Cracking of cumene over silica-alumina catalysts

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Received on September 7, 1978; Revised on November 20, 1978

Abstract

Cracking of cumene was studied in a fixed bed reactor over silica-alumina catalysts under isothermal conditions in the temperature range 350–500° C. Catalytic activity of silica-alumina was found to depend on its composition and temperature of activation. Detailed studies were carried out over silica-alumina containing 9·2% alumina after it was heat-treated at 350° C for 3 hours. In the range of variables studied, single site adsorption of cumene (benzene adsorbed) was found to be the most probable rate controlling step.

Key words: Cumene, cracking, silica-alumina, catalytic activity, rate controlling step.

1. Introduction

Many solid catalysts are described as having acid sites on their surfaces and these acid sites govern their activity for reactions such as dehydration, cracking, isomerization, etc. Cracking of hydrocarbons is catalysed by acid catalysts such as silica, and silica-alumina amongst others. Cracking of cumene has received considerable attention as a reaction typical of one class of cracking reactions, namely, dealkylation of aromatics[8]. Over acid catalysts, the reaction is expected to be clean yielding essentially benzene and propylene as the products of the reaction[8].

Obelentsev and Gryazev,[1, 2] and Ballod *et al.*[3] studied cracking of cumene as a function of space velocity in an integral reactor at constant pressure over silica-alumina catalysts in the temperature range 300–350° C and 400–450° C respectively. Topchieva and Panchenkov[4] studied the reaction over silica-alumina (10% alumina) as a function of pressure at 400° C while Corrigan *et al.*[5] studied it in the temperature range 455–488° C. Weisz and Prater[6] studied the reaction as a function of pressure and concentration of inhibitors in a differential reactor over silica-alumina (10% alumina) in the temperature range 360–420° C. Plank and Nace[7] studied the effect of nitrogen compounds over silica-alumina (10% alumina) in the temperature range 426–482° C. Prater and Lago[8] studied the kinetics of this reaction in a differential reactor over silica-alumina (12% alumina) in the temperature range 307–690° C, while Chernov and Antipina[9] studied it in the temperature range 370–492° C. Nikitan[10] studied the effect of catalyst pretreatment while Topochieva, Romanovskii and Timoshenko *et al.*[11] studied the effect of the method of preparation of the catalyst.

The present investigation was undertaken to study cumene cracking over silica-alumina catalysts in order to establish the most probable rate controlling mechanism.

2. Experimental

The experimental set-up used in the present investigation is given in Fig. 1. It mainly consisted of cumene feeding and metering unit, pretreater and reactor assembly and product collection unit.

Analar grade cumene was used after removing any cumene hydroperoxide that may be present by treatment with silica gel.

Silica and alumina gels were prepared by standard procedures and silica-alumina catalysts of varying compositions were prepared by mixing the gels in the required proportion[14, 15].

Acidity of the catalyst was measured by amine titration using *p*-dimethyl aminoazo benzene as the indicator[16].

The product gas mainly consisting of propylene was analysed in an Orsat apparatus. Unconverted cumene and product benzene were analysed by gas-chromatography.

2.1. *Pretreatment of the catalyst*

Silica-alumina catalyst prepared as given above was heat-treated in a muffle furnace at different temperatures for varying intervals of time in order to study the effect of pretreatment on catalyst acidity. At a constant temperature, acidity of the catalyst was found to decrease initially with time and after a lapse of 2–3 hours attained a constant value[15, 17]. Acidity was found to pass through a maximum depending on the temperature of treatment and composition of the catalyst. Maximum acidity was exhibited by the catalyst containing 9·2% alumina when it was heat-treated at 350° C for 3 hours. All further samples were heat-treated at a temperature of 350° C for 3 hours.

2.2. *Kinetic data*

Catalytic activity of silica-alumina for the cracking of cumene was studied by measuring the conversion of cumene to benzene and propylene as a function of time factor and reaction temperature. Before collecting kinetic data it was ensured that diffusional

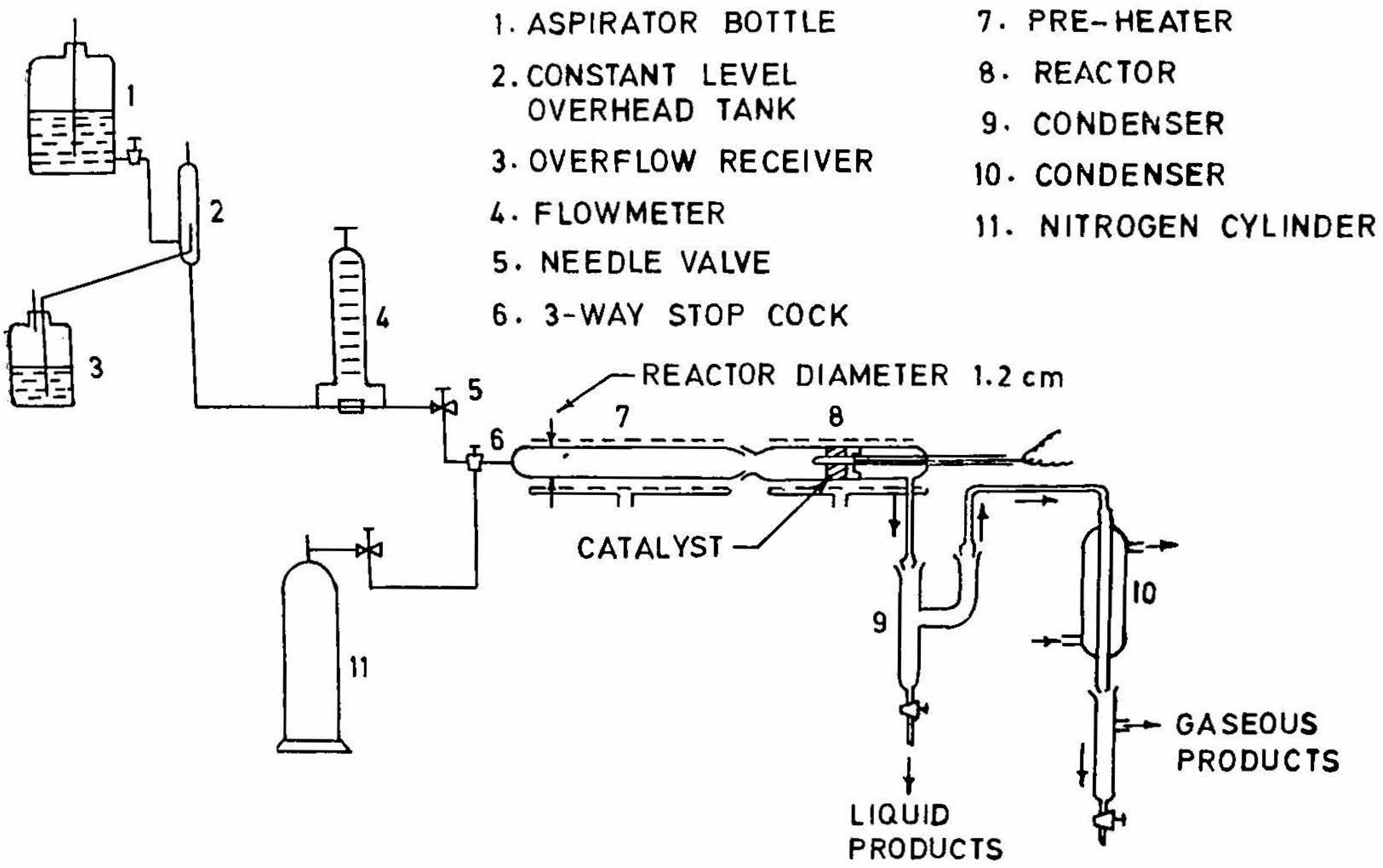

Fig. 1. Schematic diagram of the experimenal set-up.

effects, *viz.*, bulk and pore diffusion were not significant. Under the following conditions diffusional effects were found to be at a minimum:

Cumene flow rate : $\not<$ 1·2 moles/hr.

Particle size of the
catalyst : $\not>$ 0·1775 mm (−65 + 100 Tyler mesh).

Subsequent calculations according to the methods suggested by Yoshida *et al.*[12] have shown that with this particle size the effectiveness factor was nearly unity.

The effect of time factor and reaction temperature was studied in the following range of variables :

W/F : 1, 2, 3, 4 and 5 g cat. hr./g mole

Temperature : 350, 400, 450 and 500° C.

The data are presented in Table I. It can be seen that the conversion increases as a function of time factor as well as temperature.

2.3. *Kinetic analysis*

For a flow reactor of the type employed in the present study, the basic design equation can be written as

$$W/F = \int_0^x dx/r. \tag{1}$$

Table I

Effect of time factor on conversion

W/F g. cat. hr./ g. mole	Conversion, x			
	Temperature ° C 350	400	450	500
1·0	0·022	0·030	0·032	0·041
2·0	0·055	0·070	0·081	0·087
3·0	0·070	0·085	0·115	0·123
4·0	0·084	0·110	0·133	0·157
5·0	0·116	0·130	0·174	0·205

For a first order reaction, r can be expressed as

$$r = k \cdot C_A. \tag{2}$$

Expressing C_A in terms of conversion, eqn. (1) on integration gives

$$k \frac{P_T}{RT} \frac{W}{F} = [-x - 2ln(1-x)]. \tag{3}$$

The experimental data plotted in Fig. 2 were found to follow eqn. (3). From the slopes of the above plots, the reaction velocity constants were evaluated. These constants given in Table II were related to the temperature effect by means of the Arrhenius equation. Activation energy (E) and frequency factor (A) were evaluated

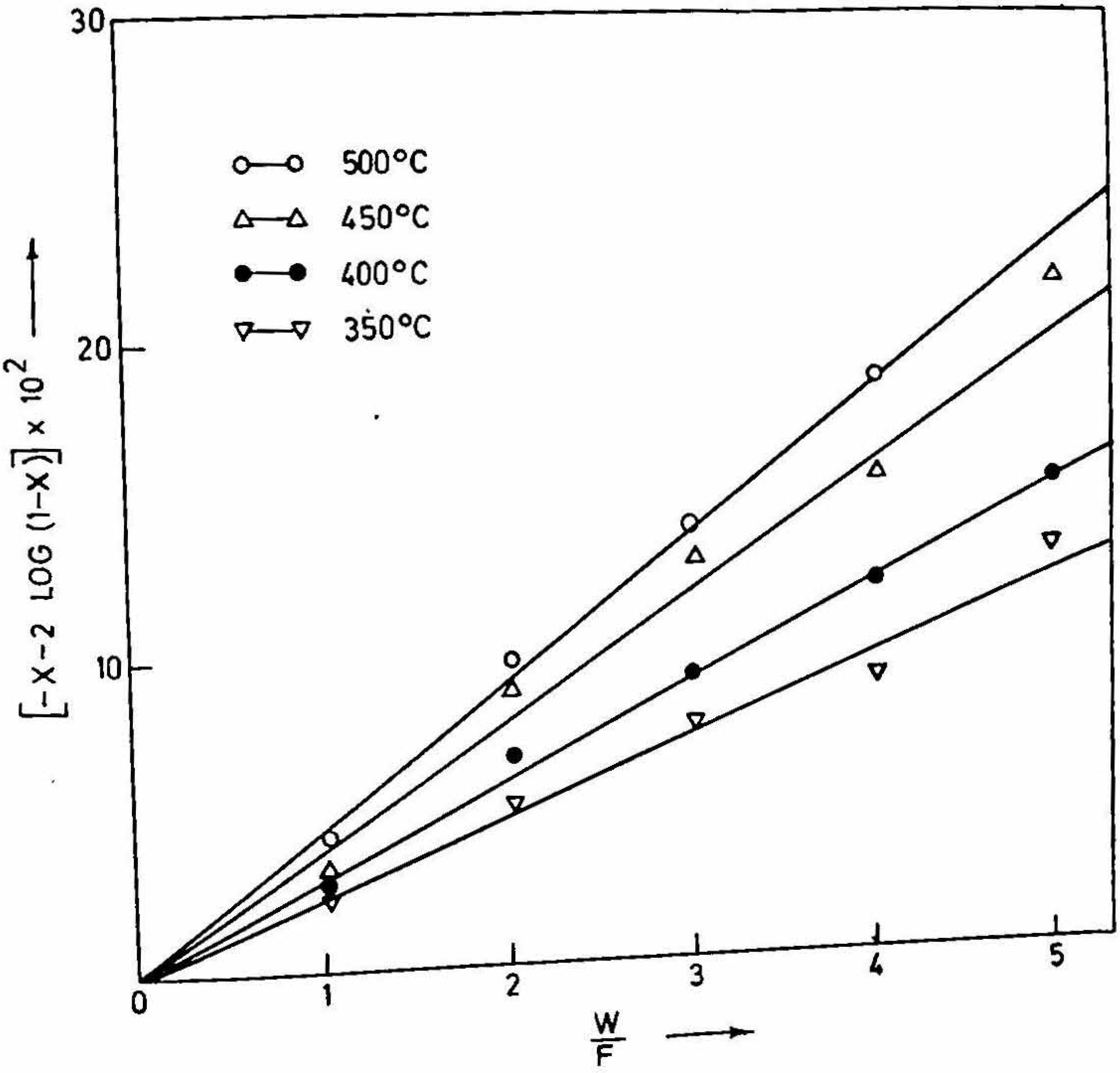

FIG. 2. Test for the first order rate expression,

by linear regression analysis. Substituting the values of E and A, the rate equati can be given as:

$$1 \cdot 7 \times 10^2 e^{-6265/RT} (P_T/RT)(W/F) = [-x - 2ln(1 - x)].$$

The validity of the above expression was checked by substituting the pertinent valı of x, T and other constants and evaluating the values of W/F. The good agreem between the experimental and calculated values of W/F plotted in Fig. 3 shows tl the kinetics of cumene cracking could be adequately expressed by the first order r expression given in equation (4).

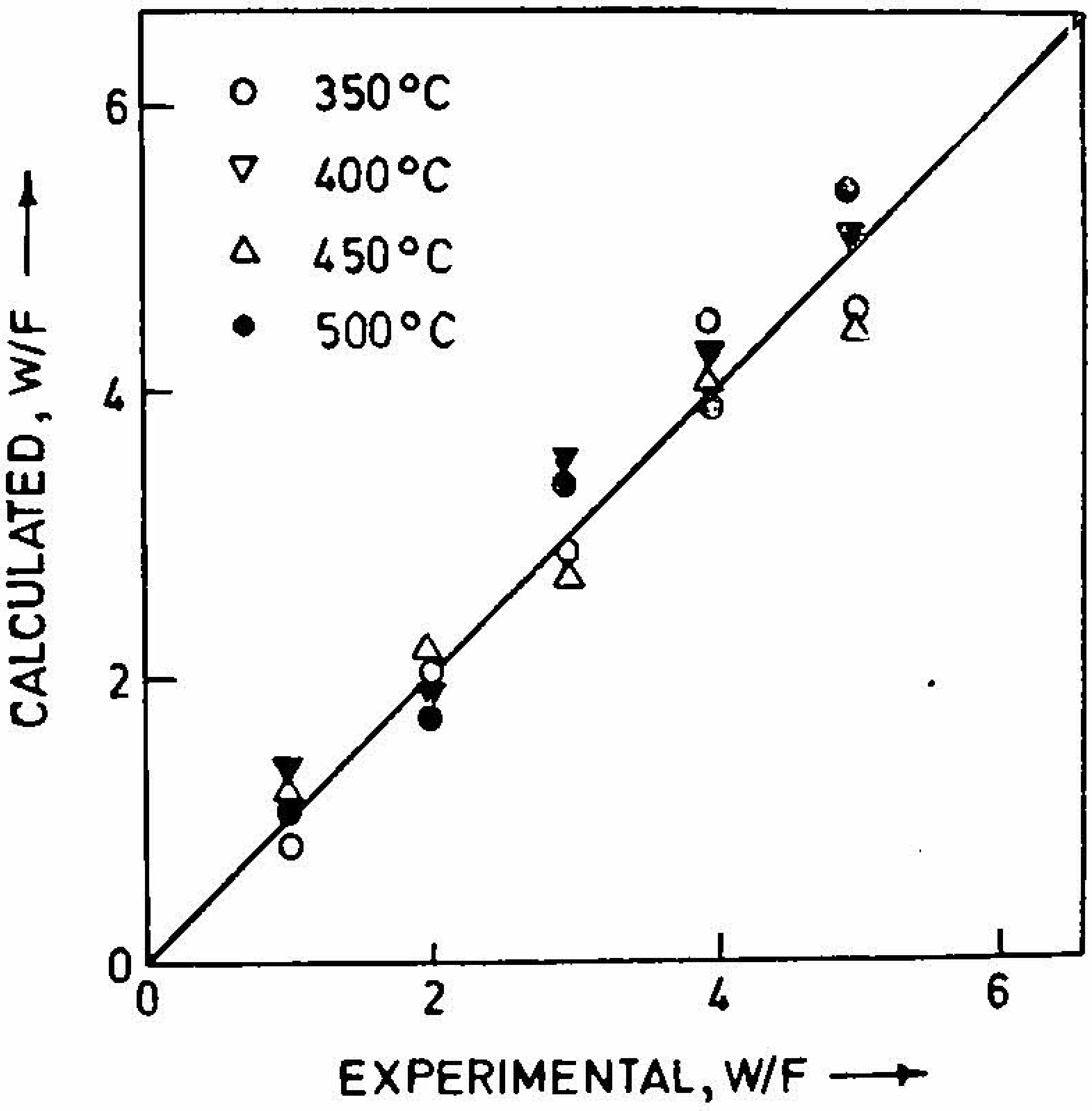

FIG. 3. Experimental *vs.* calculated W/F.

2.4. *Rate controlling mechanism*

As stated earlier in this paper while collecting kinetic data it was ensured that physic steps, *viz.*, bulk and pore diffusional effects were not controlling the overall reactio An attempt was made to determine the most probable rate controlling mechanism b applying the mechanism equations reported by Yang and Hougen[18]. For a pure fee values of P_R and P_S in these equations are the same but have different coefficient However, to determine these coefficients separately, one should use feed containin one of the products. In the present study, product benzene was added to cumene an runs were conducted under the same range of variables as with the pure feed. Th conversion *vs.* W/F data plotted in Fig. 4 are fitted to a second degree polynomial a

$$x = a(W/F) + b(W/F)^2.$$

Table II

Reaction velocity constants

Temp. °C	k lit/gm. cat. hr.
350	1·245
400	1·664
450	2·348
500	3·292

Constants a and b were evaluated by the method of least squares. The correlation coefficient for the least square fit was 0·99 thereby proving that the polynomial fit to the data was very good. Knowing the values of these constants the instantaneous rate at any W/F could be evaluated as:

$$\frac{dx}{d(W/F)} = a + 2b\,(W/F).$$

The partial pressures at any conversion level can be computed as:

$$P_A = \frac{(1-z)(1-x)}{(1-z)(1+x)+z}\,P_T$$

$$P_R = \frac{(1-z)(x+z)}{(1-z)(1+x)+z}\,P_T$$

$$P_S = \frac{(1-z)\,x}{(1-z)(1+x)+z}\,P_T$$

where z is the mole fraction of benzene in the feed. Knowing r, P_A, P_R, P_S the coefficients in the mechanism equations were evaluated by the method of least squares. The criteria for any one of the mechanism equations to be controlling can be given as:

(1) all the coefficients in the equation must be positive.

(2) the constants should be temperature dependent, and

(3) if more than one mechanism is rate controlling, then, whichever gives better agreement between the experimental and calculated reaction rates is to be selected as the correct mechanism.

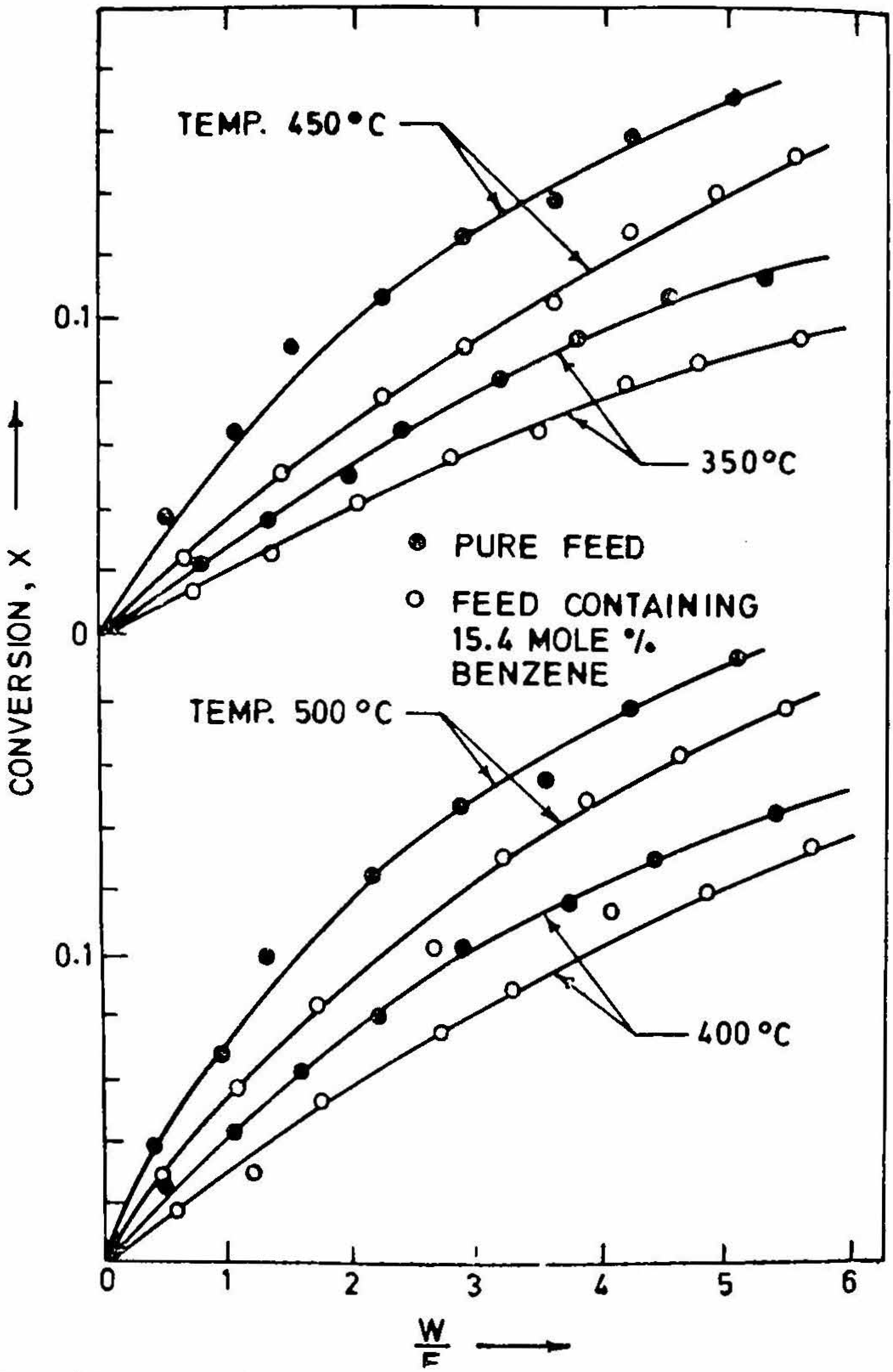

FIG. 4. Effect of benzene addition to feed on conversion.

Positive constants at all the temperatures were observed with two mechanisms, *viz.*, (1) adsorption of cumene controlling, single site, benzene adsorbed; and (2) adsorption of cumene controlling, single site, propylene adsorbed; showing that either of these may be rate controlling. The constants are given in Table III. The precise rate controlling step between the two was determined by the non-intrinsic parametric method of Watson *et al.*[13] according to which:

Table III

Coefficients in mechanism equations

		Temp. ° C			
		350	400	450	500
Mechanism 1					
Adsorption of cumene (single site)	a	45·84	36·11	32·21	29·22
Benzene adsorbed	b	0·3714	0·4889	0·5818	0·6702
Mechanism 2					
Adsorption of cumene (single site)	a	45·54	35·79	31·86	28·86
Propylene adsorbed	b	0·1517	0·1676	0·1754	0·1828

$$r - 0{\cdot}5\,(r_1 + r_2) = \lambda\,(r_2 - r_1)$$

where

λ is the non-intrinsic parameter.

($\lambda = -0{\cdot}5$ if mechanism (1) controlling,

$\lambda = +0{\cdot}5$ if mechanism (2) controlling),

r is the observed reaction rate and r_1 and r_2 are the rates given by mechanisms 1 and 2 respectively.

From the above equation, value of λ was determined by the method of least squares. It was found that λ was approximately equal to $-0{\cdot}5$. Thus single site adsorption of cumene-benzene adsorbed (Mechanism 1) seems to be the most probable rate controlling step. Knowing the constants a and b, the reaction rate and adsorption equilibrium constants were evaluated and were plotted in Fig. 5 for the effect of temperature. From the above plot values of E and A were evaluated. Substituting these values in the mechanism equation, the final rate equation for cumene cracking can be given as:

$$r = \frac{k\,(P_A - P_R\,P_S\,/K)}{(1 + K_S\,P_S)}$$

$$= \frac{[4{\cdot}488 \times 10^4\,e^{-2303/RT}\,(P_A - P_R\,P_S/K)]}{[1 + 8{\cdot}487 \times 10^4\,e^{2096/RT}\,P_S]}$$

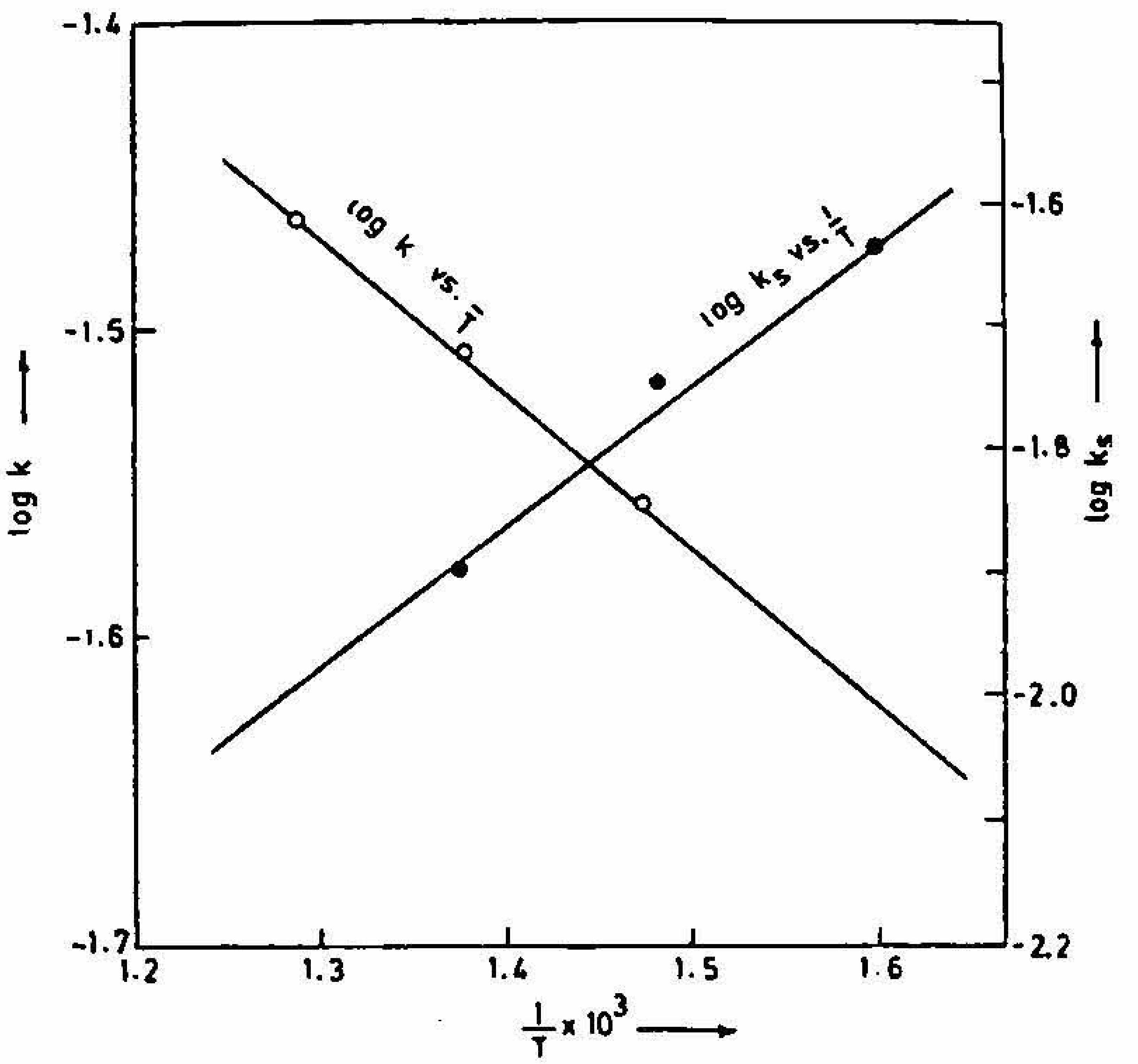

FIG. 5. Arrhenius plots for reaction rate and adsorption equilibrium constants.

Nomenclature

$a, b, c, d \ldots$	Constants in the polynomial and mechanism equations
C_A	Concentration of cumene, g moles/litre
F	Flow rate of cumene g moles/hr.
k	Reaction velocity constant, litres/gm. cat. hr.
K	Equilibrium constant
k_A, k_B, k_S	Adsorption equilibrium constants for cumene, benzene and propylene, respectively
P_A, P_B, P_S	Partial pressures of cumene, benzene and propylene respectively, atm,
P_T	Total pressure, atm.
R	Universal gas constant
r, r_1, r_2	Reaction rate, gm. moles/g. cat. hr.
T	Absolute temperature
W	Weight of catalyst. gm.
x	conversion, $\frac{\text{gm. moles of product formed}}{\text{gm. moles of feed}}$
λ	Non-intrinsic parameter.

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