I, K_H	rate coefficient for main and hydrocracking reaction (mol/hr.g.cat)
K_c	rate coefficient for coke formation (g.coke/hr.g cat)
K_B	adsorption parameter
η	exponent in fouling function
η_1, η_2	exponents in hydrocracking and coke reaction rate expressions
P_t	total pressure (atm.)
R	gas constant (cal/mol ^oK)
r_A, r_H, r_I	reaction rate for total reaction,hydrocracking and main reaction, respectively(mol/hr.g cat)
r_C	reaction rate for coke formation (g coke/ hr. g cat)
T	Temperature (K)
t	dimensionless time variable
t'	time (hr)
Y_A, Y_B, Y_H, Y_W	molfraction of n-pentane,isopentane, cracking products and hydrogen respectively
Z	dimensionless axial coordinate
Z'	axial coordinate (cm)
α	fouling parameter (g cat/g coke)$^{1/2}$
ε	void fraction
ρ_B	catalyst bulk density (g cat/cm^3)
ϕ	fouling function
Ω	cross section of the reactor (cm^2)

Subscript

0	non fouling conditions

concluded that the hydrocracking parameters were not so well determined and were taken mainly to satisfy the material balance.

Khang and Levenspiel (45) have extended the phenomenological description of the reactions given by Eqs. (2.22) to (2.24), to situations where r_p and/or r_d are affected by intraphase mass diffusion for the simultaneous, consecutive, and parallel deactivations. For diffusion of the reactant and/or poison precursor, the respective Thiele moduli for reactant and poison, ϕ_r and ϕ_p , determines the distribution of poison within the porous catalyst and, therefore, the activity - selectivity behaviour. For simultaneous and parallel sources of reactions- decay the poison distribution as a function of time for small, moderate, and large values of ϕ given by them is schematically shown in Fig. 2.3.1. Fig. 2.3.2 shows poison distribution for consecutive deactivation. Khang and Levenspiel solved the diffusion - reaction equations for each of these poisoning networks, for activity and concentration profiles, in the pellet with progress of reaction in time, and concluded that the order of deactivation m in the equation assumes the following range of values (for n = 1).

- Simultaneous deactivation; m varies from 1 to 3 as ϕ increases.
- Consecutive deactivation; m is equal to unity so long as the bulkstream contains the intermediate.
- Parallel deactivation.

where $\phi_r \ll 1$ and $\phi_p \ll 1$, $m = 1$

$$\phi_r \left\{ \begin{array}{lll} = \phi_p & = 1 & , m < 1 \\ \gg \phi_p & > 1 & , m \rightarrow 2 \\ = \phi_p & > 1 & , m \rightarrow 3 \end{array} \right.$$

and $\phi_p > \phi_r > 1$, m is not constant.

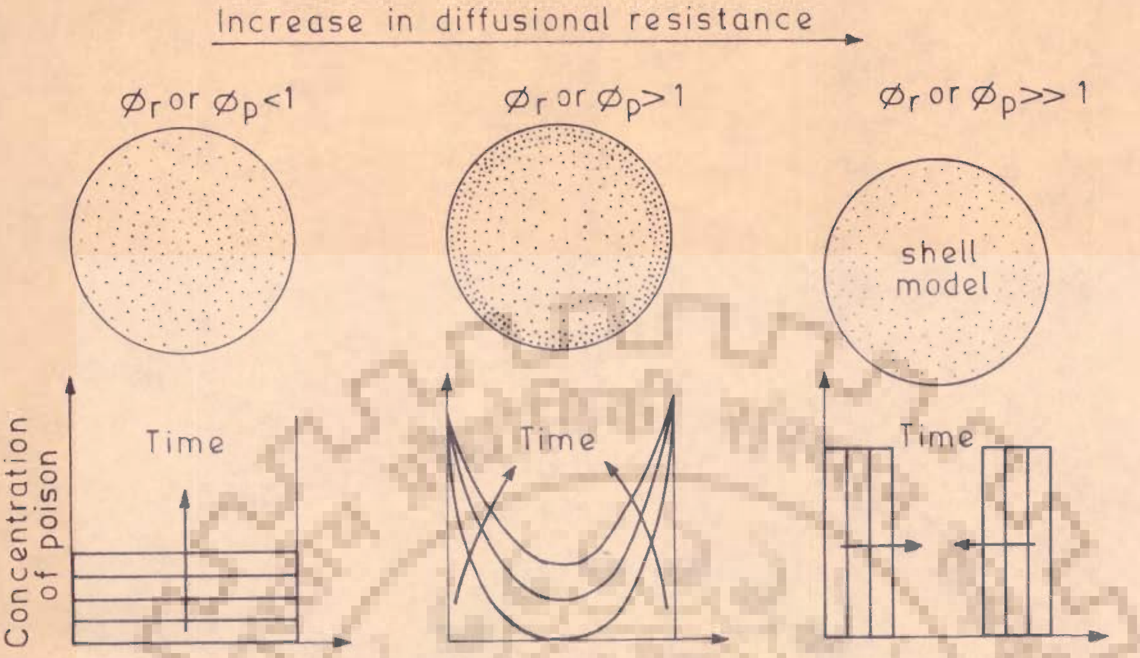


FIG.2.3.1 Resistance to pore diffusion determines where the poison deposits for parallel or simultaneous deactivation.

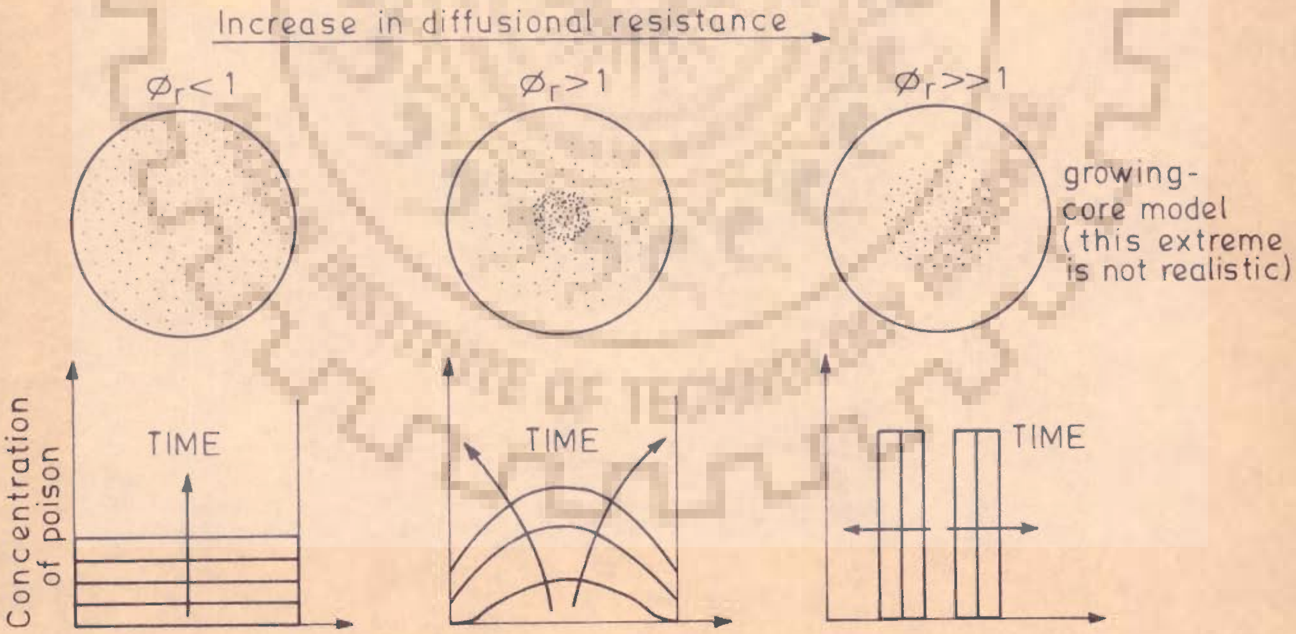


FIG.2.3.2 Resistance to pore diffusion determines where the poison deposits for series deactivation.

— Independent deactivation : if this is due to reactants and products, and if the cause is thermal, m ≃ 1. While if it is independent of intraphase mass diffusion, it will be sensitive to intraphase temperature gradient and m ≃ 2, if the interval Δ T is negligible. They also advised that as the analysis is based on linearity of the principal reactions and since the deactivation exponent proves to be somewhat variable, one should ascertain the value of m from experiment only.

Wojciechowski (91) has summarized various deactivation relationships and has given an alternative description of deactivation, the time-on-stream theory of catalyst decay. Various types of deactivation rate equations are tabulated in Table 2.4 with their limits of integration implied in the decay function as used by original authors. The general hyperbolic relationship of Wojciechowski reduces to linear deactivation for $m = 0$ and is approximated to exponential decay when $m \simeq 1$, while hyperbolic deactivation behaviour is obtained for $m \simeq 2$. In case k_d is assumed to be free from concentration effects, the equation is as for independent deactivation and is applicable to sintering or such deactivation phenomena where concentration effects are negligible.

Mahoney (55) carried out studies on dehydrocyclization of n-heptane on a commercial reforming catalyst in a basket reactor referred to as internally recycled gradientless reactor. The experimental deactivating data was extrapolated back to zero time to get initial values of rate constants. For other times the apparent or effective rate constants were calculated and plotted using Voorhie's (84) equation. The hydrocracking rate constants- Voorhie's plot indicated that the rate constants were constant with time and were equal to the initial rate constant. But, the dehydrocyclization rate constants' Voorhie's plot gave two straight lines, one having a larger slope at the start and the other with smaller slope at the end of the run. The effect of pore

Table-2.4 Deactivation Equations

Type of decay	Reference	Equation	Differential form	Limits of Intergration implied by decay function as used by original authors
Linear	Maxted(57), Elay and Rideal(24), Crowe(20), Crowe and Lee(21)	$\theta=\theta_o - At$	$-\frac{d\theta}{dt} = A$	Limit $\theta=\theta_o$ at $t=0$
Exponential	Pease and Stewart(67) Weekman(85), Ogunye and Ray(65)	$\theta=\theta_o\ e^{-At}$	$-\frac{d\theta}{dt} = A\theta$	Limit $\theta=\theta_o$ at $t=0$
Hyperbolic	Ogunye and Ray(66) Miertschin and Jackson(62)	$\frac{1}{\theta}\ \frac{1}{\theta_o} + At$	$-\frac{d\theta}{dt} = A\theta^2$	Limit $\theta=\theta_o$ at $t=0$
	Voorhies(84)	$\theta=A/\sqrt{t}$	$-\frac{d\theta}{dt} = A\ \frac{\theta^3}{2}$	Limit $\theta=\infty$ at $t=0$
Reciprocal Power function	Blanding(9)	$\theta= A\ t^{-B}$	$-\frac{d\theta}{dt} = B(A)^{1/B}\ \theta^{\frac{Bn}{B}}$	Limit $\theta=\infty$ at $t=0$
	Volts et al(83)	$\theta= t^{-m}$	$-\frac{d\theta}{dt} = A\ \theta^m$	Limit $\theta=\infty$ at $t=0$
General Hyperbolic	Wojciechowski(90)	$\theta=(1+Gt)^{-M}$ $= \left(\frac{1}{1+(m-1)k_d t}\right)^{\frac{1}{m-1}}$	$-\frac{d\theta}{dt} = k_d\theta^m$	Limit $\theta=1$ at $t=0$

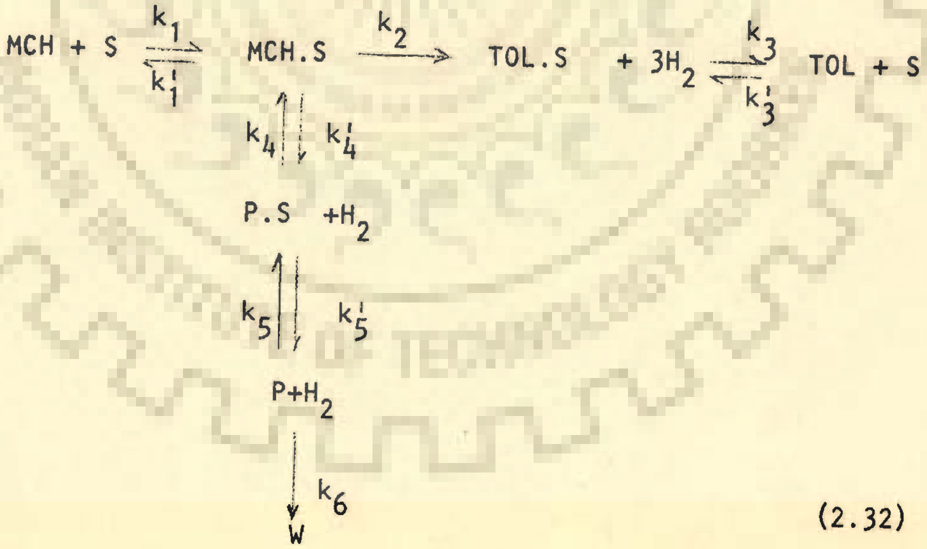
Where $\theta=C_s/C_{s0}$

C_s - current concentration of any component A at time t

C_{s0} - Initial concentration of any component A

θ - Fraction of sites available at any time t diffusion on dehydrocyclization reaction was also considered and have reported higher effective rate constants with powder than with commercial 1/12 inch extrudates.

Wolf and Peterson (89) used single pellet diffusion reactor (SPDR) for reaction-deactivation studies to elucidate the mechanism of poisoning for methyl cyclohexane (MCH) dehydrogenation reaction on 0.6 percent platinum-on-alumina catalyst at atmospheric pressure between temperature range of 350-400°C, and MCH and hydrogen partial pressure from 15-60 and 0-800 Torr, respectively. They observed that, there are two types of poisons, reversible (P) and irreversible (W). Reversible poisons are removed by hydrogen while irreversible poisons are not, and the poison precursor appears to be the adsorbed reactant. Based on the above observations they proposed the following reaction mechanism :



(2.32)

Surface reaction was found to be the rate controlling step and the rate of main reaction is given by -

$$r = k_2 \left[MCH.S \right]$$

$$= k_2 k_1 \left[S \right]_{to} \left[1 - \frac{[P] + [W]}{[S]_{to}} \right] [MCH] \qquad (2.33)$$

The rate of formation of reversible poison, P, is given by-

$$\frac{d[P]}{dt} = k_5 k_1 k_4 \, [S]_{to} \left[1 - \frac{[P] + [W]}{[S]_{to}} \right] \frac{(MCH)}{(H_2)} - k_5 [P][H_2] - k_6 [P] \tag{2.34}$$

where k_1 and k_4 are adsorption equilibrium constants for the corresponding reactions, and $[S]_{to}$ is initially measured activity which depends on operating conditions. The catalyst pellet was considered as an infinite flat slab of finite thickness. Diffusion of reactants was assumed to be one-dimensional and at quasi-steady state because the time scale for diffusion is smaller than the time constant of the poisoning reactions. The values of lumped rate constants were determined by solution of non-linear simultaneous differential equations. Their results are useful to predict the mechanism of deactivation and main reactions, and show the importance of hydrogen in reforming reactions. The individual rate constants of different reaction steps and the activation energies are not reported.

2.5 EXTERNAL AND INTERNAL HEAT AND MASS TRANSPORT RESISTANCES

In studies of heterogeneous catalytic reaction system, one of the main objectives is to determine whether the intrinsic kinetics or the interaction between the kinetics and transport resistances controls the overall rate of reaction. The effect of temperature and concentration gradients is generally studied in two domains :

(1) Intraparticle - within individual catalyst particles, and

(2) Interparticles or Intraphase - between the external surface of the particles and fluid adjacent to them.

A number of reviews have appeared for inter, and intra pellet heat and mass transfer effects (29,59,60). The various criteria used for testing the effects are given in Table 2.5. In operating any of the reactor it should be ensured that the criteria as calculated from these equations are satisfied if the kinetic data obtained are to reflect the intrinsic kinetic behaviour of the reaction involved. For using these equations the diffusion coefficient, heat of reaction, and the physical properties of the catalyst are needed, together with an experimental value of apparent reaction rate constant and observed initial reaction rate of dehydrogenation reaction. Using these values, the applicability of the various criteria can be easily tested.

Table 2.5 Criteria for the absence of mass and heat transfer effects

Inter phase Transport	Intraphase Transport
Mass Transfer	Mass Transfer :
$\frac{\bar{r}}{C_A . k_m a} = \frac{k_1'}{k_m a} < 0.15$	$\left(\frac{V'}{Se} \right)^2 \frac{k_1' \; \rho_p}{De} < 1$
Mears (60)	Weisz and Prater (87)
Heat Transfer	For Isothermal Pellet:
$\frac{E}{R_g \; T_b^2} (T_s - T_b) < 0.15$	$\frac{\bar{r} . \rho_p . R^2 . (\Delta H)}{T_b . ke} \left(\frac{E}{R_g T_b} \right) < 0.75$
Mears (59)	Anderson (1)
	Maximum temperature gradient in the pellet : -
$(T_b - T_s) = \frac{0.7 \; (\Delta H) \; \bar{r}}{C_p . \; \rho . k_m a}$	$\beta_m = \frac{(\Delta H) . D_e . \; C_s}{k_e . \; T_s}$
Smith (77)	Carberry (14)

2.6 CRITERIA FOR CATALYST BED DILUTION EFFECTS

The main reason for errors in the analysis of integral reactor data is the lack of isothermality in the reactor bed which is particularly serious with highly exothermic and endothermic reactions. One remedy for this problem is to dilute the catalyst bed with inert solids. Rihani et al. (73) have successfully employed a diluted fixed bed in studying the kinetics of a highly exothermic catalytic reaction vapor-phase hydrogenation of nitrobenzene to aniline. By trial and error they determined the different degrees of dilution in different parts of the bed to ensure isothermal operation. Calderbank (11) employed catalyst dilution and had developed equations to be used for calculating the dilution required to maintain isothermal conditions. The dilution is a function of distance along the packed bed.

A closer examination of a diluted bed will show that several distributions of the diluent are possible, and that the exit reactant concentration can be influenced by the type of distribution. vanden Bleek et al. (82) have given the following general criterion for neglecting the effect of catalyst dilution :

$$B = \frac{b\, d_p}{(1-b)\, \delta\, L} < 4 \times 10^{-3} \qquad (2.35)$$

where δ is the experimental error percent, b is the inert fraction, dp is the particle size, and L is length of the bed.

2.7 INTEGRAL CATALYTIC REACTOR CRITERIA

Carberry (15) has indicated that if the tube-to-pellet diameter ratio is less than 6, radial temperature gradients will be less. Heat release per unit volume of bed can be reduced by diluting the catalyst bed with inert particles. The laboratory packed-bed catalytic reactor should thus consist of a bed of large length to-tube diameter ratio (usually more than 8) and small tube-to-pellet diameter ratio with operation at high Reynold numbers.

A summary of criteria for the fixed bed catalytic laboratory reactors has been given by Doraiswamy and Tajbl (23). They have analysed results on the basis of criteria discussed by Mears (60). They have further reported that L/dp ratio should be more than 30 and dt/dp shouldbe less than 6 for integral catalytic laboratory reactors.

2.8 CONCLUSIONS FROM LITERATURE REVIEW FOR THE DEVELOPMENT OF KINETIC AND DEACTIVATION MODEL

The published literature provides the following guidelines for the development of a kinetic and deactivation model for cyclohexane dehydrogenation on platnium-on-alumina catalyst.

Dehydrogenation of cyclohexane at atmospheric pressure and temperatures above 300°C will not produce any intermediate product and the main product will only be aromatics. Further, it is safe to consider dehydrogenation of cyclohexane reaction as irreversible first order.

As not much information is available for hydrocracking reaction and in all the publishsed work it has been assumed to be an irreversible first order reaction, it may be reasonable to assume the same for the development of kinetic model in the present study.

The hydrocracking rate constant is independent of time-on-stream and, therefore, deactivation of catalyst has no effect on hydrocracking rates. The values of effective or apparent rate constant for cyclohexane dehydrogenation will decrease with time-on-stream due to fall in activity of catalyst. All the changes in dehydrogenation rate with time-on-stream will be accounted for by the activity changes in the catalyst.

Intraparticle mass transfer limitations for pelleted catalysts are important and must be considered in the development of model (55).

In view of the above the equations for the dehydrogenation and hydrocracking reactions can be written as -

Dehydrogenation : $r_1 = k_1 \eta_1 \, a \, C_A$ (2.36)

Hydrocracking : $r_2 = k_2 \eta_2 C_A$ (2.37)

where $a = 1$ at $t = 0$. Intrinsic rate coefficients and effectiveness factors $k_1 \eta_1$ and $k_2 \eta_2$ can be taken as constant for the entire operation under isothermal condition. Activity 'a' and reactant concentration C_A will change with time-on-stream and position in the bed.

A close look at the analysis of Khang and Levenspiel (45), and Wolf and Peterson (89) indicates that basically the approach of both is same, and show the advantage of using separate equations for main and deactivating reactions.

The deactivation equations used by Khang and Levenspiel are :

$$-\frac{da}{dt} = k_d C_{AS} a^m \qquad (2.38)$$

$$-\frac{d\alpha}{dt} = k_d \alpha C_A \qquad (2.39)$$

and $$a = \frac{3}{R^3 C_{AS} \eta} \int_0^R \alpha . C_A . r^2 \, dr \qquad (2.40)$$

where α is activity at any point in the catalyst pellet and the rate of decrease of activity α is proportional to first power of concentration of the poisoning component. Activity a is defined as mean activity of the whole pellet and is obtained by equation (2.40), that is, by integrating the point activities throughout the pellet.

Wolf and Peterson have used the following deactivation equation :

$$\frac{d[P]}{dt} = k_5 K_1 K_4 [S]_{to} \left[1 - \frac{[P] + [W]}{[S]_{to}} \right] \frac{(MCH)}{(H_2)} - k_5 (P)(H_2) - k_6 (P)$$

(2.34)

If the last two terms of Eqn. (2.34) are left and then comparison with Eqn. (2.38) gives :

$$k_d = k_5 K_1 K_4 (S)_{to}$$

$$a = \left[1 - \frac{(P) + (W)}{(S)_{to}} \right]$$

$$m = 1$$

and

$$C_{AS} = \frac{(MCH)}{(H_2)}$$

Thus, a general equation for deactivation rate during the dehydrogenation of component A can be written as -

$$-\frac{da}{dt} = k_d a^m \frac{(A)}{(H_2)} \qquad (2.41)$$

While the rates for dehydrogenation and hydrocracking reactions are given by Eqns. (2.36) and (2.37), respectively.

CHAPTER - 3

EXPERIMENTAL SET-UP AND PROCEDURE

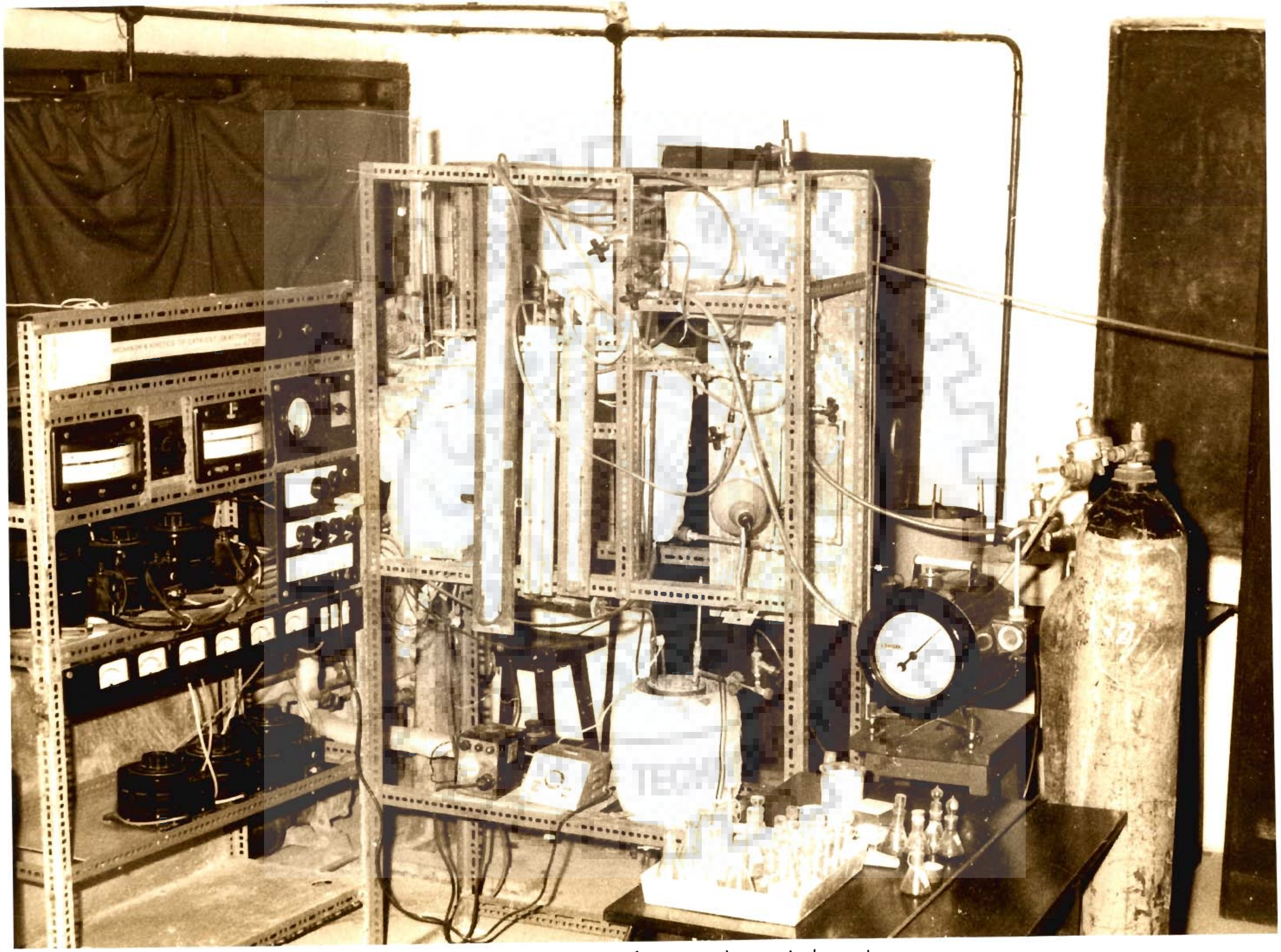
3.1 THE EXPERIMENTAL SET-UP CONSISTED OF THE FOLLOWING SECTIONS:

(i) Feeding arrangement for cyclohexane and Hydrogen
(ii) Vaporizer and preheater
(iii) Reactor section
(iv) Condenser section

An overall view of the experimental set up is shown in photograph 3.1. On the right is the operational panel showing all the above sections and on the left is the control panel showing the various ammeters, voltmeters, variable-transformers, temperature indicator-controllers and selector switches for thermocouples.

3.1.1 Feeding Arrangement for Cyclohexane and Hydrogen

Feeding arrangement for cyclohexane and hydrogen has been shown in detail in Fig. 3.1. The cyclohexane was continuously fed from a storage tank A through valve V_4 and rotameter R. The constant flow rate of cyclohexane was maintained by applying a constant nitrogen pressure over the liquid level. Any increase in system pressure during the reaction was compensated by changing the nitrogen pressure with the help of valves V_1 and V_2. The flow rate of cyclohexane was measured by precalibrated rotameter R. Dry hydrogen was fed to the system from a hydrogen cylinder through a silica-gel bed. Pressure of the hydrogen gas was kept constant with the help of a regulator and valve V_5 and was precisely measured by manometer M_2. During the operation the flow rate of hydrogen was maintained constant with the simultaneous operation of valves V_5 and V_6. As the



Photograph 3.1 Overall view of experimental set up

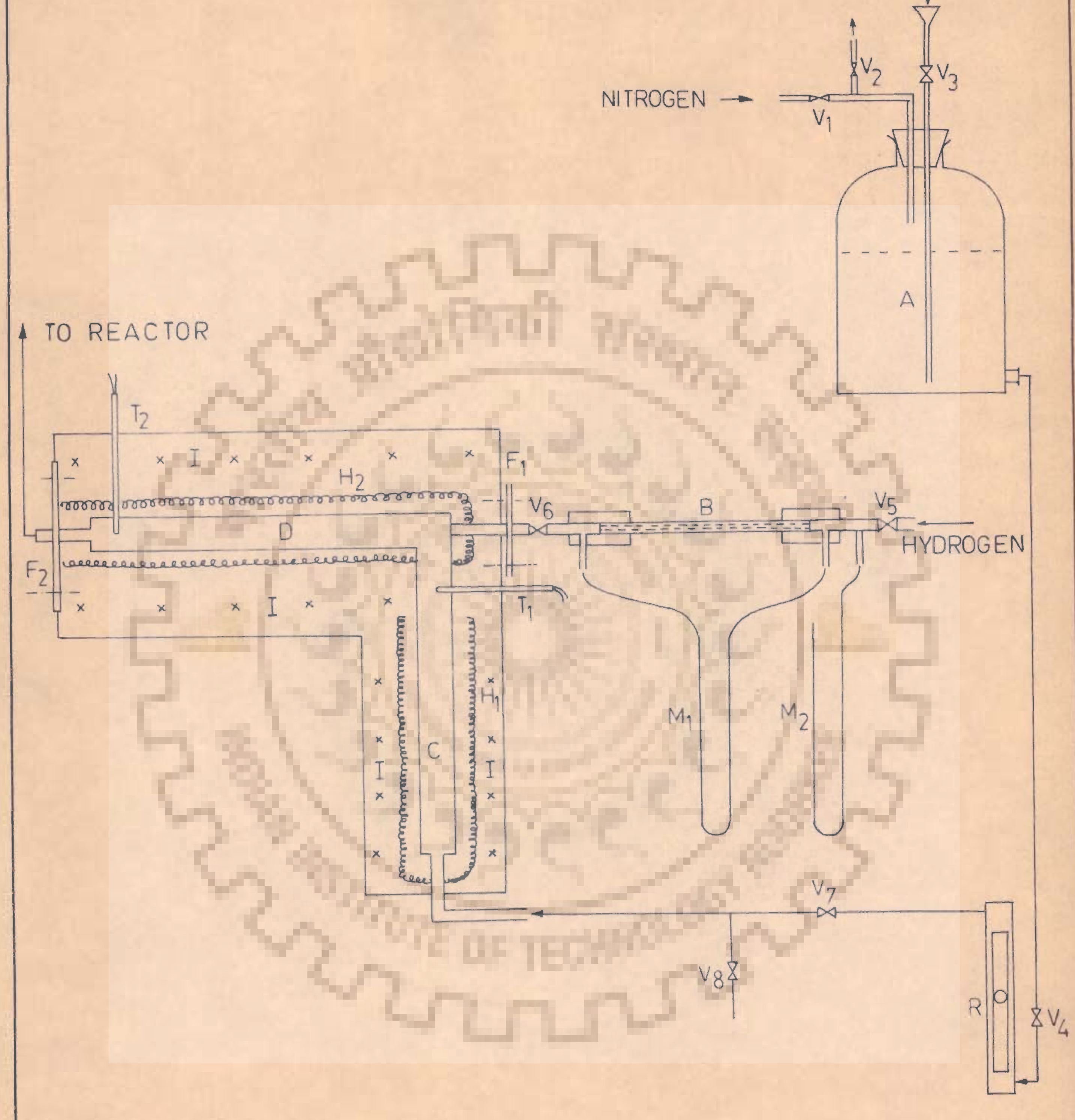


FIG.3.1 FEEDING ARRANGEMENT, VAPORIZER AND PREHEATER

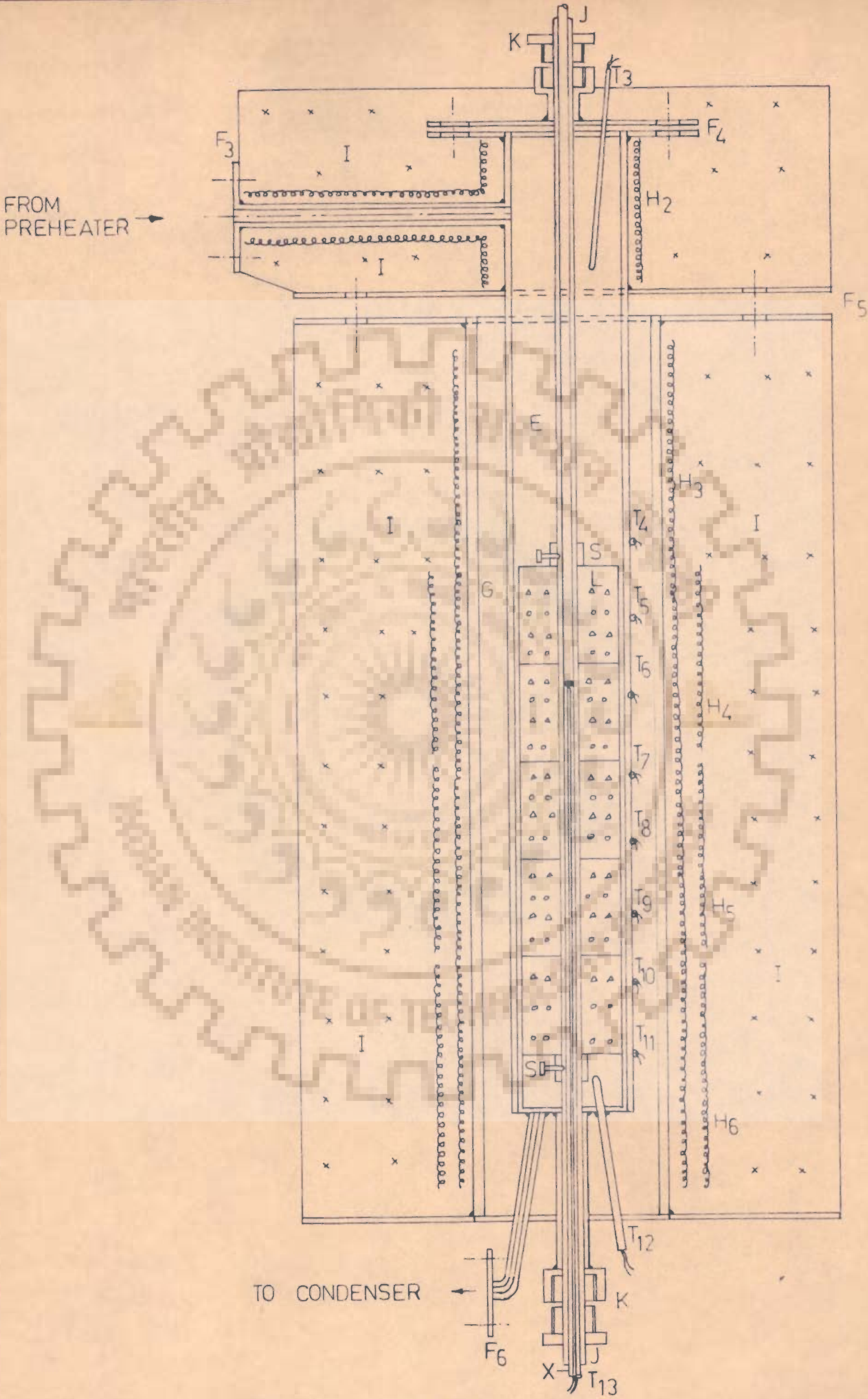


FIG. 3.2 REACTOR SECTION

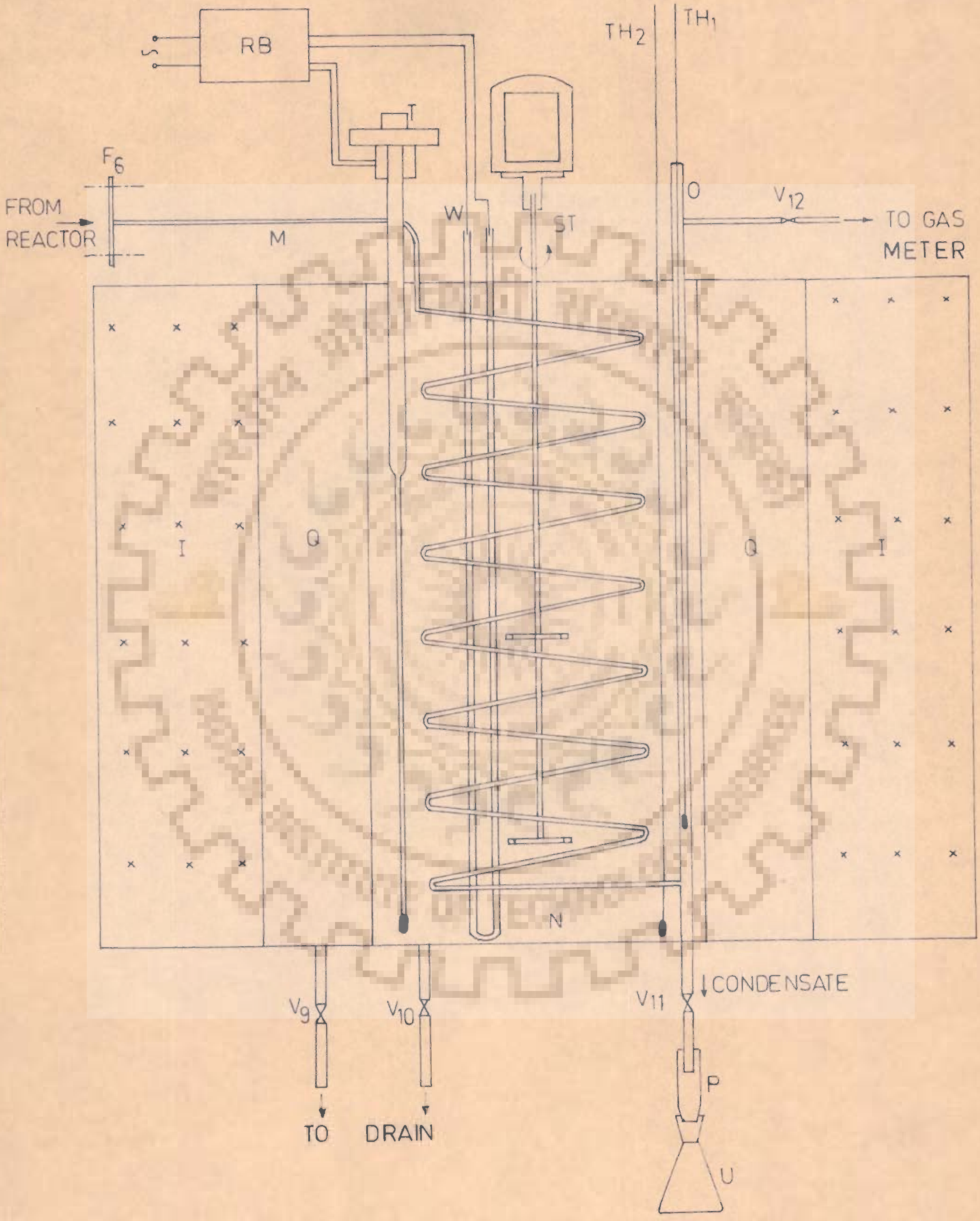


FIG. 3.3 CONDENSER SECTION

KEY TO FIGURES 3.1 to 3.3

A	Feeding tank
B	Needle meter
C	Vaporizer
D	Preheater
E	Reactor tube
F_1 to F_6	Flanges
G	Heater tube in reactor Section
H_1 to H_6	Heaters
I	Insulation
J	Central supporting tube
K	Gland-nut assembly
L	Catalyst cups with supporting plates and mesh
M	Condenser Coil
M_1, M_2	Manometers
N	Cold Water Bath
O	Condenser outlet tube
P	Standard Glass Joint
Q	Ice Bath
RB	Relay Box assembly
ST	Stirrer
T	Mercury contact thermometer
U	Conical flask
V_1 to V_{12}	Needle valves
W	Immersion heater in condenser section
X	Moving thermocouple tube

ambient temperature changes during the operation were negligible, the maintenance of constant pressure in the manometer M_2 and constant pressure drop across needle meter B, measured with the help of manometer M_1 assured a constant flow rate of hydrogen.

3.1.2 Vaporizer and Preheater

Measured cyclohexane stream was vaporized before mixing with the hydrogen gas.

The vaporizer section C was heated by a heater H_1, the heat flux was adjusted with the help of a variable transformer. Vaporizer exit temperature was indicated by thermocouple T_1 .

The hydrogen and cyclohexane vapours were mixed and heated to the reaction temperature in a preheater D, with the help of heater H_2. Temperature at the exit of preheater was measured by thermocouple T_2.

3.1.3 REACTOR SECTION

Preheated mixture of cyclohexane and hydrogen was fed to the reactor. Flange F_3 connects the preheater section with the reactor section. The details of the reactor section have been schematically shown in Fig. 3.2.

The reaction section consisted of an annular space between two concentric tubes, J (I.D. 6.4 mm, OD 9.6 mm) and E (I.D. 32 mm, OD 38 mm). The catalyst was charged to reactor section in cups L (ID 29.5 mm, OD 31.5 mm, Height 45 mm). The bottom of the cup consisted of a BSS 100 mesh stainless steel screen supported by a perforated plate (Dia 29.5 mm, Thickness 1.5 mm). Eight thermocouples, T_4 through T_{11} were silver soldered at the periphery of tube N at different axial positions. One thermocouple T_{13} was soldered in a sliding tube X. The tube X was movable in the central tube J to indicate temperature at various axial positions. The reactor inlet and exit temperatures are recorded with the help of thermocouples T_3 and T_{12} respectively. The gases from the reactor enter the condenser section. The reactor section was connected to the condenser section through flange F_6. In the reactor section, the flow of reaction mixture was from top to bottom.

The complete reactor tube E with exit flange F_6 was so designed that the assembly could be inserted in mild steel heater tube G(52 mm ID, 60 mm OD) and kept in position with the help of flange F_5.

The cups assembly consisted of cups L with a central hole in perforated bottom plate and stainless steel screen to slide around tube J. They were kept in position by stoppers S and the whole assembly was placed in tube E and kept in position by flange F_4.

For leak proof arrangement the ends of tube J were fixed with help of gland arrangement K_1 to the lower end of reactor tube E and with the help of gland arrangement K_2 to the flange F_4 at the top.

A scale was provided on top of the reactor section to indicate the axial position of the moving thermocouple T_{13}, placed in sliding tube X, in the reactor section.

The tube G was heated by four heaters H_3 through H_6.

The material of construction used in vaporizer, preheater and reactor section was stainless steel grade 316.

Ammeters were provided for measuring the currents in all the heaters individually.

The thermocouples were made from chromel-alumel wires. The joints were made by silver soldering. Reference junction was always at atmospheric temperature. Emf of the thermocouples were measured by indicating type of pyrometers calibrated for chromel-alumel thermocouples.

Heaters were made of nichrome wire placed in porcelain beads to provide electric insulation from metallic wall. The heat flux of the individual heaters was varied by variable transformers.

Vaporizer, preheater and reactor were insulated with asbestos rope, then by a layer of asbestos, magnesia and plaster of paris powders mixed in proper proportions and finally by glass wool to ensure minimum heat loss.

3.1.4 CONDENSER SECTION

The gaseous products from the reactor exit were partially condensed in a condenser as shown in Fig. 3.3. The condenser consisted of a helical copper coil M (ID 35 mm, OD 6.3 mm, Length 5,500.00 mm, coil diameter 70 mm) immersed in a thermostat N. The thermostatic water bath N was cooled by ice-bath

The water was maintained at a uniform temperature with the help of a stirrer ST. The subatmospheric temperature of the water bath was maintained through an auxillary heater W controlled by mercury contact thermometer T and relay box RB arrangement.

The outlet of the coil M was connected to a tube O (ID 5.5 mm, OD 12.2 mm) where gases were separated from condensate. By keeping the valve V_{11} open, the condensate was collected in a glass conical flask U attached to the lower end of tube O with the help of standard B-29 glass joint P. The flow rate of the uncondensed gases was measured with the help of a recording type of wet gas meter.

Temperatures of the bath N and Q of the gases at the point of separation from condensate were measured by thermometers TH_2 and TH_1 respectively.

3.2 EXPERIMENTAL PROCEDURE

A weighed amount of the catalyst was charged to the reactor.

The total amount of the catalyst was distributed in four or five cups in increasing quantity from top to bottom, so as to achieve near uniform conversion in each cup section of reactor. Glass beads, of nearly same diameter as that of catalyst pallet, were uniformly mixed with the catalyst in each of the cups in decreasing proportion from top to bottom. Care was taken in selecting the inert fractions in different cups so as to satisfy the bed criteria of equation 2.1. Further, the annular space available for catalyst in the cups is 7.5 mm and diameter of the catalyst pellet is 1.5 mm, therefore, the ratio d_t/d_p is less than 6. In all the cases the length of the bed is more than 30 times the pellet diameter, therefore, the integral reactor criteria given in section 2.5.1 is also satisfied.

The top and bottom cups were filled with only glass beads. The objective of placing bottom most cup (60 mm length) with glass beads was to minimize the end heat losses in the bottom of the reactor section E which was open to atmosphere as shown in Fig. 3.2, and of filling the top most cup (80 mm length) with glass beads was to preheat the reactants to the desired reaction temperature before they entered the reactions section.

The cups after filling with catalyst and glass beads were kept in position around tube J and the assembly was inserted into tube E. Flange F_4 and gland nuts K_1 and K_2 were then tightened carefully. The system was maintained under hydrogen pressure and was checked for any leakage.

A small flow of hydrogen was started and the heaters were switched on. The heat fluxes were adjusted by manipulating variable transformers so as to heat the reactor and preheater to the reaction temperature and the vaporizer to about 200°C. The system was then left for about four to five hours with suitable adjustments as necessary until the temperature of reactor stabilized at the desired value.

Meanwhile, the thermostatic bath was filled with water and ice in their respective chambers. The electrical current in the auxiliary heater was adjusted according to the requirements and the bath was left for stabilization.

The tank A was filled with liquid cyclohexane through valve V_3 keeping valve V_2 open to atmosphere.

After the steady state was achieved, the flow rate of hydrogen was increased to the desired value and allowed to attain the steady flow. Cumulative flow rate readings were recorded with time by the recording wet gas meter. The flow of liquid cyclohexane was then started from the tank A, regulated by valve V_4 and was measured by rotameter R.

As the cyclohexane flow rates were maintained between 0.5 and 3.0 ml/min, great accuracy in operation was needed to maintain steady flow rate. Further, the pressure drop in the system increased with the progress of reaction due to deactivation of catalyst and this required even greater care to maintain uniform flow of cyclohexane in experiments. This drop in pressure was compensated by proportionate increase in the nitrogen pressure over the liquid cyclohexane in tank A. The valves V_5 and V_6 were also adjusted simultaneously during the reaction to maintain the steady flow of hydrogen gas. Steady values of pressure drop across the needle meter B and the gage pressure M_2 ensured steady rate of hydrogen flow to the reactor.

The most important problem during the operation was that of maintaining the reactor under isothermal condition. The main heater H_2 was wound around complete length of the mild steel tube G to supply the constant heat flux to the complete reactor. Three auxiliary heaters H_4, H_5 and H_6 were wound in three axial sections around tube G to meet the additional heat requirements in any reactor section. As most of the reaction takes place in the inlet section of the reactor, the heat supplied by heater H_4 was more than that by H_5 or H_6. With the deactivation of catalyst during the reaction, the zone of maximum heat requirement gradually progresses downward. Thus, it was also necessary to change the currents in auxiliary heaters with time-on-stream so as to keep uniform temperature throughout the catalyst bed in the reactor.

The reaction products leaving the reactor were cooled and condensed in the condenser. The temperature of the condenser was maintained close to 6°C to ensure near complete condensation without any crystallization of cyclohexane or benzene. Care was taken that this temperature did not fall below the freezing point of benzene or cyclohexane. The uncondensed gases from the condenser were passed through the recording type wet gas meter and the meter readings were recorded with time. The liquid samples were collected in conical flasks from the condenser bottom periodically at a time interval of 20 to 30 minutes. The time of each sample was separately recorded.

3.3 ANALYSIS OF PRODUCTS

The analysis of liquid products and reactants was carried out in Gas-chromatograph (AIMIL make MK III-A supplied by M/s Associated Instruments Manufacturers of India Ltd., New Delhi) using carbowax-4000 (10 percent on wt basis) on celite column (3 meters long - 6.25 mm diameter) with flame ionization detector (FID). Following average operating conditions were maintained:

-	Injection Temperature	85°C
-	Column Temperature	75°C
-	FID Temperature	120°C
-	Column Gas Pressure	$0.3\ \frac{kg}{cm^2}$ gage
-	Strip chart recorder speed	60 cm/hr.

The sensitivity of the recorder (Eliott Instruments, England) was maintained at a level so as to achieve good separation for cyclohexane and benzene. Liquid sample quantity varied from 2 to 5 micro litre.

Cyclohexane and benzene peak areas were standardised by using spectroscopic grade chemicals under gas-chromatograph conditions, similar to those used for liquid product analysis. For same quantity, benzene peak area was observed to be higher as compared to cyclohexane.

For some of the runs chromatographic analysis of gases leaving the condenser was attempted, but the results were not satisfactory and error involved was relatively large. With the liquid sample analysis and assuming vapor – liquid equilibria at condenser exit, the material balances for hydrogen and cyclohexane were satisfied to well within ± 8 percent.

3.4 REGENERATION OF DEACTIVATED CATALYSTS

The deactivated catalyst regeneration is carried out by passing measured amount of dried air through valve V_8 and measured amount of nitrogen through valve V_5, to maintain the desired concentration of oxygen in the inlet gas. During the start up of regeneration the concentration of oxygen was kept around 2 percent and gradually the concentration was increased upto 15 percent keeping a close watch on temperatures in the catalyst bed so as to keep them well below the sintering limit during catalyst regeneration. Total time required for regeneration was around 6 to 8 hours.

In the experimental runs reported in this thesis, however, fresh catalyst was used for each run so as to ensure the identical intrinsic catalyst activity for each run.

3.5 SPECIFICATIONS OF MATERIALS USED :

3.5.1 Reforming Catalyst :

Name	RD - 150 Sinclair - Baker
Composition	0.6 percent platinum on η - alumina
Total Surface area	330 m^2/g
Pore Volume	0.42 cm^3/g
Average pore radius	32 Å
Porosity	0.504
Tortuosity factor	3.8
Size of pellet	1.6 mm dia, 4.8 mm length
Density of pellet	1.2 g/cm^3
Effective thermal conductivity	$1.04 \frac{Cal}{hr.cm.gm.}$

3.5.2 Cyclohexane :

Specific gravity at 20°C	0.776 - 0.780
Boiling range (95 percent)	80 - 82°C
Freezing point	5.0 - 6.5°C
Non-volatile matter	Less than 0.005 percent
Manufacturer	BDH Division, Glaxo Laboratories (India) Ltd., Bombay - 18.

No impurity was detectable by gas chromatograph even at higher sensitivities in this cyclohexane.

3.5.3 Nitrogen and Hydrogen gases :

Purity more than 99 percent

Manufacturer	Indian Oxygen Ltd., New Delhi.

CHAPTER - 4

EXPERIMENTAL OBSERVATIONS AND ANALYSIS OF INTEGRAL REACTOR DATA

4.1 PRELIMINARY EXPERIMENTATION

Some preliminary runs were carried out without catalyst at high temperature and low mole ratios of hydrogen-to-cyclohexane to check if the stainless-steel used for the fabrication of experimental set up is having any effect on the conversion of cyclohexane to benzene. No trace of benzene was found in reactor effluents as confirmed by the chromatographic analysis of liquid condensate from the condenser.

Material balance for cyclohexane was also checked for these runs and the difference in the amount of cyclohexane recovered and fed was always within ± 5 percent. It was, therefore, concluded that the system was leak proof, stainless steel did not result in conversion of cyclohexane at the conditions of the experiments and the flow rate measurements were accurate. Further, at steady state operation, readings of all the thermocouples in the reactor section (T_4 to T_{11}) and the central thermocouple (T_{13}) indicated same temperature confirming the accuracy and sensitivity of the thermocouples.

4.2 EXPERIMENTAL DATA AND THE RANGE OF PARAMETERS INVESTIGATED

4.2.1 Experimental Data :

The experimental data are tabulated in Appendix - A, Tables A-1 to A-19. Each table gives experimental results for a given set of experimental conditions, namely, volumetric feed rate of liquid cyclohexane and hydrogen, ambient temperature and pressure, average temperature in the reactor and condenser, and weight of the catalyst used in the reactor. Weight of the glass beads added to the catalyst is not reported.

The conversion-time data is reported as mass of liquid sample collected from condenser and its composition as obtained from gas-chromatographic analysis, and average flow rate of uncondensed gases from condenser for different time intervals from the start of the run.

During experiments it was observed that the variation in rotameter R readings was within ± 0.1 ml/min, the pressure variation in manometers M_1 and M_2 were within ± 1 cm of carbon-tetrachloride and mercury respectively and temperature variation in catalyst bed was within ± 5°C.

4.2.2 Range of Parameters Studied :

From the experimental data, range for the three main variables, as obtained, is as follows :

Mole Ratio	0.94 - 4.8
Space Velocity –	
– LHSV, hr^{-1}	1.28 - 4.77
– W/F, (g cat)(hr) /(gmole)	17.64 - 65.91
Average Reactor Temperature, °C	310 - 435

4.3 CYCLOHEXANE CONVERSION CALCULATIONS

The vapor phase concentration of cyclohexane and benzene was calculated by assuming that the equilibrium had been achieved in the condenser bath N between condensate and the uncondensed vapors leaving the condenser M at the temperature indicated by thermometer TH_1. The temperature difference between that of bath N and of the gases leaving the condenser as measured by thermometers TH_2 and TH_1 respectively, was always less than 0.5°C. The condensate compositions were accurately known from chromatographic analysis and were found to be reliable and accurate to within ± 2 percent. The chromatographic analysis indicated the presence of benzene and cyclohexane in liquid products. Hydrocracking gives indiscriminate rupture of C-C linkage and may result in some pentane formation The maximum hydrocracking was 13.5 percent of the cyclohexane fed and minimum hydrogen-to-cyclohexane mole ratio was 0.935. Assuming that the entire cyclohexane was hydrocracked to pentane and methane and no increase in the number of hydrogen moles due to benzene formation, then maximum possible mole fraction and partial pressure of pentane in reactor effluent would have been 0.075 and 56 mm Hg respectively. The vapour pressure of pentane at the minimum condenser temperature of 6°C is 220 mm Hg. Since the vapour pressure of pentane is very much higher than its maximum possible partial pressure, pentane is therefore, not expected in the condensate, as confirmed by the chromatographic analysis of liquid product. The following equations (43) are used for the calculation of mole fractions of benzene and cyclohexane in gaseous products.

$$\mathrm{Ln}\ \gamma_B = -\ln(x_B+A_{12}x_{CH})+x_{CH}\left[\frac{A_{12}}{x_B+A_{12}x_{CH}} - \frac{A_{21}}{A_{21}x_B+x_{CH}}\right]$$

$$\ln \gamma_{CH} = \ln(x_{CH}+A_{21}x_B) - x_B\left[\frac{A_{12}}{x_B+A_{12}x_{CH}} - \frac{A_{21}}{A_{21}x_B+x_{CH}}\right]$$

$$\log_{10} p_B = 6.90565 - \frac{1211.033}{T + 220.79}$$

$$\log_{10} p_{CH} = 6.84498 - \frac{1203.526}{T + 222.863}$$

$$y_B = \gamma_B\, x_B\, p_B / P$$

$$y_{CH} = \gamma_{CH}\, x_{CH}\, p_{CH} / P$$

where, A_{21} = 0.65926 A_{12} = 1.00918

p - Vapor pressure, mm Hg

P - Total pressure, mm Hg

T - Temperature, °C
x - Liquid phase composition
y - Gas phase composition
γ - Activity coefficients

Suitable values, as given above, were taken for Wilson-parameters A_{12} and A_{21}, and for Antoine constants for benzene - cyclohexane mixture. Use of above equations for the calculation of benzene and cyclohexane mole fractions is well justified in view of reasonably good check on material balance for hydrogen as indicated by P E R H values in Tables A-1 to A-19, Appendix - A.

Since accurate chromatographic analysis of gaseous products was not possible, direct information about the quantity or nature of hydrocracked gaseous products was not available. No direct measurement was possible for estimating the fraction of cyclohexane converted to poison (coke), but it is safe to assume that the loss of cyclohexane into carbonaceous products was negligible. The fraction of cyclohexane hydrocracked has been obtained from the material balance for cyclohexane. However, for nearly ten percent data points the sum of moles of cyclohexane and benzene in product was found to be more than or equal to the moles of cyclohexane fed, thus resulting in a negative or zero value for the moles of cyclohexane hydrocracked. Obviously this cannot be true and such data points were discarded as they indicate the cumulative effect of errors in the flow rates measurement and chromatographic analysis of liquid product. These points are marked by an asterisk in Appendix A and are circled in Fig. 4.1.1 to 4.1.19 as rogue points.

Tables A-1 to A-19 in Appendix A give the measured values of liquid product quantity and its analysis, and gaseous product average flow rate along with calculated values of moles of cyclohexane fed, moles of benzene and cyclohexane in product, percent cyclohexane unconverted and that converted to benzene, and percent error in hydrogen balance during a given time-on-stream period.

The moles of exit gases and hydrogen fed were corrected by assuming them to be saturated with water vapor while flowing through the wet gas-meter. An independent material balance was carried out for hydrogen to check for the accuracy of measurements and the details of these calculations are shown in Appendix - G. The error in hydrogen balance was found to be within-2 to +6 percent for ninety percent of data points, indicating good measurement accuracy. The calculated values of the extent of cyclohexane hydrocracked are also within reasonable limit of 10 percent of cyclohexane fed for more than eighty percent condensate samples.

4.4 EXTRAPOLATION OF DEACTIVATION DATA TO GET INITIAL RATE DATA

The experimental data given in Appendix - A has been plotted on Fig. 4.1.1 to 4.1.19 and smooth curves were drawn from the experimental points for benzene and cyclohexane by visual observation. The figures show the values of X_B and X_A at the mid point of the start and end of collection time for each condensate sample. Fitting of data by polynomials of high order was not considered useful in view of limited number of data points and the inherent accuracy of experimental measurements. The extrapolation of smoothened curve gives conversion at time $t \rightarrow 0$ for undeactivated catalyst. Blanding (9) and Mahoney (55) have also used a similar procedure to get the initial rate data for undeactivated catalyst. Table B-1 to B-19 in Appendix - B give percent conversion of cyclohexane to benzene, and percent cyclohexane unconverted as obtained from smoothened experimental data of Fig. 4.1 to 4.19, and these values are referred subsequently as experimental data for model development and further

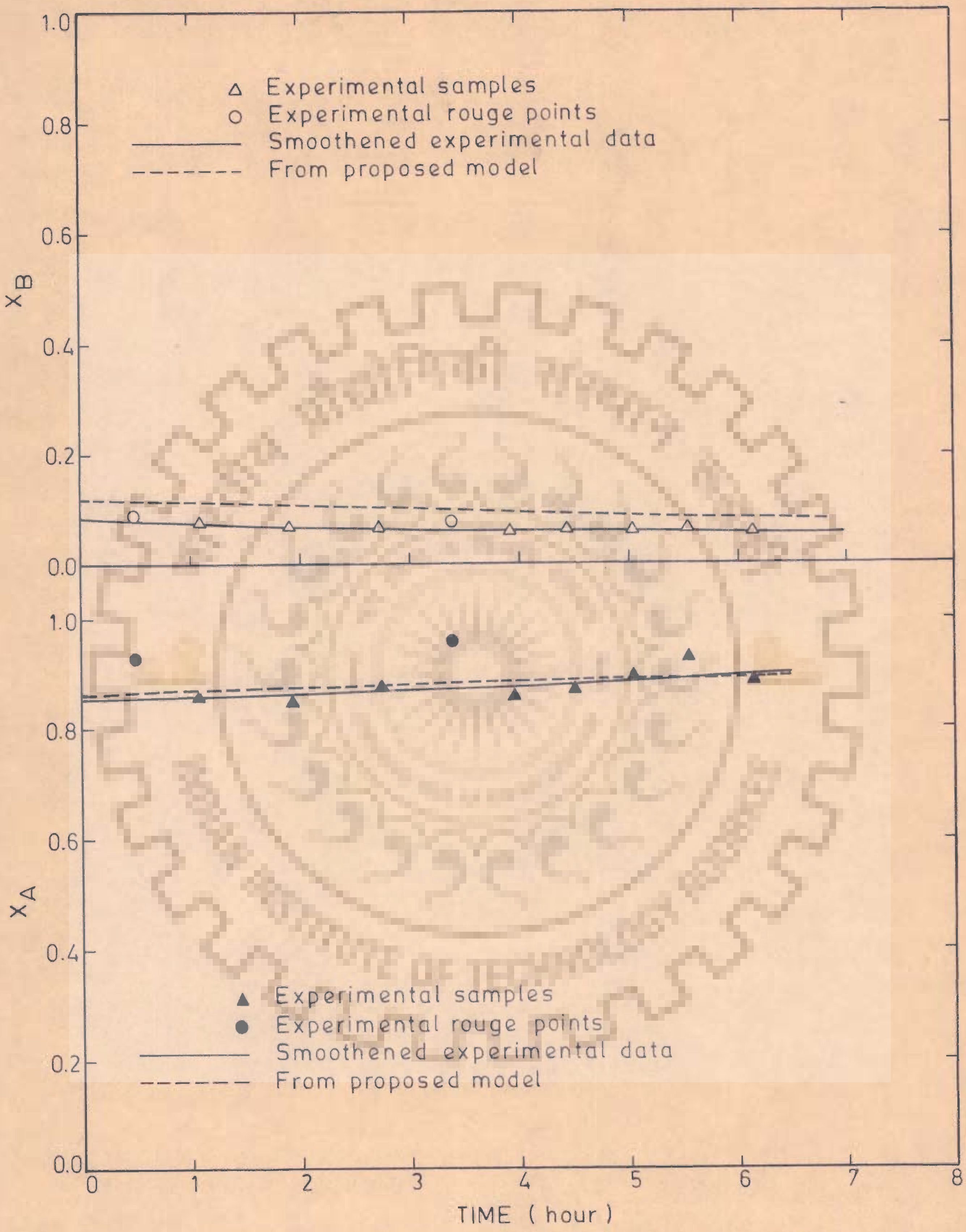


FIG. 4.1.1 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 310 °C, L H S V = 4.565, MOLE RATIO = 4.348)

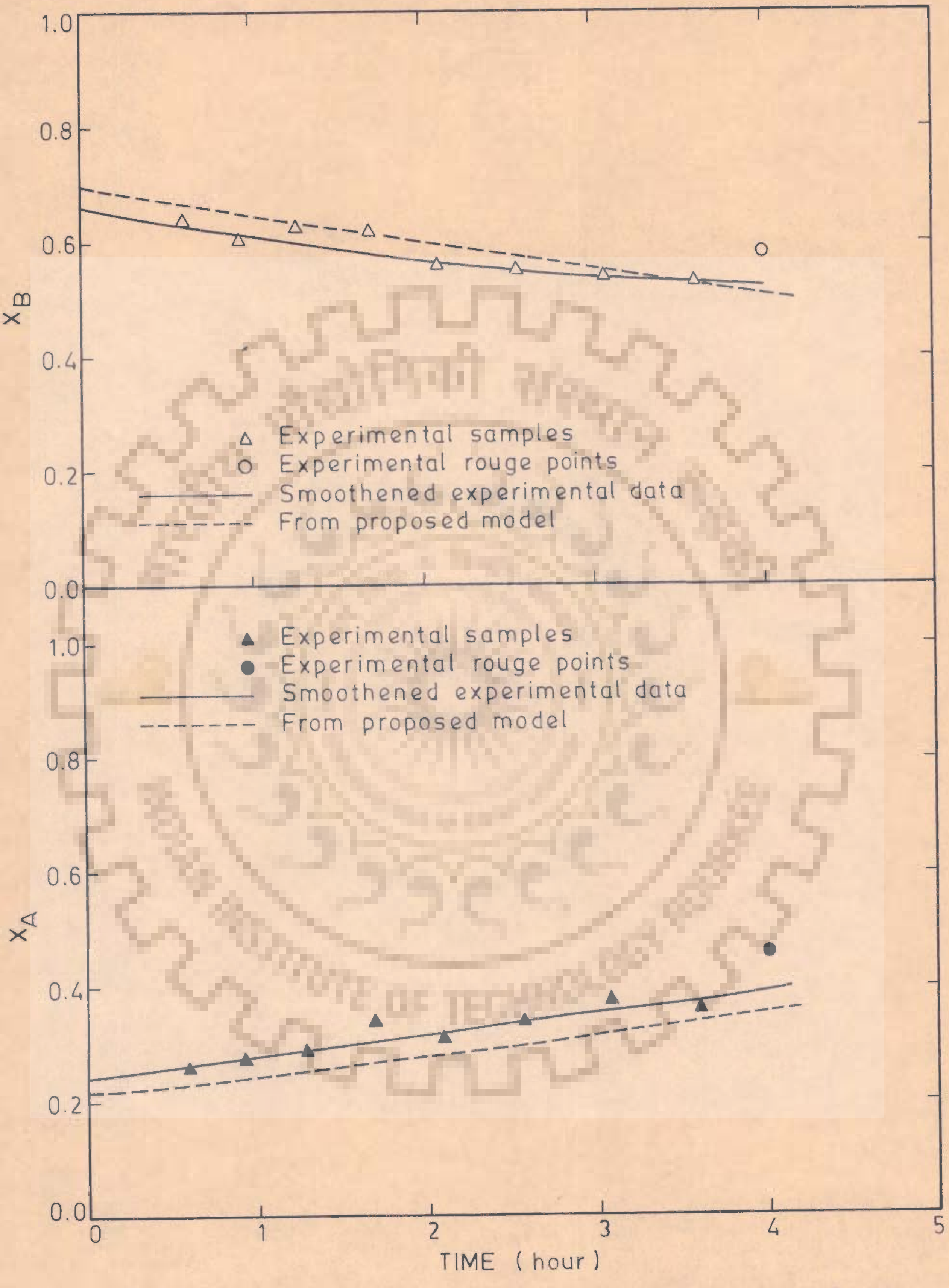


FIG. 4.1.2 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 355°C, L H S V = 2.052, MOLE RATIO = 1.002)

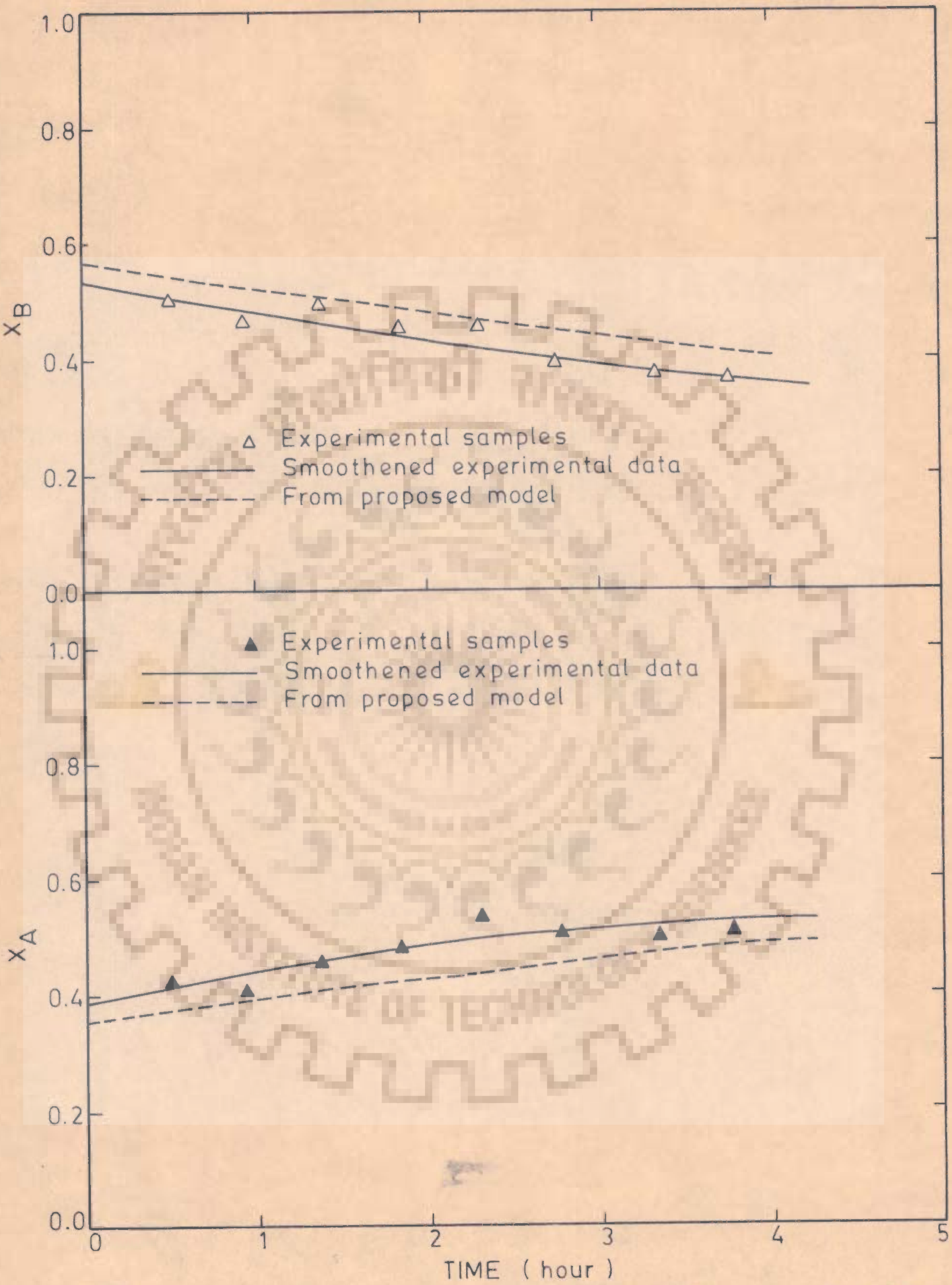


FIG. 4.1.3 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 355 °C, L H S V = 2.437, MOLE RATIO = 2.176)

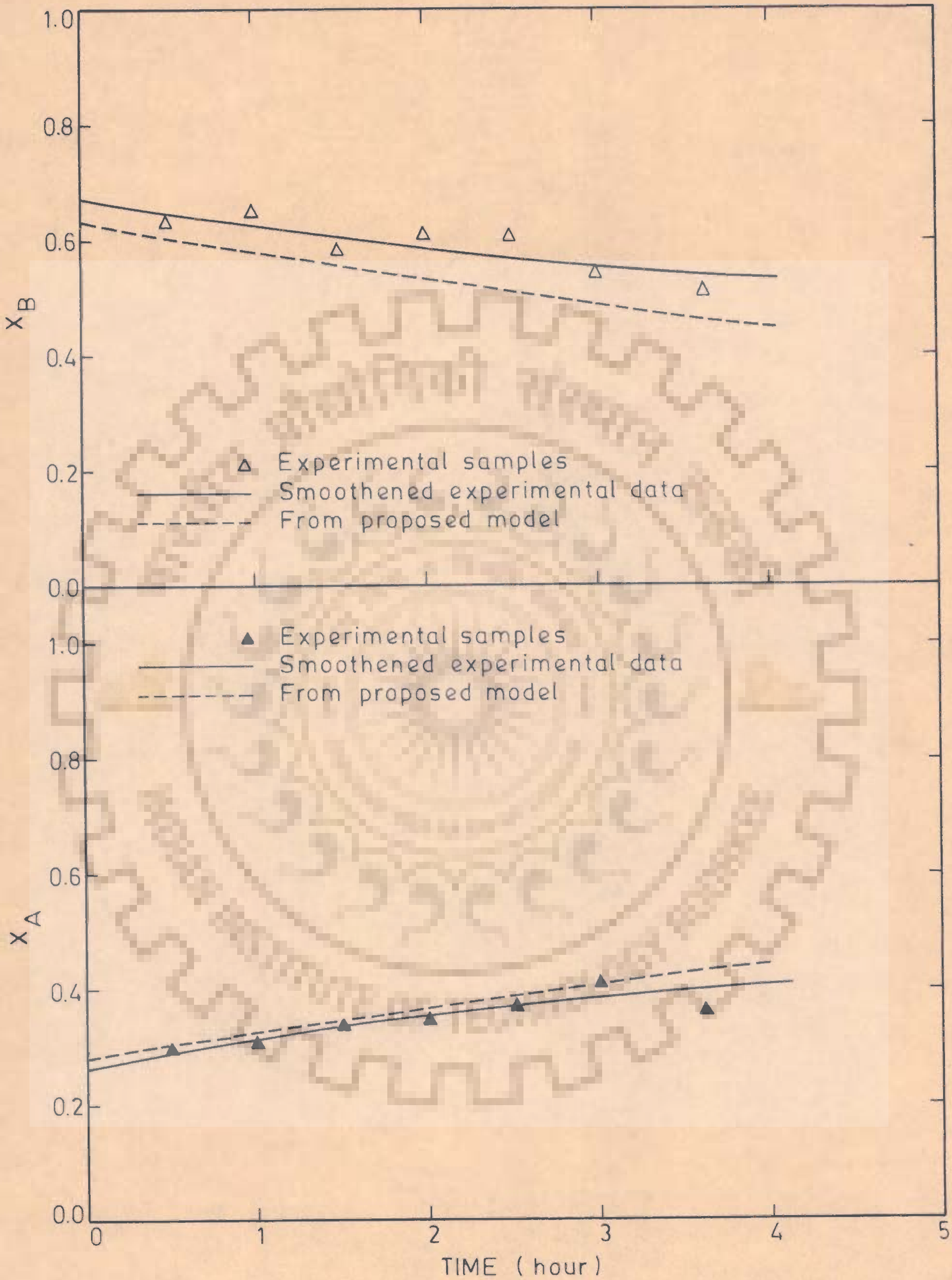


FIG. 4.1.4 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 350 °C, L H S V = 2.425, MOLE RATIO = 0.935)

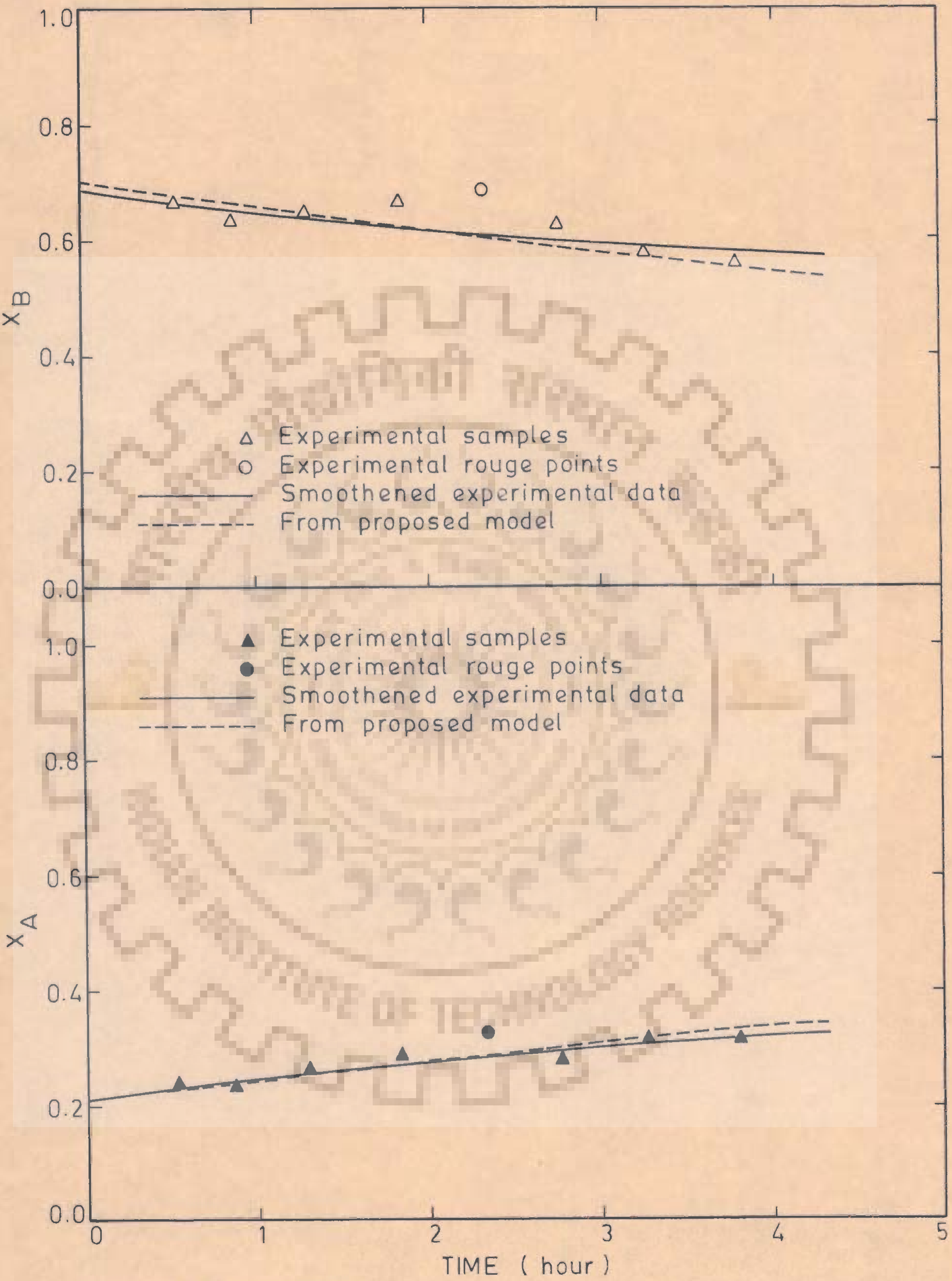


FIG. 4.1.5 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 390 °C, L H S V = 2.347, MOLE RATIO = 2.844)

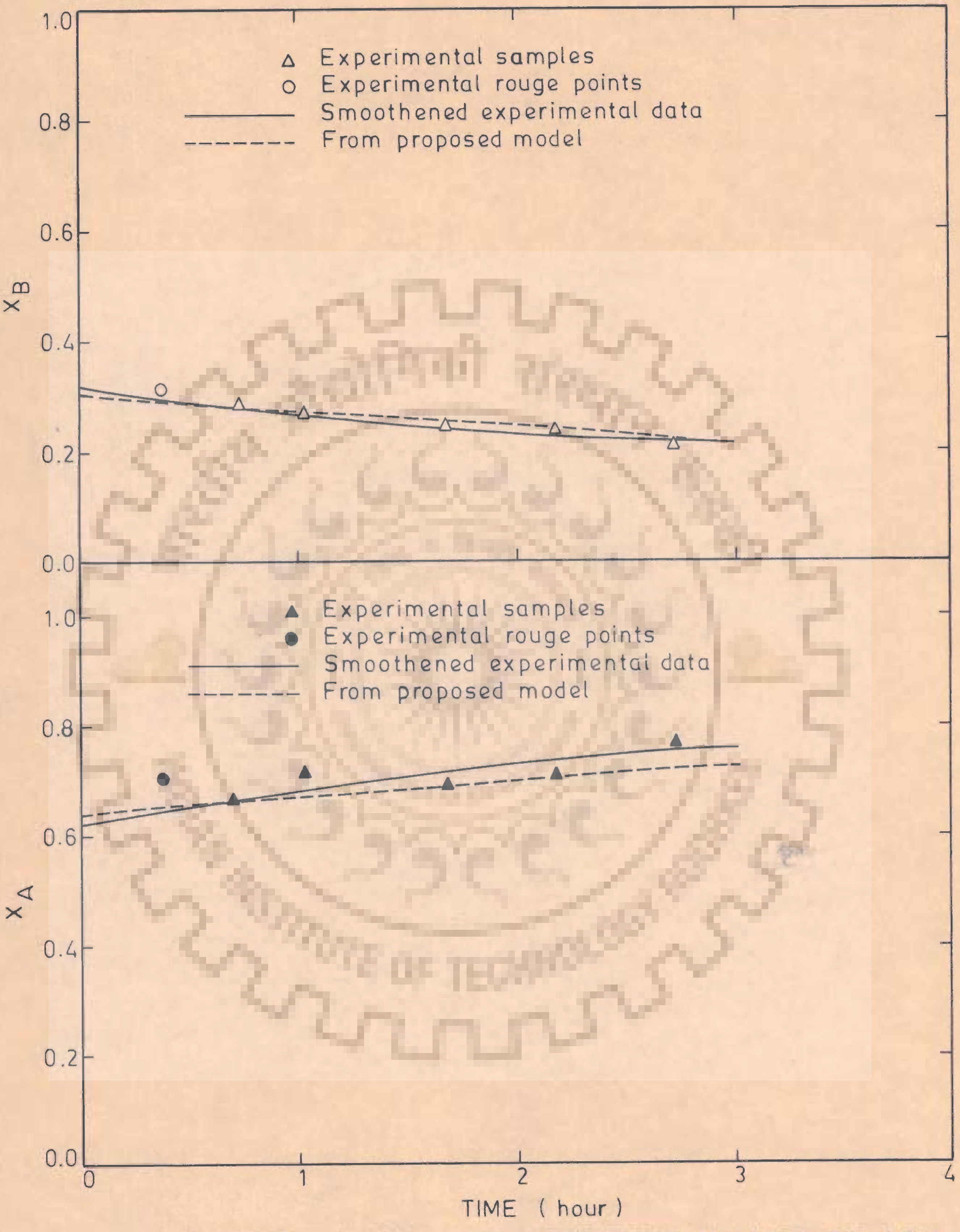


FIG. 4.1.6 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT EXIT WITH TIME. (TEMPERATURE = 315 °C, L H S V = 3.36 MOLE RATIO = 1.422)

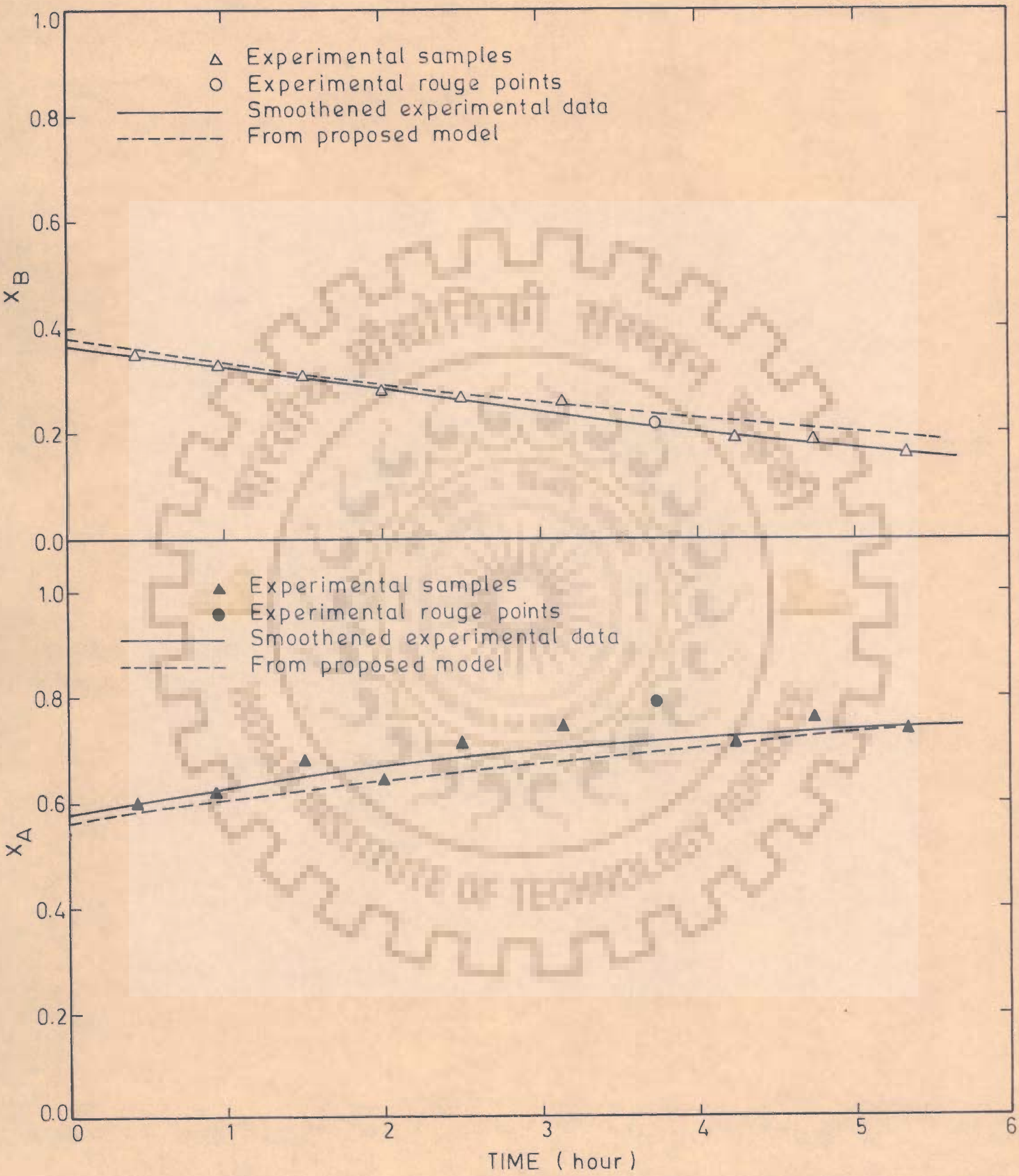


FIG. 4.1.7 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 345°C, LHSV = 4.256, MOLE RATIO = 1.865)

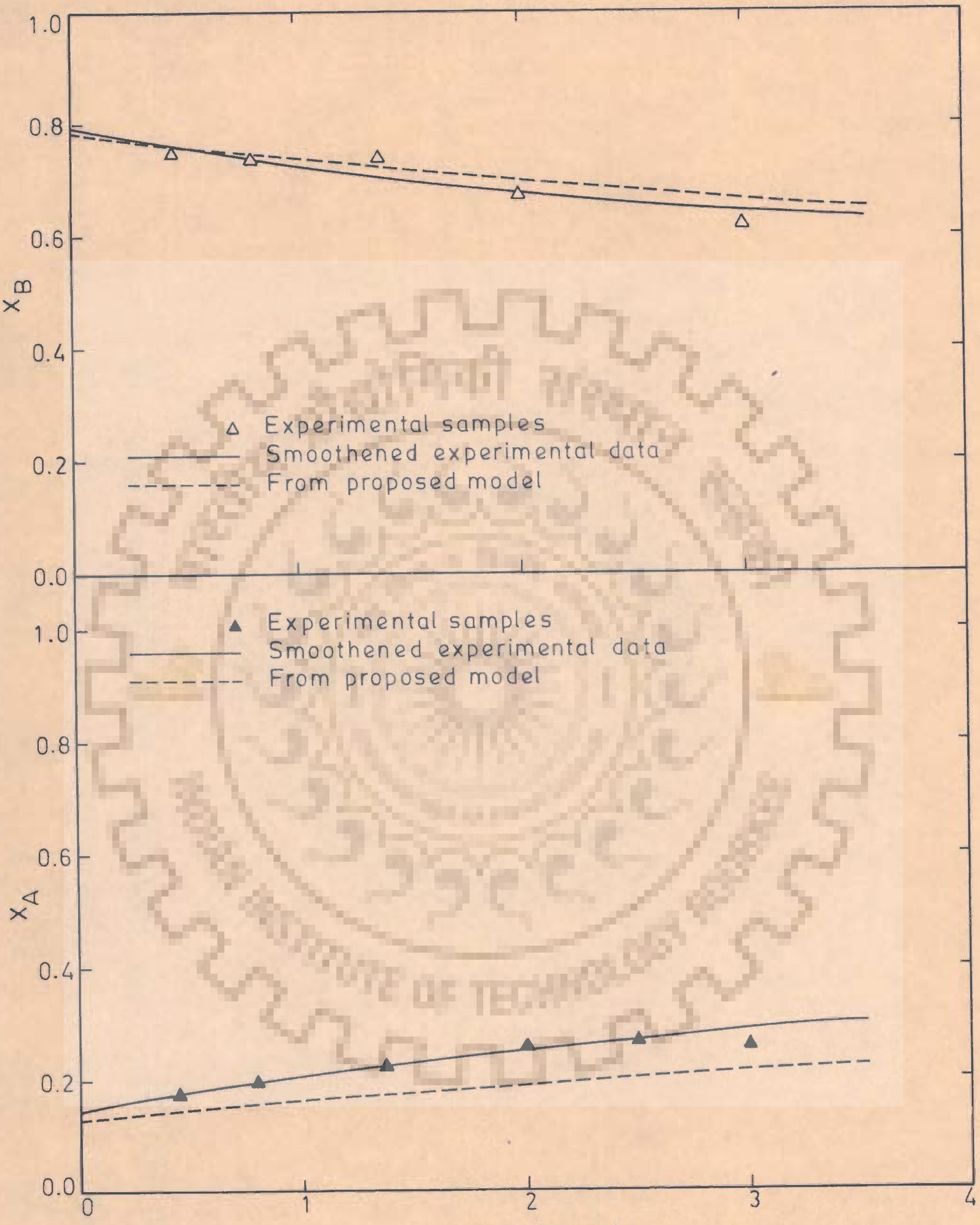


FIG. 4.1.8 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 410 °C, LHSV = 2.367, MOLE RATIO = 2.66)

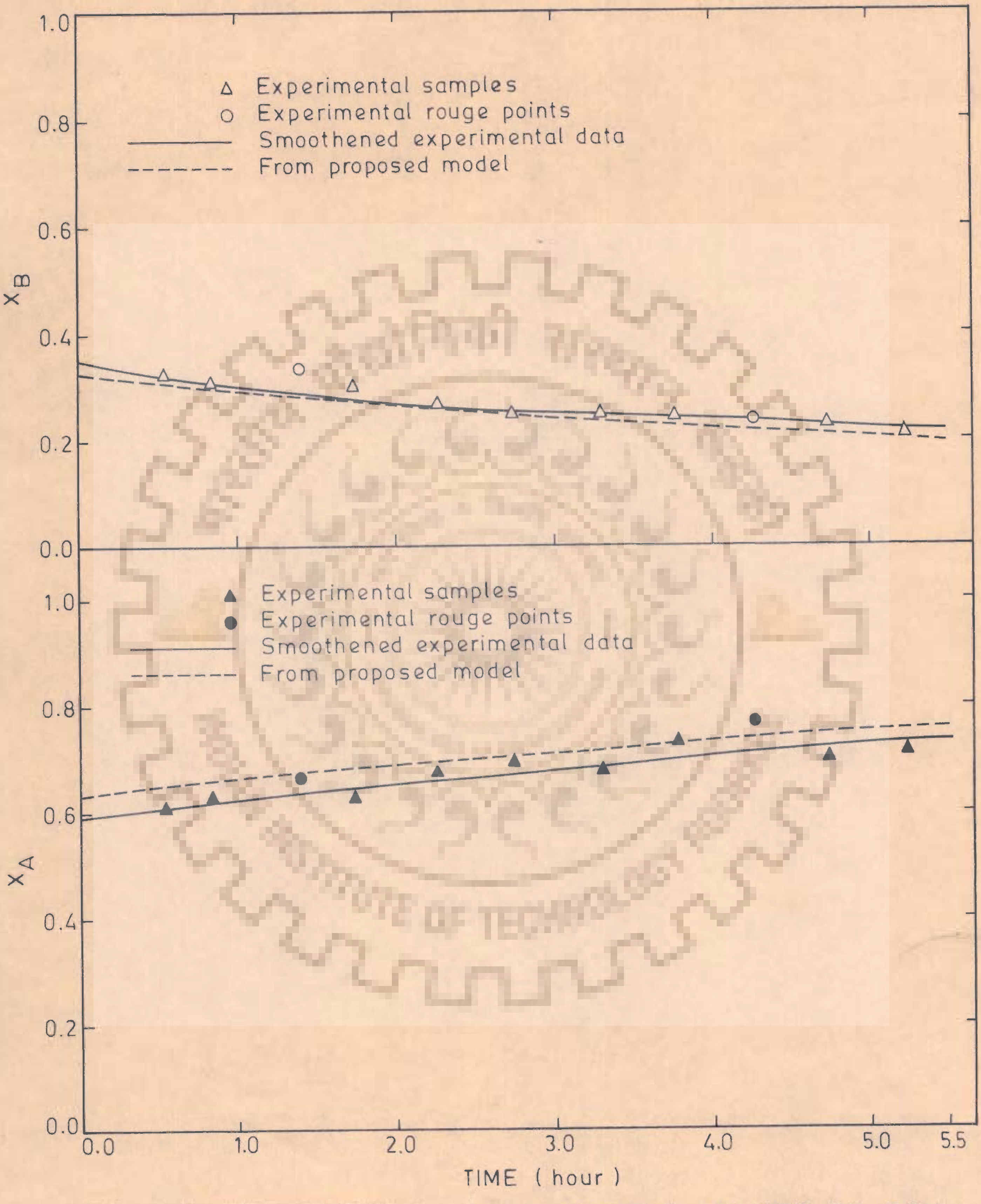


FIG. 4.1.9 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 370 °C, L H S V = 4.798, MOLE RATIO = 4.571)

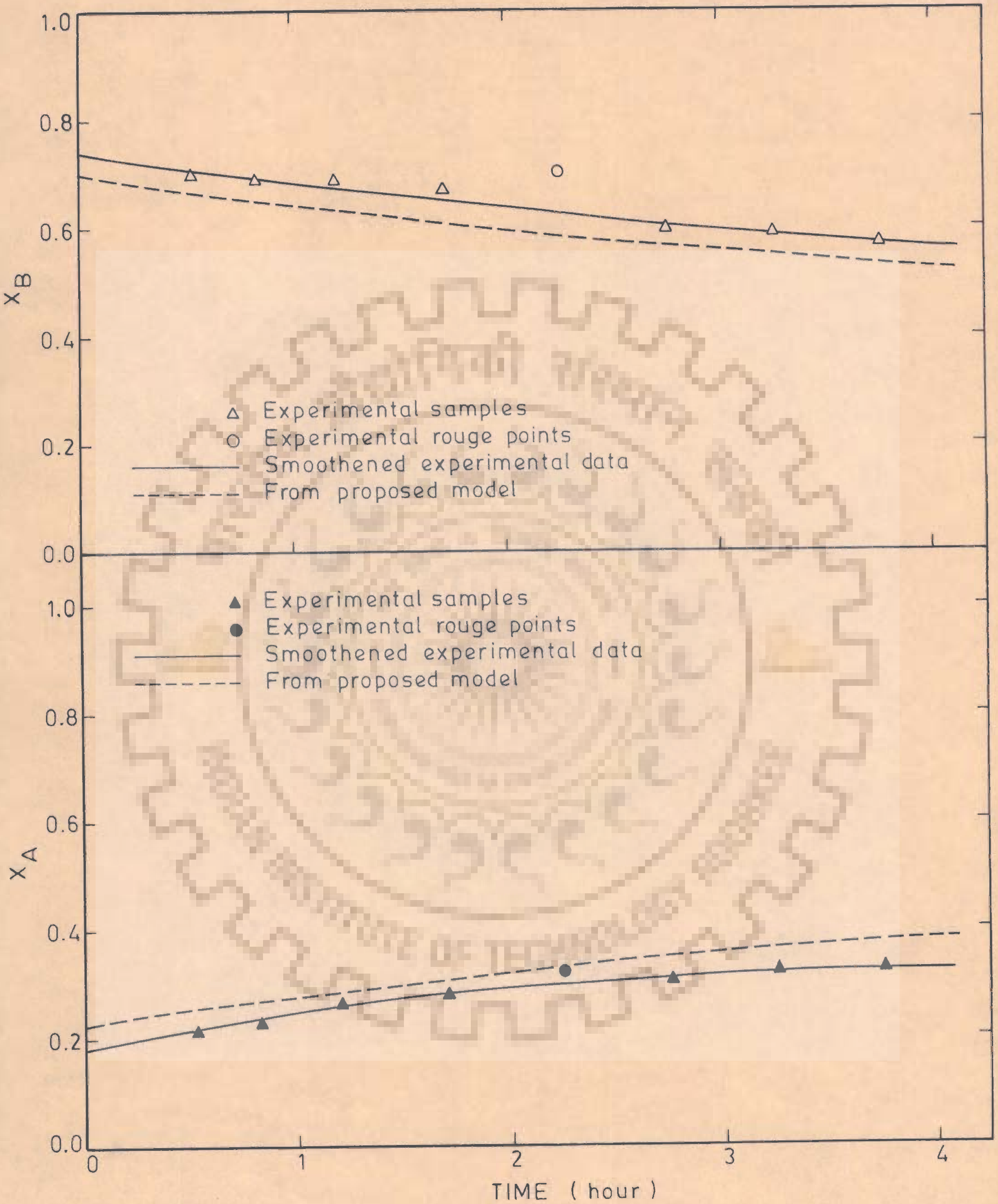


FIG. 4.1.10 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 435 °C, LHSV = 3.737, MOLE RATIO = 3.924)

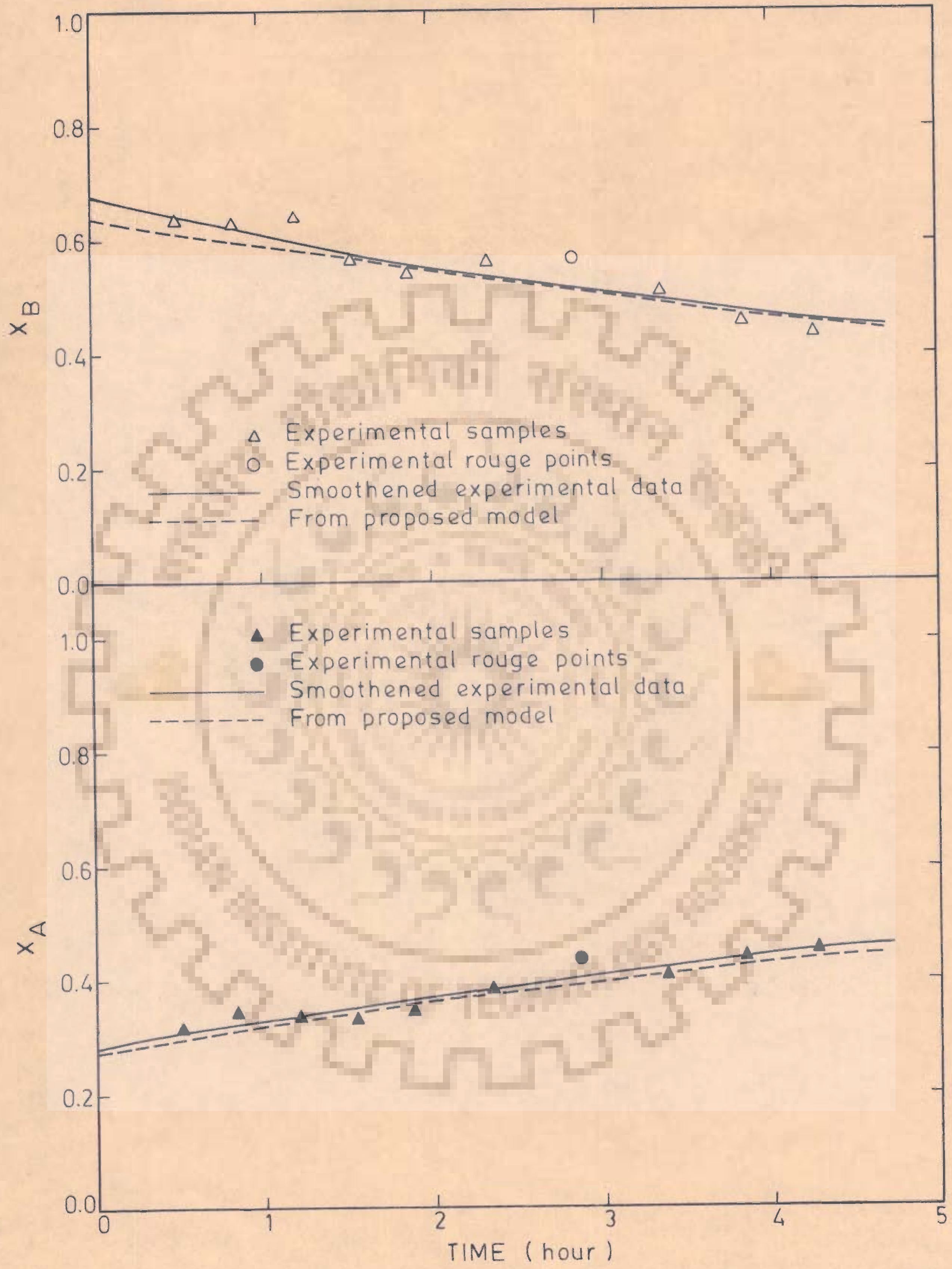


FIG. 4.1.11 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 385 °C, L H S V = 2.815, MOLE RATIO = 2.716)

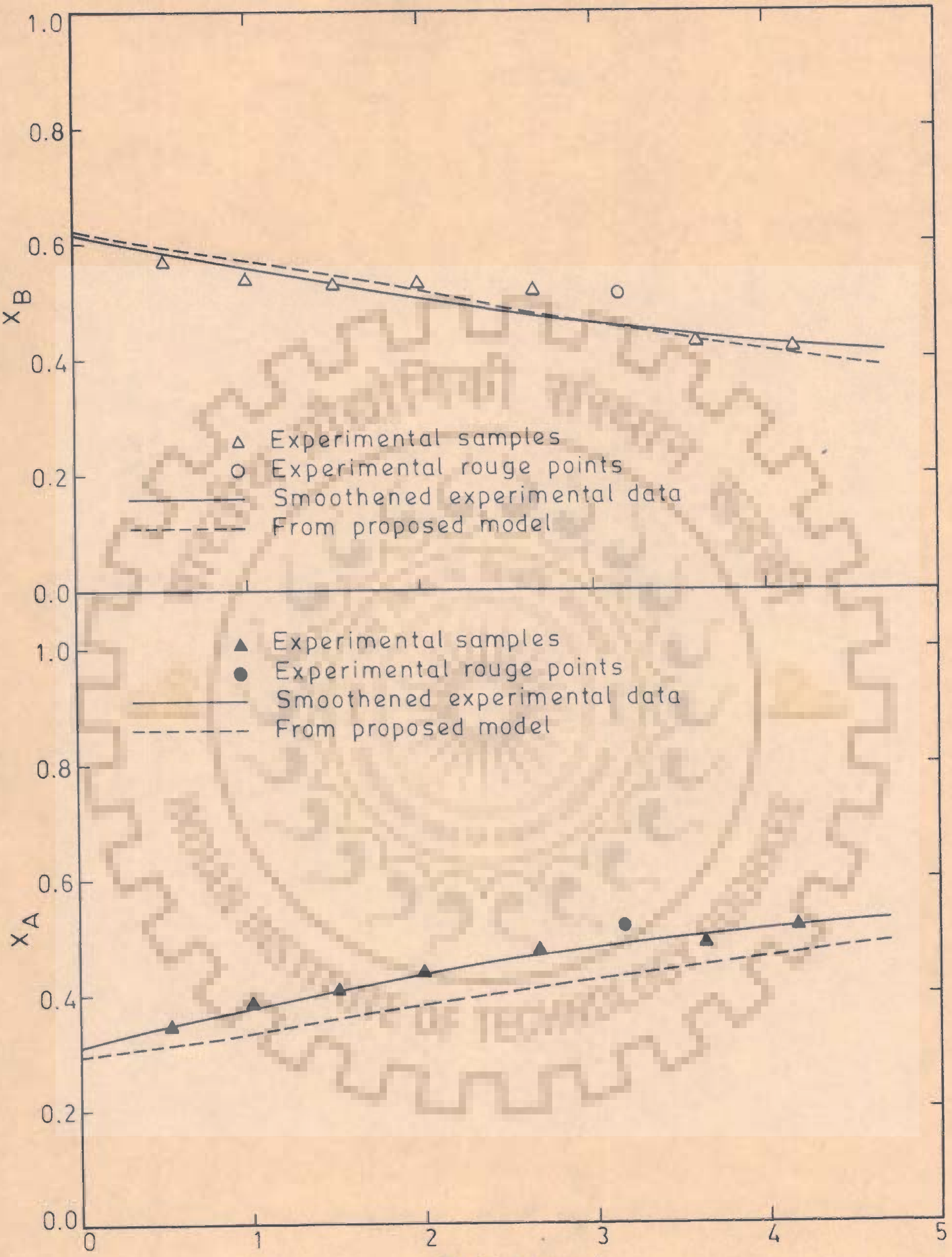


FIG. 4.1.12 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 360°C, LHSV = 2.76, MOLE RATIO = 1.304)

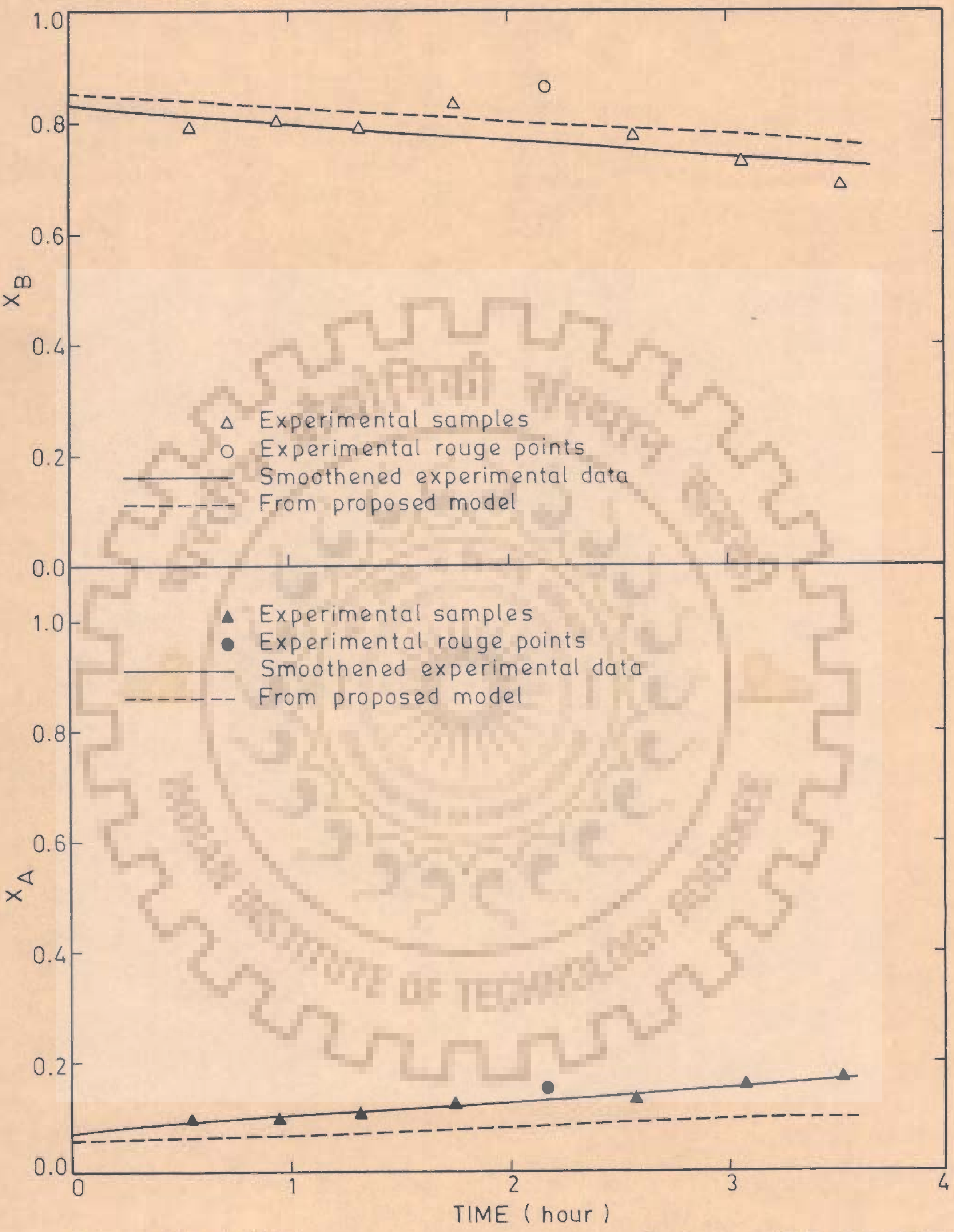


FIG. 4.1.13 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 420°C, L H S V = 1.666, MOLE RATIO = 3.082)

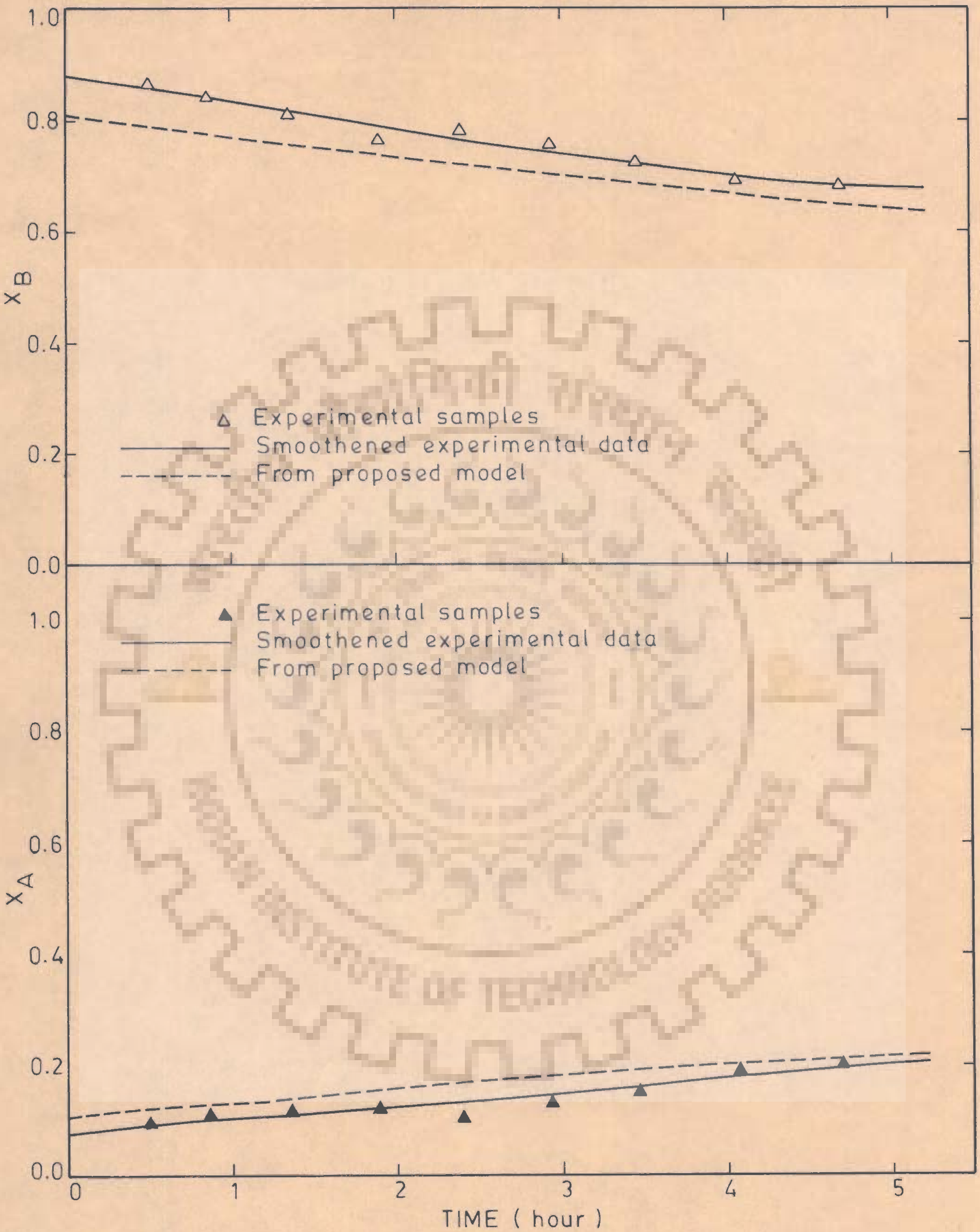


FIG. 4.1.14 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 425 °C, L H S V = 2.473, MOLE RATIO = 2.868)

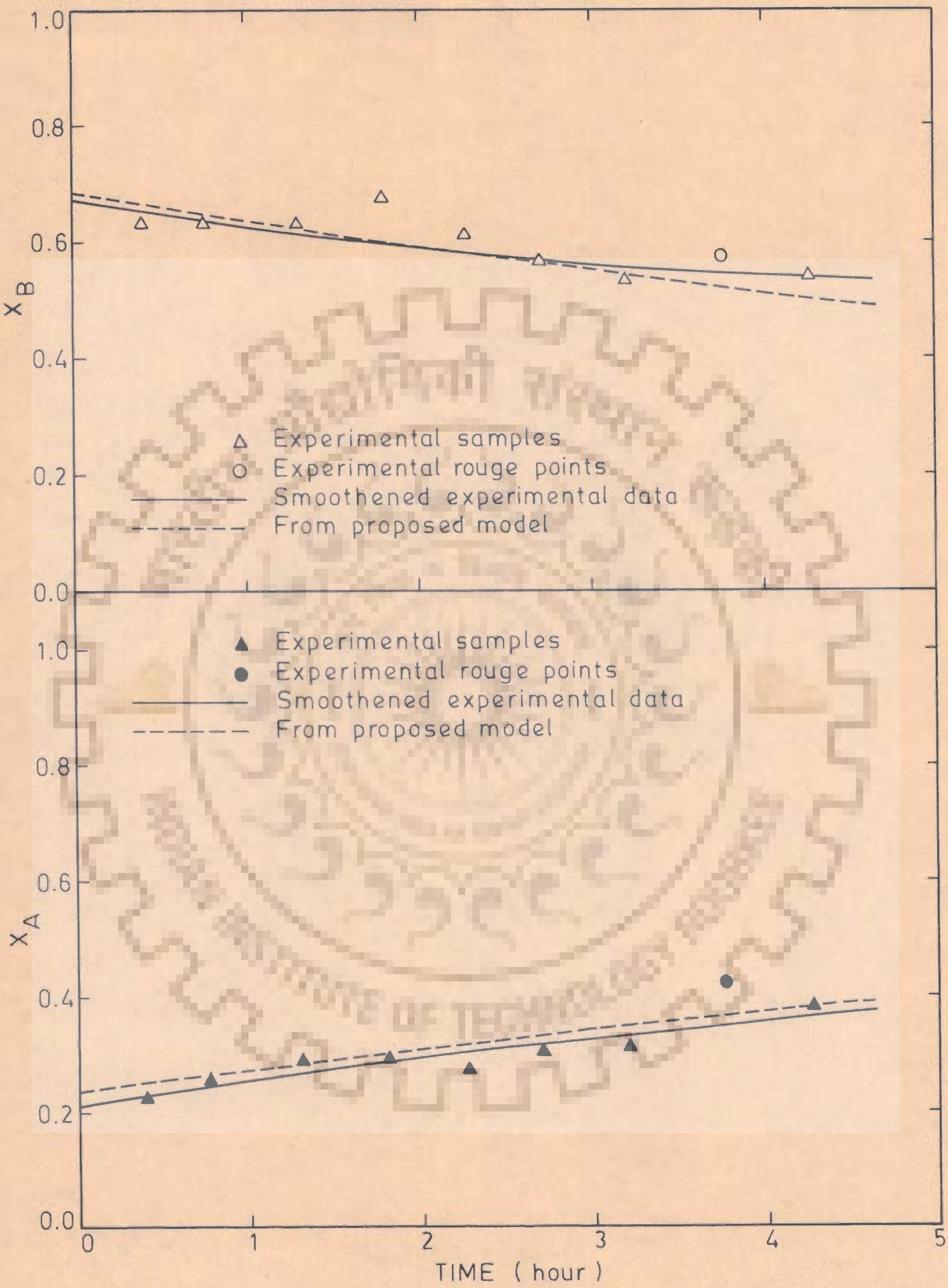


FIG. 4.1.15 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 400°C, L H S V = 2.721, MOLE RATIO = 2.79)

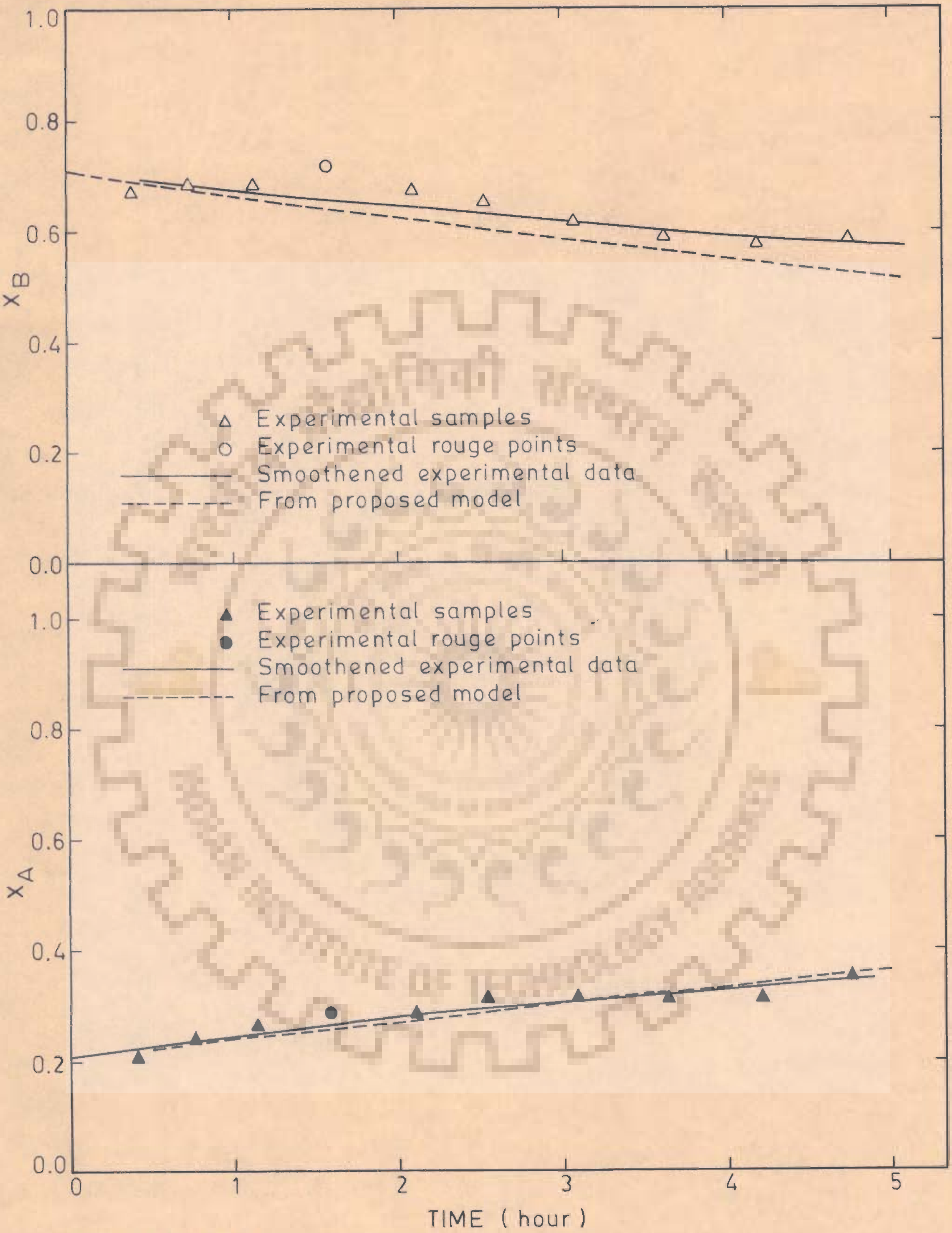


FIG. 4.1.16 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 400°C, L H S V = 2.473, MOLE RATIO = 2.831)

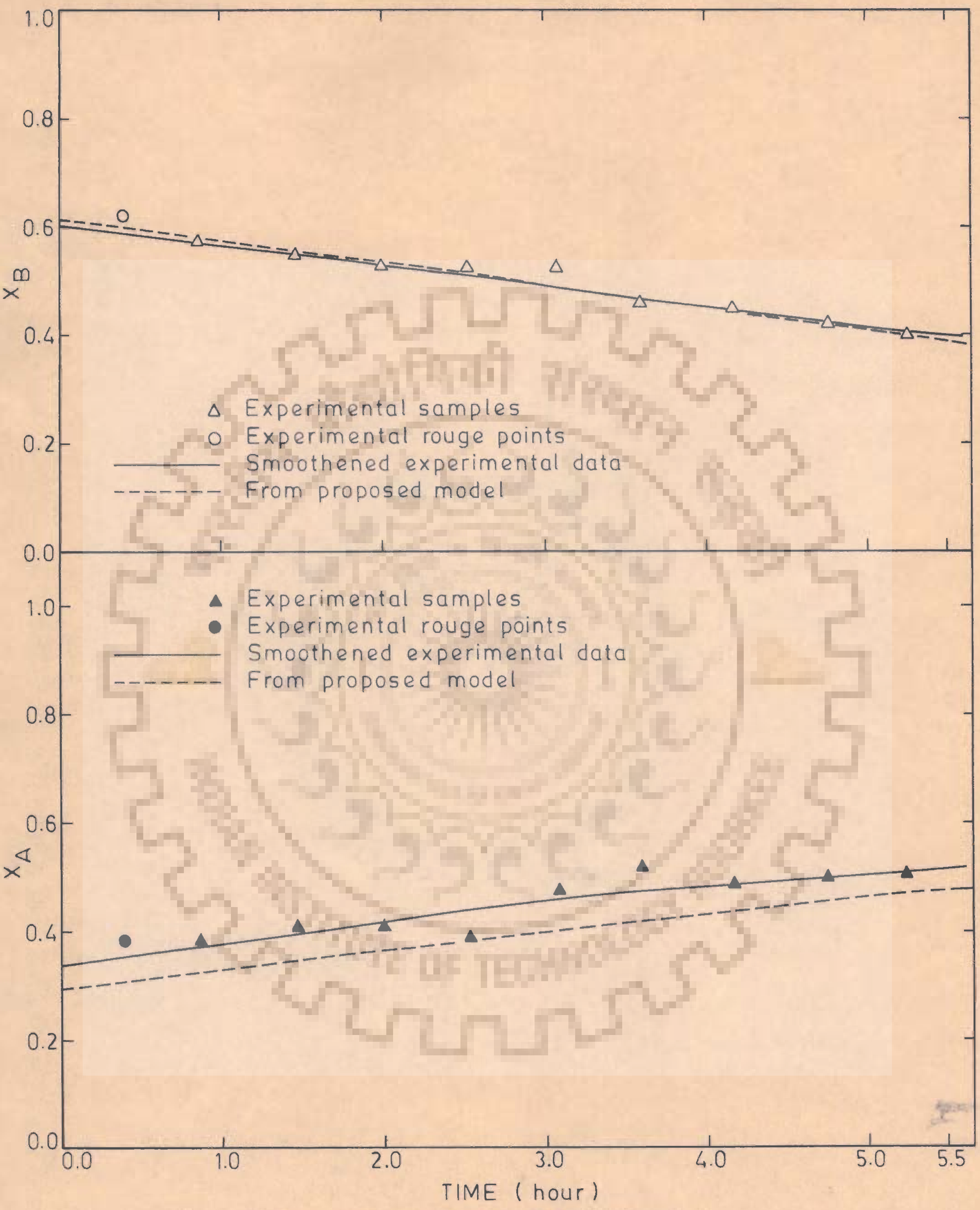


FIG. 4.1.17 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME. (TEMPERATURE = 340°C, L H S V = 1.904, MOLE RATIO = 1.229)

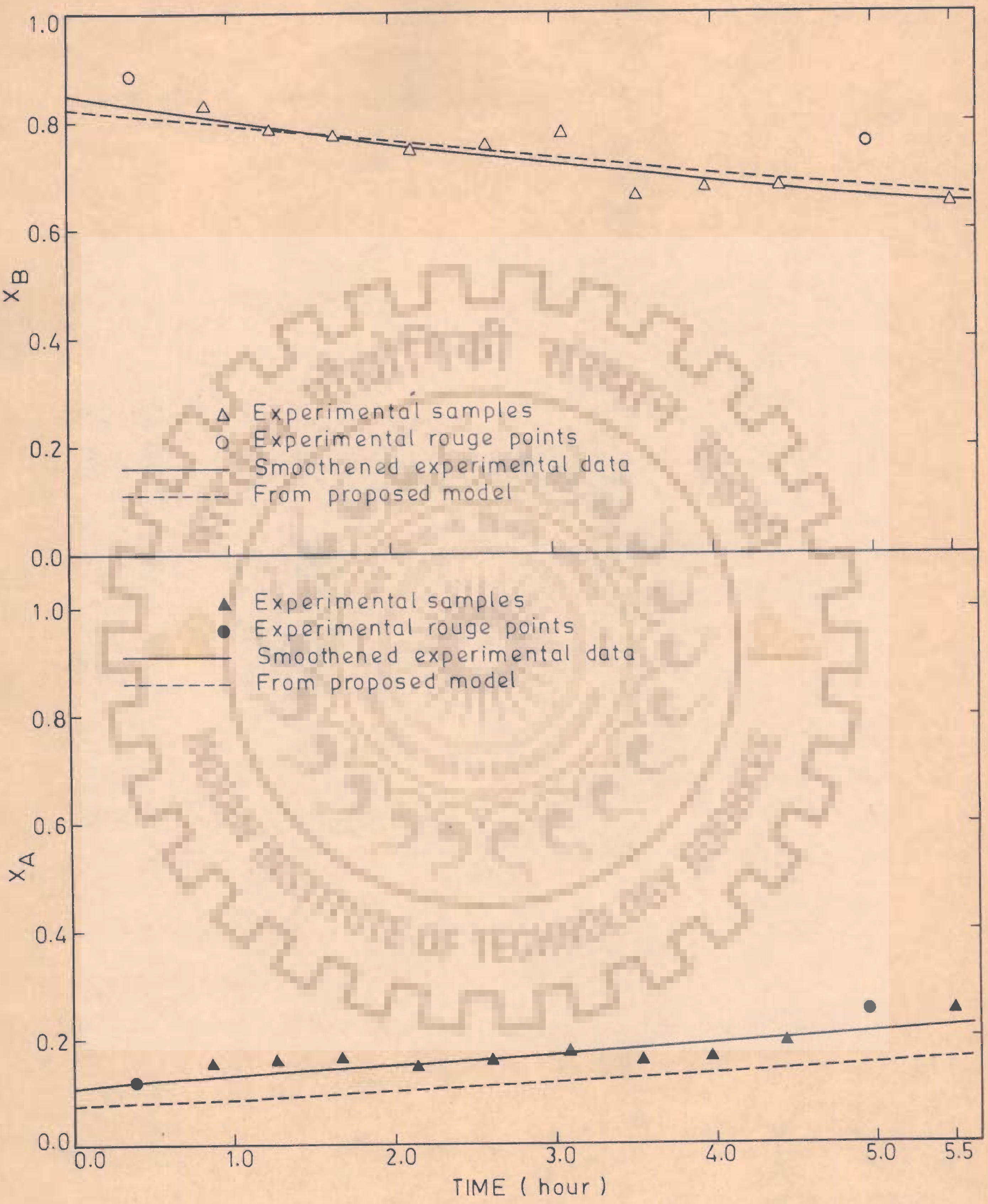


FIG. 4.1.18 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR EXIT WITH TIME (TEMPERATURE = 385 °C, L H S V = 1.529, MOLE RATIO = 1.659)

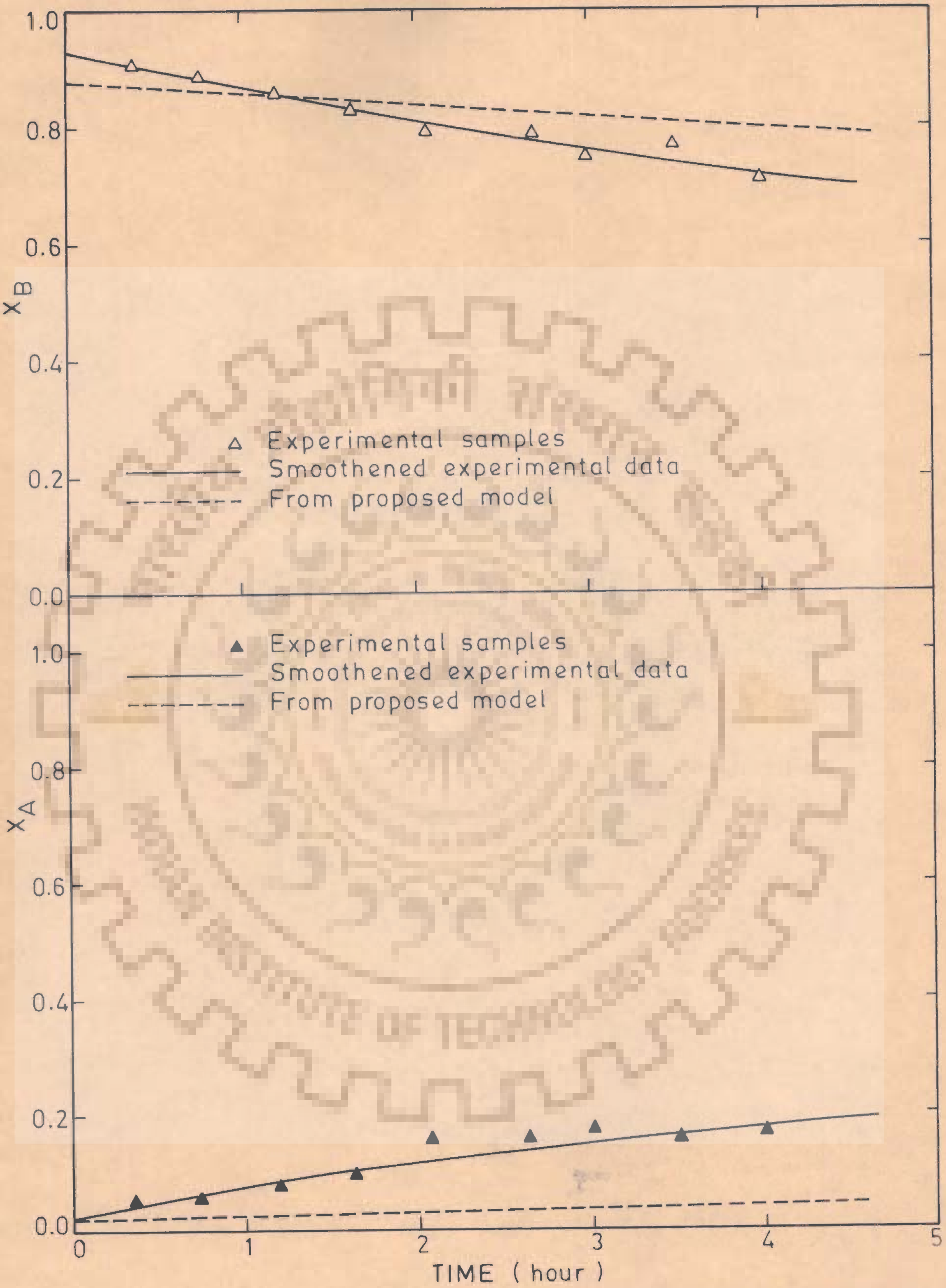


FIG. 4.1.19 EXPERIMENTAL AND PREDICTED VALUES OF CONVERSION AT REACTOR WITH TIME. (TEMPERATURE=405 °C LHSV=1.275 MOLE RATIO=1.743)

calculations. Table B-1 to B-19 also give percent conversion of cyclohexane to hydrocracked products and these values are obtained simply by subtracting from 100 the values of percent conversion to benzene and percent cyclohexane unconverted.

4.5 FORMULATION AND ESTIMATION OF APPARENT REACTION RATE CONSTANTS FOR UNDEACTIVATED CATALYST

The kinetic model used in the analysis of data for undeactivated catalyst is :

Dehydrogenation : $C_6H_{12} \xrightarrow{k_1} C_6H_6 + 3H_2$

Hydrocracking – $C_6H_{12} + 2H_2 \xrightarrow{k_2} 2C_3H_8$

or $C_4H_{10} + C_2H_6$

or $C_5H_{12} + CH_4$ (4.1)

The data was analysed assuming first-order irreversible kinetics for both the above reactions and plug flow behaviour in the reactor. These assumptions result in the following conversion - space velocity relationship for initial rate data :

$$X_B + \left[\frac{1 + \dfrac{(1+\gamma)\ (1+K)}{3-K}}{1+K}\right] \ln \left[1-(1+K)X_B\right] = - k_1 . \mathrm{CO} . \frac{1+K}{3-K} . \frac{W}{F} \tag{4.2}$$

The details of the assumptions and derivation are given in Appendix - C.

From the operating conditions F,W,P,T, and γ are known (reported in Appendix-A) and from the smoothened experimental data X_A, X_B and X_C (reported in Appendix-B) are known for undeactivated catalyst (at t = 0), and thus the apparent reaction rate constants k_1' and k_2' are calculated by using equation 4.2, since $K = k_2'/k_1' = (1-X_A-X_B)/X_B$. The apparent rate constants are tabulated in Appendix-D.

Sample calculations are given in Appendix-G.

4.6 ESTIMATION OF EXTERNAL AND INTERNAL MASS TRANSPORT EFFECTS

Kinetic analysis of heterogeneously catalysed fluid reactions is never complete unless the role of inter-and intra-particle heat and mass transfer rates is properly investigated. The average pore radius of the catalyst used in this investigation is quite small (32 A^o) and the reaction is highly endothermic (Δ H = 50.8 kcal/gmol). This necessitates a careful estimation of various mass and heat transfer rate parameters in order to find the intrinsic kinetic parameters.

4.6.1 Estimation of External Mass-Transfer Coefficient

The estimation of external mass transfer coefficient requires the values of catalyst pellet diameter, and density of gas mixture, bulk-diffusivity, viscosity and mass-velocity at operating conditions. From the above data Reynold's number is first calculated and then external mass transfer coefficient is estimated by evaluating j_D factor.

The bulk diffusivity of cyclohexane in hydrogen is calculated using Chapman-Enskog equation (77). Hydrogen is taken as the other component, even though some benzene is also present, because hydrogen is the predominant component for most of the experimental runs. The gas viscosities for cyclohexane and hydrogen were obtained from standard charts (68) for different temperatures. As the viscosities of hydrogen and cyclohexane are not too different, therefore, an arithmatic average value is taken for the reaction mixture. The density of the gas mixture at reactor inlet conditions is used in the calculations. It is assumed that the change in density is small since the changes in pressure, temperature and average molecular-weight of reaction mixture are not very significant. From the known values of catalyst pellet diameter and mass velocity, Reynold's number is calculated using the physical properties of reaction mixture as indicated above. The Colburn mass-transfer factor j_D is then estimated from standard charts (77). The value of j_D is used to calculate the mass transfer coefficient $k_m a$ by using the defining relationship for j_D as shown below

$$j_D = (k_m a)\left(\frac{\rho}{G}\right)\left(\frac{\mu}{\rho D_{AB}}\right)^{2/3} = f\left(\frac{d_p G}{\mu}\right)$$

The values of Reynold's number, Colburn mass-transfer factor j_D and external mass-transfer coefficient $k_m a$ are tabulated in Appendix-E for all the sets.

4.6.2 Estimation of Effective Diffusivity in Catalyst Pellet

The values of diffusivity, pellet-porosity and tortuosity-factor are required to estimate effective diffusivity of cyclohexane in the catalyst pellet. Since the mean pore radius is 32 $\overset{o}{A}$, the Knudsen diffusion will prevail and the Knudsen diffusivity for cyclohexane is obtained by standard method (77). The effective diffusivity D_e of cyclohexane in pellet is obtained by (77) :

$$D_e = D_K \frac{\epsilon}{\tau}$$

where D_K is Knudsen diffusivity, ϵ is porosity and τ is tortuosity factor of the pellet. For the catalyst used in this investigation, the porosity is found to be 0.504 and the reported value of tortuosity-factor (75) is 3.58.

The values of effective diffusivity of cyclohexane are given in Appendix-E for all sets.

4.6.3 Estimation of Cyclohexane Dehydrogenation Reaction Rate at the Inlet of Reactor

The rate of dehydrogenation of cyclohexane at the reactor inlet is given by :

$$\bar{r} = k_1' C_{A0} = k_1' \frac{P}{RT} \cdot \frac{1}{1+\gamma}$$

As the values of k_1', P, T and γ are already known, the values of reaction rate $\bar{r}$ were calculated and are tabulated in Appendix-E.

4.7 APPLICATION OF DIFFERENT CRITERION TO CONSIDER THE LIMITING INTER-AND INTRA-PARTICLE HEAT AND MASS TRANSFER RATES

After estimating the external mass-transfer coefficient, effective diffusivity and inlet reaction rates, different criterion were then applied to determine the limiting heat or mass transfer rate.

4.7.1 Criteria for External Mass Transport Effects

The criteria to determine whether the external mass transport effects are important or not, is given by (60) :

$$\frac{\bar{r}}{C_A . k_m a} = \frac{k_1'}{k_m a} < 0.15$$

Since the values of k_1' and $k_m a$ are known, the calculated values of the ratio are given in Appendix-E and in all the cases it is found that the value of the ratio is less than 0.15. This indicates quite clearly that the resistance due to external mass transfer is insignificant and can, therefore, be neglected. As the values of k_2' are always lower than k_1' the criteria will always be satisfied for hydrocracking reaction also.

4.7.2 Criteria for Internal Mass-Transport Effects :

The criteria for internal mass transport effects is given by (87) :

$$F_1 = \left[\frac{V'}{S_e} \right]^2 \cdot \frac{k_1' \rho_p}{D_e} < 1$$

where S_e is the external surface area of the catalyst pellet, V' is the volume of catalyst pellet and ρ_p is pellet density of catalyst. The values of these parameters are given in section 3.5. From the known values of catalyst properties, effective diffusity and k_1', the values of factor F_1 are computed and these are tabulated in Appendix-E. It is evident that in all the cases the values of the factor F_1 are more than one, except for very low reaction temperature, that is, for set No.1 and 6. This indicates that the resistance due to internal mass transport is significant and it must be taken into consideration while calculating the intrinsic rate constants from the experimental data.

4.7.3 Criteria for External Heat Transport Effects

The criteria for estimating the significance of the external heat transport effect is given by (59) :

$$F_2 = \frac{E}{R_g \, T_b^2} \, (T_s - T_b) < 0.15$$

where

$$T_b - T_s = \frac{0.7 \; (\Delta H) \; (C_b - C_s)}{C_p \cdot \rho}$$

$$= \frac{0.7 \; (\Delta H) \; \bar{r}}{C_p \cdot \rho \cdot k_m a}$$

and for dehydrogenation of cyclohexane ΔH is 50.8 kcal/gmol, specific heat of reaction mixture is 3.25 cal/g.°C and $\frac{E}{R_g}$ is approximated (40) as 15,200 °K.

Since the values of $k_m a$ and $\bar{r}$ are known, the values of $(T_b - T_s)$ and the factor F_2 can be calculated for all the sets. These values are tabulated in Appendix-E and it is seen that in all the cases the values of F_2 is less than 0.15 indicating that the external heat transfer resistance is negligible for all the experimental runs. Further, the value of $(T_b - T_s)$ indicate the difference in bulk and surface temperature and the maximum value is only 1.76°C which is well within the limits of experimental errors in temperature measurement.

4.7.4 Criteria for Non-Isothermal Pellet

The criteria for estimating the Non-isothermality of catalyst pellet is given by (1) :

$$F_3 = \frac{\bar{r} . \rho_p . R^2 . (\Delta H)}{T_b . k_e} . \left(\frac{E}{R_g . T_b} \right) < 0.75$$

The effective thermal conductivity for the catalyst pellet used in this investigation is approximated as 1.04 cal/hr. cm. K (77). For the known values of constants E/R_g, ΔH and ρ_p, and the calculated values of $\bar{r}$ and T_b the factor F_3 is calculated and the same is tabulated in Appendix-E. All the values are less than 0.75. It is, therefore, clear that the catalyst pellets can be considered as isothermal.

4.7.5 Criteria for Maximum Temperature Gradient in Catalyst Pellet

The maximum temperature gradient in catalyst pellet is given by (14) :

$$\beta_m = \frac{(\Delta H) . D_e . C_s}{k_e . T_s}$$

As the external mass and heat transfer resistances are negligible, we can take the values of surface concentrations and temperatures as those of bulk concentrations and temperatures respectively. Thus, we have

$$\beta_m = \frac{(\Delta H) . D_e . C_b}{k_e . T_b}$$

The values of factor β_m are calculated for all the sets and is tabulated in Appendix-E. The maximum temperature gradient is found to be 2°C and this further confirms that the catalyst pellet is essentially isothermal.

4.8 SIGNIFICANCE OF HEAT AND MASS TRANSPORT LIMITATIONS

From the above analysis it can be concluded that -

(1) the external mass-and heat-transfer limitations are negligible,

(2) the difference between bulk and surface temperature is insignificant and the catalyst pellet is essentially isothermal, and

(3) the internal mass transport limitation is significant and it must be considered while estimating the intrinsic rate constants.

4.9 ESTIMATION OF EFFECTIVENESS FACTORS AND INTRINSIC RATE CONSTANTS

The computed values of apparent rate constants $k_1^{'}$ and $k_2^{'}$, physical properties of catalysts and effective diffusivity of reactant are used to calculate the effectiveness factors η_1 and η_2, and intrinsic rate constants k_1 and k_2 following the procedure given in Appendix-C. Tables D-1 and D-2, Appendix D, show the apparent and intrinsic rate constants and effectiveness factors at different temperatures for dehydrogenation and hydrocracking reactions, respectively. The values of $k_1^{'}$, $k_2^{'}$, k_1 and k_2 obtained from experimental measurements at very low or very high cyclohexane conversion to benzene which are not considered very accurate due to the reasons explained in Appendix-C are marked by asterisk in Table D-1 and D-2 and these values of k_1 and k_2 are not used in the estimation of activation energies. These values belong to sets No.1, 14, 18 and 19.

Activation energy for dehydrogenation and hydrocracking rate constants are determined by assuming Arrhenius temperature dependance. Fig. 4.2 shows the plot of ln k_1 and ln k_2 as a function of 1/T and the straight lines are drawn by regression analysis of all data points except

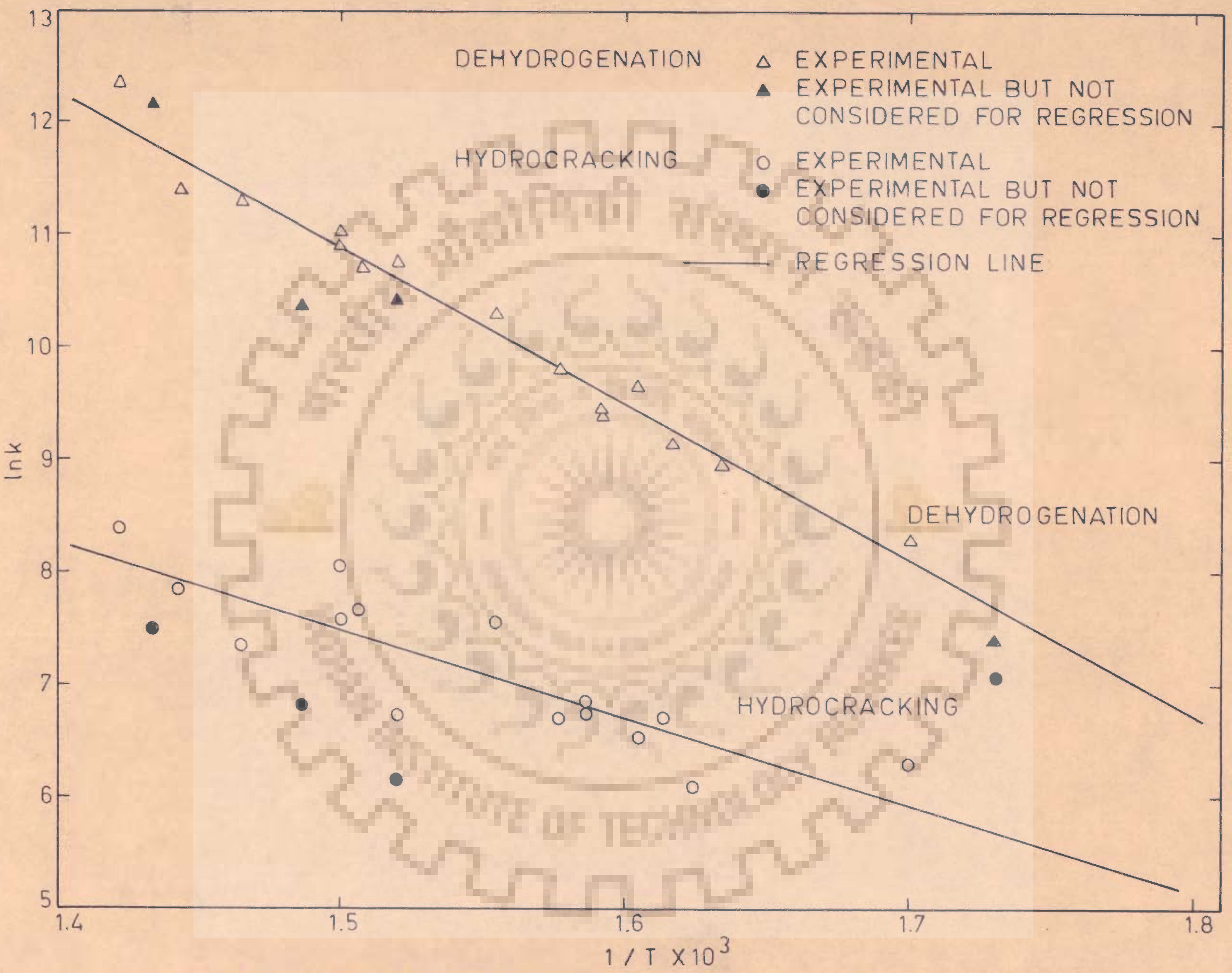


FIG. 4.2 ARHENIUS PLOT OF DEHYDROGENATION AND HYDROCRACKING RATE CONSTANTS WITH TEMPERATURE.

those encircled which were not considered very accurate for reasons explained earlier. The temperature dependance of rate constants obtained from the regression analysis is

$$\text{Dehydrogenation : } k_1 = \exp\left(31.57 - \frac{13,800}{T}\right) \qquad (4.7)$$

$$\text{Hydrocracking : } k_2 = \exp\left(18.97 - \frac{7,654}{T}\right) \qquad (4.8)$$

CHAPTER - 5

DEVELOPMENT OF KINETIC AND DEACTIVATION MODEL

In the kinetic analysis presented in previous Chapter, the intrinsic rate constants are calculated for dehydrogenation and hydrocracking reactions for undeactivating catalyst (at t= 0) assuming the catalyst activity to be unity throughout the bed. This is a safe assumption at the start of the run, but due to deposition of poisons on the catalyst, the catalyst activity will fall with time and will also change along the bed. The fall in activity will be maximum at the inlet of the reactor and minimum at the reactor exit since the reactant concentration, which also causes deactivation is maximum at the reactor inlet. Thus the complete kinetic model is :

$$\text{Dehydrogenation : } \quad C_6H_{12} \xrightarrow{k_1} C_6H_6 + 2H_2$$

$$\text{Hydrocracking : } \quad C_6H_{12} + 2H_2 \xrightarrow{k_2} 2C_3H_8$$

$$\text{or } C_4H_{10} + C_2H_6$$

$$\text{or } C_5H_{12} + CH_4$$

$$\text{Deactivation: } \quad C_6H_{12} \xrightarrow{k_d} \text{Catalyst poison (coke)} \qquad (5.1)$$

It is assumed that the loss of cyclohexane due to deactivation reaction is negligible, but the changes in catalyst activity due to the deposition of the poisons is quite significant.

In chapter 4 it has been concluded that only internal mass transfer limitations needs to be considered while analysing the experimental rate data. The values of intrinsic rate constants k_1 and k_2 for dehydrogenation and hydrocracking reactions respectively and their temperature dependence has already been reported in chapter 4.

5.1 DEACTIVATION MODEL DEVELOPMENT :

It has been assumed that the coke formation on catalyst will result in loss of catalyst activity for only dehydrogenation reaction involving platinum sites and not for hydrocracking reaction which takes place on acidic (alumina) sites. This is a valid assumption since cracking reactions are not very specific as far as the nature of catalyst surface is concerned. This assumption has been recently used by Mahoney (55) to successfully analyse his data for dehydrocyclization of n - heptane on platinum - on - alumina reforming catalyst. Thus, the rates for dehydrogenation and hydrocracking reactions with catalyst deactivation can be represented as follows :

$$r_1 = k_1 \eta_1 a C_A \tag{5.2}$$

$$r_2 = k_2 \eta_2 C_A \tag{5.3}$$

Where a is the activity of the catalyst which has been assumed to be unity for undeactivated catalyst at $t = 0$, and in general, is a function of time-on-stream and position in the bed. It may be noted that the effectiveness factors used in the equations (5.2) and (5.3) correspond to those for undeactivated catalyst.

The variation of activity with position is primarily due to the fact that the rate of catalyst deactivation depends on reactant (cyclohexane) concentration and cyclohexane concentration decreases as it gets converted in the reactor into benzene and hydrocracked products. Continuity equations, similar to those used by Lambrecht, Nussey and Froment (49) can be written for benzene, hydrocracking products and catalyst activity, and these can be solved simultaneously using proper form of rate equations for dehydrogenation equation (5.2), hydrocracking equation (5.3), and activity change. However, simultaneous solution of these non-linear partial differential equations is quite time consuming even on a fast computer as observed by Lambrecht et al. The works of Khang and Levenspiel (45) and Wolf and Peterson (89) for similar reaction systems indicate that the change in reactant concentration with catalyst bed position is much faster and predominant as compared to the change in concentration with time at any bed position. Thus a simplified procedure is adopted to solve the continuity equations. This assumes a quasi-steady state behaviour with respect to catalyst activity for dehydrogenation reaction while solving the differential equation describing material balance for benzene and cyclohexane in the reactor, that is,

$$dX_B = k_1 \eta_1 C_A \, a \, d\,(W/F) \tag{5.4}$$

and

$$dX_A = -(k_1 \eta_1 a \, C_A + k_2 \eta_2 C_A) \, d(W/F) \tag{5.5}$$

The change in activity with time at different positions in reactor bed are then computed with the help of deactivation rate equation given below :

$$- r_d = - \frac{da}{dt} = k_d \, a^m \left(\frac{C_A}{C_H} \right) \tag{5.6}$$

For an appropriate time interval, at any position in the bed, the values of reactant concentration C_A and C_H can be considered as constant and decrease in catalyst activity at that position computed. After obtaining the new activity profile of catalyst in the reactor bed, the material balance equations (5.4) and (5.5) are solved using these activity values. The new concentration profiles are then used in equation (5.6) to compute decay in catalyst activity for the next time interval at any given position of the catalyst bed in the reactor. Alternate solution of material balance equations and catalyst deactivation rate equation continues till the end of the run. For these computations, a time interval of 5 minutes was choosen to obtain the desired accuracy with minimum computation time. The details of computation on accuracy are discussed in the next chapter entitled Discussion and Results.

5.2 ESTIMATION OF DEACTIVATION PARAMETERS :

Assumed values of m and k_d were used to calculate the cyclohexane and benzene mole fractions at reactor exit at different times by solving the material balance equations and catalyst deactivation rate equation alternately, as described earlier. For different operating conditions, the solution was carried out on IBM 370/145 of the Oil and Natural Gas Commission, Dehradun, and DEC 2050 system of Regional Computer Centre, Chandigarh using fourth order Runge Kutta method for numerical integration of equations (5.4) to (5.6). It may be noted from equations (5.4) and (5.5) that

$$-\frac{dX_A}{dX_B} = 1 + \frac{k_2 \eta_2}{k_1 \eta_1 a} = 1 + \frac{K}{a} \qquad (5.7)$$

For (i + 1) th bed increment, the above equation can easily be integrated by assuming average catalyst activity for that bed increment to give -

$$(X_A)_i - (X_A)_{i+1} = \left[1 + \frac{k}{(a_{avg})_{i+1}}\right]\left[(X_B)_{i+1} - (X_B)_i\right] \qquad (5.8)$$

where $$\frac{1}{(a_{avg})_{i+1}} = \frac{1}{2}\left[\frac{1}{a_i} + \frac{1}{a_{i+1}}\right]$$

Fraction of cyclohexane converted to hydrocracked products is calculated by cyclohexane material balance, that is,

$$X_C = 1 - X_A - X_B$$

This is an initial value type numerical integration with 40 equal increments in the catalyst bed from reactor inlet to exit, and for this case the initial values are given by :

at the inlet of the reactor : $X_A = 1$, $X_B = 0$, $X_C = 0$

and at $t = 0$, $a = 1$ for all positions in the bed. The accuracy of computation is discussed in the next chapter entitled Discussion of Results.

The optimal values of k_d and m were obtained for each set by minimizing the variance of percentage error between calculated and the experimental values of fraction of cyclohexane converted into benzene, at the reactor exit conditions, at different times-on-stream for each set where the percentage error is defined as :

$$\text{Percentage error} = \frac{(\text{experimental value})-(\text{calculated value})}{(\text{experimental value})} \times 100 \qquad (5.9)$$

These experimental values were obtained from smoothened experimental data and are tabulated in Appendix-B as already discussed. The reason for selecting the minimization of variance for benzene percentage error was that for most of the samples the concentration of benzene was quite high and the accuracy for chromatographic analysis for benzene is more than cyclohexane as explained in section 3.3 on analysis of liquid product. The values of k_d and m were optimized to within ± 5 and ± 2 percent of their optimum value, respectively. The optimal values of k_d and m thus obtained are tabulated in Table 5.1. The calculated values of fraction of cyclohexane remained unconverted and that converted into benzene, and corresponding variance of percentage error are also tabulated in Appendix-B.

Complete analysis was also carried out for the equation :

$$- r_d = - \frac{da}{dt} = k_d \, a^m \, C_A \qquad (5.10)$$

taking into consideration, the concentration of cyclohexane only instead of the ratio of cyclohexane to hydrogen C_A/C_H, used in equation (5.6).

Table 5.1: Experimental rate constants, effectiveness factors, Thiele parameters, and optimized deactivation parameters m and k_d

SET NO.	TR	k_1	η_1	k_2	η_2	ϕ_1	ϕ_2	k_d	m
1	310	1700	0.767	1190	0.820	0.755	0.630	0.408	1.405
2	355	12000	0.423	924	0.855	1.970	0.547	0.550	1.756
3	355	12700	0.413	864	0.865	2.021	0.526	0.779	1.548
4	350	15200	0.381	646	0.882	2.221	0.458	0.433	1.280
5	390	43300	0.241	2170	0.738	3.728	0.829	0.797	1.941
6	315	3970	0.621	542	0.906	1.146	0.419	0.508	1.383
7	345	9300	0.467	825	0.842	1.738	0.518	0.555	1.129
8	410	81900	0.187	1500	0.800	5.020	0.679	2.639	3.113
9	370	29500	0.290	1900	0.757	3.074	0.781	1.075	2.321
10	435	224000	0.116	4440	0.608	8.267	1.186	2.330	2.720
11	385	45400	0.240	839	0.868	3.795	0.516	1.324	1.766
12	360	16650	0.370	800	0.872	2.311	0.506	0.909	2.553
13	420	88100	0.180	2600	0.712	5.207	0.895	1.658	2.049
14	425	197000	0.122	1810	0.795	7.787	0.689	2.372	1.742
15	400	59400	0.208	3100	0.678	4.307	0.984	0.989	1.975
16	400	57550	0.210	1900	0.761	4.240	0.771	0.836	2.305
17	340	7600	0.507	416	0.925	1.570	0.368	0.433	1.257
18	385	33900	0.270	469	0.920	3.278	0.386	1.191	1.623
19	405	47500	0.330	932	0.867	3.822	0.518	4.527	1.927

Table 5.2: Calculated rate constants, effectiveness factors, Thiele parameters, and deactivation parameters - as obtained from the proposed model

SET NO.	TR	k_1	η_1	ϕ_1	k_2	η_2	ϕ_2	k_d	m
1	310	2709	0.696	0.935	346	0.9[illegible]9	0.334	0.318	1.190
2	355	14770	0.388	2.181	886	0.862	0.534	0.681	1.495
3	355	14770	0.388	2.181	886	0.862	0.534	0.681	1.495
4	350	12380	0.417	1.998	803	0.873	0.509	0.629	1.451
5	390	47100	0.235	3.897	1686	0.776	0.737	1.145	1.884
6	315	3313	0.659	1.034	387	0.932	0.353	0.348	1.215
7	345	10350	0.448	1.827	727	0.883	0.484	0.580	1.410
8	410	86630	0.177	5.285	2364	0.720	0.873	1.506	2.174
9	370	24660	0.313	2.819	1177	0.828	0.616	0.857	1.644
10	435	176800	0.127	7.550	3511	0.649	1.064	2.074	2.600
11	385	40210	0.252	3.601	1544	0.789	0.706	1.067	1.819
12	360	17570	0.361	2.380	975	0.851	0.561	0.736	1.542
13	420	115900	0.155	6.114	2780	0.692	0.947	1.716	2.337
14	425	133700	0.145	6.566	3007	0.677	0.985	1.829	2.422
15	400	55040	0.219	4.212	1840	0.762	0.770	1.228	1.952
16	400	55040	0.219	4.212	1840	0.762	0.770	1.228	1.952
17	340	8627	0.480	1.668	657	0.892	0.460	0.535	1=371
18	385	40210	0.252	3.601	1544	0.789	0.706	1.067	1.819
19	405	74640	0.190	4.906	2176	0.735	0.838	1.408	2.097

The variance in general were more with equation (5.10) than those obtained with equation (5.6) for most of sets. But more important reason for rejecting the use of equation (5.10) was the fact that it assumes that the deactivation phenomena is independent of hydrogen concentration. This assumption is not true because beneficial effect of high hydrogen concentration in reducing the catalyst deactivation rate in reforming process is well established. Accordingly, the concentration ratio C_A/C_H is also used by Lambrecht et al. (49), and Wolf and Peterson (89). Therefore, only equation (5.6) is used in the final deactivation model.

5.2.1 Estimation of Arrhenius Equation for Deactivation Rate Constants

The optimized values of k_d were used to make an Arrhenius plot as shown in Fig. 5.1 between ln k_d and 1/T. The four points belonging to sets number 1, 14, 18 and 19, which were neglected for regression in section 4.9 for dehydrogenation and hydrocracking rate constants for reasons explained earlier, were again not considered for regression analysis of deactivation rate constant data. The points 1 and 19 are again found to deviate from the straight line significantly, Fig. 5.1, which supports the reasoning given earlier for neglecting them for evaluating the Arrhenius constants for dehydrogenation and hydrocracking rate constants. The deviation of k_d values corresponding to sets 14 and 18 was not too much because the experimental conversion values for various time-on-stream remained within the limits imposed by the accuracy criteria, as explained in Appendix-C, except for initial one hour. The straight line is drawn in Fig. 5.1 using the constants determined by regression analysis, and the relationship is given by :

$$k_d = \exp\left(9.4751 - \frac{6,192}{T}\right) \qquad (5.11)$$

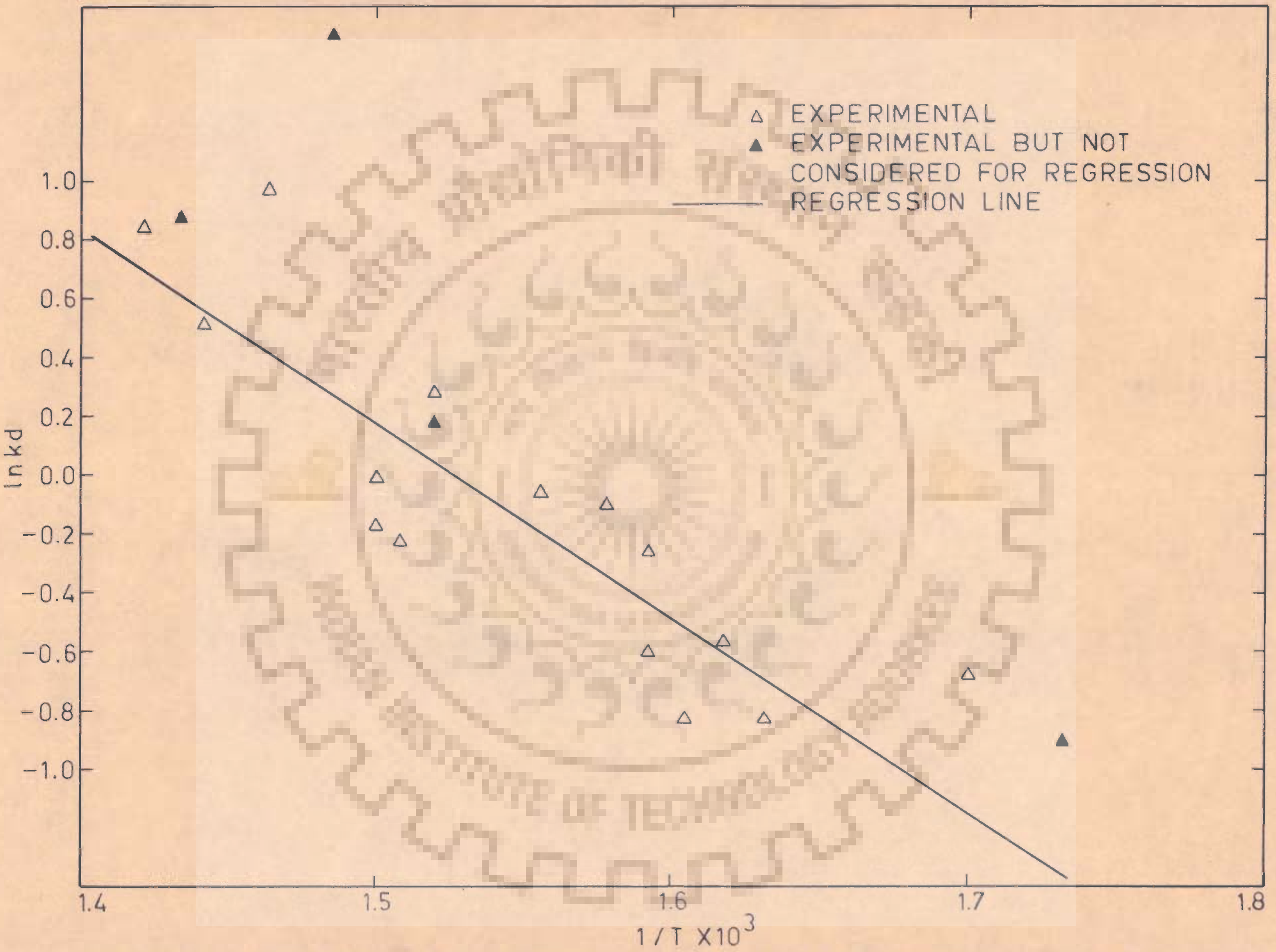


FIG. 5.1 ARHENIUS PLOT OF DEACTIVATION RATE CONSTANT, kd, WITH TEMPERATURE.

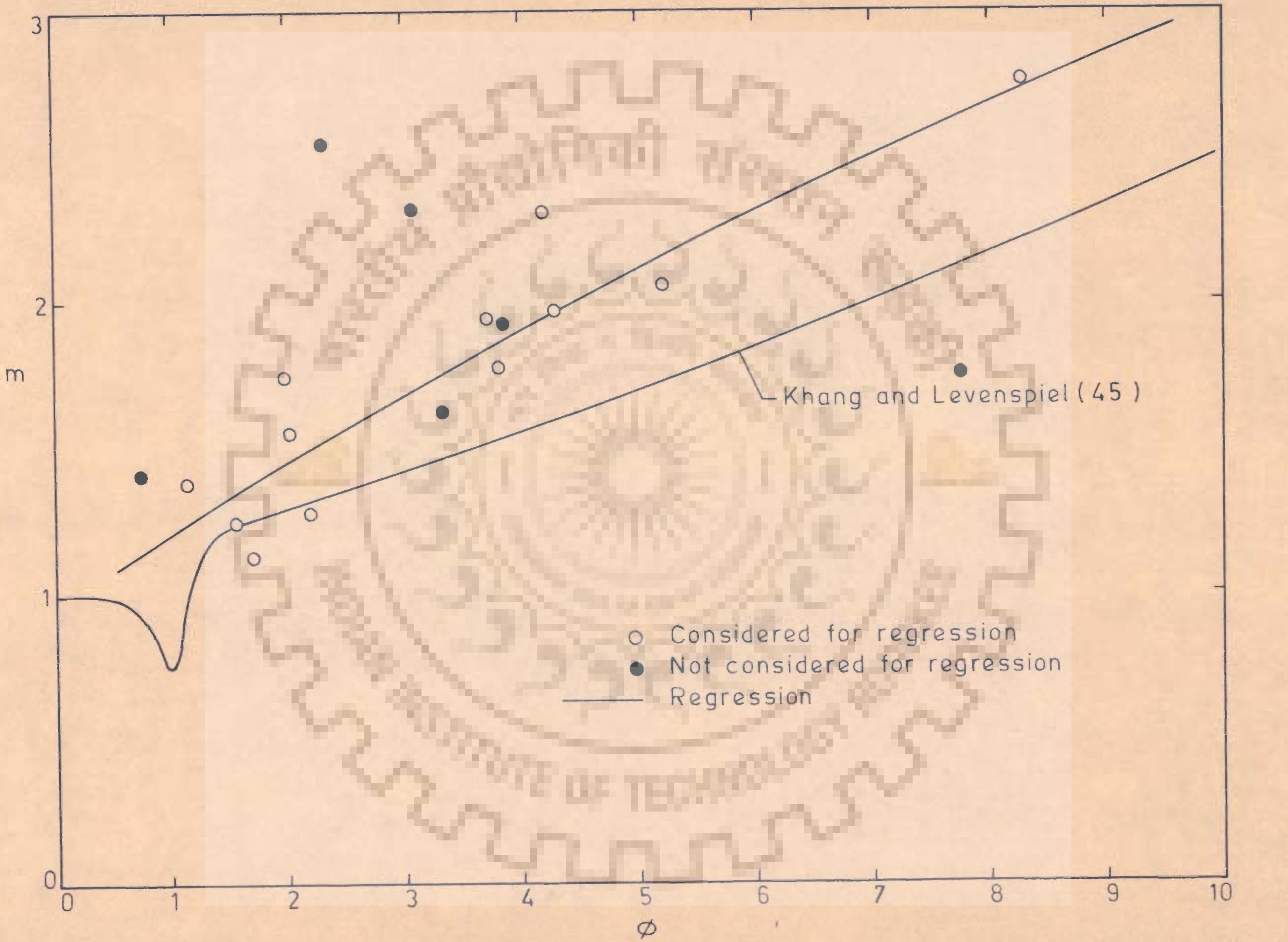


FIG. 5.2 VARIATION OF ORDER OF DEACTIVATION m WITH THIELE MODULUS ϕ

5.2.2 Estimation of Constants for ϕ and m Polynomial :

Khang and Levenspiel (45) have reported that the constant m used in deactivation rate equation (5.6) is related to Thiele parameter ϕ of the main reaction for a deactivating catalyst system. Accordingly, a second order polynomial was used to correlate the optimized values of m as given in table 5.1 with the experimental values of Thiele parameter for dehydrogenation reaction ϕ_1 as given in Table D-1 in Appendix-D.

The values of m and ϕ_1 are plotted in Fig. 5.2. From the figure it is clear that the values are too off for sets 8, 9, 12 and 14. The four points belonging to sets number 1, 14, 18 and 19 are again not considered for regression in view of their doubtful accuracy along with the three additional points belonging to sets number 8, 9 and 12. The values of constants in polynomial were thus determined by regression analysis for the remaining 12 points. The relationship of m with ϕ_1 is given by :

$$m = 0.9502 + 0.2623\,\phi_1 - 0.005806\,\phi_1^2 \tag{5.12}$$

and is shown as a curve on Fig. 5.2. The relative percentage error variances for X_A and X_B for sets 8, 9 and 12 corresponding to optimal m values and m values obtained by equation (5.12) are also given in Table B-8, 9 and 12 in Appendix-B. Comparison of these variances indicate relatively lesser sensitivity for m values, that is, shallow minima for these sets. Therefore, leaving out of these widely deviating points, set 8, 9 and 12 for m - ϕ_1 regression analysis can be justified. For comparison, the m - ϕ_1 relationship of Khang and Levenspiel (45) is also shown in Fig. 5.2.

5.3 APPLICATION OF THE PROPOSED MODEL FOR THEPREDICTION OF CONCENTRATION AND ACTIVITY PROFILES :

The material balance equationsfor plug flow reactor for dehydrogenation and hydrocracking reactions, equation (5.4) and (5.5), along with deactivation rate equation (5.6) are used to predict the concentration and activity profiles in the catalyst bed for different values of times-on-stream, for a particular set of operating conditions and catalyst. The kinetic and deactivation model consists of equation (4.7), (4.8), (5.10) and (5.11) to calculate the intrinsic dehydrogenation and hydrocrackihg rate constants, deactivation rate constants and m respectively. The value of Thiele parameter needed to calculate m and effectiveness factor is defined by equation (C-3) and effectiveness - factor $\eta - \phi$ relationship is given by equation (C - 4), Appendix C. The model consisting of these six equations is used to calculate the concentration and activity profiles along the catalyst bed for different times-on-stream by following the numerical integration procedure discussed earlier, section 5.2. The values of fraction of cyclohexane converted into benzene and the fraction remained unconverted at the reactor exit are calculated by the proposed model and these computed values are used to calculate the variance of the percentage error between the experimental and computed values. Appendix-B also gives the computed values of X_A and X_B by the proposed model along with smoothened experimental values and those obtained by using optimal values of m and k_d. The relative and absolute variances of percentage error for X_A and X_B are also given at the bottom of the table for each set. The absolute error is defined as the difference between the experimental and calculated value as obtained from the proposed model, and the relative percentage error has already been defined by equation (5.9). The errors have been calculated for every thirty minutes interval from the start of the run, at the exit of the reactor, though for the solution of simultaneous equations assuming pseudo-steady - state behaviour the time interval is five minutes.

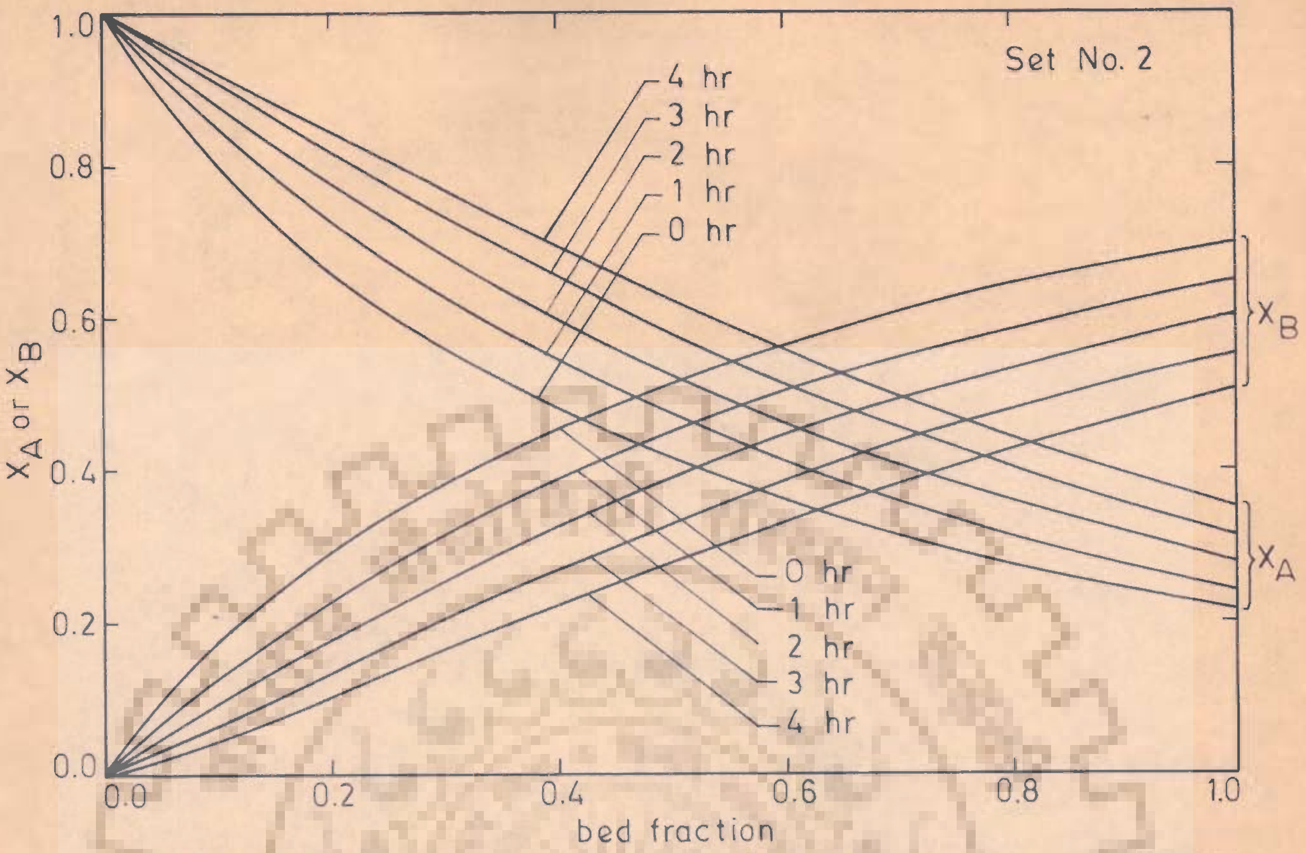


FIG. 5.3.2 Conversion profiles in the bed at different times.

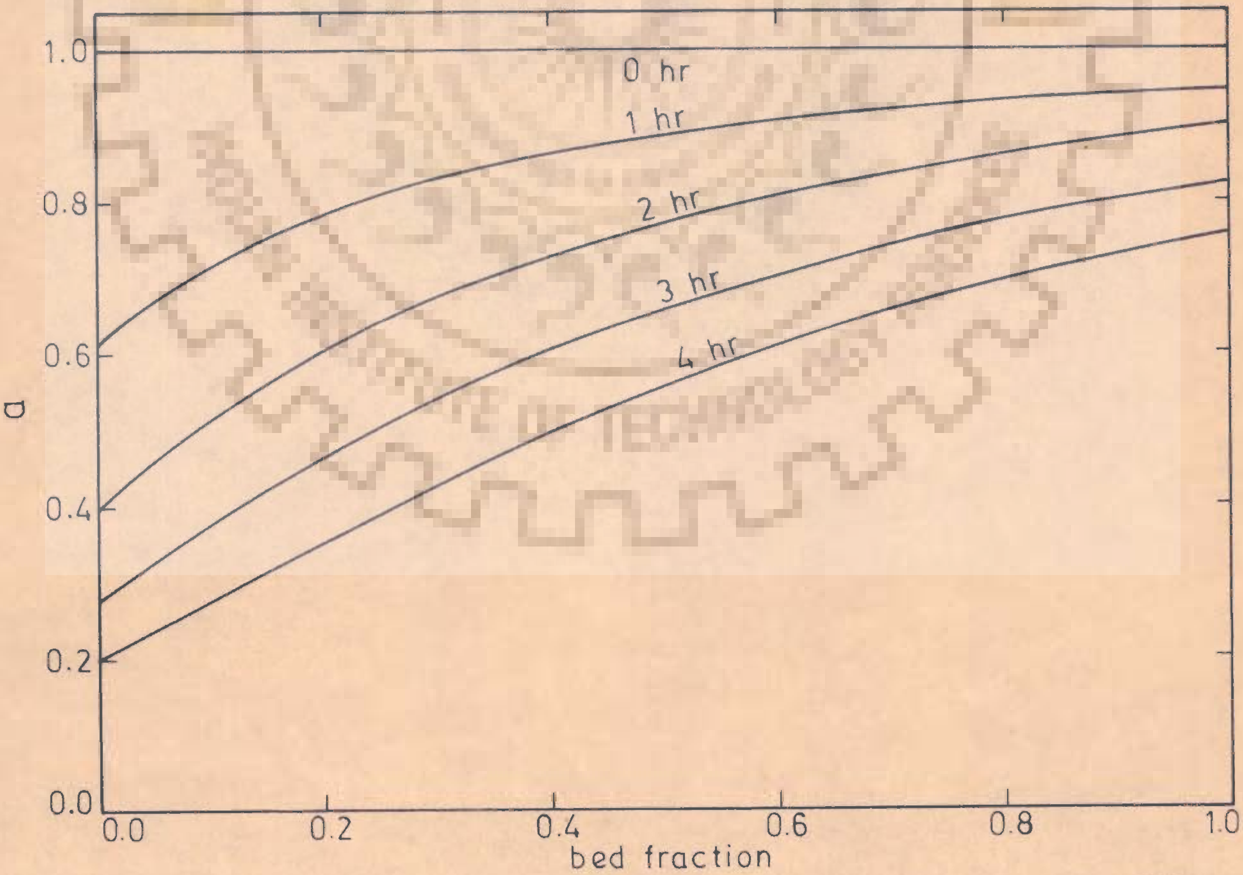


FIG. 5.4.2 Profiles of catalyst activity in the bed at different times.

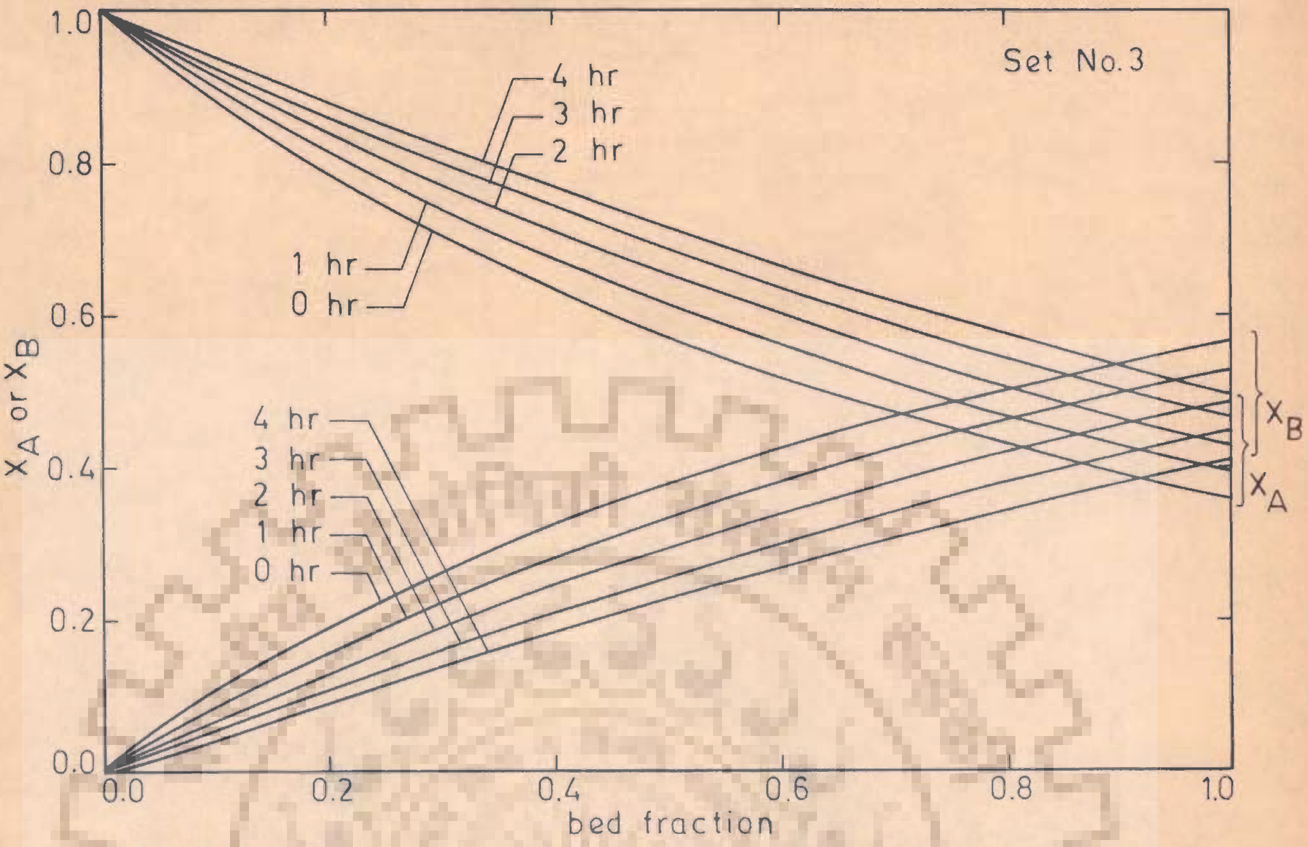


FIG. 5.3.3 Conversion profiles in the bed at different times.

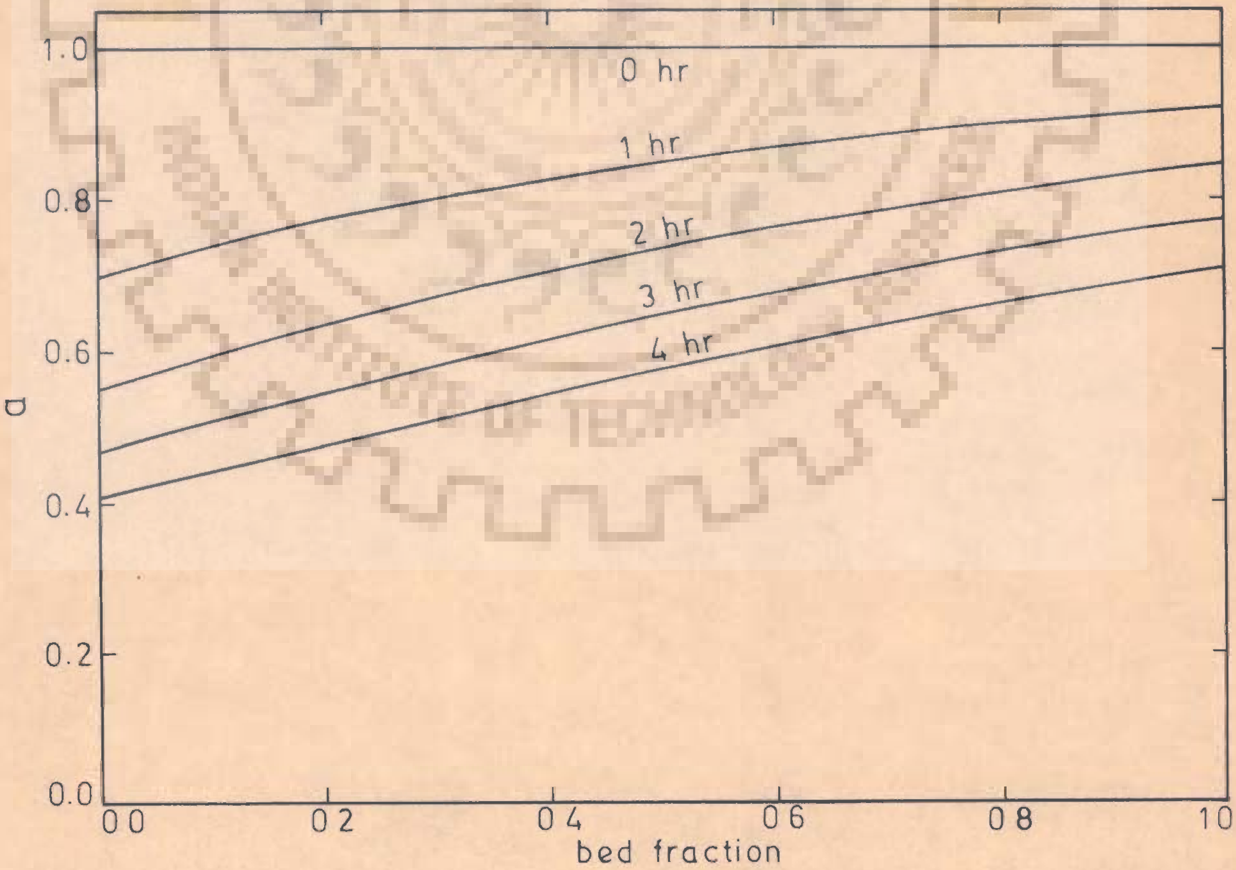


FIG. 5.4.3 Profiles of catalyst activity in the bed at different times.

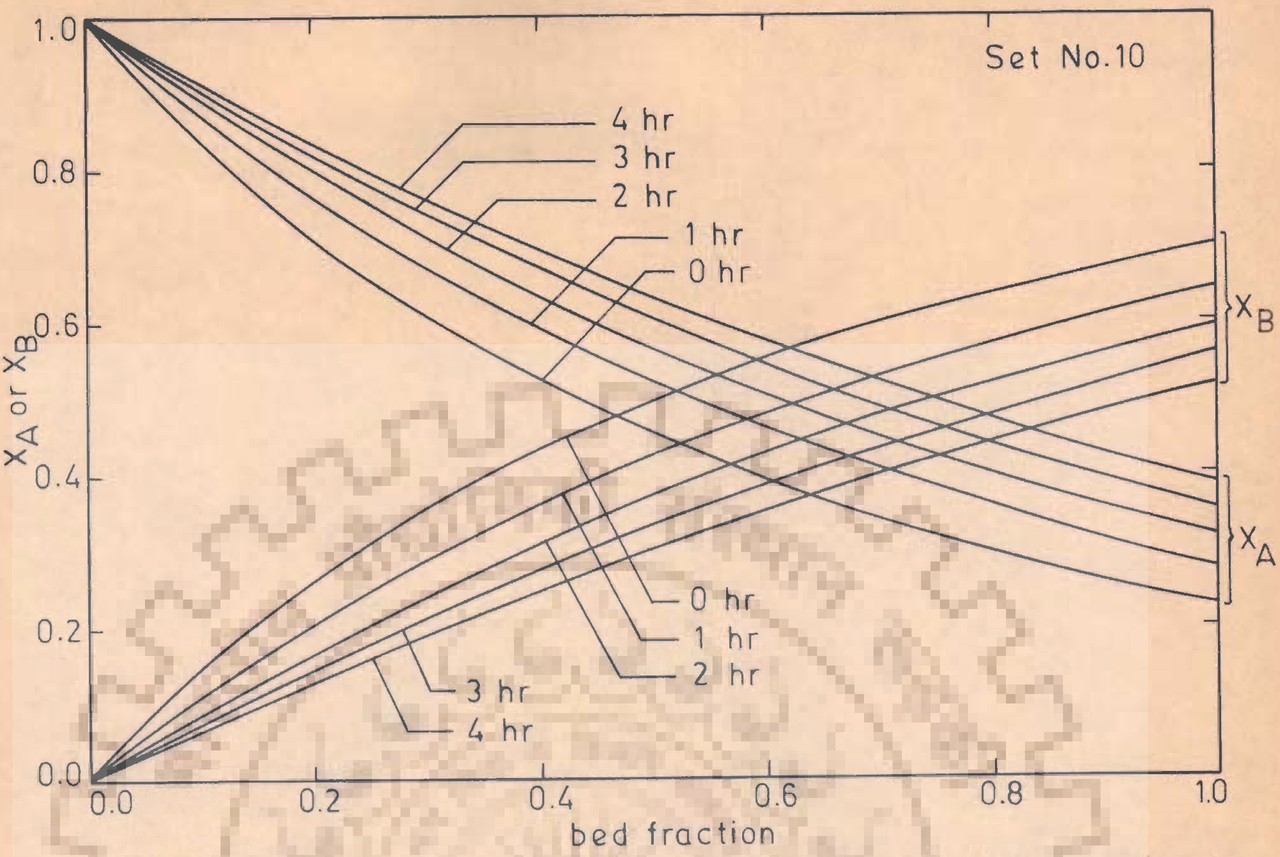


FIG. 5.3.10 Conversion profiles in the bed at different times.

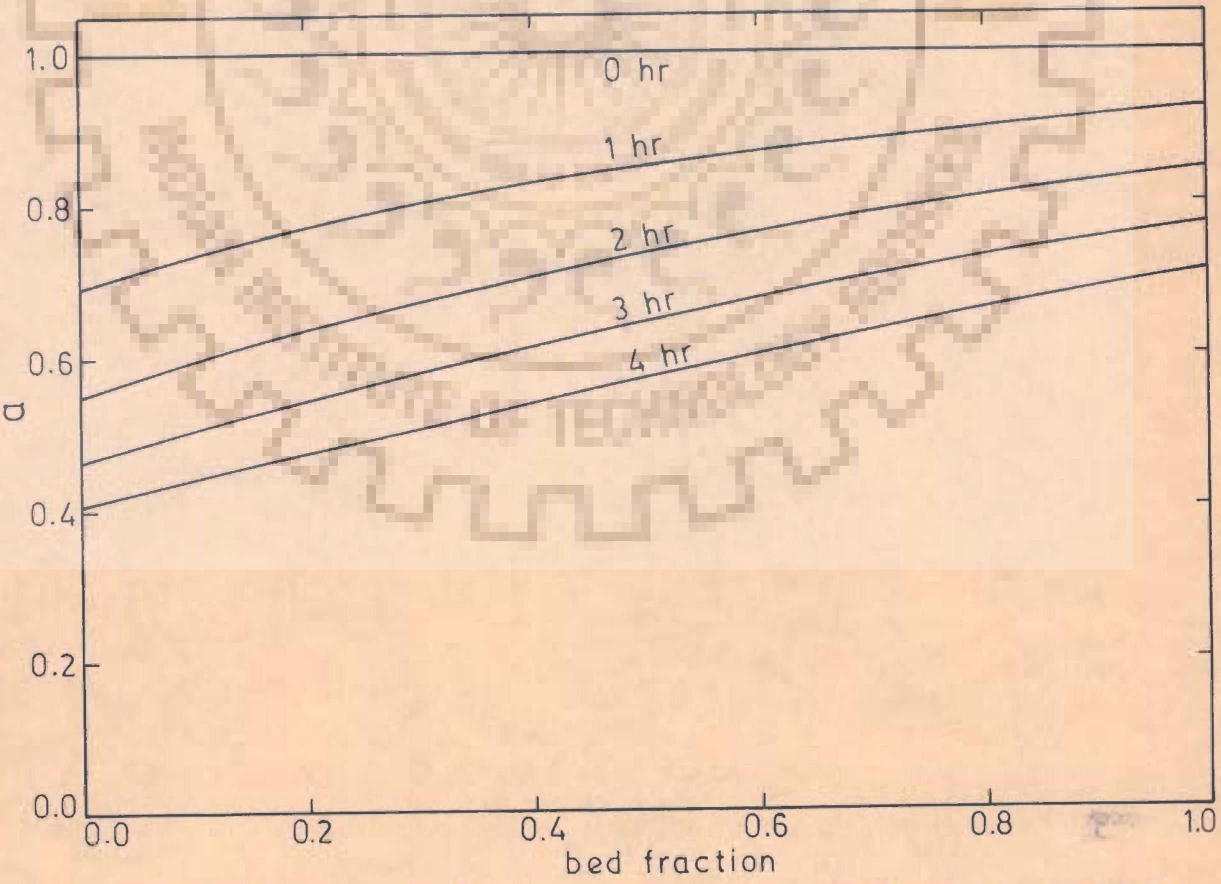


FIG. 5.4.10 Profiles of catalyst activity in the bed at different times.

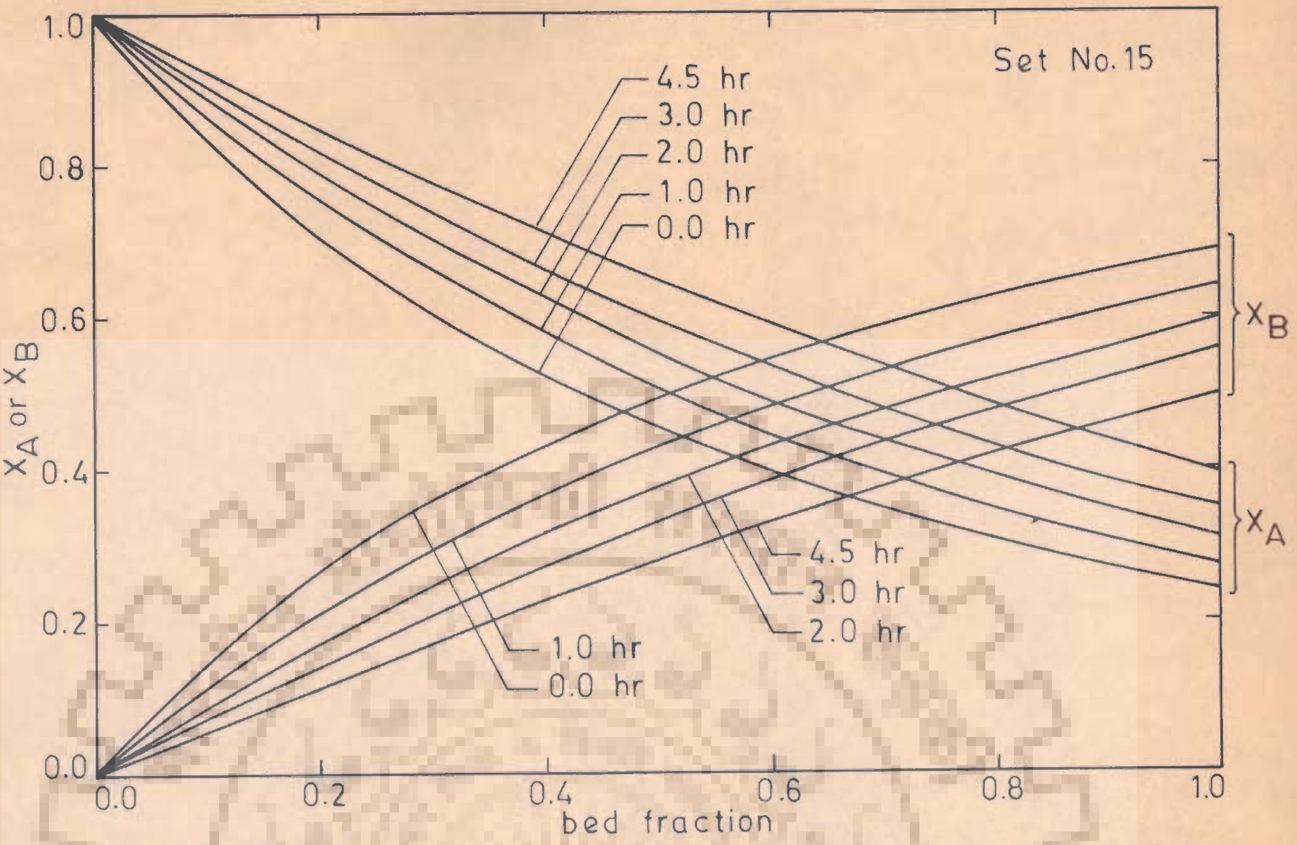


FIG. 5.3.15 Conversion profiles in the bed at different times.

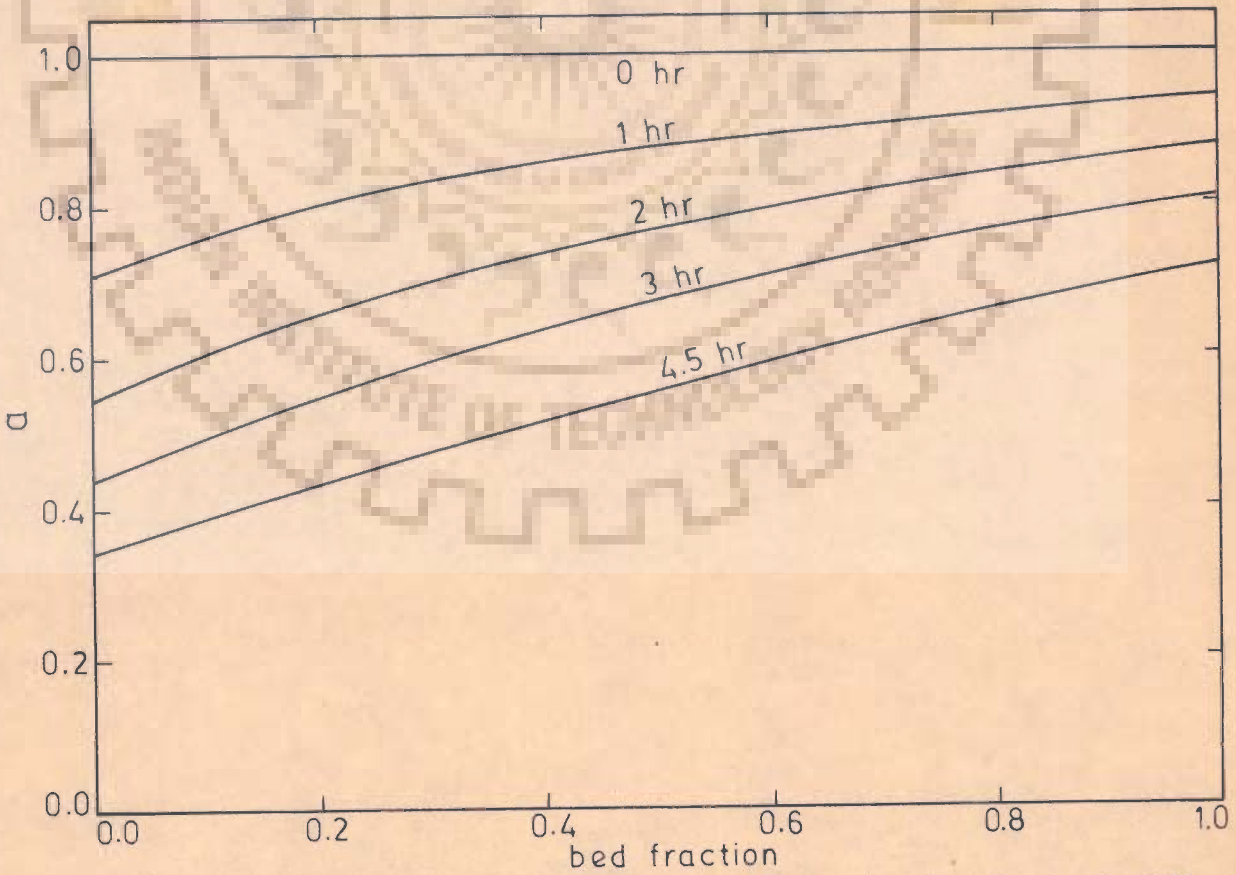


FIG. 5.4.15 Profiles of catalyst activity in the bed at different times.

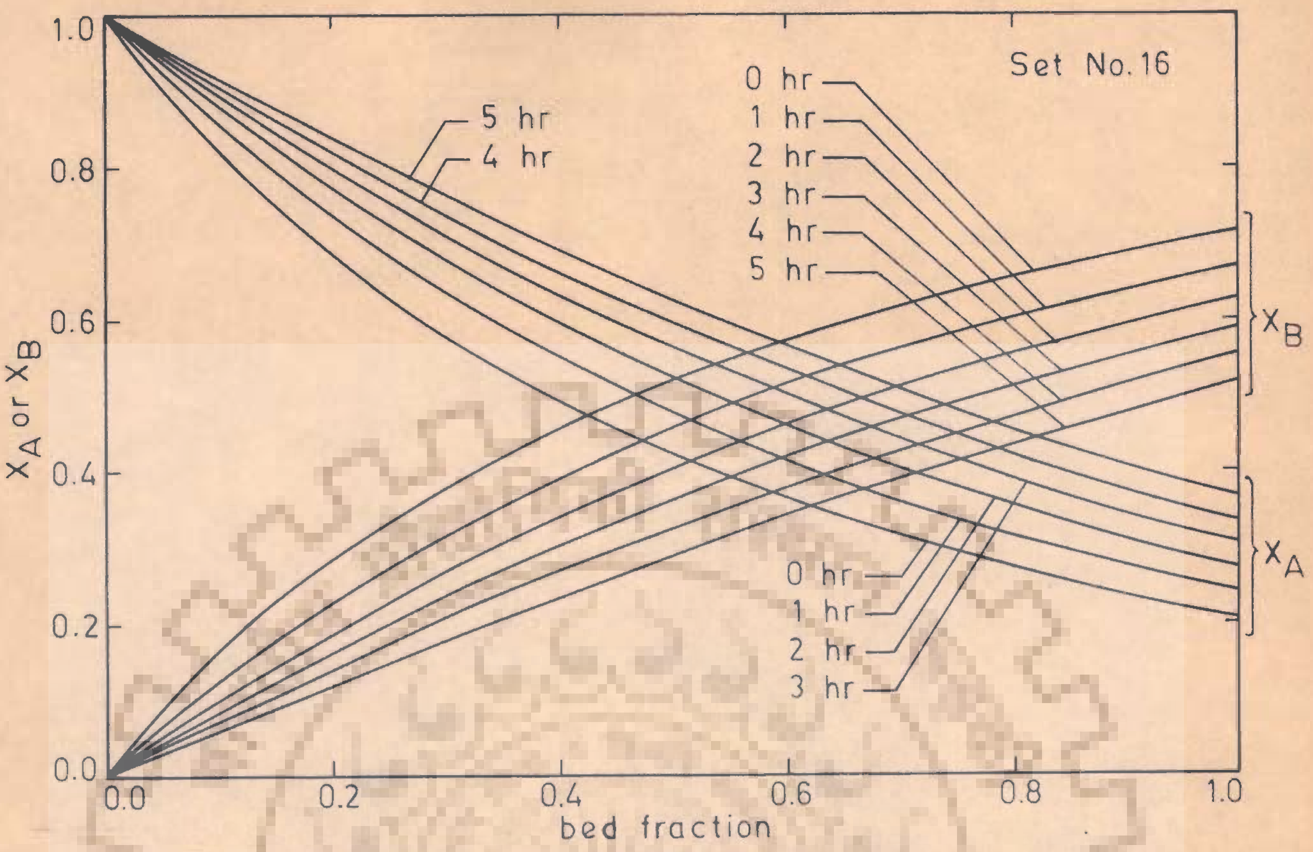


FIG. 5.3.16 Conversion profiles in the bed at different times.

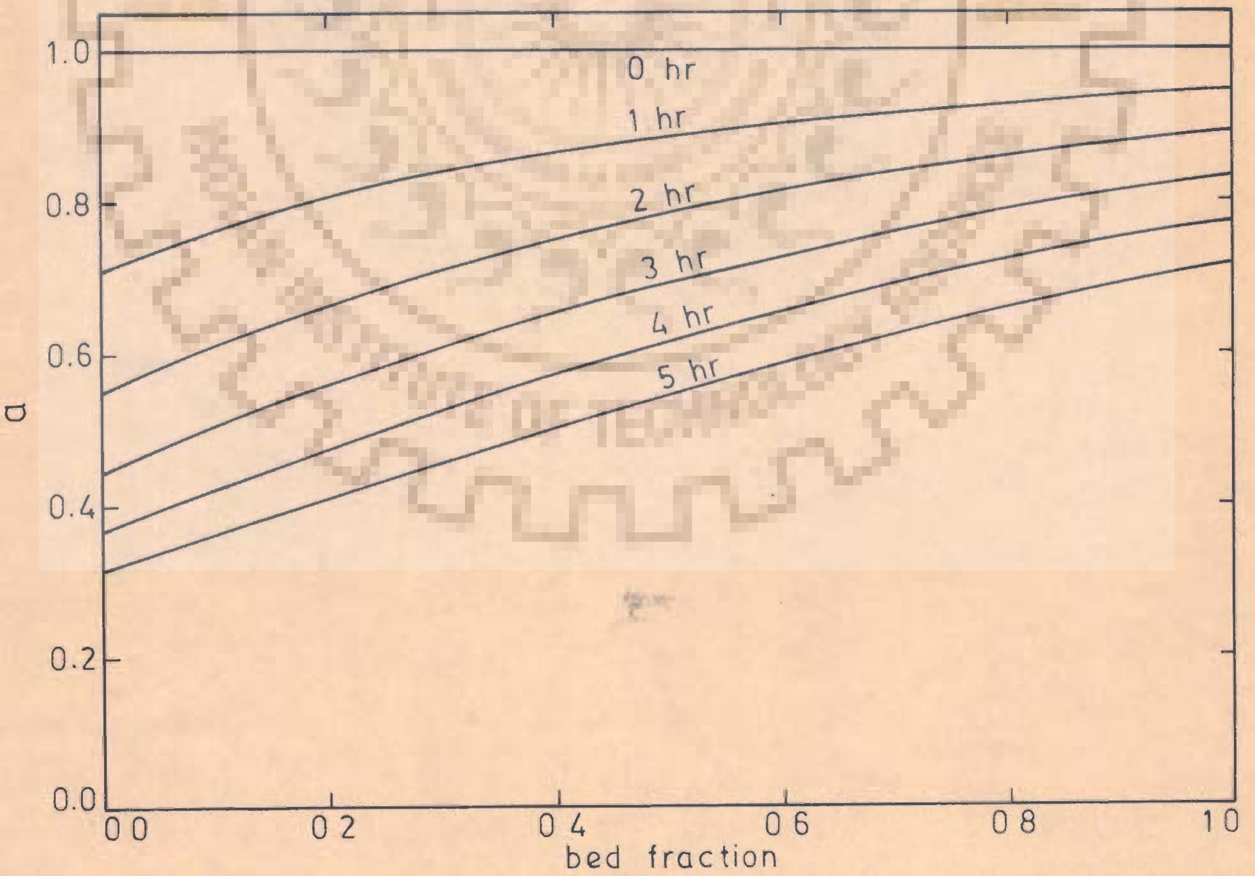


FIG. 5.4.16 Profiles of catalyst activity in the bed at different times.

The advantage of comparing the two values, from the smoothened and calculated curves, at every five minutes interval was not significant. Fig. 4.1.1 to 4.1.19 also show the computed values of X_A and X_B by the model for comparison with experimental values.

The values of X_A and X_B at different positions in the bed and for different times-on-stream, as predicted by the proposed model are plotted in Figs. 5.3 for five representative sets. The predicted values of catalyst activity by the model for different axial positions of the catalyst bed in the reactor, and for different times-on-stream are also plotted on Fig. 5.4 for five representative sets to indicate the trends of changes in these values. Appendix F gives the values of catalyst activity a, and fractions X_A and X_B at different bed fractions and times - on - stream for all the nineteen sets.

CHAPTER - 6

DISCUSSION OF RESULTS

The techniques and the assumptions involved in the analysis of the integral reactor data and the development of kinetic and deactivation model are discussed in their justifications. The results, in the form of various correlations, obtained are also presented in these chapters and these results will now be discussed in the following sections of this chapter.

6.1 DEHYDROGENATION AND HYDROCRACKING REACTION KINETICS :

Intrinsic rate constants for dehydrogenation and hydrocracking reactions were calculated assuming first order irreversible kinetics as per the procedure explained earlier. These intrinsic rate constants are plotted in Fig. 4.2 to calculate activation energies assuming Arrhenius temperature dependance. From this figure it is clear that these intrinsic rate constants depend only on temperature and not on other operating conditions, such as, liquid hourly space velocity and hydrogen-to-cyclohexane mole ratio. This confirms the validity of first order irreversible kinetics for dehydrogenation and hydrocracking reactions at atmospheric pressure operation in the temperature range of 580 to 710 K. The first order irreversible kinetics was also observed by earlier investigations for these reactions under similar operating conditions (6,23,32,89,40).

The temperature dependance of intrinsic rate constant for dehydrogenation reaction, as obtained by regression analysis, is given by equation (4.7) -

$$k_1 = \exp\left(31.57 - \frac{327,300}{RT}\right) \frac{cc}{hr.gm\ cat}$$

and the correlation coefficient for the regression line was obtained

Table 6.1 Comparison of Activation Energies for Dehydrogenation Reactions:

Worker	Reactant	Catalyst	Activation Energy(cal/gmole)
Haensel and Berger [32]	Cyclohexane	Pt - on - alumina	18,100
	Methyl cyclopentane	Pt - on - alumina	32,800
Smith [78]	Naphthenes	0.6% Pt-on-alumina	38,225
Panchenkov et al [94]	Cyclohexane	Pt - on - alumina	18,000
Barnett [6]	Cyclohexane	Pt - on - alumina	41,600
Graham et al [28]	Cyclohexane	Pt - on - alumina	58,000
Henningsen et al [40]	C_8 naphthenes	Pt - on - alumina	30,000
Christoffel et al [17]	Cyclohexane	Pt - on - Zeolite	41,500
From the present Work	Cyclohexane	0.6% Pt-on-alumina	27,300

Table 6.2 Comparison of Activation Energies for Hydrocracking Reactions:

Henningsen et al [40]	C_8 naphthenes	Pt - on - alumina	45,000
Smith [78]	Naphthenes	0.6% Pt-on-alumina	68,530
From the present work	Cyclohexane	0.6% Pt-on-alumina	15,150

as -0.991, which indicates a very good fit of data for the dehydrogenation rate constants. The values of activation energy for dehydrogenation, as reported by various investigators, are compared in Table 6.1. The very high value of 58,000 cal/gmole for the activation energy of dehydrogenation of cyclohexane as reported by Graham et al. (28) cannot be considered by very reliable due to very low catalyst concentrations, assumption of complete external mass transfer control with reaction in equilibrium at catalyst surface, and at the same time reporting very low values of intra-pellet effectiveness factors. Barnett (6) reported a value of 41,600 cal/gmole, twice the value of apparent (experimental) activation energy obtained by him for 1/8 inch pellet assuming Knudsen diffusion with a tortuosity factor of 1/8. His assumption that the dehydrogenation reaction was completely intrapellet diffusion controlled may not be fully valid and therefore, the intrinsic activation energy value may be less than twice the apparent (experimental) activation energy value. The value 41,500 cal/gmole reported by Christoffel et al. was reported for platinum -on-zeolite catalyst where benzene and methylcyclopentane were the products of reaction. Other reported values of activation energy for the dehydrogenation of cyclohexane/naphthenes range from 18,000 to 38,225 cal/gmole and the value of 27,300 cal/gmole obtained in the present investigation, therefore, appears reasonable. Eventhough, various investigators have studied the effect of dehydrogenation reaction at different pressures, but the effect of pressure on activation energy is expected to be insignificant (28).

The temperature dependance of intrinsic rate constant for hydrocracking reaction, as obtained by regression analysis, is given by equation (4.8) -

$$k_2 = \exp\left(18.97 - \frac{15,150}{RT}\right) \quad \frac{cc}{hr.gm\ cat}$$

and the correlation coefficient for the regression line was obtained as -0.902, which indicates a good fit of data for the hydrocracking rate constants. The values of activation energy, as reported by other investigators, is given in Table 6.2. Lambrecht et al. (49) had indicated the unreliability of hydrocracking reaction rates, as obtained from material balance analysis, and have not reported the values of hydrocracking rate - constants. Same appears to be true in the present work also, as the conversion to hydrocracked products was calculated to match the material balance of cyclohexane feed, and any error in measurements will ultimately effect the fraction of cyclohexane converted to hydrocracked products. The intrinsic hydrocracking rate constants were calculated from the fractional conversions to hydrocracked products as obtained by extrapolation of data for undeactivated catalyst, and this can also result in some error. Since the fractional conversions to hydrocracked products are small, even small error in measurements or extrapolations will greatly effect the values of hydrocracracking rate constants. Because of this difficulty very few workers have estimated the values of hydrocracking rate constants and the activation energy. A comparison of the only available three values, Table 6.2, for the activation energy for hydrocracking reactions show a wide variation in values. An activation energy of 15,150 cal/gmole for hydrocracking reactions obtained in the present investigation appears to be rather low. More careful experimental measurements and direct analysis of the hydrocracked products may provide more accurate hydrocracking rate constant and activation energy values.

6.2 ACCURACY OF COMPUTATION PROCEDURE

The solution of equations 5.4 and 5.5 was first carried out for 20, 30, 40, 50 and 100 bed increments for set number 16 at initial (undeactivated catalyst) conditions. This set has quite high conversions out of all the sets considered reliable for analysis and will, therefore, show maximum computation error. Fig. 6.1 shows the values of X_A and X_B at the reactor exit as a function of the number of bed increments used for numerical integration. It shows the values for X_B as 0.70285 and 0.70236 and for X_A as 0.21302 and 0.21354 for 40 and 1000 bed increments. The values corresponding to 1000 bed increments are obtained by extrapolation of curves. Thus, a difference of about 0.05 percent for X_B and X_A is found when number of bed increments are increased from 40 to 1000 for numerical integration. The accuracy of analytical measurements is no better than ± 2 percent and, therefore, 40 bed increments were considered sufficient to reduce the computation time. Further, Smith (77) has indicated that the proper bed increment can be taken as one pellet diameter which also gives nearly 40 increments in the bed.

After deciding, the bed increments as 40, an analysis was next carried out to check the effect of time interval in the solution of equations 5.4 to 5.6 on the X_A and X_B values at the exit of reactor. For this analysis time intervals of 5, 10, 15 and 30 minutes were taken and the exit X_A and X_B values are plotted as a function of time intervals in Fig. 6.2. As expected, this shows that the smaller is the time interval, the better will be the accuracy of X_A and X_B values but the computer time will increase proportionately. The values at the exit of reactor after 5 hours time-on-stream for the same set are 0.4486 and 0.4476 for X_B, and 0.4194 and 0.4206 for X_A using 5.0 and 0.1 minute time interval respectively. The value for 0.1 minute time interval was found from Fig. 6.2 by extrapolation. Thus a better accuracy of about 0.10 percent for X_B and 0.12 percent for X_A values after 5 hours time-on-stream is obtained when the time interval for computation is reduced to 0.1 minute from 5 minutes for numerical integration but will require 50 times more computation time. Again, considering the accuracy of analytical

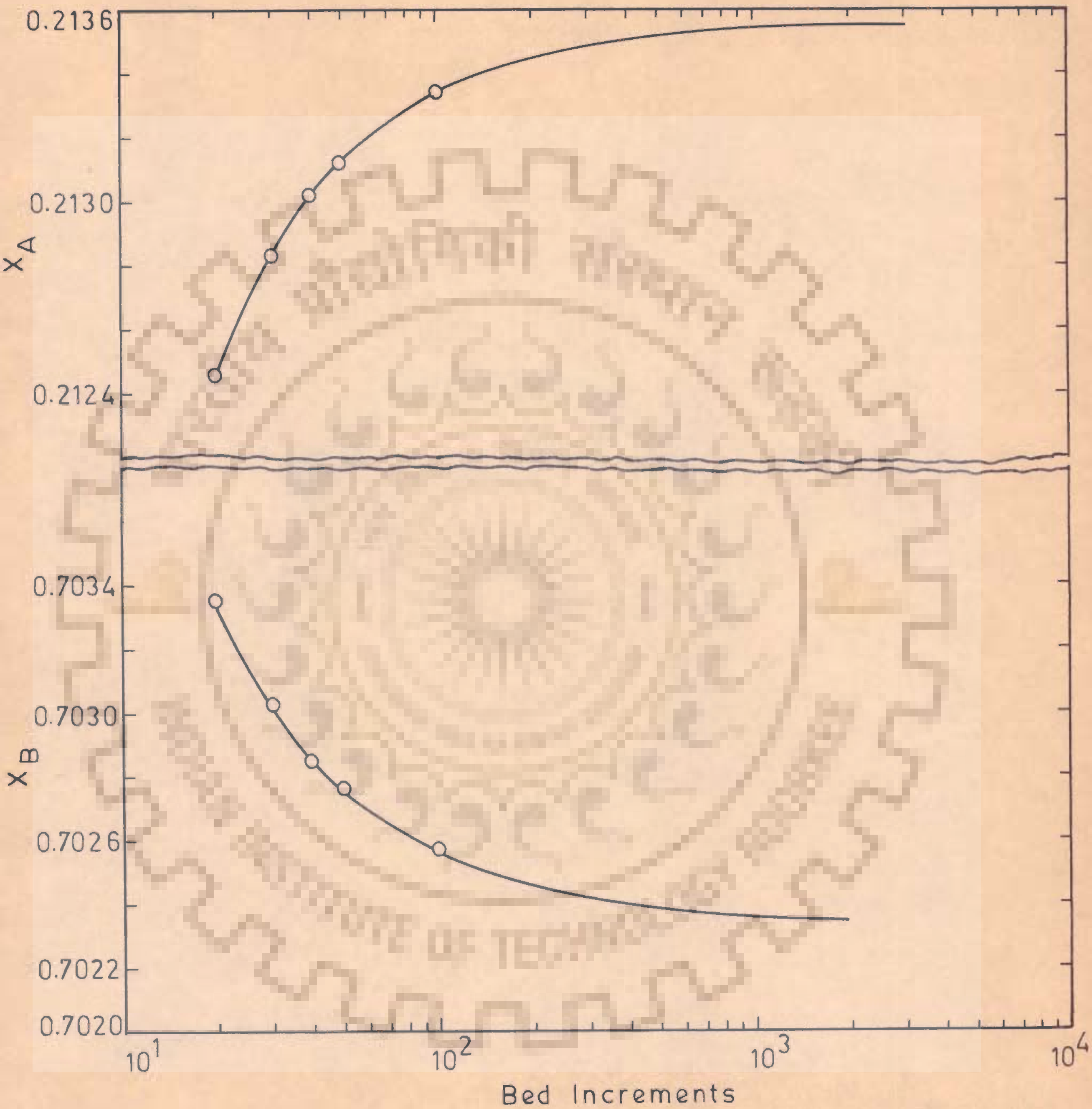


FIG. 6.1 EFFECT OF BED INCREMENTS ON THE CONVERSION AT THE EXIT OF REACTOR.

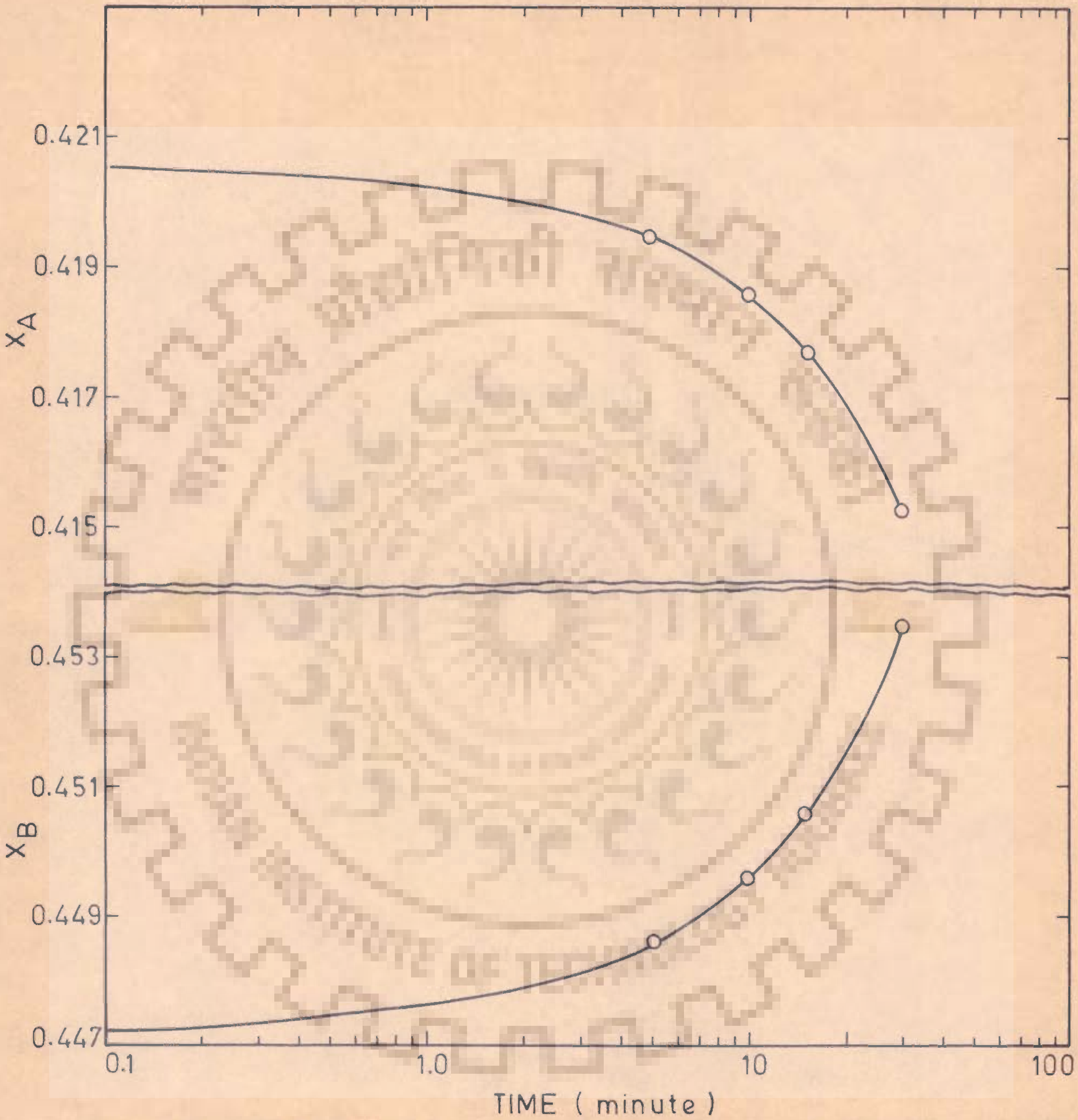


FIG. 6.2 EFFECT OF TIME INTERVAL ON THE CONVERSION AT THE EXIT OF REACTOR.

and other measurements, 5 minutes time interval for numerical integration is considered appropriate.

The computed values of X_A, X_B and activity for different bed positions and times-on-stream are given in Tables F-1 to F-19 in Appendix F. These tabulated values clearly justify the assumption of quasi-steady state because changes with axial positions are much faster and predominant compared to the changes with time at any bed position. Thus, a time interval of 5 minutes with 40 bed increments were choosen and the results of computation are considered sufficiently accurate for the analysis in the present investigation.

The optimal values of deactivation parameters m and k_d were determined by minimuzation of variance in the X_B values as discussed in section 5.2. Pattern search technique was used for this optimization. Since no a priori information was available about the expected values of m and k_d, the reduction in computation time was achieved first by using 30 minutes time interval with 20 bed increments and then using these m and k_d values for final optimization using 5 minutes time interval with 40 bed increments.

It is important to note that the total time requirement for the computation of kinetic and deactivation parameters for one set is nearly two minutes on IBM 370/145 system as compared to 5½ to 6 hours required by Lambrecht et al. (49) on IBM 360/30 for determining one set of parameter values. It may also be pointed out that one complete calculation cycle for computing X_A, X_B and activity profiles along the bed at any given time-on-stream requires only 1.01 seconds approximately on IBM 370/145 system.

6.3 DEACTIVATION RATE CONSTANTS

The temperature dependance of deactivation rate constant is given by equation (5.11) -

$$k_d = \exp\left(9.475 - \frac{12,260}{RT}\right) \qquad (hr)^{-1}$$

and the correlation coefficient for the regression line was obtained as -0.872, which indicates a reasonably good fit of data for the deactivation rate constants obtained from the proposed deactivation equation (5.6). It is not possible to compare the activation energy for deactivation reaction with the work of earlier investigators because no such information is available from the available published literature. However, Lambrecht et al. (49) have reported the Arrhenius relationship for the fouling reaction by the equation :

$$k_d = \exp\left(19.3 - \frac{35,500}{RT}\right) \quad \frac{\text{g coke}}{\text{hr.g cat}}$$

by analysing the coke profile for n- pentane isomerization reaction after the end of the run. But their Arrhenius plot for k_d shows considerable scatter and C_5 hydrocarbon reactions are expected to require higher activation energy as compared to C_6 hydrocarbons.

In this work, it is important to note that the deactivation parameters have been determined by using reactor exit X_A and X_B profiles as a function of time-on-stream using a suitable optimization procedure. Since no other assumption has been introduced and also in view of good correlation coefficient for deactivation rate constant, the equation (5.11) can be considered reliable for k_d.

6.4 RELATIONSHIP BETWEEN m AND $\emptyset_1$

The m - $\emptyset_1$ relationship is given by equation (5.12).

$$m = 0.9502 + 0.2623\,\emptyset_1 - 0.005806\,\emptyset_1^2$$

for the Thiele parameter (based on dehydrogenation rate coefficient) range of 0.75 to 8.2. This relationship is very nearly linear in view of very low value of coefficient of $\emptyset_1^2$. In Fig. 5.2 m and $\emptyset_1$ relationship is plotted along with that obtained by Khang and Levenspiel (45) for comparison. The nature of two curves is similar for $\emptyset_1$ values larger than 1.0 but the m values determined in this study are higher, as compared to those obtained by Khang and Levenspiel. This difference may be due to the strong simplification made in the kinetic scheme for deactivation by considering it as a single reaction in this investigation. Khang and Levenspiel have reported a minima in m - $\emptyset_1$ curve, at $\emptyset_1$ value of near to unity. But no such minima is observed in this work for $\emptyset_1$ value as low as 0.77. Further considerable scatter in values is observed in Fig. 5.2. The values of m in the range of 1 and 3 for the experimental Thiele parameter range of 0.75 to 8.2 indicate that deactivation reaction is simultaneous to the main dehydrogenation reaction and support this assumption used in the model development. In this study the value of m has not gone below unity and this indicates that even at the $\emptyset_1$ value of 0.77 the pore mouth poisoning may be important.

6.5 ACCURACY OF THE PROPOSED MODEL

The conversion values at the exit of reactor as calculated by the proposed model along with experimental points are shown in Fig. 4.1.1 to 4.1.19. Tables B-1 to B-19, in Appendix B also give the relative- and absolute-percentage error variances. The variance of absolute percentage error in X_A and X_B are less than 4.51 and 5.88 respectively for all the sets except set 19 where it is 9.42 for X_A. The variance of relative percentage error is 41.45 for X_A for set 19 and is 31.16 for X_B for set 1. This confirms that the data of sets number 1 and 19 are unreliable for model development due to very low and high conversions respectively. The same is true for set numbers 14 and 18 but to a lesser extent. This justifies the exclusion of data points corresponding to set numbers 1, 14, 18 and 19 in the determination of kinetic and deactivation parameters. The tabulated and plotted values of X_A and X_B indicate that the proposed model the proposed model agrees very well with experimental values.

Figs. 5.3 and 5.4 shows the X_A, X_B and activity profiles along the reactor bed for different time-on-stream for five representative sets. The experimental conditions for these five sets are :

SET NO.	TEMP.°C	LHSV	MOLE RATIO
2	355	2.052	1.002
3	355	2.437	2.176
10	435	3.737	3.924
15	400	2.721	2.790
16	400	2.473	2.831

The figures corresponding to set numbers 15 and 16 indicate that due to lower LHSV in set number 16, higher conversions to benzene are obtained while there is not much difference in the final activities of the bed (at 4.5 hours times-on-stream it is 0.34 at the inlet and 0.713 at the exit of the reactor for set number 15 and the corresponding values for set number 16 are 0.32 and 0.715 respectively). The figures corresponding to sets 2 and 3 show the combined effect of higher LHSV and mole-ratio in set number 3 with respect to those for set number 2 and these figures indicate that the fall in activity is more, except for bottom 80 percent of the bed, in set number 2 as compared to set number 3 (at 4.0 hours time-on-stream it is 0.2 at the inlet and 0.75 at the exit of reactor for set number 2 and the corresponding values for set number 3 are 0.39 and 0.73 respectively).

The effect of higher mole ratio, LHSV and temperature is combined in set number 10. For this set, even though the value of X_B at the reactor exit at the end of 4 hours is similar to that for set number 15 (0.518 and 0.513 respectively) the drop in catalyst activity is more

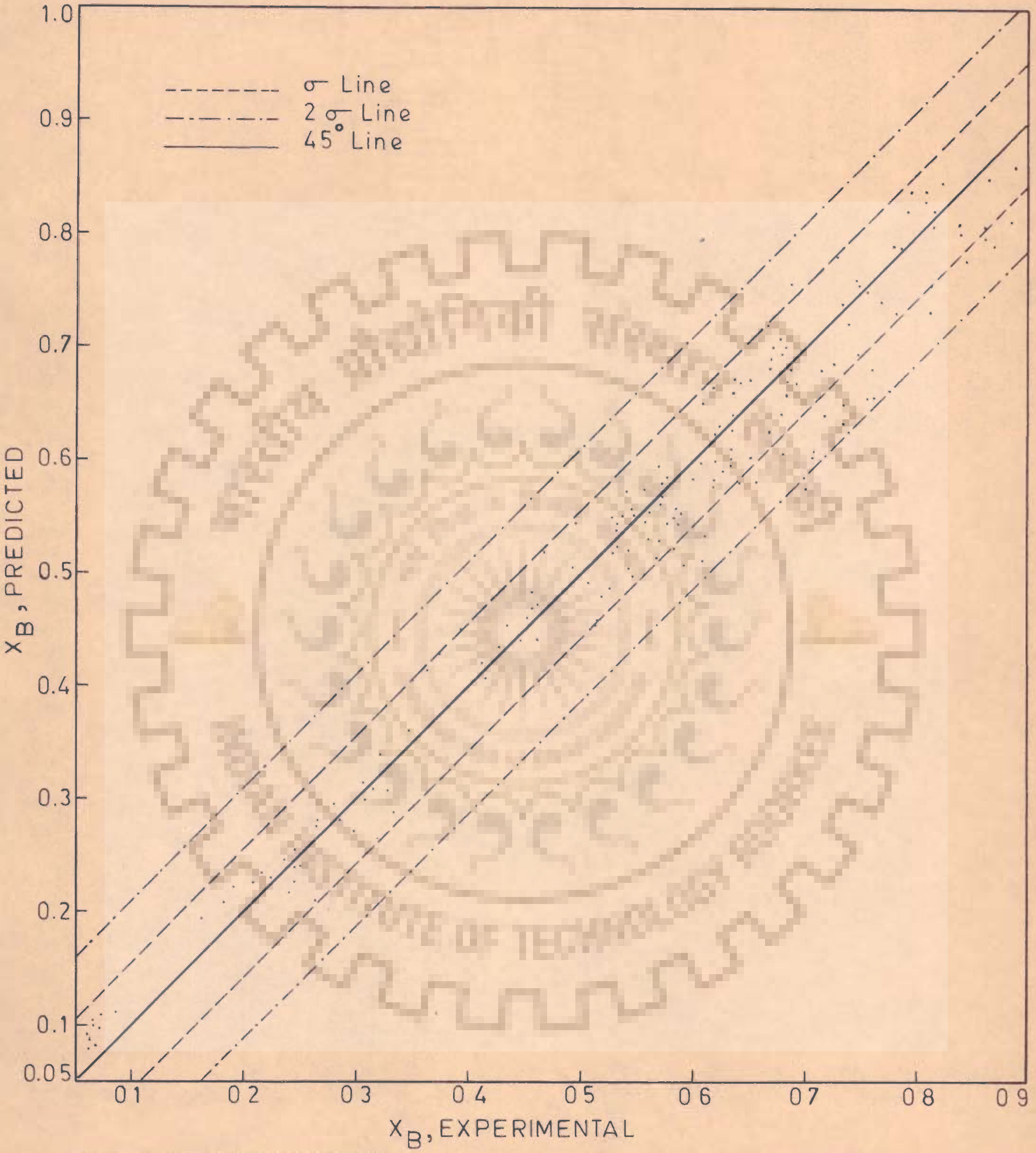


FIG. 6.3 COMPARISON OF EXPERIMENTAL AND PREDICTED VALUES OF CONVERSIONS OF BENZENE AT REACTOR EXIT.

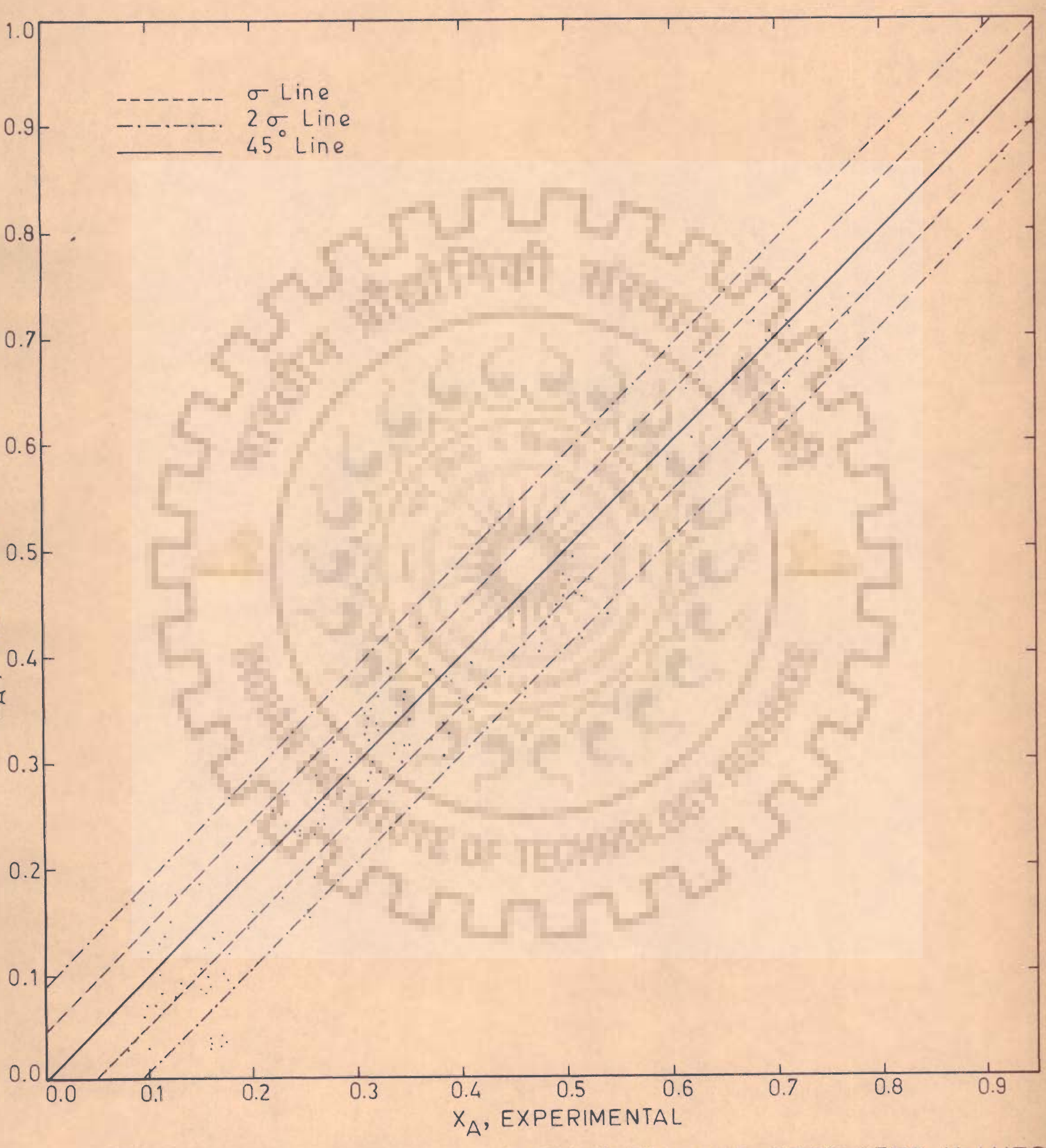


FIG. 6.4 COMPARISON OF EXPERIMENTAL AND PREDICTED VALUES OF UNCONVERTED CYCLOHEXANE AT REACTOR EXIT.

rapid for bottom 50 percent of bed (at 4.0 hours time-on-stream it is 0.406 at the inlet and 0.706 at the exit of reactor for set 10 and the corresponding values for set 15 are 0.368 and 0.743). Thus, it can be observed that the effect of temperature and mole ratio on catalyst deactivation is more pronounced to that of LHSV.

The experimental values and the corresponding values from the model for all the 168 data points are plotted for X_B in Fig. 6.3 and X_A in Fig. 6.4 to show their scatter around 45° line. The absolute percentage error variance between the experimental and predicted values of X_B and X_A is 5.498 and 4.723 respectively but no trend is discernible. The variance values are of the same order as the experimental inaccuracies and, therefore, the kinetic and deactivation model is quite accurate and reliable.

CHAPTER - 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The following conclusions can be derived from the present investigation :

1. For obtaining kinetic and deactivation parameters, smoothening and extrapolation of experimental conversion data under deactivating conditions to zero time for determining conversion values for undeactivated catalyst provide a reliable and accurate procedure

2. The following kinetic and deactivation scheme adequately describes the reforming reactions under deactivating conditions with special reference to cyclohexane dehydrogenation on platinum-on-alumina reforming catalyst :

   Dehydrogenation: $C_6H_{12} \xrightarrow{k_1} C_6H_6 + 3H_2$; $r_1 = k_1 \eta_1 \, a \, C_A$

   Hydrocracking : $C_6H_{12} \xrightarrow{k_2}$ hydrocracked products ; $-r_2 = k_2 \eta_2 C_A$

   Deactivation : $C_6H_{12} \xrightarrow{k_d}$ catalyst poison (coke) ; $-r_d = -\frac{da}{dt} = k_d \, a^m (C_A/C_H)$

3. Estimates of interphase and intrapellet heat and mass transfer resistances under experimental conditions indicate that only intrapellet mass transfer resistance is significant and effectiveness factor values were in the range of 0.12 to 0.77 for the main dehydrogenation reaction, and in the range of 0.60 to 0.93 for the hydrocracking reactions.

4. The values of kinetic and deactivation parameters for Sinclair Baker RD 150 containing 0.6 percent Pt-on-alumina catalyst, are :

$$k_1 = \exp\left(31.57 - \frac{27,300}{RT}\right) \qquad \frac{cm^3}{(hr)\ (g\ catalyst)}$$

$$k_2 = \exp\left(18.97 - \frac{15,150}{RT}\right) \qquad \frac{cm^3}{(hr)\ (g\ catalyst)}$$

$$k_d = \exp\left(9.475 - \frac{12,260}{RT}\right) \qquad (hr)^{-1}$$

$$m = 0.9502 + 0.2623\ \phi_1 - 0.005806\ \phi_1^2$$

where Thiele parameter ϕ_1 is based on k_1 .

5. Estimation of hydrocracking rate constants from conversion values, as obtained from the materal balance of cyclohexane feed, is not very reliable. Direct measurement of hydrocracked products is desirable for better estimates of these constants.

6. The values of m in the range of 1.0 to 3.0 obtained in this investigation indicate pore mouth poisoning and confirms simultaneous deactivation.

7. Quasi steady-state procedure for simultaneous solution of kinetic and deactivation rate equations given in 2 above is quite accurate and reliable. The computer time requirement for this procedure to obtain parameter values for a set of experimental data is extremely small as compared to that required for unsteady state procedure involving partial differential equation. In this work, use of 40 increments for total bed (bed increment of the order of one pellet diameter) gave a computation accuracy of better than 0.05 percent in exit conversion values and use of 5 minutes time interval resulted in a computation accuracy of better than

0.12 percent in exit conversion values at the end of five hours time - on - stream.

8. The proposed kinetic and deactivation model predicts experimental data with sufficient accuracy and absolute percentage error variance between the experimental and predicted values of conversion is 5.5 for X_B and 4.7 for X_A .

7.2 RECOMMENDATIONS :

Based on the present investigation , the following recommendations are made for further studies :

1. Maintenance of isothermal conditions in the reactor is very important and better heating system, such as, salt bath, may be desirable.
2. More accurate flow measurements for liquid feed at very low rates is essential.
3. Experimental studies if carried out at pressures close to those used industrially may provide more valuable information regarding kinetic and deactivation parameters. But use of high pressure will reduce the catalyst deactivation rate and, therefore, each experimental run will require much longer time-on-stream to study deactivation phenomena.
4. It is desirable to analyse reactor effluents not only liquid products but also for hydrocracked gases for more accurate determination of hydrocracking rate constants. Direct analysis of reactor effluents, without condensing them, by using on-line gas-chromatograph is more useful.

5. Studies with other feed stocks, such as, pentane, hexane, heptane, octane, methyl cyclopentane, methyl cyclohexane and industrial naphthas of various boiling ranges, may be desirable to simulate in industrial catalytic reformers.

6. Other catalysts used industrially may also be used to estimate the effect of catalyst type on kinetic and deactivation parameters.

NOMENCLATURE FOR APPENDICES

AO,A1,A2 - constants for second order polynomial between m and φ_1

AMF - cyclohexane fed on average flow rate basis, moles

AMG - cyclohexane in uncondensed exit gases, moles

AML - cyclohexane condensed in liquid phases, moles

AMU - cyclohexane remained unconverted, moles

BMF - benzene formed, moles

BMG - benzene in uncondensed gases, moles

BML - benzene condensed in liquid phase, moles

CF1 - concentration $P/R_g T$

CHC - cyclohexane converted into hydrocracked gases, moles

CHCG - hydrocracked gases moles, from gas analysis

ED - effective diffusivity, $\frac{cm^2}{hr}$

EGM - exit uncondensed gases, moles

ETA - effective diffusivity

FA,FB,FCR - fraction of cyclohexane, benzene and hydrocracked gases in products with respect to average cyclohexane feed.

FR - feed rate of cyclohexane, ml/minute

GAMA - mole ratio of hydrogen to cyclohexane in feed.

GCAT - weight of catalyst fed in the reactor, gms.

HFE - hydrogen feed, moles

HFO - hydrogen formed, moles

M - No of bed increments

P - atmospheric pressure, mm of mercury

PCH,PH - percentage of cyclohexane and benzene in products with respect to average cyclohexane feed

PERH - percentage error from hydrogen material balance

PHE - Thiele modulus

PMG - product moles in gas phase

QCF, QHF - cyclohexane and hydrogen feed rate respectively in moles per minute

R - gas constant

RHOP - pellet density , gm/cm^3

T - time for which the sample has been collected, min

TA - ambient temperature , ^{o}C

TE - exit temperature of gases from condenser, ^{o}C

TIME - duration for which sample has been collected with time-on-stream in minutes. For example 90 - 125 means the liquid sample has been collected between 90 and 125 minutes time-on-stream and corresponding T is 35 minutes.

TPM - Total accountable moles of benzene and cyclohexane

TR - reactor temperature , $^{\circ}$C.

VAL,VBL - volumetric fraction of benzene and cyclohexane in liquid condensate sample, respectively

VCF,VHP - volumetric feed rate of liquid cyclohexane, and hydrogen gas at ambient conditions respectively, cm^3 per minute.

VEG - volumetric flow rate of exit gases from condenser at ambient conditions.

VPA,VPB - vapour pressure of cyclohexane and benzene at condenser temperature, mm of mercury

VPW - vapour pressure of water at ambient temperature

VSE - characteristic length of pellet, cm.

W - same as GCAT

WLS - mass of liquid sample collected at exit of condenser in time T.

X_A,X_B - mole fraction of cyclohexane and benzene in liquid sample, respectively.

YA,YB - activity coefficients of cyclohexane and benzene at condenser exit conditions.

YAG,YBG - mole fractions of cyclohexane and benzene in gas phase, respectively.

APPENDIX-A

Experimental Results and Calculated Values of Conversion and Material Balance

TABLE A-1 SET NO 1

VCF-1.0 GCAT-10.2263 TR-310 VHF-1028 P-739 TC-6.0 TA-22.C

Set No.	MEASURED VALUES				CALCULATED VALUES						
		Liquid Product		Gaseous Product	Feed	Product					
	Time min.	WLS g	VBL %	VEG Lit/min	CMF gmol	BMF gmol	AMU gmol	CHC gmol	PCH %	PB %	PERH %
*1	18-42	13.7919	6.69	1.163	0.2219	0.0191	0.2041	-0.0013	92.00	8.60	1.15
2	42-90	24.7980	6.18	1.153	0.4437	0.0328	0.3790	-0.0319	85.42	7.38	1.08
3	90-145	20.0328	5.61	1.135	0.5084	0.0337	0.4322	-0.0425	85.01	6.64	-0.37
4	145-188	22.8940	5.49	1.148	0.3975	0.0266	0.3495	0.0214	87.93	6.70	1.10
*5	188-218	17.8360	5.60	1.156	0.2773	0.0205	0.2647	-0.0079	95.46	7.39	1.36
6	218-255	18.6008	5.12	1.144	0.3420	0.0205	0.2895	0.0320	84.64	6.01	1.22
7	255-290	18.2884	5.10	1.145	0.3235	0.0199	0.2818	0.0218	87.08	6.15	1.21
8	290-318	15.1527	4.95	1.140	0.2588	0.0158	0.2314	0.0116	89.40	6.10	0.79
9	318-350	18.2603	5.13	1.150	0.2958	0.0195	0.2750	0.0013	92.98	6.58	1.38
10	350-390	21.2580	4.87	1.145	0.3698	0.0220	0.3269	0.0209	88.41	5.94	1.36

TABLE A-2 SET NO 2

VCF-1.5 GCAT-34.1307 TR-355 VHF-362.5 P-736 TC-6.8 TA-25.0

Set No.	Time min.	WLS g	VBL %	VEG Lit/min	CMF gmol	BMF gmol	AMU gmol	CHC gmol	PCH %	PB %	PERH %
1	25-45	15.8403	67.6	1.137	0.2773	0.1764	0.0722	0.0287	26.05	63.62	5.19
2	45-65	15.6193	65.4	1.096	0.2773	0.1682	0.0757	0.0334	27.30	60.67	3.33
3	65-90	20.2772	64.6	1.141	0.3467	0.2161	0.1006	0.0300	29.03	62.35	9.96
4	90-115	21.3536	61.3	1.130	0.3467	0.2148	0.1145	0.0174	33.02	61.97	8.18
5	115-140	19.4595	60.1	1.048	0.3467	0.1930	0.1080	0.0457	31.15	55.66	5.71
6	140-170	24.3444	57.6	1.052	0.4160	0.2308	0.1426	0.0426	34.28	55.49	7.24
7	170-200	25.1006	54.9	1.034	0.4160	0.2260	0.1551	0.0349	37.29	54.34	5.96
8	200-230	24.0714	55.9	1.004	0.4160	0.2208	0.1457	0.0495	35.04	53.08	1.96
*9	230-250	22.3552	54.5	1.170	0.2773	0.1717	0.1194	-0.0138	46.01	58.98	6.15

TABLE A-3 SET NO 3

VCF-1.5 GCAT-28.7307 TR-355 VHF-810.5 P-735. TC-10.0 TA-30.

1	20-43	16.6413	49.4	1.483	0.3189	0.1585	0.1354	0.0250	42.45	49.69	1.78
2	43-67	16.405	48.7	1.447	0.3328	0.1558	0.1367	0.0403	41.07	46.81	1.62
3	67-95	21.3585	47.2	1.446	0.3883	0.1918	0.1780	0.0185	45.84	49.40	-0.43
4	95-125	22.5050	43.9	1.433	0.4160	0.1892	0.1991	0.0277	47.87	45.47	1.84
5	125-150	20.2540	41.2	1.455	0.3467	0.1581	0.1849	0.0037	53.33	45.61	4.17
6	150-180	25.6395	38.5	1.360	0.4853	0.1901	0.2474	0.0478	50.98	39.17	2.16
7	180-215	21.0806	37.9	1.340	0.4160	0.1553	0.2070	0.0537	49.77	37.33	2.39
8	215-240	17.4033	36.9	1.355	0.3467	0.1259	0.1748	0.0460	50.42	36.32	5.51

TABLE A-4 SET NO 4

VCF-1.25 GCAT-24.0616 TR-350. VHF-277 P-730 TC-6.0 TA-20.

1	14-45	21.7128	64.5	0.893	0.3582	0.2263	0.1055	0.0264	29.46	63.18	1.70
2	45-75	21.8025	64.3	0.912	0.3467	0.2260	0.1062	0.0145	30.64	65.20	1.70
3	75-105	21.2140	59.1	0.846	0.3467	0.2023	0.1176	0.0268	33.91	58.37	1.01
4	105-135	21.7413	59.8	0.886	0.3467	0.2119	0.1197	0.0157	34.55	61.14	5.77
5	135-165	22.3740	58.0	0.902	0.3467	0.2102	0.1276	0.0089	36.82	60.64	10.77
6	165-195	22.2307	53.0	0.800	0.3467	0.1891	0.1395	0.0181	40.24	54.55	-2.50
7	195-240	30.1037	54.2	0.806	0.5200	0.2660	0.1875	0.0665	36.06	51.15	10.45

TABLE A-5 SET NO 5

VCF-1.5 GCAT-29.8309 TR-390 VHF-1066 P-735 TC-7.7 TA-31.

1	21-45	15.9580	70.7	1.944	0.3328	0.2225	0.0817	0.0286	24.54	66.85	0.92
2	45-60	9.2820	70.5	1.900	0.2080	0.1312	0.0487	0.0281	23.42	63.08	1.01
3	60-95	23.7718	68.2	1.902	0.4853	0.3169	0.1297	0.0387	26.73	65.30	-1.19
4	95-125	21.3565	67.0	1.938	0.4160	0.2779	0.1196	0.0185	28.76	66.81	3.71
*5	125-155	22.8940	64.6	1.950	0.4160	0.2831	0.1344	-0.0015	32.32	68.06	0.66
6	155-180	16.7211	66.1	1.870	0.3467	0.2170	0.0971	0.0326	28.01	62.57	-1.17
7	180-212	21.0500	61.3	1.860	0.4437	0.2568	0.1398	0.0471	31.52	57.89	2.82
8	212-240	18.1092	60.3	1.828	0.3883	0.2178	0.1234	0.0471	31.78	56.11	1.87

TABLE A-6 SET NO 6

VCF-1.5 GCAT-20.8413 TR-315 VHF-502 P-735 TC-6.5 TA-20.

*1	15-30	14.9676	26.5	0.906	0.2080	0.0656	0.1469	-0.0045	70.64	31.53	3.61
2	30-55	23.0850	25.3	0.870	0.3467	0.0992	0.2302	0.0173	66.39	28.61	3.01
3	55-87	31.0567	22.9	0.839	0.4437	0.1176	0.3189	0.0072	71.88	26.51	1.67
4	87-115	25.8510	22.2	0.815	0.3582	0.0953	0.2688	0.0241	69.25	24.56	1.28
5	115-145	28.0855	21.1	0.810	0.4160	0.0984	0.2958	0.0218	71.11	23.65	2.26
6	145-180	34.2750	17.8	0.790	0.4853	0.1010	0.3741	0.0102	77.09	20.81	4.56

TABLE A-7 SET NO 7

VCF-1.0 GCAT-10.9685 TR-345 VHF-442 P-730 TC-6.5 TA-20.

1	14-40	15.0920	32.0	0.742	0.2403	0.0835	0.1436	0.0132	59.76	34.72	2.28
2	40-70	17.4208	29.6	0.725	0.2773	0.0895	0.1719	0.0159	61.98	32.27	2.62
3	70-110	24.6226	26.6	0.714	0.3698	0.0190	0.2507	0.0061	67.81	30.52	3.12
4	110-130	11.4578	25.9	0.691	0.1849	0.0516	0.1187	0.0146	64.19	27.91	2.42
5	130-170	24.7366	23.0	0.685	0.3698	0.0980	0.2632	0.0086	71.19	26.51	3.42
6	170-205	22.3579	21.5	0.675	0.3235	0.0824	0.2411	0.0000	74.51	25.47	2.98
*7	205-240	22.6466	18.0	0.651	0.3235	0.0698	0.2542	-0.0005	75.56	21.59	4.15
8	240-270	17.2885	17.5	0.629	0.2773	0.0527	0.1978	0.0..68	71.34	18.99	3.64
9	270-300	18.1480	16.1	0.620	0.2773	0.0504	0.2095	0.0174	75.53	18.19	3.03
10	300-340	23.0326	14.8	0.610	0.3698	0.0594	0.2718	0.0386	73.50	16.07	4.34

TABLE A-8 SET NO 8

VCF-1.5 GCAT-29.5788 TR-410 VHF-997 P-735 TC-8.3 TA-31.

1	17-37	13.2118	79.7	1.942	0.2773	0.2065	0.0479	0.0229	17.27	74.47	-1.03
2	37-60	15.5250	76.9	1.940	0.3189	0.2337	0.0633	0.0219	19.85	73.37	0.62
3	60-105	31.8117	74.7	1.955	0.6240	0.4597	0.1413	0.0230	22.65	73.67	2.95
4	105-135	20.7513	69.7	1.860	0.4160	0.2811	0.1076	0.0273	25.87	67.57	-1.20
5	135-165	21.8371	70.3	1.932	0.4160	0.2967	0.1105	0.0088	26.57	71.33	1.33
6	165-195	19.0854	67.6	1.816	0.4160	0.2567	0.1081	0.0512	25.98	61.72	1.21

TABLE A-9 SET NO 9

VCF-2.7 GCAT-26.2677 TR-370 VHF-3096 P-730 TC-7.5 TA-30.5

1	24-40	19.0316	29.0	4.017	0.3993	0.1303	0.2461	0.0229	61.63	32.63	0.41
2	40-60	23.6922	28.0	3.987	0.4992	0.1541	0.3133	0.0318	62.76	30.87	0.67
*3	60-90	39.3024	28.4	4.035	0.7488	0.2501	0.5002	-0.0015	66.80	33.41	0.46
4	90-120	35.0823	27.1	3.957	0.7488	0.2220	0.4709	0.0559	62.89	29.65	0.57
5	120-150	34.0496	24.2	4.004	0.7488	0.1977	0.4840	0.0671	64.63	26.41	0.41
6	150-180	36.9970	21.6	3.851	0.7488	0.1843	0.5210	0.0435	69.58	24.62	0.70
7	180-215	42.0568	22.2	3.856	0.8736	0.2172	0.5932	0.0632	67.91	24.86	0.68
8	215-240	32.6665	20.7	3.850	0.6240	0.1530	0.4563	0.0147	73.14	24.53	0.74
*9	240-270	41.4179	19.5	3.831	0.7488	0.1795	0.5763	-0.0070	76.97	23.98	0.54
10	270-300	36.2496	20.0	3.843	0.7488	0.1694	0.5252	0.0542	70.14	22.63	1.78
11	300-330	36.3431	18.5	3.780	0.7488	0.1568	0.5335	0.0585	71.25	20.94	1.00

TABLE A-10 SET NO 10

VCF-2.06 GCAT-25.7319 TR-435 VHF-1980 P-725 TC-6.3 TA-25.0

1	22-40	15 0981	74.4	3.234	0.3428	0.2388	0.0746	0.0294	21.76	69.66	2.93
2	40-60	16.8588	72.7	3.206	0.3809	0.2601	0.0881	0.0327	23.14	68.30	1.61
3	60-85	22.3695	69.5	3.200	0.4761	0.3248	0.1269	0.0244	26.65	68.22	-0.32
4	85-120	33.1567	69.0	3.255	0.6665	0.4716	0.1880	0.0069	28.21	70.76	1.70
*5	120-150	29.8457	65.7	3.237	0.5713	0.3995	0.1828	-0.0110	32.00	69.93	0.75
6	150-180	25.3237	62.8	3.058	0.5713	0.3390	0.1753	0.0570	30.68	59.33	-0.26
7	180-210	25.4674	61.2	3.062	0.5713	0.3329	0.1834	0.0550	32.10	58.28	1.24
8	210-240	25.2778	60.0	3.039	0.5713	0.3249	0.1875	0.0589	32.83	56.88	1.21

TABLE A-11 SET NO 11

VCF-1.5 GCAT-24.8715 TR-385 VHF-1016 P-732 TC-6.0 TA-30.0

1	21-40	14.3716	63.1	1.821	0.2635	0.1670	0.0840	0.0125	31.88	63.40	-0.78
2	40-60	15.6634	61.1	1.832	0.2773	0.1756	0.0956	0.0061	34.48	63.33	0.29
3	60-85	19.4531	62.2	1.845	0.3467	0.2224	0.1159	0.0084	33.43	64.14	1.67
4	85-100	10.7096	59.3	1.764	0.2080	0.1188	0.0696	0.0196	33.44	57.10	0.62
5	100-125	17.3809	56.8	1.720	0.3467	0.1857	0.1199	0.0411	34.58	53.57	-0.88
6	125-155	22.9319	54.9	1.747	0.4160	0.2327	0.1613	0.0220	38.77	55.94	2.63

*7	155-185	24.7826	52.2	1.752	0.4160	0.2359	0.1810	-0.0009	43.51	56.70	0.50
6	185-220	25.8856	50.9	1.696	0.4853	0.2460	0.1985	0.0408	40.91	50.68	0.10
9	220-240	14.5872	46.3	1.662	0.2773	0.1272	0.1223	0.0278	44.91	45.88	0.16
10	240-270	21.6436	44.1	1.624	0.4160	0.1802	0.1885	0.0473	45.30	43.31	0.37

TABLE A-12 SET NO 12

VCF-1.25 GCAT-21.1381 TR-365 VHF-380 P-742 TC-6.0 TA-20.0

1	20-45	16.9690	57.9	0.972	0.2889	0.1641	0.1004	0.0244	34.75	56.82	10.96
2	45-75	20.9118	54.0	0.907	0.3467	0.1867	0.1328	0.0272	38.30	53.85	1.59
3	75-105	21.0610	52.5	0.915	0.3467	0.1834	0.1382	0.0251	39.88	52.90	5.76
4	105-145	22.6216	50.5	0.902	0.3467	0.1877	0.1527	00.0063	44.06	54.14	-1.14
5	145-175	23.1117	47.4	0.901	0.3467	0.1800	0.1652	0.0015	47.64	51.93	4.47
*6	175-205	24.0367	45.0	0.392	0.3467	0.1771	0.1784	-0.0088	51.46	51.09	4.15
7	205-230	17.8901	41.7	0.803	0.2889	0.1231	0.1413	0.0245	48.91	42.62	-1.52
8	230-270	29.4048	39.7	0.819	0.4622	0.1928	0.2398	0.0296	51.89	41.71	5.09

TABLE A-13 SET NO 13

VCF-1.25 GCAT-35.0256 TR-420 VHF-965 P-731 TC-8.5 TA-30.5

1	21-45	11.6225	88.3	1.856	0.2773	0.2202	0.0266	0.0305	9.61	79.40	3.46
2	45-70	12.5840	88.7	1.830	0.2889	0.2334	0.0284	0.0271	9.82	80.79	-0.43
3	70-90	9.8646	87.5	1.848	0.2311	0.1829	0.0249	0.0233	10.77	79.17	2.86
4	90-120	16.3233	86.3	1.870	0.3467	0.2896	0.0433	0.0138	12.49	83.55	0.68
5	120-140	11.7224	84.2	1.885	0.2311	0.1989	0.0347	-0.0025	15.02	86.06	-0.37
6	140-170	15.2068	84.7	1.809	0.3467	0.2693	0.0457	0.0317	13.18	77.69	0.40
7	170-200	14.7861	81.0	1.763	0.3467	0.2524	0.0549	0.0394	15.84	72.81	0.57
8	200-225	11.8757	78.5	1.745	0.2889	0.1985	0.0501	0.0403	17.33	68.73	2.77

TABLE A-14 SET NO 14

VCF-1.5 GCAT-28.3169 TR-420 VHF-1064 P-738 TC-8.0 TA-30.0

1	20-40	13.5803	89.4	2.190	0.2773	0.2408	0.0270	0.0095	9.73	86.82	3.10
2	40-65	16.8394	87.8	2.130	0.3467	0.2920	0.0381	0.0166	10.99	84.23	0.43

3	65-100	22.6310	86.8	2.136	0.4853	0.3946	0.0563	0.0344	11.61	81.30	3.99
4	100-130	18.4993	85.8	2.046	0.4160	0.3199	0.0496	0.0465	11.91	76.89	0.61
5	130-160	18.3807	88.1	2.028	0.4160	0.3248	0.0414	0.0498	9.95	78.07	-2.15
6	160-190	18.4002	85.2	2.027	0.4160	0.3158	0.0512	0.0490	12.32	75.92	-0.08
7	190-225	21.0764	82.0	2.017	0.4853	0.3518	0.0714	0.0621	14.72	72.50	2.52
8	225-265	24.1884	77.4	2.008	0.5547	0.3833	0.1020	0.0694	18.38	69.11	5.14
9	265-300	21.9102	75.5	1.930	0.4853	0.3313	0.0969	0.0571	19.97	68.26	-0.91

TABLE A-15 SET NO 15

VCF-1.5 GCAT-25.7305 TR-400. VHF-1050 P-730 TC-6.0 TA-30.5

1	16-30	9.0847	71.2	1.887	0.1941	0.1237	0.0442	0.0262	22.76	63.70	1.32
2	30-60	20.5517	68.1	1.852	0.4160	0.2643	0.1082	0.0435	26.01	63.53	-0.41
3	60-95	25.1568	65.3	1.880	0.4853	0.3080	0.1418	0.0355	29.23	63.47	0.85
4	95-120	19.5460	67.7	1.968	0.3467	0.2442	0.1014	0.0011	29.25	70.46	1.29
5	120-150	20.5894	65.8	1.854	0.4160	0.2566	0.1159	0.0435	27.85	61.67	1.35
6	150-175	16.9670	61.4	1.809	0.3467	0.1980	0.1070	0.0417	30.86	57.13	1.23
7	175-210	22.7755	59.1	1.767	0.4853	0.2586	0.1530	00.0737	31.53	53.28	1.56
8	210-240	24.6317	53.8	1.816	0.4160	0.2432	0.1757	-0.0029	42.23	58.46	0.35
9	240-270	22.1022	54.0	1.788	0.4160	0.2256	0.1602	0.0302	38.51	54.24	2.38

TABLE A-16 SET NO 16

VCF-1.5 GCAT-28.2129 TR-400. VHF-1050 P-738 TC-8.0 TA-30.0

1	13-35	13.5121	74.5	1.960	0.3051	0.2044	0.0630	0.0377	20.66	67.01	4.40
2	35-55	13.4309	71.7	1.932	0.2773	0.1899	0.0666	0.0208	24.00	68.47	0.29
3	55-80	17.2964	69.6	1.958	0.3467	0.2359	0.0909	0.0199	26.21	68.05	2.32
4	80-110	22.5163	68.7	1.975	0.4160	0.2983	0.1192	-0.0015	28.66	71.70	0.65
5	110-135	17.7242	67.8	1.931	0.3467	0.2347	0.0977	0.0143	28.18	67.70	0.95
6	135-170	25.2985	64.3	1.880	0.4853	0.3154	0.1519	0.0180	31.29	65.00	-0.82
7	170-200	20.7020	62.8	1.885	0.4160	0.2569	0.1317	0.0274	31.65	61.75	3.05
8	200-235	23.1244	62.0	1.830	0.4853	0.2851	0.1510	0.0492	31.11	58.74	1.31
9	235-270	22.9349	61.5	1.801	0.4853	0.2801	0.1512	00.0540	31.16	57.71	-0.19
10	270-300	20.9630	58.6	1.830	0.4160	0.2418	0.1461	0.0281	35.11	51.22	1.93

TABLE A-17 SET NO 17

VCF-1.25 GCAT-30.6438 TR-340 VHF-364 P-730 TC-6.5 TA-20.

* 1	16-32	12.0137	57.6	0.990	0.1849	0.1144	0.0708	-0.0003	38.27	61.91	5.13
2	32-70	27.5460	55.5	0.943	0.4391	0.2532	0.1699	0.0160	38.70	57.67	3.28
3	70-105	25.3139	52.8	0.913	0.4044	0.2213	0.1649	0.0182	40.77	54.72	2.68
4	105-135	21.2233	52.0	0.898	0.3467	0.1832	0.1408	0.0227	40.62	52.85	3.36
5	135-170	24.0360	53.4	0.890	0.4044	0.2133	0.1553	0.0358	38.41	52.74	1.57
6	170-200	23.0279	47.9	0.903	0.3467	0.1821	0.1639	0.0007	47.27	52.53	5.41
7	200-230	22.6600	42.0	0.827	0.3467	0.1570	0.1780	0.0117	51.36	45.29	3.39
8	230-270	28.8412	43.2	0.812	0.4622	0.2060	0.2228	0.0334	48.20	44.58	1.26
9	270-300	21.3937	40.5	0.766	0.3467	0.1433	0.1726	0.0308	49.80	41.35	-0.85
10	300-330	20.8560	39.2	0.803	0.3467	0.1369	0.1737	0.0361	50.12	39.49	11.34

TABLE A-18 SET NO 18

VCF-1.25 GCAT-38.1509 TR-380 VHF-487 P-740 TC-7.5 TA-21.0

1	16-40	16.1641	87.0	1.363	0.2773	0.2452	0.0332	-0.0011	11.98	88.43	4.06
2	40-65	16.7735	82.8	1.307	0.2889	0.2415	0.0449	0.0025	15.54	83.60	1.76
3	65-85	12.7075	81.4	1.276	0.2311	0.1817	0.0371	0.0123	16.05	78.61	4.73
4	85-115	19.4425	79.0	1.242	0.3467	0.2700	0.0607	0.0160	17.51	77.90	-0.62
5	115-140	14.9594	81.8	1.230	0.2889	0.2160	0.0431	0.0298	14.91	74.79	2.75
6	140-170	18.2487	81.2	1.250	0.3467	0.2619	0.0542	0.0306	15.65	75.54	5.24
7	170-200	20.1048	80.4	1.290	0.3467	0.2814	0.0610	0.0043	17.60	81.16	2.78
8	200-225	13.1572	79.5	1.222	0.2889	0.1921	0.0445	0.0523	15.40	66.49	8.44
9	225-250	13.3880	78.3	1.232	0.2889	0.1943	0.0469	0.0477	16.23	67.26	12.44
10	250-280	17.5921	75.4	1.120	0.3467	0.2355	0.0677	0.0435	19.54	67.93	-1.26
*11	280-315	24.5280	72.4	1.245	0.4044	0.3074	0.1020	-0.0050	25.23	76.01	3.13
12	315-345	18.3121	69.2	1.180	0.3467	0.2252	0.0870	0.0344	25.10	64.98	7.45

TABLE A-19 SET NO 19

VCF-1.0 GCAT-36.6219 TR-405 VHF-412 P-732 TC-8.5 TA-20.0

1	15-30	7.5115	94.3	1.164	0.1387	0.1289	0.0073	0.0025	5.28	90.94	5.92
2	30-60	14.8804	91.8	1.106	0.2773	0.2465	0.0204	0.0104	5.37	88.68	-0.49
3	60-85	11.7427	91.0	1.130	0.2311	0.2000	0.0185	0.0126	8.01	86.53	10.40
4	85-110	11.6729	88.4	1.050	0.2311	0.1900	0.0229	0.0182	9.91	82.18	-1.90
5	110-140	15.1247	82.1	1.070	0.2773	0.2244	0.0441	0.0088	15.91	80.94	4.49
6	140-165	12.1510	83.9	1.012	0.2311	0.1828	0.0317	0.0166	13.72	79.08	-5.46
7	165-195	15.5717	80.9	1.070	0.2773	0.2264	0.0479	0.0030	17.28	81.63	3.26
8	195-225	15.2610	82.3	1.060	0.2773	0.2258	0.0437	0.0078	15.77	81.43	1.38
9	225-255	13.6046	79.1	0.984	0.2773	0.1967	0.0466	0.0340	16.79	70.94	1.99

APPENDIX - B

Comparison of Smoothened Experimental Conversion Values with those Predicted by the Proposed Model

		TABLE B-1			SET NO 1			
Sl. No.	Time min.	Smoothened Data X_B	X_A	$X_C = 1 - X_A - X_B$	With Optimized m and k_d X_B	X_A	From Model X_B	X_A
1	0	0.082	0.855	0.062	0.0832	0.8547	0.1189	0.8606
2	30	0.080	0.857	0.063	0.0799	0.8578	0.1154	0.8641
3	60	0.076	0.859	0.065	0.0768	0.8607	0.1120	0.8674
4	90	0.070	0.860	0.070	0.0739	0.8635	0.1088	0.8706
5	120	0.069	0.862	0.069	0.0711	0.8662	0.1056	0.8737
6	150	0.066	0.865	0.069	0.0685	0.8687	0.1025	0.8767
7	180	0.063	0.870	0.067	0.0659	0.8711	0.0995	0.8797
8	210	0.061	0.875	0.064	0.0635	0.8735	0.0966	0.8825
9	240	0.060	0.879	0.061	0.0612	0.8756	0.0938	0.8853
10	270	0.059	0.881	0.060	0.0591	0.8776	0.0911	0.8880
11	300	0.058	0.885	0.057	0.0570	0.8794	0.0884	0.8906
12	330	0.057	0.891	0.052	0.0550	0.8814	0.0859	0.8931
13	360	0.056	0.900	0.044	0.0531	0.8832	0.0834	0.8955
14	390	0.055	0.901	0.044	0.0513	0.8850	0.0810	0.8979
PERCENTAGE ERROR VARIANCE :								
			RELATIVE –		2.182	0.484	31.16	0.536
			ABSOLUTE –		0.134	0.538	2.024	0.773
		TABLE B-2			SET NO 2			
1	0	0.660	0.237	0.103	0.6604	0.2365	0.6945	0.2130
2	30	0.626	0.260	0.114	0.6395	0.2509	0.6707	0.2296
3	60	0.610	0.280	0.110	0.6192	0.2651	0.2464	0.6467
4	90	0.588	0.300	0.112	0.5993	0.2791	0.6227	0.2634
5	120	0.570	0.318	0.112	0.5798	0.2928	0.5985	0.2806
6	150	0.552	0.339	0.109	0.5608	0.3065	0.5743	0.2980
7	180	0.539	0.356	0.105	0.5421	0.3199	0.5501	0.3155
8	210	0.530	0.369	0.101	0.5238	0.3332	0.5259	0.3332
9	240	0.522	0.380	0.098	0.5058	0.3462	0.5019	0.3509
PERCENTAGE ERROR VARIANCE:								
			RELATIVE –		1.069	4.656	2.96	6.77
			ABSOLUTE –		0.605	2.61	1.778	3.855
		TABLE B-3			SET NO 3			
1	0	0.535	0.389	0.076	0.5352	0.3887	0.5651	0.3597
2	30	0.510	0.415	0.075	0.5104	0.4101	0.5441	0.3775
3	60	0.486	0.440	0.074	0.4863	0.4309	0.5234	0.3952
4	90	0.460	0.466	0.074	0.4629	0.4511	0.5031	0.4127
5	120	0.435	0.487	0.078	0.4403	0.4708	0.4831	0.4298
6	150	0.413	0.501	0.086	0.4185	0.4898	0.4636	0.4467
7	180	0.393	0.515	0.092	0.3975	0.5082	0.4445	0.4632
8	210	0.377	0.525	0.098	0.3773	0.5259	0.4259	0.4794
9	240	0.360	0.531	0.109	0.3579	0.5428	0.4078	0.4952
PERCENTAGE ERROR VARIANCE :								
			RELETIVE –		0.47	1.269	6.493	5.951
			ABSOLUTE –		0.195	0.951	2.702	5.851

TABLE B-4 SET NO 4

1	0	0.670	0.264	0.066	0.6702	0.2638	0.6320	0.2822
2	30	0.648	0.290	0.062	0.6528	0.2777	0.6048	0.3028
3	60	0.625	0.312	0.063	0.635	0.2919	0.5776	0.3236
4	90	0.606	0.335	0.059	0.6168	0.3064	0.5504	0.3445
5	120	0.585	0.352	0.063	0.5984	0.3212	0.5232	0.3654
6	150	0.570	0.369	0.061	0.5797	0.3363	0.4962	0.3863
7	180	0.555	0.382	0.063	0.5607	0.3516	0.4695	0.4072
8	210	0.543	0.396	0.061	0.5414	0.3672	0.4430	0.4279
9	240	0.534	0.405	0.061	0.5220	0.3830	0.4170	0.4485
PERCENTAGE ERROR VARIANCE :								
			RELATIVE -		0.927	4.251	8.046	3.815
			ABSOLUTE		0.537	2.575	4.514	1.834

TABLE B-5 SET NO 5

1	0	0.685	0.211	0.104	0.6855	0.2106	0.7033	0.2134
2	30	0.668	0.230	0.102	0-6700	0.2219	0.6817	0.2302
3	60	0.650	0.249	0.101	0.6550	0.2329	0.6607	0.2467
4	90	0.635	0.261	0.104	0.6403	0.2438	0.6402	0.2629
5	120	0.620	0.275	0.105	0.6260	0.2546	0.6203	0.2789
6	150	0.608	0.289	0.103	0.6120	0.2652	0.6008	0.2946
7	180	0.597	0.300	0.103	0.5983	0.2756	0.5818	0.3100
8	210	0.589	0.312	0.099	0.5850	0.2858	0.5634	0.3251
9	240	0.580	0.321	0.099	0.5719	0.2959	0.5454	0.3399
PERCENTAGE ERROR VARIANCE :								
			RELATIVE -		0.467	4.176	1.794	1.732
			ABSOLUTE		0.284	2.021	1.081	0.328

TABLE B-6 SET NO 6

1	0	0.317	0.620	0.063	0.3266	0.6085	0.3069	0.6425
2	30	0.291	0.650	0.059	0.3030	0.6298	0.2905	0.6576
3	60	0.268	0.680	0.052	0.2806	0.6501	0.2746	0.6724
4	90	0.248	0.708	0.044	0.2595	0.6692	0.2592	0.6866
5	120	0.231	0.730	0.039	0.2397	0.6871	0.2444	0.7004
6	150	0.223	0.747	0.030	0.2213	0.7038	0.2300	0.7137
7	180	0.215	0.760	0.025	0.2041	0.7194	0.2163	0.7265
PERCENTAGE ERROR VARIANCE :								
			RELATIVE -		2.477	2.973	2.115	2.116
			ABSOLUTE -		0.634	2.78	0.528	0.647

TABLE B-7 SET NO 7

1	0	0.363	0.519	0.058	0.3632	0.5787	0.3819	0.5652
2	30	0.343	0.602	0.055	0.3413	0.5989	0.3591	0.5862
3	60	0.325	0.628	0.047	0.3197	0.6186	0.3373	0.6063
4	90	0.307	0.650	0.043	0.2987	0.6379	0.3165	0.6255
5	120	0.286	0.670	0.044	0.2783	0.6566	0.2968	0.6438
6	150	0.262	0.687	0.051	0.2586	0.6747	0.2780	0.6611
7	180	0.240	0.700	0.060	0.2396	0.6922	0.2603	0.6775
8	210	0.219	0.708	0.073	0.2215	0.7089	0.2436	0.6930
9	240	0.200	0.721	0.079	0.2042	0.7248	0.2278	0.7076
10	270	0.185	0.730	0.085	0.1879	0.7398	0.2131	0.7213

11	300	0.170	0.738	0.092	0.1724	0.7541	0.1992	0.7341
12	330	0.157	0.745	0.098	0.1579	0.7675	0.1863	0.7461

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0.951	0.959	6.492	1.635
ABSOLUTE -	0.252	1.014	1.290	1.750

TABLE B-8 SET NO 8

1	0	0.793	0.145	0.062	0.7933	0.1447	0.7827	0.1305
2	30	0.760	0.179	0.061	0.7594	0.1709	0.7613	0.1449
3	60	0.726	0.205	0.069	0.7307	0.1937	0.7409	0.1590
4	90	0.700	0.230	0.070	0.7054	0.2144	0.7212	0.1729
5	120	0.678	0.250	0.072	0.6825	0.2333	0.7022	0.1866
6	150	0.659	0.269	0.072	0.6616	0.2507	0.6837	0.2001
7	180	0.645	0.289	0.066	0.6425	0.2668	0.6658	0.2134
8	210	0.633	0.301	0.066	0.6248	0.2817	0.6483	0.2265

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0.404	3.705	1.665	14.10
ABSOLUTE -	0.268	1.597	1.122	4.34

TABLE B-9 SET NO 9

1	0	0.350	0.591	0.059	0.3462	0.5955	0.3255	0.6334
2	30	0.327	0.609	0.064	0.3264	0.6140	0.3093	0.6488
3	60	0.302	0.622	0.076	0.3089	0.6304	0.2942	0.6633
4	90	0.288	0.640	0.072	0.2932	0.6451	0.2799	0.6770
5	120	0.270	0.651	0.079	0.2791	0.6583	0.2665	0.6898
6	150	0.259	0.665	0.076	0.2665	0.6702	0.2540	0.7018
7	180	0.251	0.679	0.070	0.2549	0.6810	0.2422	0.7131
8	210	0.245	0.690	0.065	0.2444	0.6909	0.2311	0.7238
9	240	0.239	0.705	0.056	0.2348	0.7000	0.2207	0.7338
10	270	0.231	0.715	0.054	0.2259	0.7083	0.2109	0.7431
11	300	0.220	0.725	0.055	0.2178	0.7160	0.2017	0.7520
12	330	0.218	0.730	0.052	0.2102	0.7231	0.1930	0.7603

PERCENTAGE ERROR VARIANCE :

RELATIVE -	1.273	0.537	3.804	3.258
ABSOLUTE -	0.327	0.585	0.961	3.808

TABLE B-10 SET NO 10

1	0	0.740	0.183	0.077	0.7405	0.1825	0.7005	0.2283
2	30	0.711	0.218	0.071	0.7107	0.2058	0.6699	0.2536
3	60	0.685	0.248	0.067	0.6842	0.2270	0.6424	0.2767
4	90	0.662	0.273	0.065	0.6600	0.2467	0.6173	0.2979
5	120	0.640	0.291	0.069	0.6377	0.2650	0.5943	0.3176
6	150	0.618	0.302	0.080	0.6177	0.2822	0.5730	0.3360
7	180	0.596	0.314	0.090	0.5979	0.2983	0.5533	0.3531
8	210	0.579	0.322	0.099	0.5799	0.3134	0.5350	0.3690
9	240	0.562	0.327	0.111	0.5632	0.3276	0.5179	0.3839

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0.138	3.821	4.189	9.077
ABSOLUTE -	0.084	1.619	2.652	4.225

TABLE B-11 SET NO 11

1	0	0.675	0.280	0.045	0.6752	0.2798	0.6386	0.2846
2	30	0.642	0.307	0.051	0.6460	0.3052	0.6140	0.3050
3	60	0.610	0.329	0.061	0.6176	0.3313	0.5902	0.3249
4	90	0.580	0.349	0.071	0.5900	0.3563	0.5673	0.3442
5	120	0.550	0.368	0.082	0.5631	0.3806	0.5451	0.3629
6	150	0.530	0.388	0.082	0.537	0.4043	0.5237	0.3811
7	180	0.510	0.405	0.085	0.5121	0.4272	0.5031	0.3987
8	210	0.489	0.425	0.086	0.4879	0.4492	0.4833	0.4158
9	240	0.470	0.442	0.088	0.4648	0.4704	0.4642	0.4322
10	270	0.451	0.458	0.091	0.4427	0.4907	0.4460	0.4480

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0 799	2.647	1.628	1.027
ABSOLUTE -	0.430	1.632	1.029	0.542

TABLE B-12 SET NO 12

1	0	0.615	0.315	0.070	0.6168	0.3130	0.6232	0.2953
2	30	0.589	0.348	0.063	0.5846	0.3397	0.5959	0.3170
3	60	0.560	0.377	0.063	0.5564	0.3633	0.5688	0.3385
4	90	0.532	0.406	0.062	0.5311	0.3846	0.5421	0.3600
5	120	0.508	0.431	0.061	0.5082	0.4041	0.5159	0.3812
6	150	0.483	0.460	0.057	0.4873	0.4219	0.4901	0.4021
7	180	0.462	0.480	0.058	0.4682	0.4383	0.4649	0.4227
8	210	0.448	0.497	0.055	0.4505	0.4535	0.4403	0.4428
9	240	0.430	0.510	0.060	0.4342	0.4675	0.4163	0.4625
10	270	0.418	0.523	0.059	0.419	0.4805	0.3932	0.4816

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0.429	4.049	1.522	6.249
ABSOLUTE -	0.208	3.118	0.688	4.942

TABLE B-13 SET NO 13

1	0	0.831	0.072	0.097	0.8314	0.0715	0.8540	0.0544
2	30	0.811	0.091	0.098	0.8155	0.0797	0.8402	0.0608
3	60	0.800	0.105	0.095	0.8001	0.0879	0.8271	0.0672
4	90	0.782	0.115	0.103	0.7851	0.0962	0.8146	0.0735
5	120	0.769	0.127	0.104	0.7703	0.1046	0.8025	0.0799
6	150	0.754	0.139	0.107	0.7558	0.1131	0.7907	0.0863
7	180	0.740	0.153	0.107	0.7415	0.1218	0.7792	0.0928
8	210	0.728	0.170	0.102	0.7273	0.1305	0.7679	0.0993

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0.170	10.47	2.674	22.24
ABSOLUTE -	0.135	2.38	2.043	14.61

TABLE B-14 SET NO 14

1	0	0.880	0.075	0.045	0.8805	0.0748	0.8109	0.1036
2	30	0.860	0.089	0.051	0.8607	0.0887	0.7899	0.1170
3	60	0.835	0.101	0.064	0.8405	0.1035	0.7702	0.1298
4	90	0.806	0.110	0.084	0.8196	0.1190	0.7516	0.1424
5	120	0.782	0.120	0.098	0.7979	0.1360	0.7338	0.1548
6	150	0.761	0.131	0.108	0.7755	0.1536	0.7166	0.1669
7	180	0.742	0.142	0.116	0.7524	0.1721	0.7001	0.1788

8	210	0.720	0.157	0.123	0.7287	0.1914	0.6840	0.1905
9	240	0.700	0.175	0.125	0.7046	0.2114	0.6685	0.2020
10	270	0.688	0.188	0.124	0.6800	0.2320	0.6535	0.2133
11	300	0.680	0.200	0.120	0.6551	0.2530	0.6389	0.2243

PERCENTAGE ERROR VARIANCE:

RELATIVE -	0.993	10.27	3.85	15.72
ABSOLUTE -	0.722	2.488	3.05	3.95

TABLE B-15 SET NO 15

1	0	0.675	0.210	0.115	0.6756	0.2093	0.6865	0.2335
2	30	0.651	0.235	0.114	0.6560	0.2231	0.6620	0.2531
3	60	0.631	0.254	0.115	0.6372	0.2366	0.6384	0.2721
4	90	0.610	0.274	0.116	0.6191	0.2497	0.6156	0.2906
5	120	0.590	0.291	0.119	0.6015	0.2626	0.5936	0.3087
6	150	0.577	0.309	0.114	0.5845	0.2751	0.5725	0.3262
7	180	0.562	0.324	0.114	0.5681	0.2874	0.5520	0.3432
8	210	0.551	0.340	0.109	0.5521	0.2994	0.5324	0.3596
9	240	0.545	0.357	0.098	0.5367	0.3111	0.5134	0.3755
10	270	0.528	0.371	0.091	0.5217	0.3225	0.4952	0.3909

PERCENTAGE ERROR VARIANCE:

RELATIVE -	0.903	6.004	2.110	4.145
ABSOLUTE -	0.513	3.202	1.161	2.09

TABLE B-16 SET NO 16

1	0	0.710	0.205	0.085	0.7029	0.2130	0.7121	0.2050
2	30	0.692	0.227	0.081	0.6872	0.2252	0.6896	0.2223
3	60	0.675	0.245	0.080	0.6772	0.2368	0.6678	0.2393
4	90	0.660	0.262	0.078	0.6578	0.2482	0.6466	0.2560
5	120	0.645	0.280	0.075	0.6440	0.2891	0.6261	0.2724
6	150	0.630	0.295	0.075	0.6307	0.2698	0.6061	0.2884
7	180	0.615	0.306	0.079	0.6178	0.2802	0.5868	0.3041
8	210	0.601	0.318	0.081	0.6053	0.2902	0.5680	0.3194
9	240	0.590	0.330	0.080	0.5933	0.3000	0.5498	0.3344
10	270	0.581	0.340	0.079	0.5816	0.3096	0.5322	0.3489
11	300	0.571	0.350	0.079	0.5703	0.3188	0.5151	0.3630

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0.309	4.370	3.106	1.292
ABSOLUTE -	0.205	2.392	1.832	0.602

TABLE B-17 SET NO 17

1	0	0.601	0.339	0.060	0.6011	0.3389	0.6163	0.2964
2	30	0.582	0.358	0.060	0.5831	0.3543	0.5952	0.3127
3	60	0.563	0.376	0.061	0.5649	0.3699	0.5741	0.3292
4	90	0.549	0.395	0.056	0.5465	0.3856	0.5529	0.3458
5	120	0.528	0.416	0.056	0.5279	0.4016	0.5317	0.3625
6	150	0.510	0.436	0.054	0.5093	0.4176	0.5105	0.3792
7	180	0.489	0.455	0.056	0.4905	0.4338	0.4894	0.3960
8	210	0.468	0.469	0.063	0.4717	0.4500	0.4684	0.4127
9	240	0.450	0.480	0.070	0.4529	0.4663	0.4475	0.4294
10	270	0.430	0.491	0.079	0.4342	0.4826	0.4269	0.4459

11	300	0.411	0.501	0.088	0.4155	0.4988	0.4066	0.4623
12	330	0.402	0.515	0.083	0.3970	0.5149	0.3865	0.4785

PERCENTAGE ERROR VARIANCE :

RELATIVE -	0.398	1.638	1.005	6.921
ABSOLUTE -	0.173	2.231	0.503	5.276

TABLE B-18 SET NO 18

1	0	0.850	0.110	0.040	0.8502	0.1098	0.8274	0.0731
2	30	0.827	0.120	0.053	0.8329	0.1231	0.8120	0.0803
3	60	0.801	0.129	0.070	0.8152	0.1371	0.7968	0.0876
4	90	0.780	0.140	0.080	0.7970	0.1516	0.7818	0.0950
5	120	0.760	0.151	0.089	0.7782	0.1667	0.7668	0.1026
6	150	0.741	0.160	0.099	0.7589	0.1827	0.7520	0.1103
7	180	0.721	0.170	0.109	0.7391	0.1987	0.7373	0.1182
8	210	0.708	0.181	0.111	0.7189	0.2156	0.7225	0.1263
9	240	0.690	0.190	0.120	0.6982	0.2329	0.7079	0.1345
10	270	0.675	0.199	0.126	0.6771	0.2509	0.6932	0.1429
11	300	0.663	0.210	0.127	0.6558	0.2689	0.6786	0.1515
12	330	0.652	0.220	0.128	0.6342	0.2875	0.6640	0.1602

PERCENTAGE ERROR VARIANCE :

RELATIVE -	1.084	10.99	1.179	18.50
ABSOLUTE -	0.791	5.427	0.859	5.437

TABLE B-19 SET NO 19

1	0	0.930	0.022	0.048	0.9302	0.0218	0.8800	0.0209
2	30	0.900	0.050	0.050	0.9060	0.0312	0.8678	0.0233
3	60	0.870	0.075	0.055	0.8822	0.0422	0.8563	0.0258
4	90	0.840	0.100	0.060	0.8571	0.0549	0.8452	0.0283
5	120	0.811	0.116	0.073	0.8307	0.0697	0.8346	0.0309
6	150	0.785	0.133	0.082	0.8028	0.0867	0.8242	0.0336
7	180	0.761	0.150	0.089	0.7734	0.1058	0.8141	0.0363
8	210	0.739	0.162	0.099	0.7424	0.1270	0.8041	0.0391
9	240	0.718	0.175	0.107	0.7102	0.1501	0.7944	0.0420
10	270	0.700	0.190	0.110	0.6769	0.1747	0.7848	0.0450

PERCENTAGE ERROR VARIANCE :

RELATIVE -	1.098	19.016	4.146	41.45
ABSOLUTE -	0.849	3.432	3.099	9.42

APPENDIX - C

Formulation of Kinetic Model to Estimate Intrinsic Rate Constants for Undeactivated Catalyst:

Dehydrogenation : $\underset{A}{C_6H_{12}} \xrightarrow{k_1} \underset{B}{C_6H_6} + \underset{H}{3H_2}$

Hydrocracking : $C_6H_{12} + 2H_2 \xrightarrow{k_2} 2\ C_3H_8$

or $C_4H_{10} + C_2H_6$

or $C_5H_{12} + CH_4$

Suppose at the inlet of reactor section: A = 1, $\frac{C_H}{C_A} = \gamma$

Cyclohexana : X_A

benzene : X_B

hydrogen : $\gamma + 5\ x_B + 2X_A - 2$

hydro cracked gases: $2 - 2\ X_B - 2X_A$

Total Moles : $\gamma + 4\ X_B + X_A$

$$CO = \frac{P}{Rg\ T}$$

$$C_A = CO\ \frac{X_A}{\gamma+4X_B+X_A}$$

For plug flow behaviour and irrerersible first order kinetics:

$$F\ dX_B = k_1\eta_1\ a\ C_A\ dw = k_1 CO\ \frac{X_A}{\gamma+4X_B+X_A}\ dw \qquad \ldots(C-1)$$

$$-F\ dX_A = (k_1\eta_1 a + k_2\eta_2)\ C_A\ dw = (k_1' + k_2')\ Co\ \frac{X_A}{\gamma + 4X_B + X_A}\ dw$$

...(C-2)

as at t = 0, for undeactivated catalyst , a = 1 and

$k_1' = k_1\ \eta_1$, and $k_2' = k_2\ \eta_2$.

Dividing (C-2) by (C-1), and at isothermal and steady state conditions:

$$-\frac{dX_A}{dX_B} = \frac{k_1' + k_2'}{k_1'}$$

on integration:

$$\text{or} \quad -\int_1^{X_A} dX_A = \frac{k_1' + k_2'}{k_1'} \int_0^{X_B} d\ X_B$$

$$\text{or} \quad \frac{1 - X_A}{X_B} = \frac{k_1' + k_2'}{k_1'}$$

$$\text{or} \quad \frac{1 - X_A - X_B}{X_B} = \frac{k_2'}{k_1'} = K \qquad \text{...(C-3)}$$

$$\text{or} \quad X_A = 1 - (1+K)\ X_B \qquad \text{...(C-4)}$$

Substituting from (C-4) in (C-1), we have:

$$\frac{F\ dX_B}{k_1'\ C_o} = \frac{1 - (1+K)X_B}{1 + \gamma + (3-K)X_B}\ dw$$

$$\text{or} \quad \left[-1 + \frac{\dfrac{(1+\gamma)\ (1+K)}{3-K} + 1}{1 - X_B\ (1+K)} \right] dX_B = k_1' Co\ \frac{1+K}{3-K}\ \frac{dw}{F}$$

on integrating :

$$K_B + \left[\frac{1+\frac{(1+\gamma)(1+K)}{3-K}}{1+K}\right] \ln[1-(1+K)X_B] = -k_1' C0 \left(\frac{1+K}{3-K}\right)\left(\frac{W}{F}\right) \qquad \ldots(C-5)$$

From the operating conditions F, W, P, T and γ are known and from the extrapolated smoothened experimental data, conversion X_A and X_B are also known for undeactivated catalyst, that is at t = 0. Thus, K is first calculated from Eq. (C-3), k_1' is then calculated from Eqn. (C-5) and k_2' is calculated by noting that $k_2' = K\, k_1'$.

In order to estimate the intrinsic rate constants k_1 and k_2, it is necessary to find the effectiveness factors η_1 and η_2 for dehydrogenation and hydrocracking reactions from the experimental rate measurements. For this, the procedure of Weisz and Prater [87] is used. Following is the brief description of this procedure.

The Thiele parameter ϕ is defined as:

$$\phi = \left(\frac{V'}{Se}\right) \sqrt{\frac{k\,\rho_p}{D_e}} \qquad \ldots(C-6)$$

and for first order irreversible reaction in a spherical pellet, the relationship between effectiveness factor η and Thiele parameter ϕ is given by

$$\eta = \frac{1}{\phi}\left[\frac{1}{\tanh 3\phi} - \frac{1}{3\phi}\right] \qquad \ldots(C-7)$$

It is, therefore, clear that

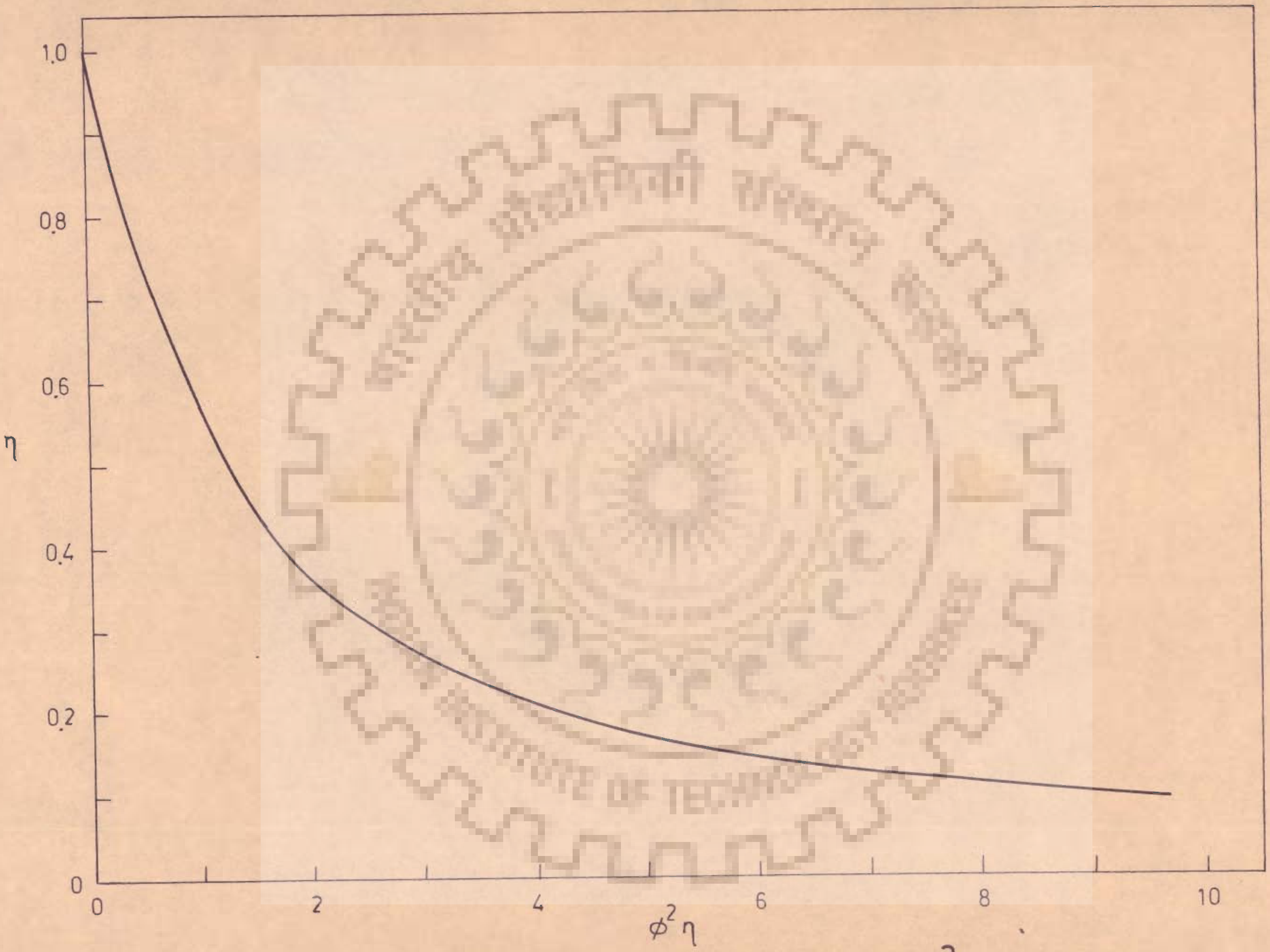


Fig. C-1 Variation of effectiveness factor η with $\phi^2\eta$ parameter

$$\phi^2\eta = \left(\frac{V'}{S_e}\right)^2 \frac{k'\rho_p}{D_e} \qquad \ldots(C-8)$$

where $k' = k\eta$ ...(C-9)

$\phi^2\eta$ can be calculated from the physical properties of the catalyst, effective diffusivity of reactant and the apparent rate constant k'. The value of effectiveness factor was estimated from the plot of η versus $\phi^2\eta$ which was obtained from Eq.(C-7) and is shown in Fig. C-1. The value of ϕ can then be calculated. Using the values of η and k', the intrinsic rate constant k can be obtained by noting that $k=k'/\eta$.

The calculated values of apparent rate constants k_1' and k_2' depend on the constant K, which is estimated from X_A and X_B using Eqn.(C-3). For very low values of X_B , say X_B less than 0.1, the denominator of Eqn.(C-3) being very small the values of K may not be very accurate due to inherent inaccuracy in the estimation of X_B due to errors in flow rate measurement and chromatographic analysis. Similarly, for very high values of X_B the difference $[(1-X_B)-X_A]$ may not be very accurate due to inherent inaccuracy in the estimation of low values of X_A, say X_A less than 0.1. This indicates that chances of error are significant for both cases, that is, for large and also for very low conversion of cyclohexane into benzene.

APPENDIX - D

Table-D-1: Calculated Values of Dehydrogenation Rate Constant from Experimental Data

Set No	TR	k'_1	$\phi_1^2 \eta_1$	η_1	ϕ_1	k_1
*1	310	1300	0.437	0.767	0.755	1700
2	355	5060	1.642	0.423	1.970	12000
3	355	5260	1.687	0.413	2.021	12700
4	350	5790	1.880	0.381	2.221	15200
5	390	10560	3.349	0.241	3.728	43800
6	315	2470	0.815	0.621	1.146	3970
7	345	4345	1.410	0.467	1.738	9300
8	410	15300	4.712	0.187	5.020	81900
9	370	8550	2.740	0.290	3.074	29500
10	435	25960	7.928	0.116	8.267	224000
11	385	10900	3.457	0.240	3.795	45400
12	360	6160	1.976	0.370	2.311	16650
13	420	15860	4.880	0.180	5.207	88100
*14	425	24040	7.397	0.122	7.787	197000
15	400	12350	3.859	0.208	4.307	59400
16	400	12090	3.775	0.210	4.240	57550
17	340	3850	1.250	0.507	1.570	7600
*18	385	9155	2.902	0.270	3.278	33900
*19	405	15670	4.820	0.330	3.822	47500

Table-D-2: Calculated Values of Hydrocracking Rate Constants from Experimental Data

Set No.	TR	k'_2	$\phi_2^2 \eta_2$	η_2	ϕ_2	k_2
*1	310	973	0.326	0.820	0.630	1190
2	355	790	0.256	0.855	0.547	924
3	355	747	0.239	0.865	0.526	864
4	350	570	0.185	0.882	0.458	646
5	390	1600	0.507	0.738	0.829	2170
6	315	491	0.159	0.906	0.419	542
7	345	695	0.226	0.842	0.518	825
8	410	1200	0.369	0.800	0.679	1500
9	370	1440	0.462	0.757	0.781	1900
10	435	2700	0.856	0.608	1.186	4440
11	385	728	0.231	0.868	0.516	839
12	360	697	0.223	0.872	0.506	800
13	420	1850	0.570	0.712	0.895	2600
*14	425	1230	0.378	0.795	0.689	1810
15	400	2100	0.657	0.678	0.984	3100
16	400	1450	0.452	0.761	0.771	1900
17	340	385	0.125	0.925	0.368	416
*18	385	431	0.137	0.920	0.386	469
*19	405	808	0.233	0.867	0.518	932

Computed Values of Parameters to Estimate the External and Internal, Heat and Mass Transfer Resistances

Set No.	Re	j_D	$k_m a \times 10^{-5}$	De	$\frac{k_1'}{k_m a} \times 10^3$	F_1	$\tilde{T}_s - T_b$	F_2	$\bar{r}$	F_3	β_n
1	10.9	0.69	12.32	4.14	1.080	0.46	0.13	0.006	0.0051	0.015	0.79
2	9.87	0.70	15.55	4.28	4.33	2.02	0.55	0.022	0.0563	0.151	2.01
3	10.47	0.69	13.95	4.331	5.81	2.79	0.79	0.031	0.0484	0.124	1.250
4	10.62	0.69	13.55	4.28	3.87	1.81	0.49	0.021	0.0525	0.154	2.09
5	14.62	0.50	13.56	4.381	7.43	3.98	0.91	0.032	0.0547	0.133	0.99
6	14.84	0.50	12.65	4.208	1.89	0.82	0.24	0.016	0.0197	0.056	1.72
7	8.32	0.71	12.85	4.28	3.54	1.57	0.44	0.022	0.0310	0.080	1.42
8	14.2	0.51	17.46	4.514	9.82	5.90	1.19	0.044	0.0794	0.173	0.97
9	27.79	0.32	12.91	4.331	6.35	2.82	0.74	0.033	0.0273	0.070	0.79
10	19.10	0.41	17.46	4.547	14.88	8.96	1.76	0.055	0.0903	0.191	0.74
11	15.07	0.45	13.55	4.381	6.790	3.17	0.96	0.036	0.0529	0.133	1.03
12	12.69	0.53	12.95	4.331	5.030	2.24	0.63	0.025	0.0544	0.144	1.75
13	9.64	0.72	16.45	4.514	9.97	5.65	1.20	0.038	0.0682	0.148	0.87
14	13.51	0.61	19.25	4.514	11.13	7.38	1.35	0.043	0.0944	0.203	1.92
15	14.22	0.51	15.05	4.446	8.680	4.50	1.05	0.036	0.0600	0.139	0.97
16	14.13	0.51	15.05	4.446	9.29	4.82	1.13	0.039	0.0692	0.159	1.03
17	12.34	0.53	12.*5	4.208	3.020	1.34	0.38	0.015	0.0339	0.093	1.82
18	16.29	0.42	12.57	4.381	7.430	3.99	0.93	0.034	0.0818	0.200	1.46
19	4.47	0.85	16.45	4.446	10.18	5.77	1.27	0.041	0.1050	0.228	1.31

$$F_1 = \left(\frac{V'}{Sc}\right)^2 \frac{k_1' \rho_p}{De} \; , \quad F_2 = \frac{E}{Rg\ T_b^2} (\tilde{T}_s - T_b) \; , \quad F_3 = \frac{\bar{r} . \rho_p . R^2 . (\Delta H)}{T_b . k_e} \cdot \frac{E}{Rg\ T_b}$$

$$\beta_n = \frac{(\Delta H). De. C_b}{ke\ .\ T_b}$$

APPENDIX - F

Activity and Conversion Values for Catalyst Bed at Different Times-on-Stream

	CATALYST FRACTION								
	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.800	1.000
TABLE F-1 SET NO 1									
W	0.000	1.023	2.045	3.068	4.091	5.113	6.136	8.181	10.23
TIME ON STREAM=0 HR.									
X_A	1.000	0.985	0.970	0.955	0.941	0.927	0.913	0.886	0.861
X_B	0.000	0.013	0.026	0.038	0.051	0.063	0.074	0.097	0.119
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.985	0.970	0.956	0.942	0.929	0.915	0.889	0.864
X_B	0.000	0.013	0.025	0.037	0.049	0.061	0.072	0.094	0.115
a	0.964	0.965	0.966	0.967	0.967	0.968	0.969	0.970	0.971
TIME ON STREAM=1.0 HR.									
X_A	1.000	0.986	0.971	0.957	0.944	0.931	0.917	0.892	0.867
X_B	0.000	0.012	0.024	0.036	0.047	0.059	0.070	0.091	0.112
a	0.930	0.932	0.933	0.935	0.936	0.937	0.939	0.941	0.943
TIME ON STREAM=1.5 HR.									
X_A	1.000	0.986	0.972	0.959	0.945	0.932	0.920	0.895	0.871
X_B	0.000	0.012	0.023	0.035	0.046	0.057	0.067	0.088	0.109
a	0.898	0.900	0.902	0.904	0.906	0.908	0.909	0.913	0.916
TIME ON STREAM=2.0 HR.									
X_A	1.000	0.986	0.973	0.960	0.953	0.934	0.922	0.897	0.874
X_B	0.000	0.011	0.022	0.033	0.044	0.055	0.065	0.086	0.106
a	0.866	0.869	0.871	0.874	0.876	0.879	0.881	0.886	0.889
TIME ON STREAM=2.5 HR.									
X_A	1.000	0.987	0.974	0.961	0.948	0.936	0.924	0.900	0.877
X_B	0.000	0.011	0.022	0.032	0.043	0.053	0.063	0.083	0.102
a	0.836	0.839	0.842	0.845	0.848	0.851	0.854	0.859	0.863
TIME ON STREAM=3.0 HR.									
X_A	1.000	0.987	0.974	0.962	0.950	0.938	0.926	0.902	0.880
X_B	0.000	0.011	0.021	0.031	0.041	0.051	0.061	0.081	0.099
a	0.807	0.811	0.814	0.818	0.821	0.824	0.827	0.833	0.839
TIME ON STREAM=3.5 HR									
X_A	1.000	0.987	0.975	0.963	0.951	0.937	0.928	0.905	0.882
X_B	0.000	0.010	0.020	0.030	0.040	0.500	0.059	0.078	0.097
a	0.780	0.784	0.788	0.791	0.795	0.798	0.802	0.809	0.814
TIME ON STREAM=4.0 HR									
X_A	1.000	0.988	0.976	0.964	0.952	0.941	0.929	0.910	0.885
X_B	0.000	0.010	0.020	0.029	0.039	0.048	0.058	0.076	0.094
a	0.753	0.757	0.762	0.766	0.770	0.773	0.777	0.785	0.791
TIME ON STREAM=4.5 HR									
X_A	1.000	0.988	0.976	0.965	0.954	0.942	0.931	0.909	0.888
X_B	0.000	0.011	0.019	0.028	0.038	0.047	0.056	0.074	0.091
a	0.728	0.732	0.737	0.741	0.745	0.749	0.753	0.761	0.768
TIME ON STREAM=5.0 HR									
X_A	1.000	0.988	0.977	0.966	0.955	0.944	0.933	0.911	0.891
X_B	0.000	0.009	0.018	0.027	0.036	0.045	0.054	0.071	0.088
a	0.703	0.708	0.713	0.717	0.722	0.726	0.730	0.739	0.746

TIME ON STREAM=5.5 HR

X_A	1.000	0.939	0.978	0.967	0.956	0.945	0.934	0.913	0.893
X_B	0.000	0.009	0.018	0.027	0.035	0.044	0.052	0.069	0.086
a	0.680	0.685	0.690	0.694	0.699	0.704	0.708	0.717	0.724

TIME ON STREAM=6.0 HR

X_A	1.000	0.989	0.978	0.968	0.957	0.946	0.936	0.916	0.895
X_B	0.000	0.009	0.017	0.026	0.034	0.043	0.051	0.067	0.083
a	0.657	0.662	0.667	0.672	0.677	0.682	0.687	0.696	0.703

TIME ON STREAM=6.5 HR

X_A	1.000	0.989	0.979	0.968	0.958	0.948	0.938	0.918	0.898
X_B	0.000	0.008	0.017	0.025	0.033	0.041	0.049	0.065	0.081
a	0.636	0.641	0.646	0.651	0.656	0.661	0.666	0.675	0.683

TABLE F=2 SET NO 2

W	0.000	3.413	6.826	10.24	13.65	17.07	20.48	27.31	34.13

TIME ON STREAM=0 HR.

X_A	1.000	0.801	0.664	0.562	0.480	0.415	0.360	0.275	0.213
X_B	0.000	0.175	0.296	0.387	0.458	0.516	0.565	0.640	0.694
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.830	0.699	0.596	0.513	0.444	0.386	0.296	0.230
X_B	0.000	0.146	0.259	0.349	0.422	0.482	0.533	0.612	0.671
a	0.767	0.849	0.890	0.915	0.932	0.944	0.954	0.967	0.975

TIME ON STREAM=1.0 HR.

X_A	1.000	0.853	0.730	0.628	0.544	0.473	0.413	0.317	0.246
X_B	0.000	0.122	0.227	0.314	0.387	0.449	0.501	0.584	0.647
a	0.602	0.718	0.787	0.832	0.864	0.887	0.906	0.932	0.947

TIME ON STREAM=1.5 HR.

X_A	1.000	0.872	0.757	0.658	0.573	0.501	0.438	0.338	0.263
X_B	0.000	0.103	0.198	0.282	0.354	0.417	0.470	0.557	0.623
a	0.482	0.637	0.692	0.752	0.796	0.830	0.856	0.895	0.919

TIME ON STREAM=2.0 HR.

X_A	1.000	0.888	0.781	0.685	0.601	0.527	0.464	0.360	0.281
X_B	0.000	0.087	0.173	0.252	0.323	0.385	0.440	0.530	0.598
a	0.393	0.515	0.606	0.676	0.730	0.772	0.806	0.857	0.889

TIME ON STREAM=2.5 HR.

X_A	1.000	0.900	0.802	0.710	0.627	0.553	0.488	0.381	0.298
X_B	0.000	0.074	0.151	0.225	0.294	0.356	0.411	0.503	0.574
a	0.325	0.437	0.530	0.605	0.665	0.715	0.756	0.817	0.857

TIME ON STREAM=3.0 HR.

X_A	1.000	0.911	0.820	0.732	0.651	0.578	0.512	0.402	0.315
X_B	0.000	0.063	0.132	0.201	0.267	0.327	0.382	0.476	0.550
a	0.273	0.373	0.463	0.539	0.604	0.659	0.705	0.777	0.824

TIME ON STREAM=3.5 HR

X_A	1.000	0.919	0.835	0.752	0.674	0.601	0.535	0.423	0.333
X_B	0.000	0.054	0.116	0.179	0.242	0.301	0.355	0.450	0.526
a	0.232	0.320	0.404	0.479	0.547	0.605	0.655	0.736	0.791

TIME ON STREAM=4.0 HR

X_A	1.000	0.926	0.848	0.770	0.694	0.623	0.557	0.443	0.351
X_B	0.000	0.047	0.102	0.160	0.219	0.275	0.329	0.424	0.502
a	0.199	0.276	0.353	0.426	0.493	0.553	0.607	0.695	0.756

TABLE F-3 SET NO 3

W	0.000	2.873	5.746	8.619	11.49	14.36	17.24	22.98	28.73
TIME ON STREAM=0 HR.									
X_A	1.000	0.881	0.784	0.702	0.632	0.572	0.518	0.430	0.360
X_B	0.000	0.105	0.191	0.263	0.325	0.378	0.425	0.503	0.565
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.893	0.801	0.722	0.654	0.593	0.540	0.450	0.377
X_B	0.000	0.093	0.173	0.242	0.302	0.354	0.401	0.480	0.544
a	0.868	0.893	0.910	0.924	0.934	0.943	0.950	0.960	0.967
TIME ON STREAM=1.0 HR.									
X_A	1.000	0.903	0.817	0.741	0.674	0.614	0.561	0.470	0.395
X_B	0.000	0.083	0.157	0.222	0.280	0.332	0.379	0.458	0.523
a	0.760	0.799	0.829	0.853	0.872	0.887	0.900	0.920	0.934
TIME ON STREAM=1.5 HR.									
X_A	1.000	0.911	0.831	0.758	0.693	0.934	0.581	0.489	0.413
X_B	0.000	0.075	0.143	0.204	0.260	0.311	0.357	0.437	0.503
a	0.670	0.718	0.756	0.787	0.812	0.833	0.851	0.880	0.900
TIME ON STREAM=2.0 HR.									
X_A	1.000	0.919	0.843	0.774	0.710	0.652	0.599	0.507	0.430
X_B	0.000	0.067	0.130	0.188	0.742	0.291	0.337	0.416	0.483
a	0.594	0.647	0.689	0.725	0.756	0.782	0.804	0.841	0.866
TIME ON STREAM=2.5 HR.									
X_A	1.000	0.925	0.854	0.788	0.726	0.670	0.617	0.525	0.447
X_B	0.000	0.060	0.119	0.174	0.225	0.273	0.317	0.396	0.464
a	0.531	0.584	0.630	0.669	0.703	0.733	0.759	0.802	0.832
TIME ON STREAM=3.0 HR.									
X_A	1.000	0.931	0.864	0.801	0.741	0.686	0.634	0.542	0.463
X_B	0.000	0.055	0.109	0.160	0.209	0.256	0.299	0.377	0.444
a	0.477	0.530	0.576	0.617	0.654	0.686	0.715	0.764	0.799
TIME ON STREAM=3.5 HR									
X_A	1.000	0.935	0.873	0.812	0.755	0.701	0.650	0.559	0.479
X_B	0.000	0.050	0.099	0.148	0.195	0.239	0.281	0.358	0.426
a	0.430	0.432	0.528	0.570	0.608	0.642	0.673	0.726	0.765
TIME ON STREAM=4.0 HR									
X_A	1.000	0.940	0.881	0.723	0.768	0.715	0.666	0.575	0.495
X_B	0.000	0.046	0.091	0.137	0.181	0.224	0.265	0.341	0.408
a	0.390	0.439	0.485	0.526	0.565	0.600	0.633	0.690	0.732

TABLE F-4 SET NO 4

W	0.000	2.406	4.812	7.218	9.625	12.03	14.44	19.25	24.06
TIME ON STREAM=0 HR.									
X_A	1.000	0.837	0.718	0.625	0.550	0.487	0.433	0.348	0.282
X_B	0.000	0.144	0.248	0.330	0.396	0.452	0.499	0.574	0.632
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.862	0.751	0.659	0.583	0.518	0.463	0.372	0.303
X_B	0.000	0.118	0.214	0.293	0.360	0.416	0.465	0.544	0.605
a	0.762	0.837	0.877	0.902	0.920	0.933	0.943	0.957	0.966
TIME ON STREAM=1.0 HR.									
X_A	1.000	0.882	0.779	0.691	0.614	0.549	0.491	0.397	0.324
X_B	0.000	0.097	0.184	0.260	0.325	0.382	0.432	0.513	0.577
a	0.594	0.698	0.764	0.808	0.841	0.865	0.885	0.913	0.931

TIME ON STREAM=1.5 HR.

X_A	1.000	0.899	0.804	0.719	0.644	0.578	0.519	0.422	0.344
X_B	0.000	0.081	0.158	0.229	0.293	0.349	0.399	0.483	0.550
a	0.472	0.583	0.662	0.719	0.763	0.798	0.826	0.867	0.893

TIME ON STREAM=2.0 HR.

X_A	1.000	0.912	0.825	0.744	0.671	0.605	0.546	0.446	0.365
X_B	0.000	0.067	0.136	0.202	0.263	0.318	0.368	0.454	0.523
a	0.382	0.488	0.571	0.637	0.689	0.732	0.766	0.820	0.855

TIME ON STREAM=2.5 HR.

X_A	1.000	0.922	0.843	0.767	0.696	0.631	0.572	0.470	0.386
X_B	0.000	0.057	0.117	0.178	0.235	0.289	0.339	0.425	0.496
a	0.314	0.410	0.492	0.561	0.619	0.667	0.708	0.772	0.815

TIME ON STREAM=3.0 HR.

X_A	1.000	0.931	0.859	0.787	0.719	0.655	0.596	0.493	0.407
X_B	0.000	0.048	0.101	0.156	0.210	0.262	0.310	0.397	0.469
a	0.262	0.347	0.424	0.493	0.553	0.605	0.651	0.724	0.774

TIME ON STREAM=3.5 HR

X_A	1.000	0.937	0.871	0.805	0.740	0.678	0.620	0.516	0.428
X_B	0.000	0.041	0.088	0.137	0.187	0.237	0.284	0.369	0.443
a	0.221	0.295	0.366	0.432	0.492	0.547	0.595	0.675	0.732

TIME ON STREAM=4.0 HR

X_A	1.000	0.943	0.882	0.820	0.759	0.699	0.642	0.538	0.448
X_B	0.000	0.035	0.076	0.121	0.167	0.213	0.259	0.343	0.417
a	0.189	0.252	0.316	0.378	0.437	0.492	0.542	0.628	0.690

TABLE F-5 SET NO 5

W	0.000	2.983	5.966	8.949	11.93	14.91	17.90	23.86	29.83

TIME ON STREAM=0 HR.

X_A	1.000	0.824	0.691	0.586	0.501	0.430	0.372	0.280	0.213
X_B	0.000	0.157	0.276	0.370	0.447	0.509	0.562	0.644	0.703
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.844	0.718	0.615	0.529	0.458	0.397	0.301	0.230
X_B	0.000	0.137	0.218	0.340	0.415	0.479	0.533	0.618	0.882
a	0.843	0.879	0.904	0.922	0.935	0.946	0.954	0.966	0.974

TIME ON STREAM=1.0 HR.

X_A	1.000	0.859	0.741	0.641	0.556	0.433	0.421	0.321	0.247
X_B	0.000	0.122	0.225	0.312	0.387	0.451	0.506	0.594	0.661
a	0.725	0.779	0.819	0.849	0.873	0.893	0.908	0.932	0.948

TIME ON STREAM=1.5 HR.

X_A	1.000	0.872	0.760	0.664	0.580	0.507	0.444	0.371	0.263
X_B	0.000	0.108	0.204	0.288	0.361	0.425	0.480	0.571	0.640
a	0.634	0.696	0.744	0.783	0.815	0.842	0.864	0.898	0.920

TIME ON STREAM=2.0 HR.

X_A	1.000	0.883	0.777	0.684	0.602	0.529	0.465	0.360	0.279
X_B	0.000	0.098	0.187	0.267	0.338	0.401	0.456	0.549	0.620
a	0.562	0.626	0.679	0.724	0.761	0.793	0.820	0.863	0.892

TIME ON STREAM=2.5 HR.

X_A	1.000	0.892	0.792	0.702	0.621	0.549	0.485	0.378	0.295
X_B	0.000	0.089	0.172	0.248	0.317	0.379	0.434	0.527	0.601
a	0.504	0.567	0.622	0.669	0.710	0.746	0.778	0.829	0.864

TIME ON STREAM=3.0 HR.

X_A	1.000	0.899	0.805	0.718	0.640	0.568	0.504	0.396	0.310
X_B	0.000	0.081	0.158	0.231	0.297	0.358	0.413	0.507	0.582
a	0.456	0.517	0.571	0.620	0.664	0.702	0.737	0.794	0.835

TIME ON STREAM=3.5 HR

X_A	1.000	0.906	0.816	0.733	0.656	0.586	0.522	0.413	0.325
X_B	0.000	0.074	0.147	0.215	0.279	0.339	0.393	0.487	0.563
a	0.415	0.473	0.527	0.576	0.621	0.661	0.698	0.761	0.806

TIME ON STREAM=4.0 HR

X_A	1.000	0.911	0.826	0.746	0.671	0.602	0.539	0.429	0.340
X_B	0.000	0.069	0.136	0.201	0.263	0.321	0.374	0.468	0.545
a	0.381	0.436	0.488	0.536	0.581	0.623	0.661	0.729	0.778

TABLE F-6 SET NO 6

W	0.000	2.084	4.168	6.252	8.336	10.42	12.50	16.67	20.84

TIME ON STREAM=0 HR.

X_A	1.000	0.950	0.904	0.862	0.824	0.788	0.755	0.695	0.642
X_B	0.000	0.043	0.082	0.118	0.151	0.181	0.210	0.261	0.307
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.954	0.912	0.872	0.836	0.801	0.769	0.710	0.658
X_B	0.000	0.039	0.075	0.108	0.139	0.168	0.196	0.246	0.290
a	0.890	0.901	0.911	0.919	0.926	0.932	0.937	0.945	0.951

TIME ON STREAM=1.0 HR.

X_A	1.000	0.958	0.918	0.881	0.846	0.813	0.782	0.724	0.672
X_B	0.000	0.035	0.068	0.099	0.128	0.156	0.182	0.230	0.275
a	0.793	0.813	0.830	0.844	0.856	0.866	0.876	0.891	0.902

TIME ON STREAM=1.5 HR.

X_A	1.000	0.961	0.925	0.890	0.855	0.824	0.794	0.738	0.687
X_B	0.000	0.031	0.061	0.090	0.115	0.144	0.169	0.216	0.259
a	0.709	0.734	0.756	0.774	0.790	0.805	0.817	0.839	0.855

TIME ON STREAM=2.0 HR.

X_A	1.000	0.964	0.930	0.897	0.865	0.835	0.806	0.751	0.700
X_B	0.000	0.028	0.056	0.083	0.108	0.133	0.157	0.202	0.244
a	0.636	0.664	0.688	0.710	0.729	0.746	0.762	0.789	0.809

TIME ON STREAM=2.5 HR.

X_A	1.000	0.967	0.935	0.904	0.874	0.845	0.817	0.763	0.714
X_B	0.000	0.026	0.051	0.075	0.099	0.123	0.146	0.189	0.230
a	0.571	0.600	0.627	0.651	0.672	0.691	0.709	0.740	0.764

TIME ON STREAM=3.0 HR

X_A	1.000	0.970	0.940	0.910	0.882	0.854	0.827	0.775	0.726
X_B	0.000	0.023	0.046	0.069	0.092	0.114	0.135	0.177	0.216
a	0.514	0.544	0.571	0.596	0.619	0.640	0.659	0.694	0.720

TABLE F-7 SET NO 7

W	0.000	1.097	2.194	3.290	4.387	5.404	6.581	8.775	10.97

TIME ON STREAM=0 HR.

X_A	1.000	0.935	0.877	0.825	0.778	0.735	0.696	0.626	0.565
X_B	0.000	0.057	0.108	0.153	0.195	0.232	0.267	0.329	0.382
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.942	0.889	0.840	0.796	0.754	0.716	0.647	0.586
X_B	0.000	0.050	0.096	0.138	0.177	0.213	0.246	0.306	0.359
a	0.865	0.880	0.893	0.903	0.912	0.920	0.926	0.937	0.945

TIME ON STREAM=1.0 HR.

X_A	1.000	0.948	0.899	0.854	0.811	0.772	0.734	0.666	0.606
X_B	0.000	0.044	0.085	0.124	0.160	0.195	0.227	0.285	0.337
a	0.753	0.778	0.799	0.817	0.832	0.845	0.857	0.876	0.890

TIME ON STREAM=1.5 HR.

X_A	1.000	0.953	0.908	0.866	0.826	0.787	0.751	0.685	0.625
X_B	0.000	0.039	0.076	0.112	0.146	0.178	0.209	0.265	0.316
a	0.661	0.690	0.716	0.738	0.758	0.776	0.791	0.818	0.838

TIME ON STREAM=2.0 HR.

X_A	1.000	0.957	0.916	0.876	0.838	0.802	0.767	0.702	0.644
X_B	0.000	0.035	0.068	0.101	0.133	0.163	0.192	0.247	0.297
a	0.583	0.615	0.643	0.668	0.691	0.712	0.730	0.762	0.787

TIME ON STREAM=2.5 HR.

X_A	1.000	0.961	0.923	0.886	0.850	0.815	0.782	0.719	0.661
X_B	0.000	0.031	0.062	0.092	0.121	0.149	0.177	0.229	0.278
a	0.518	0.550	0.579	0.606	0.630	0.653	0.673	0.710	0.738

TIME ON STREAM=3.0 HR

X_A	1.000	0.964	0.929	0.894	0.860	0.827	0.795	0.734	0.678
X_B	0.000	0.028	0.056	0.083	0.110	0.137	0.163	0.213	0.260
a	0.462	0.494	0.523	0.550	0.575	0.599	0.621	0.660	0.691

TIME ON STREAM=3.5 HR

X_A	1.000	0.967	0.934	0.901	0.869	0.838	0.807	0.748	0.693
X_B	0.000	0.025	0.050	0.076	0.101	0.126	0.150	0.198	0.244
a	0.414	0.445	0.473	0.500	0.525	0.549	0.572	0.613	0.646

TIME ON STREAM=4.0 HR

X_A	1.000	0.969	0.938	0.908	0.877	0.847	0.818	0.762	0.708
X_B	0.000	0.023	0.046	0.069	0.092	0.116	0.139	0.184	0.228
a	0.373	0.402	0.429	0.455	0.480	0.504	0.527	0.569	0.603

TIME ON STREAM=4.5 HR

X_A	1.000	0.971	0.942	0.914	0.885	0.856	0.828	0.774	0.721
X_B	0.000	0.021	0.042	0.063	0.085	0.106	0.128	0.171	0.213
a	0.338	0.364	0.390	0.416	0.440	0.463	0.486	0.528	0.563

TIME ON STREAM=5.0 HR

X_A	1.000	0.973	0.946	0.919	0.892	0.865	0.838	0.785	0.734
X_B	0.000	0.019	0.038	0.058	0.078	0.098	0.118	0.159	0.199
a	0.307	0.332	0.356	0.380	0.406	0.426	0.448	0.490	0.525

TIME ON STREAM=5.5 HR

X_A	1.000	0.975	0.949	0.923	0.898	0.872	0.846	0.795	0.746
X_B	0.000	0.017	0.035	0.053	0.072	0.091	0.110	0.148	0.186
a	0.279	0.303	0.325	0.348	0.370	0.392	0.414	0.455	0.490

TABLE F-8 SET NO 8

W	0.000	2.958	5.916	8.874	11.83	14.79	17.75	23.66	29.58

TIME ON STREAM=0 HR.

X_A	1.000	0.768	0.608	0.489	0.398	0.327	0.270	0.187	0.130
X_B	0.000	0.209	0.353	0.460	0.541	0.606	0.657	0.732	0.783
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.798	0.646	0.527	0.433	0.358	0.297	0.207	0.145
X_B	0.000	0.178	0.313	0.419	0.503	0.570	0.624	0.706	0.761
a	0.803	0.858	0.893	0.917	0.934	0.947	0.957	0.971	0.979

TIME ON STREAM=1.0 HR.

X_A	1.000	0.821	0.676	0.560	0.454	0.387	0.323	0.226	0.159
X_B	0.000	0.155	0.281	0.384	0.468	0.538	0.595	0.681	0.741
a	0.672	0.747	0.801	0.848	0.871	0.895	0.913	0.941	0.957

TIME ON STREAM=1.5 HR.

X_A	1.000	0.838	0.702	0.588	0.492	0.413	0.346	0.244	0.173
X_B	0.000	0.137	0.255	0.354	0.438	0.508	0.567	0.657	0.721
a	0.579	0.660	0.722	0.772	0.812	0.844	0.870	0.909	0.934

TIME ON STREAM=2.0 HR.

X_A	1.000	0.852	0.723	0.612	0.517	0.437	0.369	0.262	0.187
X_B	0.000	0.123	0.232	0.328	0.410	0.481	0.541	0.635	0.702
a	0.509	0.589	0.655	0.750	0.756	0.795	0.827	0.877	0.909

TIME ON STREAM=2.5 HR.

X_A	1.000	0.863	0.741	0.633	0.540	0.459	0.390	0.280	0.200
X_B	0.000	0.111	0.214	0.305	0.386	0.436	0.516	0.613	0.684
a	0.455	0.531	0.598	0.655	0.705	0.748	0.786	0.845	0.884

TIME ON STREAM=3.0 HR

X_A	1.000	0.873	0.756	0.652	0.560	0.479	0.409	0.296	0.213
X_B	0.000	0.102	0.198	0.285	0.363	0.433	0.494	0.592	0.666
a	0.412	0.483	0.548	0.606	0.659	0.705	0.746	0.813	0.859

TIME ON STREAM=3.5 HR

X_A	1.000	0.880	0.770	0.669	0.579	0.498	0.427	0.313	0.226
X_B	0.000	0.094	0.184	0.267	0.343	0.412	0.472	0.572	0.648
a	0.376	0.443	0.505	0.563	0.616	0.664	0.708	0.781	0.832

TABLE F-9 SET NO 9

W	0.000	2.627	5.254	7.880	10.51	13.13	15.76	21.01	26.27

TIME ON STREAM=0 HR.

X_A	1.000	0.952	0.907	0.865	0.826	0.789	0.754	0.690	0.633
X_B	0.000	0.043	0.082	0.120	0.155	0.187	0.215	0.275	0.325
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.955	0.913	0.874	0.836	0.801	0.767	0.705	0.649
X_B	0.000	0.039	0.076	0.111	0.144	0.175	0.205	0.260	0.309
a	0.914	0.920	0.925	0.929	0.934	0.937	0.940	0.947	0.951

TIME ON STREAM=1.0 HR.

X_A	1.000	0.958	0.919	0.881	0.845	0.811	0.779	0.718	0.663
X_B	0.000	0.036	0.071	0.103	0.135	0.164	0.193	0.246	0.294
a	0.840	0.849	0.858	0.866	0.873	0.880	0.886	0.897	0.906

TIME ON STREAM=1.5 HR.

X_A	1.000	0.961	0.924	0.888	0.854	0.821	0.789	0.731	0.677
X_B	0.000	0.033	0.066	0.096	0.126	0.154	0.182	0.233	0.280
a	0.775	0.787	0.798	0.808	0.818	0.827	0.835	0.850	0.862

TIME ON STREAM=2.0 HR.

X_A	1.000	0.963	0.928	0.894	0.862	0.830	0.800	0.743	0.690
X_B	0.000	0.031	0.061	0.090	0.118	0.145	0.171	0.220	0.266
a	0.718	0.732	0.744	0.756	0.767	0.778	0.788	0.806	0.821

TIME ON STREAM=2.5 HR.

X_A	1.000	0.965	0.932	0.900	0.668	0.838	0.809	0.754	0.702
X_B	0.000	0.029	0.057	0.085	0.111	0.137	0.162	0.209	0.253
a	0.668	0.682	0.696	0.709	0.721	0.733	0.744	0.765	0.781

TIME ON STREAM=3.0 HR

X_A	1.000	0.967	0.936	0.905	0.875	0.846	0.818	0.764	0.713
X_B	0.000	0.027	0.054	0.079	0.104	0.129	0.153	0.199	0.242
a	0.623	0.638	0.652	0.666	0.679	0.692	0.704	0.726	0.745

TIME ON STREAM=3.5 HR

X_A	1.000	0.969	0.939	0.909	0.881	0.853	0.825	0.773	0.724
X_B	0.000	0.025	0.050	0.075	0.099	0.122	0.145	0.189	0.231
a	0.582	0.598	0.613	0.627	0.640	0.654	0.666	0.690	0.710

TIME ON STREAM=4.0 HR

X_A	1.000	0.971	0.942	0.915	0.886	0.859	0.833	0.782	0.734
X_B	0.000	0.024	0.047	0.071	0.093	0.116	0.138	0.180	0.221
a	0.546	0.562	0.576	0.592	0.605	0.618	0.631	0.656	0.677

TIME ON STREAM=4.5 HR

X_A	1.000	0.972	0.945	0.918	0.890	0.865	0.839	0.790	0.743
X_B	0.000	0.023	0.045	0.067	0.088	0.109	0.131	0.172	0.211
a	0.514	0.529	0.544	0.558	0.572	0.585	0.599	0.624	0.645

TIME ON STREAM=5.0 HR

X_A	1.000	0.973	0.947	0.921	0.895	0.870	0.846	0.799	0.752
X_B	0.000	0.021	0.042	0.063	0.084	0.104	0.124	0.164	0.202
a	0.484	0.499	0.515	0.528	0.542	0.556	0.569	0.595	0.616

TIME ON STREAM=5.5 HR

X_A	1.000	0.974	0.949	0.924	0.899	0.875	0.851	0.805	0.760
X_B	0.000	0.020	0.040	0.060	0.080	0.100	0.118	0.156	0.193
a	0.457	0.472	0.486	0.500	0.514	0.527	0.541	0.567	0.588

TABLE F-10 SET NO 10

W	0.000	2.573	5.146	7.720	10.29	12.87	15.44	20.59	25.73

TIME ON STREAM=0 HR.

X_A	1.000	0.837	0.710	0.607	0.522	0.451	0.392	0.298	0.228
X_B	0.000	0.148	0.2*3	0.357	0.434	0.498	0.552	0.637	0.700
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.860	0.743	0.645	0.561	0.489	0.428	0.328	0.253
X_B	0.000	0.124	0.229	0.317	0.392	0.457	0.512	0.602	0.670
a	0.812	0.846	0.871	0.892	0.908	0.921	0.932	0.949	0.960

TIME ON STREAM=1.0 HR.

X_A	1.000	0.876	0.768	0.674	0.592	0.521	0.458	0.356	0.277
X_B	0.000	0.108	0.204	0.287	0.360	0.423	0.479	0.571	0.642
a	0.694	0.737	0.773	0.803	0.829	0.851	0.869	0.900	0.920

TIME ON STREAM=1.5 HR.

X_A	1.000	0.884	0.787	0.697	0.618	0.547	0.485	0.380	0.298
X_B	0.000	0.097	0.184	0.263	0.333	0.395	0.451	0.544	0.617
a	0.611	0.656	0.696	0.731	0.761	0.738	0.812	0.852	0.880

TIME ON STREAM=2.0 HR.

X_A	1.000	0.896	0.802	0.716	0.629	0.570	0.508	0.402	0.318
X_B	0.000	0.088	0.169	0.243	0.310	0.371	0.426	0.519	0.594
a	0.550	0.594	0.634	0.670	0.703	0.733	0.761	0.808	0.842

TIME ON STREAM=2.5 HR.

X_A	1.000	0.903	0.814	0.732	0.658	0.590	0.528	0.422	0.336
X_B	0.000	0.081	0.157	0.227	0.291	0.350	0.403	0.497	0.573
a	0.502	0.544	0.583	0.620	0.654	0.685	0.714	0.766	0.805

TIME ON STREAM=3.0 HR

X_A	1.000	0.909	0.824	0.746	0.673	0.606	0.545	0.440	0.353
X_B	0.000	0.075	0.146	0.213	0.274	0.331	0.384	0.576	0.553
a	0.464	0.503	0.541	0.577	0.610	0.6*2	0.673	0.728	0.770

TIME ON STREAM=3.5 HR

X_A	1.000	0.914	0.833	0.757	0.687	0.622	0.562	0.457	0.369
X_B	0.000	0.070	0.138	0.200	0.260	0.315	0.367	0.458	0.535
a	0.432	0.469	0.505	0.540	0.573	0.605	0.635	0.692	0.737

TIME ON STREAM=4.0 HR

X_A	1.000	0.918	0.840	0.767	0.699	0.636	0.577	0.472	0.384
X_B	0.000	0.066	0.130	0.190	0.247	0.301	0.351	0.441	0.518
a	0.406	0.440	0.474	0.507	0.540	0.571	0.602	0.660	0.706

TABLE F-11 SET NO 11

W	0.000	2.487	4.974	7.461	9.950	12.44	14.92	19.90	24.87
TIME ON STREAM=0 HR.									
X_A	1.000	0.856	0.742	0.649	0.570	0.504	0.447	0.355	0.285
X_B	0.000	0.128	0.230	0.314	0.383	0.442	0.493	0.575	0.638
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.873	0.766	0.676	0.599	0.532	0.474	0.379	0.305
X_B	0.000	0.112	0.205	0.285	0.353	0.412	0.464	0.548	0.614
a	0.843	0.874	0.896	0.913	0.926	0.936	0.944	0.958	0.966
TIME ON STREAM=1.0 HR.									
X_A	1.000	0.886	0.787	0.770	0.624	0.558	0.499	0.402	0.325
X_B	0.000	0.098	0.184	0.260	0.326	0.384	0.436	0.522	0.590
a	0.732	0.771	0.806	0.834	0.857	0.875	0.891	0.915	0.931
TIME ON STREAM=1.5 HR.									
X_A	1.000	0.897	0.804	0.721	0.647	0.582	0.523	0.424	0.344
X_B	0.000	0.087	0.166	0.238	0.302	0.359	0.410	0.490	0.567
a	0.633	0.685	0.728	0.763	0.793	0.817	0.839	0.873	0.896
TIME ON STREAM=2.0 HR.									
X_A	1.000	0.905	0.819	0.740	0.668	0.603	0.545	0.445	0.363
X_B	0.000	0.078	0.151	0.218	0.280	0.336	0.386	0.474	0.545
a	0.560	0.614	0.660	0.699	0.734	0.763	0.789	0.832	0.861
TIME ON STREAM=2.5 HR.									
X_A	1.000	0.913	0.832	0.765	0.686	0.623	0.565	0.464	0.381
X_B	0.000	0.071	0.138	0.201	0.260	0.314	0.364	0.451	0.524
a	0.500	0.554	0.601	0.643	0.680	0.713	0.742	0.791	0.827
TIME ON STREAM=3.0 HR									
X_A	1.000	0.919	0.843	0.771	0.704	0.641	0.584	0.483	0.399
X_B	0.000	0.064	0.127	0.186	0.242	0.295	0.343	0.430	0.503
a	0.452	0.503	0.549	0.592	0.631	0.665	0.697	0.752	0.792
TIME ON STREAM=3.5 HR									
X_A	1.000	0.925	0.853	0.784	0.719	0.658	0.602	0.501	0.416
X_B	0.000	0.059	0.117	0.173	0.226	0.277	0.324	0.410	0.483
a	0.411	0.459	0.505	0.547	0.586	0.622	0.656	0.714	0.758
TIME ON STREAM=4.0 HR									
X_A	1.000	0.930	0.861	0.795	0.733	0.673	0.618	0.518	0.432
X_B	0.000	0.054	0.108	0.161	0.212	0.260	0.307	0.391	0.464
a	0.376	0.422	0.465	0.506	0.545	0.582	0.616	0.678	0.725
TIME ON STREAM=4.5 HR									
X_A	1.000	0.934	0.868	0.805	0.745	0.687	0.633	0.534	0.448
X_B	0.000	0.050	0.100	0.150	0.198	0.245	0.290	0.373	0.446
a	0.346	0.389	0.430	0.470	0.508	0.545	0.580	0.643	0.693

TABLE F-12 SET NO 12

W	0.000	2.114	4.228	6.341	8.455	10.57	12.68	16.91	21.14
TIME ON STREAM=0 HR.									
X_A	1.000	0.848	0.734	0.642	0.567	0.504	0.450	0.362	0.295
X_B	0.000	0.134	0.235	0.316	0.383	0.439	0.486	0.564	0.623
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.870	0.763	0.675	0.599	0.535	0.479	0.388	0.317
X_B	0.000	0.112	0.205	0.282	0.348	0.404	0.453	0.533	0.596
a	0.790	0.845	0.878	0.901	0.918	0.930	0.940	0.955	0.964
TIME ON STREAM=1.0 HR.									
X_A	1.000	0.884	0.789	0.704	0.629	0.656	0.508	0.413	0.338
X_B	0.000	0.094	0.178	0.251	0.315	0.371	0.421	0.503	0.569
a	0.638	0.716	0.770	0.809	0.838	0.861	0.880	0.907	0.925

TIME ON STREAM=1.5 HR.

X_A	1.000	0.902	0.811	0.730	0.657	0.592	0.535	0.437	0.360
X_B	0.000	0.080	0.155	0.224	0.286	0.341	0.390	0.474	0.542
a	0.525	0.610	0.674	0.723	0.763	0.794	0.820	0.860	0.887

TIME ON STREAM=2.0 HR.

X_A	1.000	0.913	0.830	0.753	0.682	0.618	0.561	0.462	0.381
X_B	0.000	0.068	0.136	0.199	0.258	0.312	0.361	0.446	0.516
a	0.439	0.523	0.591	0.646	0.691	0.730	0.762	0.813	0.847

TIME ON STREAM=2.5 HR.

X_A	1.000	0.922	0.846	0.773	0.705	0.642	0.585	0.485	0.402
X_B	0.000	0.059	0.119	0.178	0.234	0.286	0.334	0.419	0.490
a	0.373	0.451	0.518	0.576	0.625	0.668	0.705	0.765	0.806

TIME ON STREAM=3.0 HR

X_A	1.000	0.930	0.859	0.791	0.725	0.664	0.607	0.507	0.423
X_B	0.000	0.051	0.105	0.159	0.212	0.262	0.309	0.393	0.465
a	0.310	0.391	0.456	0.513	0.465	0.610	0.651	0.718	0.765

TIME ON STREAM=3.5 HR

X_A	1.000	0.936	0.871	0.806	0.744	0.685	0.629	0.528	0.443
X_B	0.000	0.045	0.093	0.143	0.192	0.239	0.285	0.368	0.440
a	0.278	0.342	0.402	0.458	0.509	0.536	0.599	0.671	0.724

TIME ON STREAM=4.0 HR

X_A	1.000	0.941	0.880	0.820	0.760	0.703	0.648	0.549	0.462
X_B	0.000	0.040	0.083	0.128	0.174	0.219	0.263	0.344	0.416
a	0.244	0.301	0.356	0.409	0.459	0.506	0.550	0.626	0.683

TIME ON STREAM=4.5 HR

X_A	1.000	0.945	0.889	0.832	0.775	0.720	0.667	0.569	0.482
X_B	0.000	0.035	0.074	0.116	0.158	0.200	0.242	0.321	0.393
a	0.216	0.266	0.316	0.366	0.414	0.460	0.504	0.583	0.643

TABLE F-13 SET NO 13

W	0.000	3.503	7.005	10.51	14.01	17.51	21.01	28.02	35.03

TIME ON STREAM=0 HR.

X_A	1.000	0.686	0.494	0.364	0.272	0.206	0.157	0.092	0.054
X_B	0.000	0.283	0.457	0.575	0.657	0.717	0.762	0.820	0.854
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.721	0.531	0.397	0.300	0.228	0.174	0.102	0.061
X_B	0.000	0.248	0.417	0.537	0.625	0.689	0.738	0.802	0.840
a	0.814	0.880	0.917	0.940	0.956	0.967	0.975	0.986	0.991

TIME ON STREAM=1.0 HR.

X_A	1.000	0.743	0.563	0.427	0.325	0.249	0.190	0.113	0.067
X_B	0.000	0.222	0.383	0.504	0.595	0.663	0.716	0.786	0.827
a	0.690	0.782	0.842	0.883	0.912	0.934	0.949	0.970	0.981

TIME ON STREAM=1.5 HR.

X_A	1.000	0.769	0.591	0.454	0.349	0.269	0.207	0.123	0.074
X_B	0.000	0.198	0.354	0.475	0.568	0.639	0.694	0.770	0.815
a	0.601	0.702	0.775	0.828	0.869	0.899	0.922	0.954	0.971

TIME ON STREAM=2.0 HR.

X_A	1.000	0.786	0.614	0.478	0.371	0.288	0.223	0.133	0.080
X_B	0.000	0.180	0.329	0.448	0.542	0.616	0.674	0.754	0.802
a	0.535	0.636	0.715	0.778	0.827	0.865	0.895	0.937	0.960

TIME ON STREAM=2.5 HR.

X_A	1.000	0.800	0.634	0.500	0.392	0.306	0.238	0.144	0.086
X_B	0.000	0.166	0.307	0.424	0.519	0.594	0.655	0.739	0.791
a	0.482	0.581	0.663	0.731	0.786	0.831	0.867	0.918	0.948

TIME ON STREAM=3.0 HR

X_A	1.000	0.812	0.652	0.519	0.411	0.323	0.253	0.154	0.092
X_B	0.000	0.153	0.288	0.403	0.497	0.574	0.636	0.724	0.779
a	0.441	0.535	0.617	0.687	0.747	0.748	0.839	0.900	0.935

TABLE F-14 SET NO 14

W	0.000	2.831	5.663	8.495	11.33	14.16	16.99	22.65	28.32
TIME ON STREAM=0 HR.									
X_A	1.000	0.746	0.575	0.453	0.360	0.289	0.234	0.155	0.104
X_B	0.000	0.230	0.384	0.495	0.579	0.643	0.693	0.765	0.811
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.780	0.618	0.494	0.398	0.322	0.262	0.174	0.117
X_B	0.000	0.194	0.339	0.450	0.537	0.605	0.659	0.738	0.790
a	0.790	0.850	0.889	0.915	0.933	0.947	0.958	0.973	0.981
TIME ON STREAM=1.0 HR.									
X_A	1.000	0.806	0.651	0.528	0.430	0.351	0.287	0.192	0.130
X_B	0.000	0.169	0.305	0.413	0.501	0.572	0.629	0.714	0.770
a	0.659	0.738	0.795	0.837	0.870	0.895	0.915	0.944	0.961
TIME ON STREAM=1.5 HR.									
X_A	1.000	0.824	0.678	0.557	0.458	0.377	0.310	0.210	0.142
X_B	0.000	0.150	0.277	0.382	0.470	0.542	0.601	0.691	0.752
a	0.570	0.653	0.717	0.769	0.811	0.845	0.872	0.913	0.939
TIME ON STREAM=2.0 HR.									
X_A	1.000	0.838	0.700	0.583	0.483	0.401	0.332	0.227	0.155
X_B	0.000	0.135	0.254	0.356	0.441	0.515	0.575	0.669	0.734
a	0.505	0.585	0.652	0.708	0.756	0.797	0.830	0.883	0.916
TIME ON STREAM=2.5 HR.									
X_A	1.000	0.850	0.718	0.704	0.506	0.422	0.352	0.243	0.167
X_B	0.000	0.123	0.235	0.332	0.417	0.490	0.552	0.649	0.717
a	0.455	0.530	0.597	0.655	0.707	0.751	0.790	0.852	0.892
TIME ON STREAM=3.0 HR.									
X_A	1.000	0.859	0.733	0.622	0.526	0.442	0.371	0.259	0.179
X_B	0.000	0.114	0.218	0.312	0.395	0.467	0.530	0.629	0.700
a	0.415	0.486	0.550	0.608	0.662	0.709	0.752	0.821	0.868
TIME ON STREAM=3.5 HR									
X_A	1.000	0.867	0.747	0.639	0.544	0.461	0.389	0.274	0.190
X_B	0.000	0.106	0.205	0.295	0.375	0.447	0.509	0.610	0.684
a	0.383	0.448	0.410	0.567	0.621	0.670	0.715	0.791	0.844
TIME ON STREAM=4.0 HR									
X_A	1.000	0.874	0.758	0.654	0.560	0.478	0.405	0.288	0.202
X_B	0.000	0.099	0.192	0.279	0.358	0.428	0.490	0.592	0.668
a	0.356	0.417	0.475	0.531	0.584	0.634	0.681	0.761	0.819
TIME ON STREAM=4.5 HR									
X_A	1.000	0.880	0.768	0.667	0.575	0.493	0.421	0.302	0.213
X_B	0.000	0.093	0.182	0.265	0.341	0.411	0.472	0.575	0.653
a	0.333	0.389	0.445	0.499	0.551	0.601	0.648	0.732	0.795
TIME ON STREAM=5.0 HR									
X_A	1.000	0.885	0.777	0.678	0.588	0.507	0.435	0.266	0.224
X_B	0.000	0.088	0.172	0.252	0.327	0.395	0.456	0.559	0.639
a	0.313	0.366	0.418	0.470	0.521	0.570	0.618	0.705	0.771

TABLE F-15 SET NO 15

W	0.000	2.573	5.146	7.719	10.29	12.86	15.44	20.58	25.73
TIME ON STREAM=0 HR.									
X_A	1.000	0.834	0.706	0.604	0.521	0.452	0.394	0.302	0.233
X_B	0.000	0.149	0.263	0.354	0.429	0.491	0.543	0.625	0.686
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.854	0.735	0.636	0.553	0.482	0.422	0.326	0.253
X_B	0.000	0.128	0.234	0.321	0.395	0.458	0.511	0.597	0.662
a	0.831	0.867	0.893	0.912	0.926	0.938	0.947	0.961	0.969
TIME ON STREAM=1.0 HR.									
X_A	1.000	0.870	0.758	0.663	0.581	0.510	0.448	0.348	0.272
X_B	0.000	0.112	0.209	0.293	0.365	0.428	0.482	0.570	0.638
a	0.708	0.761	0.801	0.832	0.857	0.878	0.895	0.921	0.938
TIME ON STREAM=1.5 HR.									
X_A	1.000	0.882	0.778	0.686	0.606	0.535	0.473	0.370	0.291
X_B	0.000	0.100	0.189	0.268	0.338	0.400	0.455	0.545	0.616
a	0.616	0.675	0.722	0.761	0.794	0.821	0.844	0.881	0.905
TIME ON STREAM=2.0 HR.									
X_A	1.000	0.892	0.795	0.707	0.628	0.558	0.496	0.391	0.309
X_B	0.000	0.089	0.172	0.247	0.315	0.375	0.429	0.521	0.594
a	0.544	0.604	0.655	0.698	0.735	0.768	0.796	0.841	0.872
TIME ON STREAM=2.5 HR.									
X_A	1.000	0.901	0.809	0.725	0.648	0.579	0.517	0.411	0.326
X_B	0.000	0.081	0.157	0.228	0.293	0.352	0.406	0.498	0.572
a	0.486	0.545	0.596	0.642	0.682	0.718	0.750	0.802	0.840
TIME ON STREAM=3.0 HR									
X_A	1.000	0.908	0.821	0.740	0.666	0.598	0.536	0.430	0.343
X_B	0.000	0.074	0.145	0.211	0.274	0.332	0.385	0.477	0.552
a	0.440	0.495	0.546	0.592	0.634	0.672	0.706	0.765	0.807
TIME ON STREAM=3.5 HR									
X_A	1.000	0.914	0.832	0.754	0.682	0.616	0.555	0.448	0.360
X_B	0.000	0.068	0.134	0.197	0.257	0.313	0.365	0.456	0.532
a	0.401	0.453	0.502	0.598	0.590	0.629	0.665	0.728	0.775
TIME ON STREAM=4.0 HR									
X_A	1.000	0.919	0.841	0.767	0.697	0.632	0.571	0.464	0.375
X_B	0.000	0.062	0.124	0.184	0.241	0.295	0.346	0.437	0.513
a	0.368	0.417	0.463	0.508	0.550	0.590	0.627	0.693	0.743
TIME ON STREAM=4.5 HR									
X_A	1.000	0.923	0.849	0.778	0.710	0.647	0.587	0.481	0.391
X_B	0.000	0.058	0.116	0.172	0.227	0.279	0.329	0.418	0.495
a	0.340	0.385	0.400	0.473	0.514	0.553	0.591	0.659	0.713

TABLE F-16 SET NO 16

W	0.000	2.831	5.663	8.495	11.33	14.16	16.93	22.65	28.32
TIME ON STREAM=0 HR.									
X_A	1.000	0.819	0.683	0.577	0.491	0.421	0.362	0.271	0.205
X_B	0.000	0.161	0.283	0.379	0.456	0.519	0.571	0.653	0.712
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
TIME ON STREAM=0.5 HR.									
X_A	1.000	0.871	0.713	0.608	0.522	0.450	0.389	0.293	0.222
X_B	0.000	0.140	0.213	0.346	0.423	0.487	0.541	0.627	0.690
a	0.833	0.873	0.899	0.916	0.932	0.943	0.952	0.965	0.974

TIME ON STREAM=1.0 HR.

X_A	1.000	0.857	0.737	0.636	0.550	0.476	0.414	0.314	0.239
X_B	0.000	0.123	0.228	0.317	0.393	0.457	0.513	0.601	0.668
a	0.712	0.769	0.811	0.843	0.868	0.888	0.905	0.930	0.946

TIME ON STREAM=1.5 HR.

X_A	1.000	0.871	0.757	0.659	0.575	0.501	0.437	0.334	0.256
X_B	0.000	0.110	0.207	0.292	0.366	0.430	0.486	0.577	0.647
a	0.621	0.684	0.734	0.775	0.808	0.836	0.859	0.894	0.918

TIME ON STREAM=2.0 HR.

X_A	1.000	0.881	0.775	0.681	0.597	0.523	0.459	0.354	0.272
X_B	0.000	0.099	0.189	0.270	0.342	0.405	0.461	0.554	0.626
a	0.549	0.614	0.668	0.714	0.752	0.785	0.813	0.859	0.889

TIME ON STREAM=2.5 HR.

X_A	1.000	0.891	0.790	0.699	0.618	0.545	0.480	0.372	0.288
X_B	0.000	0.089	0.173	0.250	0.320	0.382	0.438	0.532	0.606
a	0.492	0.555	0.610	0.659	0.701	0.738	0.770	0.823	0.860

TIME ON STREAM=3.0 HR

X_A	1.000	0.898	0.803	0.716	0.636	0.564	0.500	0.390	0.307
X_B	0.000	0.082	0.160	0.233	0.300	0.361	0.417	0.511	0.587
a	0.445	0.505	0.560	0.609	0.654	0.693	0.729	0.788	0.830

TIME ON STREAM=3.5 HR

X_A	1.000	0.905	0.815	0.730	0.653	0.583	0.518	0.408	0.319
X_B	0.000	0.075	0.148	0.217	0.282	0.341	0.396	0.491	0.568
a	0.405	0.463	0.516	0.565	0.610	0.652	0.689	0.754	0.801

TIME ON STREAM=4.0 HR

X_A	1.000	0.910	0.824	0.744	0.668	0.599	0.535	0.424	0.334
X_B	0.000	0.069	0.138	0.203	0.265	0.324	0.377	0.472	0.550
a	0.372	0.420	0.477	0.526	0.571	0.613	0.652	0.721	0.772

TIME ON STREAM=4.5 HR

X_A	1.000	0.715	0.833	0.755	0.682	0.614	0.551	0.440	0.349
X_B	0.000	0.064	0.128	0.191	0.250	0.307	0.359	0.453	0.532
a	0.344	0.395	0.443	0.490	0.535	0.577	0.617	0.689	0.743

TIME ON STREAM=5.0 HR

X_A	1.000	0.919	0.841	0.766	0.695	0.628	0.566	0.455	0.363
X_B	0.000	0.060	0.120	0.179	0.237	0.292	0.343	0.436	0.515
a	0.320	0.367	0.413	0.458	0.502	0.544	0.584	0.658	0.715

TABLE F-17 SET NO 17

W	0.000	3.064	6.129	9.193	12.26	15.32	18.39	24.52	30.64

TIME ON STREAM=0 HR.

X_A	1.000	0.848	0.734	0.643	0.568	0.505	0.451	0.364	0.236
X_B	0.000	0.133	0.233	0.313	0.379	0.434	0.481	0.557	0.616
a	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.865	0.757	0.667	0.592	0.548	0.473	0.383	0.313
X_B	0.000	0.115	0.209	0.286	0.352	0.407	0.455	0.534	0.595
a	0.830	0.877	0.905	0.924	0.937	0.947	0.954	0.966	0.973

TIME ON STREAM=1.0 HR.

X_A	1.000	0.880	0.778	0.691	0.616	0.552	0.495	0.402	0.329
X_B	0.000	0.100	0.187	0.261	0.326	0.381	0.430	0.511	0.574
a	0.695	0.769	0.817	0.853	0.874	0.893	0.908	0.930	0.944

TIME ON STREAM=1.5 HR.

X_A	1.000	0.893	0.797	0.713	0.639	0.574	0.516	0.421	0.346
X_B	0.000	0.087	0.167	0.238	0.300	0.356	0.405	0.487	0.553
a	0.587	0.674	0.735	0.779	0.813	0.840	0.861	0.894	0.914

TIME ON STREAM=2.0 HR.

X_A	1.000	0.904	0.814	0.733	0.661	0.596	0.538	0.441	0.362
X_B	0.000	0.076	0.149	0.216	0.277	0.332	0.381	0.464	0.532
a	0.499	0.591	0.659	0.712	0.754	0.737	0.814	0.856	0.884

TIME ON STREAM=2.5 HR.

X_A	1.000	0.913	0.830	0.752	0.681	0.617	0.559	0.460	0.379
X_B	0.000	0.067	0.133	0.197	0.255	0.309	0.358	0.442	0.511
a	0.428	0.518	0.591	0.649	0.696	0.735	0.768	0.819	0.852

TIME ON STREAM=3.0 HR

X_A	1.000	0.921	0.843	0.769	0.700	0.637	0.579	0.478	0.396
X_B	0.000	0.059	0.119	0.178	0.234	0.237	0.335	0.419	0.490
a	0.370	0.456	0.529	0.590	0.641	0.685	0.722	0.781	0.820

TIME ON STREAM=3.5 HR

X_A	1.000	0.928	0.855	0.785	0.718	0.656	0.598	0.497	0.413
X_B	0.000	0.052	0.107	0.162	0.215	0.266	0.313	0.397	0.468
a	0.322	0.402	0.473	0.535	0.589	0.636	0.676	0.743	0.788

TIME ON STREAM=4.0 HR

X_A	1.000	0.934	0.866	0.799	0.735	0.674	0.617	0.515	0.429
X_B	0.000	0.046	0.095	0.146	0.197	0.246	0.292	0.376	0.447
a	0.281	0.355	0.423	0.485	0.540	0.589	0.632	0.704	0.755

TIME ON STREAM=4.5 HR

X_A	1.000	0.939	0.876	0.812	0.750	0.690	0.634	0.533	0.446
X_B	0.000	0.040	0.085	0.133	0.180	0.227	0.272	0.355	0.427
a	0.247	0.314	0.378	0.438	0.494	0.544	0.589	0.666	0.721

TIME ON STREAM=5.0 HR

X_A	1.000	0.943	0.884	0.824	0.764	0.706	0.651	0.550	0.462
X_B	0.000	0.036	0.077	0.120	0.165	0.209	0.253	0.334	0.407
a	0.219	0.279	0.339	0.396	0.451	0.501	0.548	0.629	0.688

TIME ON STREAM=5.5 HR

X_A	1.000	0.947	0.891	0.834	0.777	.721	0.667	0.567	0.478
X_B	0.000	0.032	0.069	0.109	0.151	0.193	0.235	0.314	0.387
a	0.195	0.249	0.304	0.358	0.411	0.461	0.508	0.592	0.655

TABLE F-18 SET NO 18

W	0.000	3.815	7.630	11.45	15.26	19.07	22.89	30.52	38.15

TIME ON STREAM=0 HR.

X_A	1.000	0.693	0.510	0.387	0.293	0.233	0.183	0.115	0.073
X_B	0.000	0.274	0.437	0.547	0.626	0.635	0.729	0.790	0.827
a	1.000	1.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.728	0.547	0.419	0.325	0.255	0.200	0.125	0.080
X_B	0.000	0.237	0.397	0.510	0.594	0.657	0.705	0.771	0.812
a	0.791	0.876	0.917	0.941	0.956	0.967	0.975	0.985	0.990

TIME ON STREAM=1.0 HR.

X_A	1.000	0.757	0.581	0.450	0.351	0.276	0.218	0.138	0.087
X_B	0.000	0.207	0.361	0.476	0.563	0.629	0.680	0.752	0.797
a	0.645	0.769	0.838	0.881	0.911	0.932	0.947	0.968	0.979

TIME ON STREAM=1.5 HR.

X_A	1.000	0.782	0.610	0.487	0.377	0.297	0.236	0.149	0.095
X_B	0.000	0.182	0.329	0.444	0.533	0.602	0.657	0.734	0.782
a	0.539	0.677	0.764	0.823	0.865	0.896	0.919	0.950	0.967

TIME ON STREAM=2.0 HR.

X_A	1.000	0.802	0.637	0.505	0.401	0.318	0.253	0.161	0.102
X_B	0.000	0.161	0.300	0.414	0.504	0.576	0.634	0.715	0.767
a	0.459	0.598	0.696	0.767	0.819	0.859	0.889	0.930	0.954

TIME ON STREAM=2.5 HR.

X_A	1.000	0.819	0.661	0.530	0.424	0.339	0.271	0.173	0.110
X_B	0.000	0.144	0.275	0.386	0.477	0.551	0.611	0.697	0.752
a	0.398	0.531	0.633	0.712	0.774	0.821	0.858	0.910	0.940

TIME ON STREAM=3.0 HR

X_A	1.000	0.833	0.682	0.553	0.446	0.359	0.288	0.185	0.118
X_B	0.000	0.129	0.252	0.360	0.451	0.527	0.588	0.679	0.737
a	0.349	0.473	0.577	0.661	0.729	0.783	0.827	0.889	0.925

TIME ON STREAM=3.5 HR

X_A	1.000	0.845	0.701	0.574	0.467	0.378	0.305	0.197	0.126
X_B	0.000	0.116	0.232	0.336	0.427	0.503	0.566	0.660	0.722
a	0.310	0.425	0.526	0.613	0.686	0.746	0.795	0.867	0.910

TIME ON STREAM=4.0 HR

X_A	1.000	0.855	0.718	0.594	0.487	0.397	0.321	0.209	0.135
X_B	0.000	0.106	0.214	0.314	0.403	0.480	0.545	0.642	0.708
a	0.278	0.383	0.481	0.568	0.644	0.709	0.763	0.844	0.894

TIME ON STREAM=4.5 HR

X_A	1.000	0.865	0.733	0.612	0.506	0.415	0.338	0.221	0.143
X_B	0.000	0.097	0.197	0.294	0.381	0.458	0.524	0.625	0.693
a	0.251	0.347	0.440	0.526	0.604	0.672	0.731	0.821	0.877

TIME ON STREAM=5.0 HR

X_A	1.000	0.872	0.746	0.629	0.524	0.432	0.354	0.233	0.151
X_B	0.000	0.089	0.183	0.275	0.361	0.437	0.503	0.607	0.679
a	0.229	0.316	0.402	0.488	0.566	0.637	0.699	0.797	0.859

TIME ON STREAM=5.5 HR

X_A	1.000	0.878	0.758	0.644	0.540	0.449	0.369	0.246	0.160
X_B	0.000	0.082	0.170	0.258	0.341	0.417	0.484	0.589	0.664
a	0.210	0.289	0.371	0.453	0.531	0.603	0.667	0.772	0.840

TABLE F-19 SET NO 19

W	0.000	3.662	7.324	10.99	14.65	18.31	21.97	29.30	36.62

TIME ON STREAM=0 HR.

X_A	1.000	0.581	0.374	0.251	0.172	0.119	0.084	0.041	0.021
X_B	0.000	0.377	0.563	0.673	0.744	0.791	0.824	0.861	0.880
a	1.000	1.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000

TIME ON STREAM=0.5 HR.

X_A	1.000	0.626	0.412	0.280	0.193	0.134	0.094	0.047	0.023
X_B	0.000	0.330	0.519	0.638	0.716	0.768	0.804	0.847	0.868
a	0.775	0.885	0.931	0.956	0.970	0.980	0.986	0.993	0.996

TIME ON STREAM=1.0 HR.

X_A	1.000	0.662	0.447	0.307	0.213	0.149	0.104	0.052	0.026
X_B	0.000	0.291	0.480	0.605	0.689	0.746	0.786	0.833	0.856
a	0.628	0.784	0.864	0.910	0.940	0.958	0.971	0.986	0.992

TIME ON STREAM=1.5 HR.

X_A	1.000	0.692	0.479	0.333	0.232	0.163	0.115	0.057	0.028
X_B	0.000	0.260	0.445	0.574	0.663	0.725	0.768	0.820	0.845
a	0.526	0.697	0.799	0.863	0.906	0.935	0.954	0.977	0.988

TIME ON STREAM=2.0 HR.

X_A	1.000	0.717	0.507	0.357	0.252	0.177	0.125	0.062	0.031
X_B	0.000	0.234	0.414	0.545	0.638	0.704	0.750	0.807	0.835
a	0.451	0.623	0.738	0.817	0.872	0.910	0.936	0.968	0.983

TIME ON STREAM=2.5 HR.

X_A	1.000	0.738	0.533	0.380	0.270	0.192	0.136	0.067	0.034
X_B	0.000	0.212	0.385	0.517	0.614	0.683	0.733	0.794	0.824
a	0.395	0.559	0.681	0.772	0.837	0.884	0.917	0.958	0.977

TIME ON STREAM=3.0 HR.

X_A	1.000	0.756	0.555	0.402	0.289	0.206	0.146	0.073	0.036
X_B	0.000	0.193	0.360	0.491	0.590	0.663	0.716	0.781	0.814
a	0.351	0.505	0.630	0.727	0.802	0.857	0.897	0.948	0.971

TIME ON STREAM=3.5 HR

X_A	1.000	0.771	0.576	0.423	0.306	0.220	0.157	0.079	0.039
X_B	0.000	0.177	0.337	0.467	0.568	0.644	0.699	0.769	0.804
a	0.315	0.458	0.582	0.685	0.766	0.839	0.876	0.936	0.965

TIME ON STREAM=4.0 HR

X_A	1.000	0.784	0.595	0.442	0.323	0.234	0.167	0.084	0.042
X_B	0.000	0.163	0.316	0.444	0.546	0.624	0.683	0.756	0.794
a	0.287	0.418	0.539	0.645	0.732	0.801	0.855	0.924	0.958

TIME ON STREAM=4.5 HR

X_A	1.000	0.795	0.612	0.460	0.340	0.247	0.178	0.090	0.045
X_B	0.000	0.152	0.297	0.423	0.526	0.606	0.666	0.744	0.785
a	0.262	0.383	0.500	0.607	0.698	0.770	0.832	0.911	0.951

APPENDIX - G

G-1 Material Balance Calculations

Sample calculations for sample No.1 set 2

DATA

Common for all the samples of set 2

GCAT = 34.1307 gm

VHF = 362.5 ml/min.

VCF = 1.5 ml/min.

TR = 350 °C

TE = 6.8 °C

TA = 25.0 °C

P = 736 mm of Hg.

For Sample No.1 only

TIME = 25-45 minutes

T = 20 minutes

VEG = 1137 ml/min.

VBL = 0.676

WLS = 15.8403 gm

$$VPW = Exp\left[\left[7.96681 - \frac{1668.21}{TA + 228.}\right] * 2.303\right] = 23.6$$

$$VPA = Exp\left[\left[6.84498 - \frac{1203.526}{TE + 222.863}\right] * 2.303\right] = 40.25$$

$$VPB = Exp\left[\left[6.90565 - \frac{1211.033}{TE + 220.79}\right] * 2.303\right] = 38.44$$

$$CF1 = \frac{22400. * 760.}{273.} * \frac{273 + TA}{(P - VPW)} = 2.6086 * 10^{4}$$

$$LHSV = \frac{VCF * 60 * .85}{GCAT} = 2.052$$

$$QHF = \frac{VHF}{CF1} = 0.01390$$

$$QCF = \frac{VCF * 0.778}{84.16} = 0.01387$$

$$GAMA = \frac{QHF}{QCF} = 1.002$$

Above calculations are common to all the samples of this set.

$$\mathrm{AMF} = \mathrm{QCF} * \mathrm{T} = 0.2773$$

$$\mathrm{VAL} = 1.-\mathrm{VBL} = 0.324$$

$$\mathrm{BML} = \frac{\mathrm{VBL} * 0.879}{\mathrm{VBL}*0.879+\mathrm{VAL}*0.778} \cdot \frac{\mathrm{WLS}}{78} = 0.142591$$

$$\mathrm{AML} = \frac{\mathrm{VAL} * 0.778}{\mathrm{VBL}*0.879+\mathrm{VAL}*0.778} \cdot \frac{\mathrm{WLS}}{84.16} = 0.05606$$

$$X_B = \frac{\mathrm{BML}}{\mathrm{BML} + \mathrm{AML}} = 0.7178$$

$$X_A = 1.- X_B = 0.2822$$

$$\mathrm{CF} = \frac{1.00918}{X_B+1.00918*X_A} - \frac{0.65926}{0.65926*X_B+X_A}$$

$$Y_B = \mathrm{EXP}\ [-\ln\ (X_B+1.00918 * X_A)+X_A*\mathrm{CF}] = 1.0358$$

$$Y_A = \mathrm{EXP}\ [-\ln\ (X_A+0.65926*X_B) - X_B*\mathrm{CF}] = 1.2025$$

$$\mathrm{YAG} = \mathrm{VPA}*Y_A*X_A/\mathrm{P} = 0.01856$$

$$\mathrm{AMG} = \mathrm{YAG}*\mathrm{VEG}*\mathrm{T}*\mathrm{CF1} = 0.016182$$

$$\mathrm{YBG} = \mathrm{VPB}*X_B *Y_B/\mathrm{P} = 0.03883$$

$$\mathrm{BMG} = \mathrm{YBG}*\mathrm{VEG}*\mathrm{T}/\mathrm{CF1} = 0.033854$$

$$\mathrm{BMF} = \mathrm{BMG} + \mathrm{BML} = 0.176445$$

$$\mathrm{AMU} = \mathrm{AMG} + \mathrm{AML} = 0.072244$$

$$\mathrm{HFE} = \mathrm{QHF}*\mathrm{T} = 0.277928$$

$$\mathrm{HFO} = 3.*\mathrm{BMF} = 0.52933$$

$$\mathrm{TPM} = \mathrm{BMF} + \mathrm{AMU} = 0.248689$$

$$\mathrm{EGM} = \mathrm{T}*\mathrm{VEG}/\mathrm{CF1} = 0.87174$$

PMG = AMG +BMG + HFO = 0.57937

PERT = (EGM-(BMG+AMG+HFO+AMF+HFE))*100./(AMF+HFE)=2.60

PERH = (EGM-HFE-PMG)*100./HFE = 5.195

CHC = AMF - BMF - AMU = 0.02864

FA = BMF/AMF = 0.6362

FB = CMU/AMF = 0.2605

FCR = 1-FA-FB = 0.1033

CHCG = EGM-PMG-HFE = 0.01444

G.2 Sample Calculations for Apparant Rate Constants:

From G.1, for set No.2 -

Mole ratio, $\gamma = 1.002$

$\frac{1}{C_o}$ =CF1 = 2.6086×10^4 cm^3/gmole

W =GCAT= 34.1307 g

F =QCF*60 = 0.8332

From Fig. 4.1.2, from smoothened curve -

$X_A = 0.237$

$X_B = 0.660$

$X_C = 1 - X_A - X_B = 0.103$

Hence , $K = \frac{X_C}{X_B} = \frac{0.103}{0.660} = 0.156$

Substituting the values in equation (4.2)

$$0.660 + \left[\frac{1 + \frac{(1+1.002)(1+0.156)}{3-0.156}}{1+0.156} \right] \ln[1-(1+0.156)0.66]$$

$$= - k_1' * \frac{1+0.156}{3-0.156} \cdot \frac{1}{2.6086*10^4} \cdot \frac{34.1307}{0.8332}$$

and thus $k_1' = 5060$

$$k_2' = 5060 * 0.156 = 790$$

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