

# DETERMINATION OF THE KINETIC PARAMETERS AND MODELING OF THE REACTOR FOR HYDROGENATION OF M-NITROTOLUENE IN A MULTI PHASE SLURRY REACTOR

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## Abstract

Hydrogenation of m-nitrotoluene to m-toluidine has been investigated in a three phase slurry reactor, using Raney Nickel as the reaction catalyst. Effects of agitator speed, catalyst loading and temperature on the reaction rate in the methanol medium have been investigated. The kinetics of the reaction studied at atmospheric pressure in the absence of both internal and external mass transfer resistances. The overall rate of reaction has been studied by applying the Eley-Rideal mechanism. The latter has been shown to be of pseudo first order with the respect to nitro toluene concentration. The apparent activation energy for the reaction has been determined as 35 kJ/gmol. Finally, a comparison has been made between the experimental results and those predicted from the reaction model.

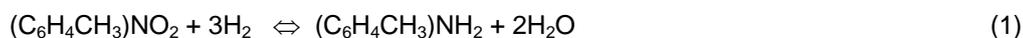
*Key Words:* m-Nitrotoluene, Toluidine, Three phase reactor, Multi phase reactions, Slurry reactors

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## 1. Introduction

Hydrogenation of m-nitrotoluene is one of the most methods to production of toluidine. This product is one of the high consumable intermediate materials to provide pigments. This conversion would be performed in slurry reactor at low temperature and pressure using appropriate catalyst. The performance of these reactors depends on a number of factors such as gas-liquid and liquid-solid mass transfer, intra particle diffusion, surface reaction kinetics, temperature, pressure and the mixing characteristic of the reactor<sup>[1]-[15]</sup>.

Toluidine can be obtained from nitrotoluene according to the following reaction:



In the present investigation, the effect of temperature, catalyst loading and agitator speed have been studied in a semi-batch reactor. Also the reaction rate model, kinetic parameters and activation energy have been determined.

## 2. Experimental

### 2.1. Material

The chemicals used in the present study were all analytical grades and supplied by Merck. These were m-nitrotoluene [(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)NO<sub>2</sub>] and methanol [CH<sub>3</sub>OH]. The purity of the used gases was 99.999 percent.

## 2.2. Catalyst

Consumed catalyst was Raney nickel by below specifications: catalyst specific surface:  $114.63 \text{ m}^2/\text{g}$ , average of catalyst particle diameter:  $10.3 \text{ micron}$ , catalyst particle density:  $4.051 \text{ g/cm}^3$

## 2.3. Experimental Procedure

Hydrogenation experiments were studied under steady state conditions in a magnetically-stirred, semi batch glass reactor (with  $180 \text{ cm}^3$  capacity) using methanol as the reaction medium. The catalyst was loaded in a reactor equipped with a manual temperature controller, variable stirrer speeds and a liquid sampling valve. The catalysts were reduced in a flowing hydrogen gas diluted with nitrogen. Experiments were performed in temperatures ranging from  $20\text{-}40 \text{ }^\circ\text{C}$  and atmospheric pressure. A schematic diagram of the experimental set-up is shown in Figure 1.

Pure hydrogen entered the top section of the reactor and distributed in reactor through sparger at the bottom of the reactor.

Reaction progress would be determined by measuring of m-nitrotoluene concentration during various time to do it. Thus, some liquid samples were withdrawn from reactor for analysis of liquid components by UV spectrophotometer, Camspec model M350<sup>[16]</sup>. The samples were analyzed several times during each experimental run.

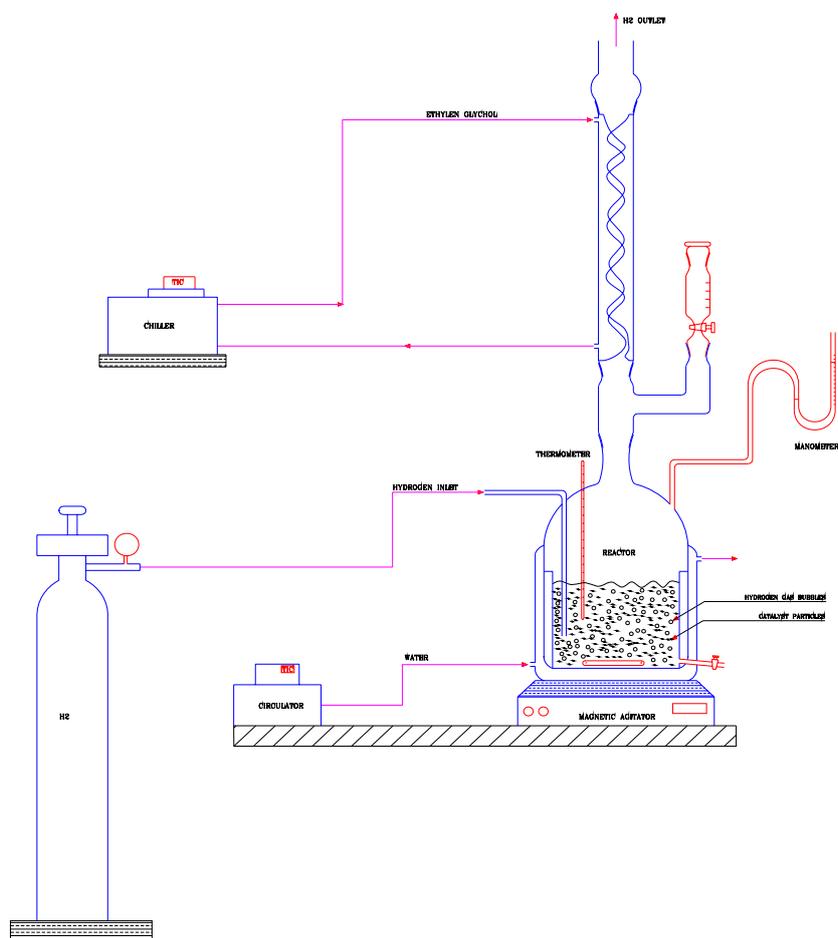


Figure 1: Schematic diagram of the reactor setup

### 3. Results and Discussion

#### 3.1. Kinetic Study

The reaction has been carried out within the temperature range of 20-40°C, atmospheric pressure. The results are presented in Figure (2).

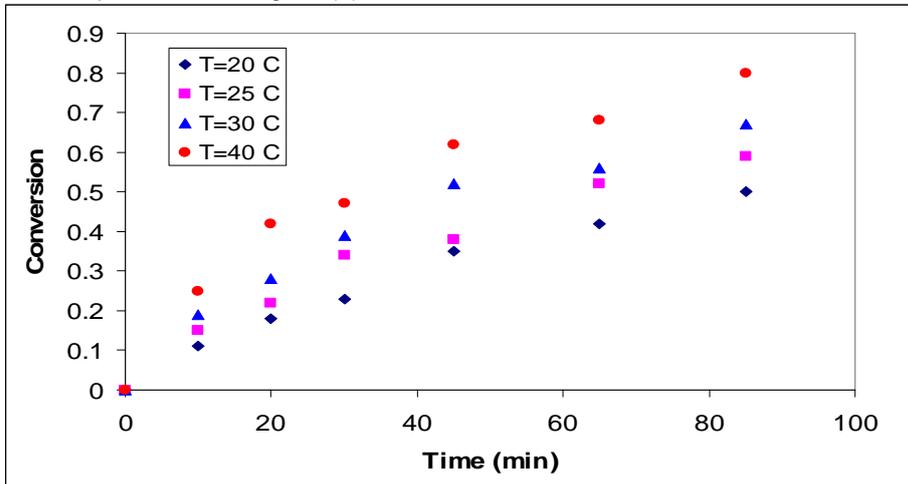


Figure 2. Conversion of m-nitrotoluene as a function of time (at different temperatures)

For determination of above reaction rate model, various mechanisms have been studied. Finally Eley-Rideal mechanism has been known as the best mechanism based on reaction data<sup>[17]</sup>. By considering the reaction of gas phase reactant A (hydrogen), the liquid reactant M (m-nitrotoluene) and product T (toluidine), stoichiometry equation of hydrogenation can be described as:



(s denotes active site of catalyst)

The equation rate for each above reaction can be written as follows, respectively:

$$-r_1 = k_1 C_M (1 - \theta_1 - \theta_2) - k_{-1} \theta_1 \quad (5)$$

$$-r_2 = k_2 \theta_1 C_A \quad (6)$$

$$-r_3 = k_3 \theta_1 - k_{-3} C_T (1 - \theta_1 - \theta_2) \quad (7)$$

$\theta_1$  is occupied active site by m-nitrotoluene and  $\theta_2$  is occupied active site by toluidine. By assuming equilibrium condition for adsorption and desorption ( $r_1=0$  and  $r_3=0$ ) and solving above equation base on  $\theta_1$  and  $\theta_2$  the rate equation was found as follows:

$$-r = \frac{(k_1 k_2 k_3 C_A) C_M}{(k_1 k_3 + k_1 k_2 C_A) C_M + (k_{-1} + k_2 C_A) (k_3 + k_{-3} C_T)} \quad (8)$$

#### 3.2. Reactor model:

By considering all mass transfer effects, a batch slurry reactor can be described by the following equation [18-20]:

$$\frac{C_{A,g}}{R_A} = \frac{H}{a_B K_L} + \frac{H}{m} \left[ \frac{1}{a_C K_c} + \frac{C_A}{\eta (-r)} \right] \text{ or} \quad (9)$$

$$\frac{C_{A,g}}{R_A} = r_b + \frac{H}{m} [r_c + r_r] \quad (10)$$

Now, by experimental data, the effect of each above resistance ( $r_b$ ,  $r_c$  and  $r_r$ ) on reaction rate and reactor model will be evaluated.

### 3.2.1. Effect of mass transfer resistances ( $r_b$ , $r_c$ and $r_r$ )

The size of sparger holes and agitator speed are effective on gas absorption in liquid. In experimental setup, the porous media sparger been used to produce very small gas bubbles. By this, mass transfer effective surface between gas and liquid would be increased and  $r_b$  would be decreased. The influence of agitator speed on the conversion of meta nitrotoluene is shown in figure (3). Above 850 rpm, the stirring speed has no effect on the reaction rate, which indicates that both gas-liquid and liquid-solid mass transfer resistances are eliminated (In other words  $r_b$  and  $r_c$  can be considered negligible).

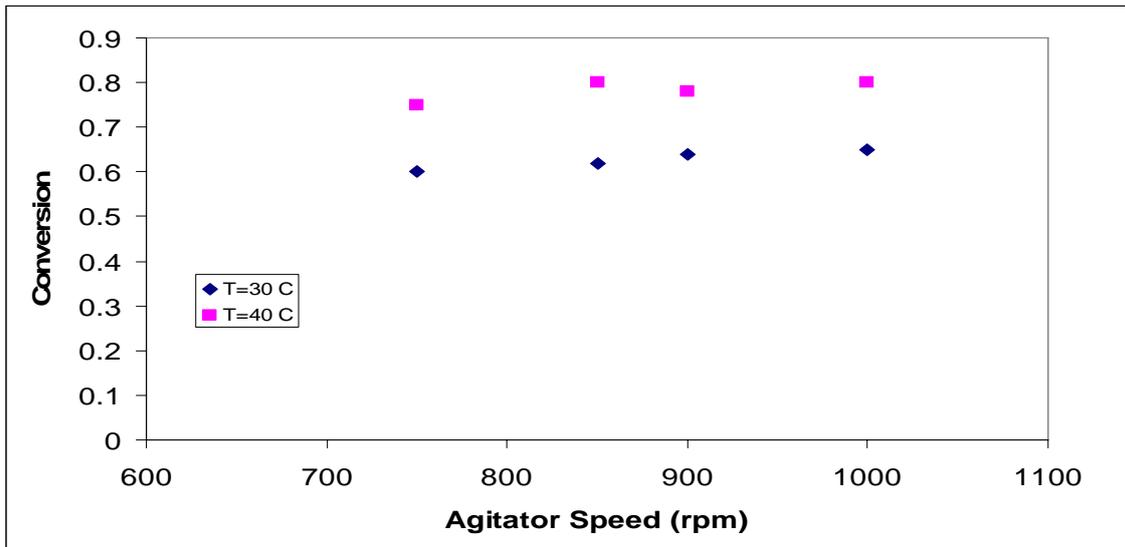


Figure 3. Conversion of m-nitrotoluene as a function of agitator speed (at different temperatures)

To compare  $r_b$  and total resistance of ( $r_c+r_r$ ), the curve of  $C_{A,g}/R_A$  would be drawn based on  $1/m$  (As equation (10)). This curve is shown in Figure (4).

Base on Figure (4):

$$r_b = 0.00222 \text{ and } (r_c + r_r) = 0.018992$$

Therefore, gas absorption resistance effect percent is ( $m = 0.015 \text{ gr/cm}^3$ ):

$$\% \frac{r_b \cdot m}{r_c + r_r} = \frac{0.00222 * 0.015}{0.018992} * 100 = \%0.175$$

According to above value, gas absorption resistance against other resistance is very small and would be ignored. This fact confirms that the reaction is not controlled by the gas-liquid mass transfer. Thus the equation (10) can be simplified as follows:

$$\frac{C_{A,g}}{R_A} = \frac{H}{m} [r_r] \quad (11)$$

The consumed catalyst was as fine powders ( $dp = 10.3 \mu\text{m}$ ). Thus, it can be assumed that, the reaction is not controlled by the liquid-solid mass transfer or by the intra particle mass transfer [6]. In other word,  $\eta$  will be assumed equal to one.

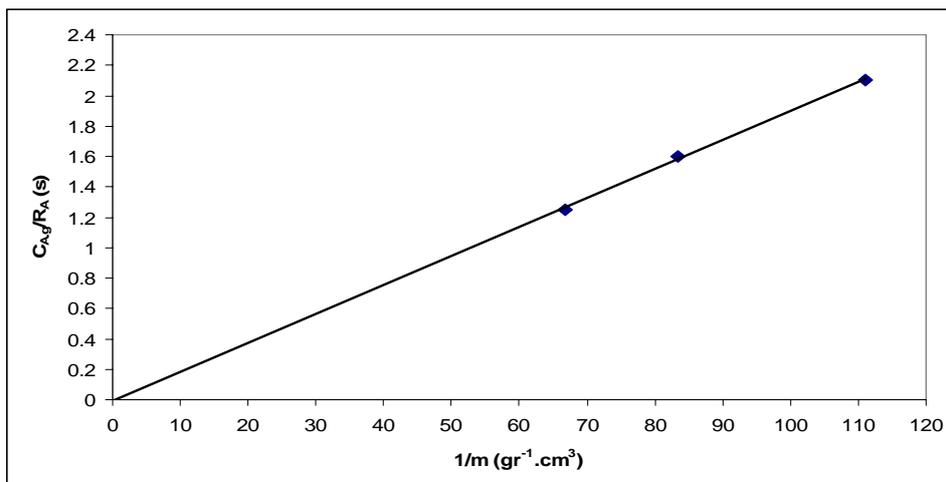


Figure 4. Conversion of m-nitrotoluene as a function of catalyst loading

The equation (11) can be written base on concentration of liquid phase reactant (meta nitrotoluene) as follows:

$$\frac{C_{M,b}}{R_M} = \frac{1}{m} \left[ \frac{C_{M,b}}{(-r)} \right] \quad (12)$$

By considering following assumption:

- (1) High amount of hydrogen has been feed to reactor and gas absorption resistance is very small comparing to other resistances, by this, it is assumed that liquid phase is saturated by hydrogen. In other word, the concentration of hydrogen in liquid phase ( $C_A$ ) will be considered constant.
- (2) Base on relation 4, it will be assumed that product desorption speed is greater than absorption of it. In other word,  $k_3 \gg k_{-3}$  and product concentration at catalyst surface is very low.

Equation (8) can be written:

$$(-r) = \frac{K_1 C_{M,b}}{1 + K_2 C_{M,b}} \quad (13)$$

where:

$$K_1 = \frac{k_1 k_2 k_3 C_A}{(k_1 + k_2 C_A) k_3} \quad K_2 = \frac{k_1 k_3 + k_1 k_2 C_A}{(k_1 + k_2 C_A) k_3}$$

by replacing equation (13) in equation (12):

$$R_M = \frac{m K_1 C_{M,b}}{1 + K_2 C_{M,b}} \quad (14)$$

or

$$\frac{1}{R_M} = \frac{1}{m K_1} * \frac{1}{C_{M,b}} + \frac{K_2}{m K_1} \quad (15)$$

Estimation of values for the kinetic parameters involved minimization of error. Using the linear regression analysis and applying the results presented in Figure (2) to the relations (15), the kinetic parameters have been calculated. The data are given in Table (1).

Table 1. Kinetic parameters

T(°C)	20	25	30	40
m.K <sub>1</sub> (1/min)	0.008594	0.010926	0.014043	0.021453
K <sub>2</sub> (mol/cm <sup>3</sup> ) <sup>-1</sup>	0.096	0.1522	0.2024	0.2156

It is clear that by replacing amounts of  $K_1$ ,  $K_2$  in equation (14), amount of  $K_2.C_{M,b}$  ( $(C_{M,B})_{max} = 0.000528 = \text{mol/cm}^3$ ) is very low ( $\ll 1$ ) and would be ignored.

Therefore, equation (14) would be summarized as below:

$$R_M = m.K_1.C_{M,b} \quad (16)$$

In other word, hydrogenation reaction of m-nitrotoluene in presence of catalyst (Rany nickel) would be apparent first order reaction based on concentration m-nitrotoluene in slurry reactor.

### 3.2.2. Kinetic parameters

The kinetic constant ( $K_1$ ) is considered base on Arrhenius relation, as follow:

$$K_1 = K_{01} \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (17)$$

The parameter of this relation (Apparent activity energy ( $E_a$ ) and pre-exponent frequency factor ( $K_{01}$ )) will be calculated using the linear regression analysis and applying the results presented in table 1 and figure 5 to the equation (17).

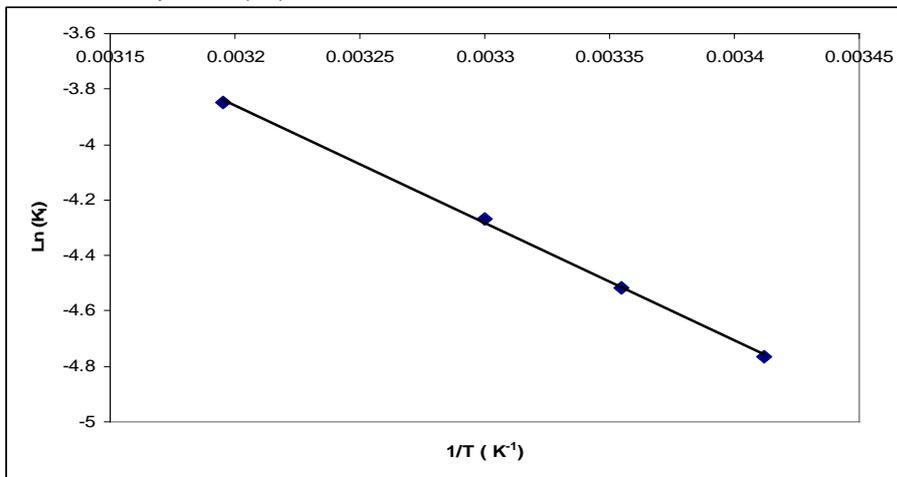


Figure 5. Kinetic parameter as a function of temperature

Calculation results are as below:

$$\frac{E_a}{R} = 4213.9(^{\circ}k) \Rightarrow E_a = 35000(j/mol)$$

$$\ln(K_{01}) = 9.62087 \Rightarrow K_{01} = 15076.16(1/min)$$

The variation of liquid reactant concentration in a batch slurry reactor can be described by the following equation:

$$\frac{-1}{V_b} \frac{dN_M}{dt} = R_M \quad (18)$$

With the initial condition that, at:

$$t = 0, C_M = C_{M0}$$

and

$$C_M = C_{M0} (1 - X_M) \quad (19)$$

It is assumed, that the system is isothermal and pressure changes due to solubility variation is negligible. By combining equations (16), (18) and (19), the following equation is obtained:

$$t = \frac{-1}{m.K_1} \ln(1 - X_M) + \frac{K_2}{m.K_1} C_{M0} \cdot X_M \quad (20)$$

### 3.3. Applications of model

#### 3.3.1. Variation of m-Nitrotoluene conversion in the reactor

In Figure 6, the experimental data for m-nitrotoluene conversion in the reactor and those predicted from the model are presented. Apart from the initial period, the correlation between the two sets of data is

satisfactory in all experimental runs. The discrepancies observed in initial period may be either due to the use of steady state experimental results in prediction of system behavior under un-steady state conditions, or to the experimental errors involved in the determination of transient m-nitrotoluene concentrations in the reactor.

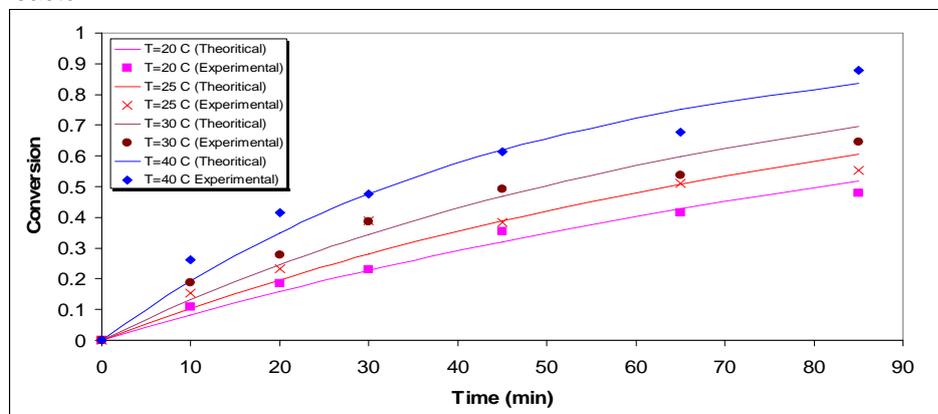


Figure 6. Conversion of m-nitrotoluene as a function of time in the reactor ( $m=0.012 \text{ g/cm}^3$ )

### 3.3.2. Variation of m-nitrotoluene conversion within the reactor at different catalyst loading

Predicted data for the m-nitrotoluene at different catalyst loading against time is plotted in Figure (7).

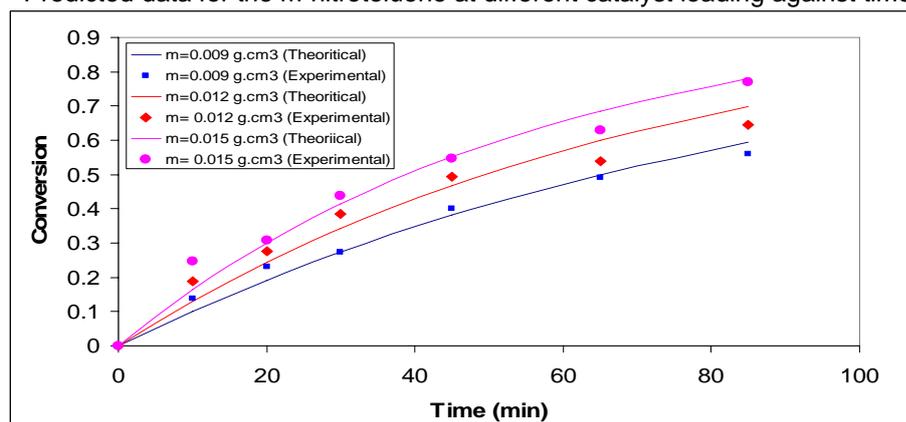


Figure 7. Conversion of m-nitrotoluene as a function of time at different catalyst loading ( $T=30 \text{ }^\circ\text{C}$ )

## 4. Conclusion

In the present study, the kinetic parameters and reactor model of toluidine from m-nitrotoluene have been studied and the following observations were made:

Gas phase is perfect mixed stream due to the phase's stream in reactor, sparger shape and its position in reactor and mixing of reactor content.

Above 850 rpm, the stirring speed has no effect on the reaction rate, which indicates that both gas-liquid and liquid-solid mass transfer resistances are eliminated.

The consumed catalyst was as fine powders. Thus, it is assumed that, the reaction is not controlled by the liquid-solid mass transfer or by the intra particle mass transfer.

Hydrogenation reaction of m-nitrotoluene in presence of catalyst (Rany nickel) would be apparent first order reaction based on concentration m-nitrotoluene in slurry reactor.

A kinetic expression for m-nitrotoluene transformation to m-toluidine has been derived and correlated with the experimental results over a range of temperatures. In order to predict the behavior for the process of conversion of m-nitrotoluene to m-toluidine in a batch slurry catalytic reactor, a simple dynamic model has been put forward. The data predicted from the model were correlated with those determined

experimentally. The degree of agreement between the two sets of data, for the steady state conditions, was 85-95% and the mean absolute error for dynamic conditions was 11%. This model may be thus, applied to predict the optimum operating temperature and loading of catalyst required for such a process.

#### Symbols

$a_B$	Gas-liquid interfacial area per unit volume of reactor ( $m^2.m^{-3}$ )	$k_C$	Liquid-solid mass transfer coefficient ( $cm.s^{-1}$ )
$a_C$	External surface area of catalyst particle per unit mass of catalyst ( $m^2.kg^{-1}$ )	$k_L$	Gas-liquid mass transfer coefficient ( $cm.s^{-1}$ )
$C_{A,g}$	Concentration of hydrogen in gas phase ( $mol.cm^{-3}$ )	$m$	Catalyst loading per unit volume of reactor ( $g.cm^{-3}$ )
$C_{A,b}$	Concentration of hydrogen in liquid phase ( $mol.cm^{-3}$ )	$R_A$	Overall reaction rate for hydrogen ( $mol.cm^{-3}.s^{-1}$ )
$C_A$	Concentration of hydrogen at catalyst surface ( $mol.cm^{-3}$ )	$R_M$	Overall reaction rate for m-nitrotoluene ( $mol.cm^{-3}.s^{-1}$ )
$C_{M0}$	Initial concentration of m-nitrotoluene ( $mol.cm^{-3}$ )	$r_b$	Gas absorption resistance
$C_{M,b}$	Concentration of m-nitrotoluene in liquid phase ( $mol.cm^{-3}$ )	$r_c$	External diffusion resistance
$C_M$	Concentration of m-nitrotoluene at catalyst surface ( $mol.cm^{-3}$ )	$r$	reaction rate ( $mol.cm^{-3}.s^{-1}$ )
$C_T$	Concentration of toluidine at catalyst surface ( $mol.cm^{-3}$ )	$t$	Time (s)
$dp$	Catalyst particle size (cm)	$s$	Active site on catalyst surface
$E_a$	Apparent activation energy ( $J.mol^{-1}$ )	$V$	Reactor volume ( $cm^3$ )
$H$	Henry constant	$X_A$	Conversion of hydrogen
$k_i$	Kinetic parameters	$X_M$	Conversion of m-nitrotoluene

#### Greek letters

$\theta_1$	Percent of catalyst surface that is occupied by m-nitrotoluene	$\rho_p$	Catalyst density ( $g.cm^{-3}$ )
$\theta_2$	Percent of catalyst surface that is occupied by toluidine	$\eta$	Effectiveness factor

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