OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

04851

Distribution
LIMITED

ID/WG.123/14
7 June 1972

Original: ENGLISH

United Nations Industrial Development Organization

Expert Group Meeting on Transfer of Know-how
in Production and Use of Catalysts

Bucharest, Romania, 26 - 30 June 1972

THE PHYSICAL AND MATHEMATICAL MODELLING OF A PROCESS FOR SOME ALKYLAROMATICS DEHYDROGENATION IN ADIABATIC SYSTEM[1/]

by

V. Mocearov
S. Popa
G. Csomontanyi
G. Panaitescu
A. Panovici

-PETROC.IN-
ROMANIAN RESEARCH INSTITUTE FOR PETROCHEMISTRY
Ploiesti
Romania

1/ The views and opinions expressed in this paper are those of the authors and do not necessarily reflect the views of the Secretariat of UNIDO. This document has been reproduced without formal editing.

14.72-3755

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

The modern trends in the transposition of the laboratory research results to pilot or commercial scales are connected to the physical and especially mathematical modelling.

In the physical modelling the nature of the phenomenon is identical in model and apparatus, the totality of the individual stages being seen as a single phenomen.

From the given equations with one variable one deduces the similarity criteria and the connections between them are established in an experimental way.

In the mathematical modelling it is necessary to compute the material and heat balance equations for the initial and local conditions of temperature, reactants concentration and the geometric features. The mathematical modelling contains three stages: the elaboration of the equations describing the process, the elaboration of the algorithm for the solution of these equations and the check of the mathematical model reliability on the studied plant.

For the optimization of the process used in obtaining styrene, which was elaborated by our group, and applied to commercial scale, our activity was led towards two targets: to accomplish the scale down of a commercial ethylbenzene dehydrogenation adiabatic reactor and to elaborate the mathematic model describing the industrial process of obtaining styrene.

Physical modelling

In order to test the various improved versions of the dehydrogenation catalyst which have to be recommanded for use in styrene process it was necessary to accomplish the physical model of the commercial reactor.

To ensure the plug flow through the reactor the following conditions must be fulfilled:

$\frac{D}{d_p} > 30$ where D is the diameter of the catalytic bed and d_p the diameter of the pellet and the $Pé_R$ (radial mass transport criterium) must be one order magnitude higher than $Pé_L$ (axial mass transport criterium)/1,2,3/.

In the commercial adiabatic plant used for alkylbenzenes dehydrogenation these conditions are fulfilled because $D/d_p \gg 30$, and for $Re_{pellet} = 60,5$ for which is corresponding a criterium $Pé_L = 0,95$ and a criterium $Pé_R = 8,5$.

The variation of the value for both Péclet numbers as functions of the modified Reynolds number is represented on the logarithmic plot in fig.1.

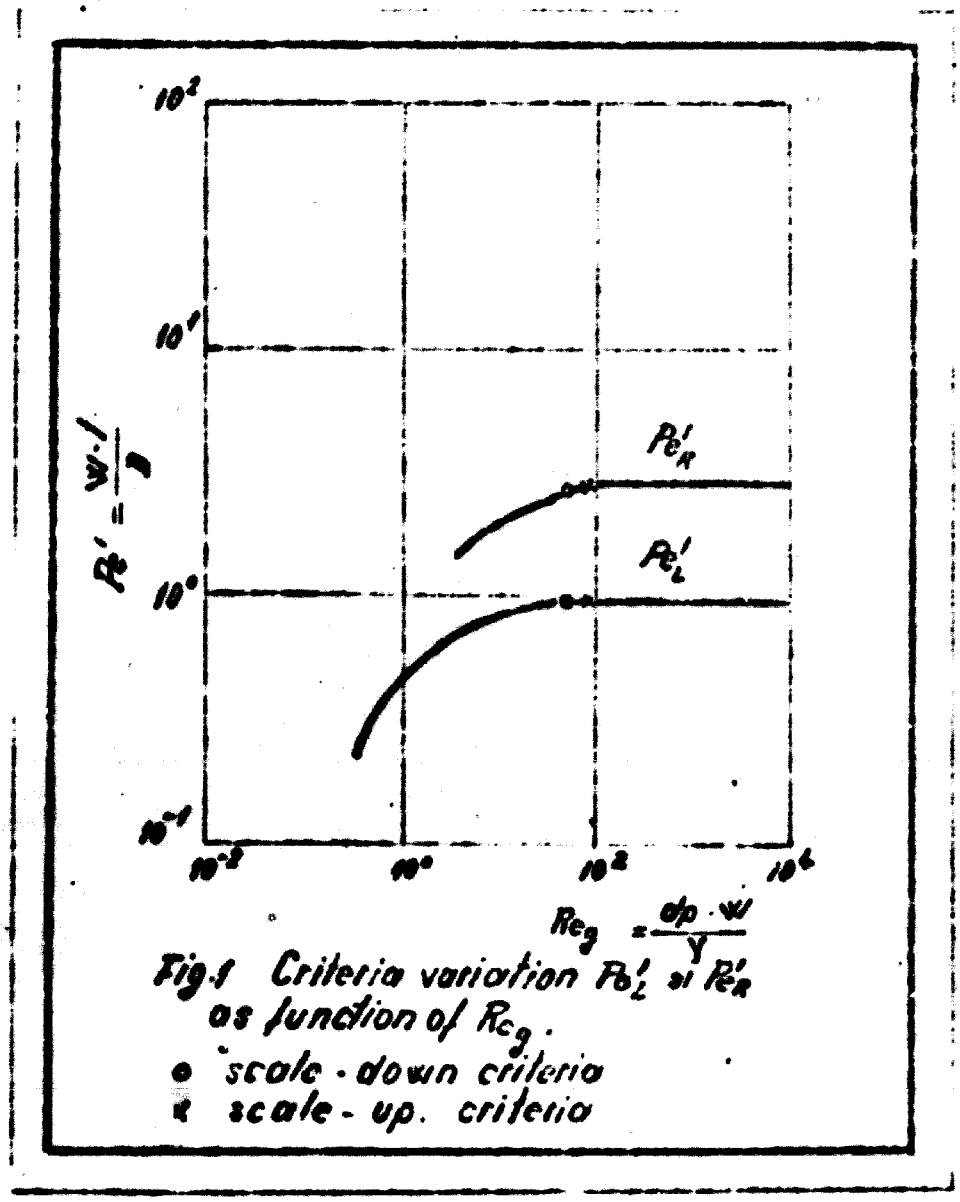


Fig.1 Criteria variation Pe'_L si Pe'_R as function of Re_g.
• scale-down criteria
x scale-up. criteria

The scale-down approach based on the criterium of maintaining the geometry of the commercial reactor namely the D/H ratio(diameter of the catalytic bed to the height of the catalytic bed)led to a physical model by which the corresponding $Pé_R$ and $Pé_L$ numbers to Re_p=8,2 have the same value,therefore the axial mixing of reactants cannot be avoided.

By the scale-down based on maintaining the hydrodinamic conditiond similar with those of the industrial reactor namely the D/dp ratio above 3o,the model fulfills the condition of the commercial apparatus.The difference between $Pé_R$ and $Pé_L$ is near to that of a commercial reactor,at a Re_p number of 5o,2.Therefore there is no danger of axial mixing of the reactant,and the flow approaches the plug type.

Thus,based on the hydrodinmaic similarity criteria it was designed and constructed an adiabatic reference device with a capacity of 1o l. catalyst.It was used for comparative tests in an adiabatic system of elaborated catalysts which were previously tested in the isothermal laboratory system in view of recommanding the best plant conditions when applying it on commercial plant.

Mathematical modelling

The mathematical modelling approach of a process for obtaining styrene was applied on the reference adiabatic reactor for the catalytic dehydrogenation of ethylbenzene which represents the scale-down of the industrial adiabatic reactor.

In order to describe the process there were proposed six catalytic reactions (I-VI) which are justifying the presence in the resulting gas effluent of ethylbenzene(1),styrene(2),hydrogen(3), toluene (4),methane(5),benzene(6),ethylene(7),carbon dioxide(8), water(9) and carbon(1o).The reactions I-IV are considered as plausible and consistent for describing ethylbenzene process in an adiabatic system,done by a series of authors who are interested in the modelling of this process/4,5,6/.

As concerning reaction V this was considered by us, as a result of a kinetic study on catalysts foulling in ethylbenzene process and reaction VI springing out of a study on catalysts

regeneration /7,8/

1.Styrene generation:

$$C_6H_5-C_2H_5 \rightleftharpoons C_6H_5-C_2H_3 + H_2 \qquad (I)$$

2.Toluene generation:

$$C_6H_5-C_2H_5 + H_2 \longrightarrow C_6H_5-CH_3 + CH_4 \qquad (II)$$

3.Benzene generation:

$$C_6H_5-C_2H_5 \longrightarrow C_6H_6 + C_2H_4 \qquad (III)$$

$$C_6H_5-CH_3 + H_2 \longrightarrow C_6H_6 + CH_4 \qquad (IV)$$

Coke generation:

$$C_6H_5-C_2H_5 \longrightarrow 3H_2 + CH_4 + 7C \qquad (V)$$

Coke regeneration:

$$C + 2H_2O \longrightarrow CO_2 + 2H_2 \qquad (VI)$$

In elaborating the mathematical model the following simplifying assumptions and calculation formula were used:

a)It was assumed that axial and radial mass and heat transfer phenomena has no influence on the kinetics of the studied reactions and as a results the terms for mass and heat transfer from the materials and heat balance equations were considered null.

b)It was assumed that the hydrogenation reactor which was proposed for the mathematic modeling has a perfect adiabaticity,or there is no heat exchange with the outside.

c)It was assumed that the pressure variations are neglijible on the catalyst bed so that in the calculations it was used a mean pressure value of 1.1o ata.

d)In calculating the molal specific heats a simplified formula was used /4/:

$$C_{p_i} = A_i + B_i T + C_i T^2 \qquad \text{(VII)}$$

where A_i, B_i, C_i, are constants, illustrated in table I for each component of the gas phase (1-1o)

Table I. The values for the coeficients A_i, B_i, C_i from molal specific heat expressions, Cp(VII)

Component	A_i	B_i	C_i
1	$-0,9289 \cdot 1o^2$	$0,3588 \cdot 1o^0$	$-0,1958 \cdot 1o^{-5}$
2	$0,9100 \cdot 1o^1$	$0,9140 \cdot 1o^{-1}$	$-0,3300 \cdot 1o^{-4}$
3	$0,6880 \cdot 1o^1$	$0,6600 \cdot 1o^{-4}$	$0,2790 \cdot 1o^{-6}$
4	$-0,7598 \cdot 1o^2$	$0,2935 \cdot 1o^0$	$-0,1591 \cdot 1o^{-3}$
5	$0,3422 \cdot 1o^1$	$0,1784 \cdot 1o^{-1}$	$-0,4170 \cdot 1o^{-5}$
6	$-0,7405 \cdot 1o^2$	$0,2702 \cdot 1o^0$	$-0,1495 \cdot 1o^{-3}$
7	$0,2706 \cdot 1o^1$	$0,2916 \cdot 1o^{-1}$	$-0,[illegible]960 \cdot 1o^{-5}$
8	$0,6850 \cdot 1o^1$	$0,8533 \cdot 1o^{-2}$	$0,2475 \cdot 1o^{-5}$
9	$0,6890 \cdot 1o^1$	$0,3283 \cdot 1o^{-2}$	$-0,3400 \cdot 1o^{-6}$
1o	$-0,1097 \cdot 1o^2$	$0,3692 \cdot 1o^{-1}$	$-0,2134 \cdot 1o^{-4}$

e)In calculating the heats of the reaction $-\Delta Hr_i$ (cal/mol there was used the simplifyed relation /4/

$$\Delta Hr_i = A_i + B_i T \qquad \text{(VIII)}$$

where A_i, B_i are constants which are characterizing the reaction components (1-1o) shown in table II.

Table II. The values of the coeficients A_i, B_i from the relation $\Delta H_i = A_i + B_i T$, cal/mol

Reaction	A_i	B_i
I	28,343	1,090
II	-12,702	-3,150
III	25,992	-1,900
IV	-9,568	-2,665
V	23,653	-2,490
VI	22,320	-2,604

f) Equilibrium constant values for obtaining styrene as temperature function, were calculated with the relation established by us on literature data/10/.

$$Kp = 0,483 \cdot 10^{6} \exp(-29.685/RT) \qquad (IX)$$

The differential equation system which describes mass and heat balances can be expressed in a condensed form when defining the matrices of the following terms: the stoechiometric coefficients (S), reaction rates (R) heat capacites (C), heats of formation for reaction products (H) and molal concentrations (X).

$$S = \begin{vmatrix} -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 3 & 0 & 1 & 0 & 0 & 0 & 0 & 7 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 1 & -2 & -1 \end{vmatrix}$$

The rows of this matrix represent the stoichiometric coeficients which are interfering in the six studied reactions (I-VI) and the columns of the matrix represent reactions stoichiometric coeficients namely those of the reaction products

(1-1o).With minus are marked compounds stoichiometric coeficients which are consumed in one of the studied reactions,and with plus the stoichiometric coeficients which are resulting from the processing.

R,C,H and X matrices are shown under the form of multidimensional vectors.

$$R=\begin{vmatrix} r_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ r_6 \end{vmatrix} \qquad C=\begin{vmatrix} C_{p_1} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ C_{p_{10}} \end{vmatrix} \qquad H=\begin{vmatrix} H_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ H_6 \end{vmatrix} \qquad X=\begin{vmatrix} x_1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ x_{10} \end{vmatrix}$$

Mass and heat balance equations expressed in finite differences have the following form:

$$\Delta X = R^* \cdot S \qquad (X)$$

$$\Delta T = \frac{R^* \cdot H}{F \cdot X^* \cdot C} \qquad (XI)$$

where:

R^* = reaction rates transposed matrix,

X^* = molal concentrations transposed matrix,

$\Delta X, \Delta T$ = finite variations for concentration and temperature on the increment of the catalytic bed height,

F = efluent molal flow (row material + diluent)

The knowlidge of the finite differences X and T gives us the possibility to calculate concentrations and temperatures values,successively,on each increment of the catalytic bed.

It is obvious that: $X_{i+1} = X_i + \Delta X$ (XII)

$T_{i+1} = T_i - \Delta T$ (XIII)

The development of relation (X) given:

$$\Delta x_1 = -r_1-r_2-r_3-r_5 \quad (X.1)$$
$$\Delta x_2 = r_1 \quad (X.2)$$
$$\Delta x_3 = r_1-r_2-r_4+3r_5+2r_6 \quad (X.3)$$
$$\Delta x_4 = r_2-r_4 \quad (X.4)$$
$$\Delta x_5 = r_3+r_4+r_5 \quad (X.5)$$
$$\Delta x_6 = r_3+r_4 \quad (X.6)$$
$$\Delta x_7 = r_3 \quad (X.7)$$
$$\Delta x_8 = r_6 \quad (X.8)$$
$$\Delta x_9 = -2r_6 \quad (X.9)$$
$$\Delta x_{10} = 7r_5-r_6 \quad (X.10)$$

and from relation (XI) ΔT takes the form of:

$$\Delta T = \frac{r_1H_1 + r_2H_2 + \dots + r_6H_6}{F(x_1C_{p_1} + x_2C_{p_2} \dots + x_{10}C_{p_{10}})} \quad (XI.1)$$

For the expressions of the reaction rates $(r_1,\dots,r_6)$ there were used, in compliance with some literature informations /4,5,9,6/ simplified forms, the studied reactions (I-VI) considering them as first order pseudo-homogeneous reactions when compared with each reaction taken separately.

$$r_1' = k_1(p_1 - \frac{p_2 \cdot p_3}{K_1}) \quad (XIV)$$

$$r_2' = k_2 \cdot p_1 \cdot p_2 \quad (XV)$$

$$r_3' = k_3 \cdot p_1 \quad (XVI)$$

$$r_4' = k_4 \cdot p_3 \cdot p_4 \quad (XVII)$$

$$r_5' = k_3 \cdot p_1 \quad (XVIII)$$

$$r_6' = k_6 \cdot p_{10} \cdot p_9^2 \quad (XIX)$$

where:

$p_i (i=1,2,\dots,10)$ = partial pressures calculated by

the multiplication of the molal concentrations vector with the average pressure of the system

$k_{i(i=1,2,....6)}$ = rate constant

$r_{i(i=1,2,...,6)}$ = reaction rate ,mole/gr.cat.H

In a kinetic study made by us on integral laboratory reactors,in pseudoisothermal conditions there were determined the values of the rate constants $k_1,k_2,...,k_6$ for the six studied reactions.The obtained results are shown in table III.

Table III.The values of the kinetic constants k_{oi},E_i for the studied reactions (I-VI)

Reaction	k_{oi} mol/gr.cat.H	E_i cal / mol
I	0,125 . 10^7	30.000
II	0,99e . 10^7	30.900
III	0,19e . 10^{10}	47.600
IV	0,72e . 10^9	45.000
V	0,175 . 10^5	30.400
VI	0,29[illegible] . 10^6	30.600

These values were adjusted in a computer in order to correspond to the macrokinetic conditions of the modeled adiabatic reactor.

By the help of the values $k_1,k_2,.....,k_6$ using the relations XIV - XIX there were calculated the values $r_1,r_2,..$ r_6 and these multiplied $\rho.A.\Delta z$

Where:

ρ =catalyst bulk density,gr/cm^3

A =area of the catalytic bed section,cm^2

$z=\frac{Z}{n}$ = increment height,where Z=the height of catalytic bed,n=the number of increments,

led us to the values $r_1, r_2 \ldots\ldots r_6$ which are interfering in vector R.

Using the above described method there was elaborated the athematic model for styrene proce s.The calculations were accomplished with the I.B.M.Disk Monitor,System Version 2 using Euler integration method and Fortran language.In figure 2 there are exemplified temperatures profiles calculated in accordance with the model on z increments from Z-the height of the catalytic bed from styrene adiabatic reactor when the effluent is entering at 630°C.Temperature values measured experimentally in three positions on the height of the catalytic bed of the adiabatic reactor(also marked on figure 2) are confirming the fact that the drown up model satisfactory follows temperature changes due to chemical processings.

A suitable agreement between the data calculated with the help of the model and the experimental one can be seen in figure 3 where is shown the variation for ethylbenzene conversion to styrene,toluene and benzene calculated on z increments, from Z-the height of the catalytic bed when effluent inlet temperature is 630°C;the experimental values obtained on styrene,benzene and toluene at effluent outlet from the catalytic bed(marked with X on fig.3) are practically superposed on those calculated corresponding to the model.

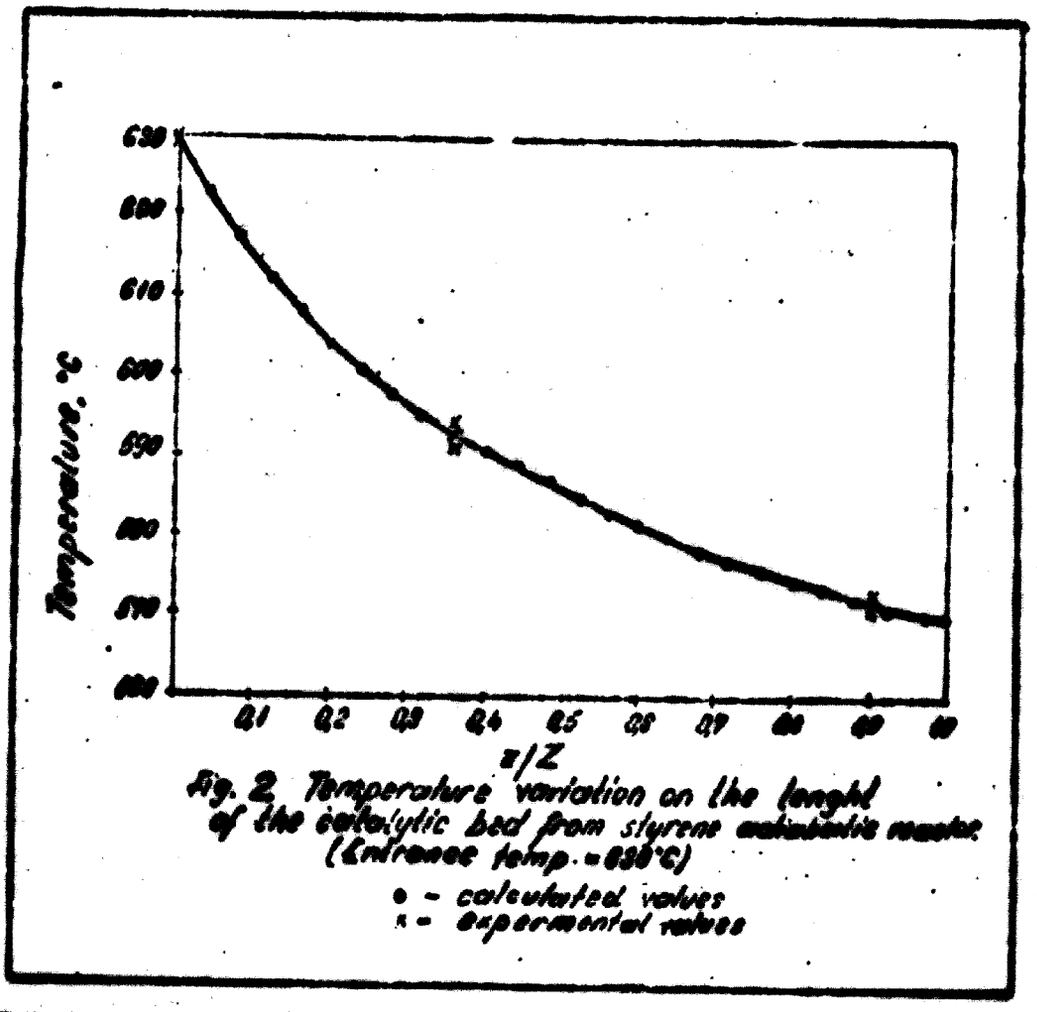


Fig. 2 Temperature variation on the lenght of the catalytic bed from styrene adiabatic reactor (Entrance temp. = 630°C)
• - calculated values
x - experimental values

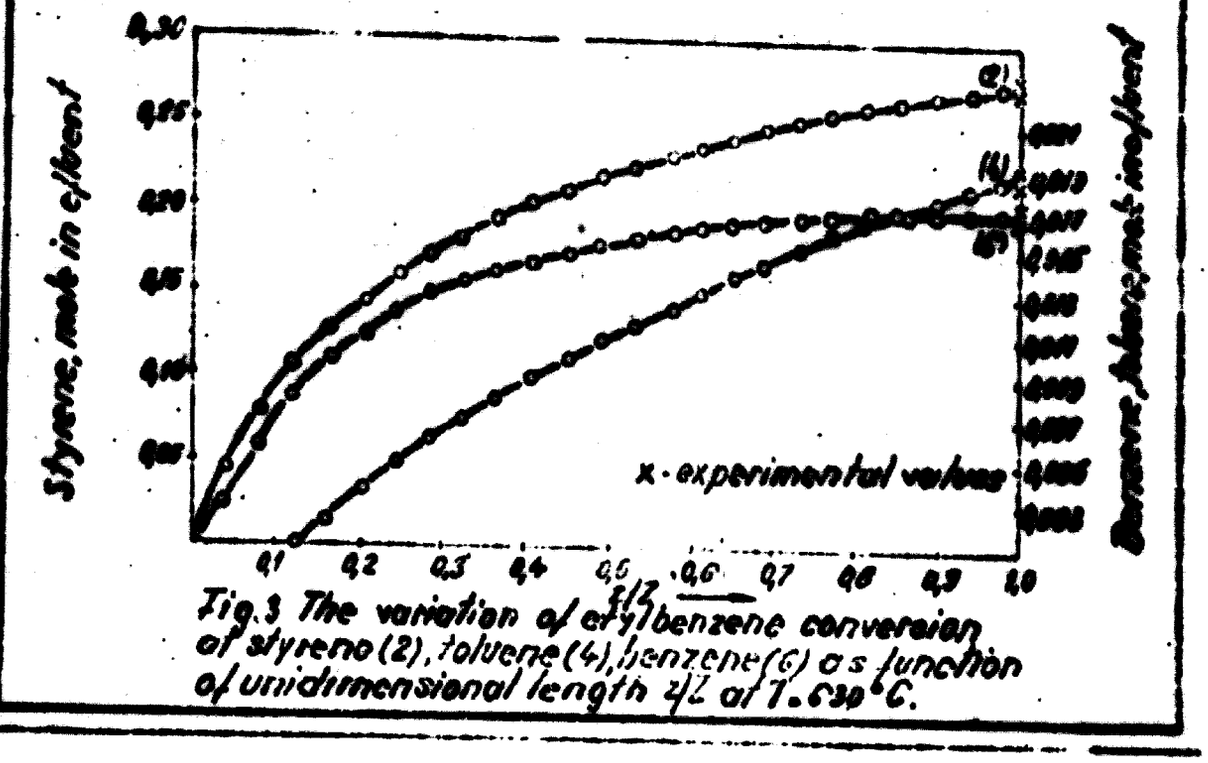


Fig. 3 The variation of ethylbenzene conversion of styrene (2), toluene (4), benzene (6) as function of unidimensional length z/Z at T = 630°C.

Conclusions:

In the present paper it is shown one of the methods which are currently used in our research work concerning the hetero-catalytic processes which are consisting of:

-catalysts kinetic characterization in a dynamic isothermal system using an integral laboratory reactor,

-the thermodynamic characterization of the principal studied reactions,

-the scale-down of the commercial reactor,

-the formulation of the analytical balance equations for heat and materials on laboratory experimental data,

-subsequent adjustements of the kinetic data which characterisation the catalyst in an isothermal system in order to correspond the microkinetic conditions from the adiabatic reactor.

With such a system of differential balance equations one proceeds subsequently to the optimization of the system based on economic criteria the optimal conditions obtained by calculations are checked in an adiabatic pilot plant which is also used to establish catalyst operating conditions in an adiabatic system.

In that paper one can see that our group is able to give in a very short period of time the best solutions in the following cases:

-the choice of the best catalyst for all kind of processes in an adiabatic system,

-the recommandation of the best operating conditions from an economic point of view,

-the discovery of possible failures existing in some adiabatic commercial reactors and the recommandations for avoiding them.

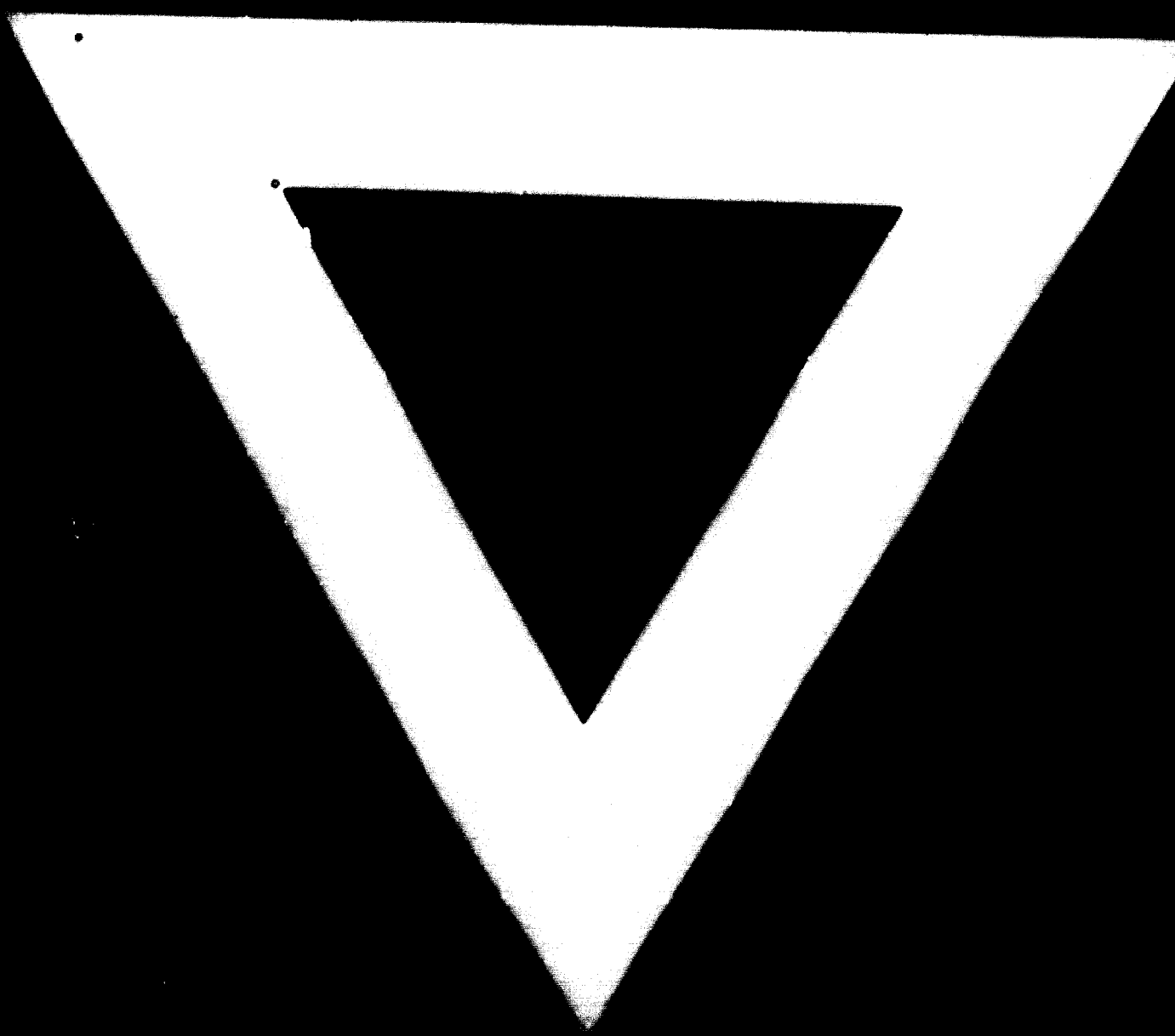
We also offer our technical aid in organising such activities in other countries and the training of a technical stuff.

Bibliography

1.-Olah A.Fouges Ind.Eng.Chem.,53,7(1961).
2.-C.Roemer et al.Ind.Eng.Chem.,[illegible],(1962)
3.-J.J.Carberry Ind.Eng.Chem. 65,11,(1964).
4.-D.Davidson,J.Res.Develop.,[illegible],(1969).
5.-J.G.P.Shell,Canad.,Soc.Eng.,47,2,(1969).
6.-J.Smith,Chem.Eng.Series,Mc.Graw-Hill,(1959).
7.-C.Coriciuc,G.Cosmontanyi,S.Popa,Rev.Roumaine Chim. 3,(1972).
8.-V.Mocearov et al.,Unpubl. Petrochim paper,(1979).
9.-O.Levenspiel,Chemical Reaction Engineering, New-York (1962).
10.-Ray A. Boundy, Raymond F.Boyer, Styren its Polymers, Copolymers and Derivatives, New York,(1952).

* * *

[redacted]



9.8.74