Iranian Journal of Science & Technology, Transaction B, Engineering, Vol. 30, No. B5
Printed in The Islamic Republic of Iran, 2006

KINETIC INVESTIGATION OF NDMA TO UDMH HYDROGENATION ON A pd/C CATALYST[*]

M. GORJI, M. KAZEMEINI[**] AND R. BOZORGMEHRI

Dept. of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, I.R. of Iran
Email: kazemini@sharif.edu

Abstract– Unsymmetrical dimethyl hydrazine (UDMH) is a strong propellant, which due to its very good physical properties and high power of repellency has been utilized as a liquid fuel for fighter jet engines for so many years. There are different methods for production of this material. One of the more efficient ones which results in higher yields compared to others is the catalytic hydrogenation of Nitroso Dimethylamine (NDMA). In this work hydrogenation of NDMA to UDMH on a 5% Pd/C in aqueous solution of NDMA was studied experimentally. Experiments were carried out in a Semi-batch three phase STR reactor under constant pressure and temperature in the range of 40 to 70°C, pressures of up to 15 bar and an NDMA concentration of 40 to 70 wt%. Products were analyzed using the Gas Chromatographic (GC) technique. Effects of temperature, pressure and NDMA concentration on NDMA conversion and yield of UDMH product in the presence of undesired dimethylamine (DMA) were studied and the optimum conditions for the selective production of UDMH were sought. A kinetic model based on the general form of the Langmuir-Hinshelwood(LH) equation was developed. Further, it was assumed that the hydrogen adsorption is dissociative and non competitive. Comparison with experimental data showed that the Eley-Rideal(ER) model has very good predictive capabilities relative to LH rate equation and therefore, it was selected for further study. Based on this relation the reaction parameters for UDMH and DMA rate equations were estimated through the non linear regression method and activation energies of UDMH and DMA reactions were determined to be 15.97 and 64.98 KJ/mol, respectively.

Keywords– Catalytic hydrogenation, UDMH, NDMA

1. INTRODUCTION

Unsymmetrical dimethyl hydrazine or the UDMH (i.e.; $(CH_3)_2NNH_2$), apart from its use as a versatile rocket fuel, finds numerous industrial applications such as enhancer of organic material synthesis, stabilizer, fuel promoter, chemicals in photography, antiskining agent in the paint industry, and inhibitors of quick growth of plants to name a few. It is also used in the preparation of polymeric derivatives of hydrazine and preparation of calcium based catalysts. This type of catalyst is useful in the polymerization of ethylene oxide. In the aerospace industry, even with the obvious advantages of hydrazine as a fuel compared to regular petroleum byproducts, and difficulties in its transportation and maintenance, for example, solidification near the zero degree centigrade or non-homogeneity with other hydrocarbon fuels, it is a rather hard material to work with. In order to overcome these problems, a great deal of attention has been paid to replacing this compound with some other hydrazine by products. For example, the Mono-Methyl Hydrazine (MMH) or UDMH are compounds with the desired repellency as jet fuel without the undesired hydrazine properties. Perhaps the highest production of hydrazine byproducts in the world belongs to the UDMH. The reason for this is the utilization of this material as a military jet fuel in many

---

[*] Received by the editors October 24, 2005; final revised form January 8, 2006.
[**] Corresponding author

countries around the world [1]. The molecular weight of the UDMH is 60.10, its melting point is-58 ^{0}C, its boiling point is 63.9 ^{0}C and its density is 791 kg/m^3. It starts fuming when placed next to ammonia and turns yellow gradually. It also may be homogeneously combined with alcohols, ethers, dimethyl formaldehyde and hydrocarbons. It may easily catch fire and has a burning point of -15 ^{0}C and a combustion degree of 249 ^{0}C. Furthermore, the burning capability is within the limits of 2-95%.

There are different production techniques for the UDMH [1, 2]

1) Reduction of the NDMA(i.e. $(CH_3)_2NNO$)
2) Rasching process
3) Hofmann rearrangement of the Unsymmetrical dimethyl urea
4) Reaction of Tri-Methyl anilinium halide with the hydrazine
5) The sodamide
6) Alkylation of reduced acetahydrazide
7) Alkylation of hydrazine.

Furthermore, several reduction methods may be used for this purpose including; chemical, catalytic, electrolytic, metal and alcohol reduction, as well as with metal hydrides [1, 2]. One of the most efficient methods is the catalytic hydrogenation of NDMA which has been utilized and many experiments have been carried out in this area [3-12]. Metals of group VIII such as platinum, palladium, rhodium, nickel and cobalt have been used as catalysts for direct hydrogenation of NDMA to UDMH. The hydrogenation reaction is susceptible to trace impurities of catalyst poisons, therefore, highly purified reactants are necessary for satisfactory yields of UDMH. Levering and Mavry used super atmospheric pressure and catalysis by Pd, Pt, Rh, Ni, and Co on the carbon, alumina, silica and titan in an organic solvent and observed that the best catalyst is Pd/C [13]. Klager, et al’s research showed that hydrogenation of nitrosamines by 10%Pt/C or Pd/C, and to some extent 5%Rh/C in the presence of salts such as ammonium acetate and lanthanum chloride, increases hydrazine production while reducing amine production [6]:

$$2R_2NNO + 3H_2 \rightarrow 2H_2 + N_2 + 2R_2NH$$

Smith and Thatcher's experiments showed that the presence of a salt in the reaction medium inhibits hydrogenation of nitrosamine to amine in the following manner [7]:

$$(CH_3)_2NNO + 3H_2 \rightarrow (CH_3)_2NH + NH_3 + H_2O$$

Which were most observed with Pd/C and Pt/C catalysts.

Gaskins and Bugalos used a gas phase hydrogenation in a fixed bed catalytic reactor with 80 to 87% reaction efficiency [8]. The main product was UDMH, i.e.;

$$(CH_3)_2NNO + 2H_2 \rightarrow (CH_3)_2NNH_2 + H_2O$$

And the undesired products were DMA (Dimethylamine), NH_3 and N_2 through the following scheme:

$$(CH_3)_2NNO + 3H_2 \rightarrow (CH_3)_2NH + NH_3 + H_2O$$
$$2(CH_3)_2NNO + 3H_2 \rightarrow 2(CH_3)_2NH + N_2 + 2H_2O$$

The DMA product not only leads to a low efficiency reaction, but also causes poisoning of the Pd catalyst. They observed that increasing the salt compound of Ferro may, to some extent, prevent undesired reactions. Tindall's experiments showed [9] that impurities in the NDMA solution lead to the poisoning of the catalyst [9]. Feldman *et al*. [12] used dearated water and Pd/C catalyst and noticed that the poisoning of the catalyst with oxygen decreases its selectivity due to undesired DMA and NH_3 production. Thatcher [12] determined that the most effective catalyst was the 5%Pd/C. Moreover, he noticed a higher extent of production of undesired products will occur due to more hydrogenation of UDMH. Generally 0.1 to about

1.0 gram of metal per mole of nitroso dimethylamine has been found to be sufficient when used as a 5% catalyst-charcoal mixture [9]. In this work hydrogenation of the aqueous solution of NDMA on a 5%Pd/C catalyst in a semi-batch CSTR reactor is carried out and the optimum temperature, pressure and NDMA concentration to obtain the best yield and conversion are determined.

2. EXPERIMENTAL

a) Material and methods

Hydrogenation of NDMA was performed in a STR reactor equipped with a magnetic stirrer. Figure 1 shows a schematic of the reactor system utilized for this purpose. The reactor material was Stainless Steel 316 with a volume of 0.6 lit. The pressure of the reactor was fixed at the desired pressure with a regulator on hydrogen stream. A jacket was provided for the heating and cooling of the reactor. Hydrogen and nitrogen gases with a purity of more than 99.9% were used. To prevent the exposure of hydrogen to oxygen, at the start of the reaction, oxygen was purged from the reactor with nitrogen. Experiments were carried out with a pure aqueous solution of 40-70 wt% NDMA and 5% Pd/C catalyst of Degussa(specific area 800 to 1000 m^2/gr). The reactor temperature and pressure of 40 to 70 °C and 7 to 15 bar respectively were implemented. In spite of the desirable effect of the pressure increase on NDMA conversion to UDMH, the authors were unable to use pressures higher than 15 bar because their reactor seal was unable to tolerate it. For each experiment, at first the NDMA solution with a specific concentration was charged to the reactor. The catalyst and Ferro sulfate were then added to the solution and the reactor containment was heated up to the desired temperature with warm water flowing into the reactor jacket and the stirrer was turned on. Next, the reactor was purged with nitrogen. After these stages, the hydrogen was introduced into the reactor till the desired pressure was reached. Then, the reaction was started and the reactor temperature was increased rapidly. For this reason, the warm water stream was closed and the cooling water was circulated in the jacket to decrease the reactor temperature to a set value. After the temperature reached the desired set point, the warm water was circulated in the jacket again. The end of the reaction is the time on which the hydrogen consumption is finished. Product samples were analyzed with an HP 6890-Agilent Gas Chromatograph (GC) using a polyethylene packed column of 1/8 inch ID and a length of 1 meter. Furthermore, a Thermal Conductivity Detector (TCD) with an injection temperature of 150°C, and a hydrogen carrier and column temperature of 60 to 90°C were utilized.

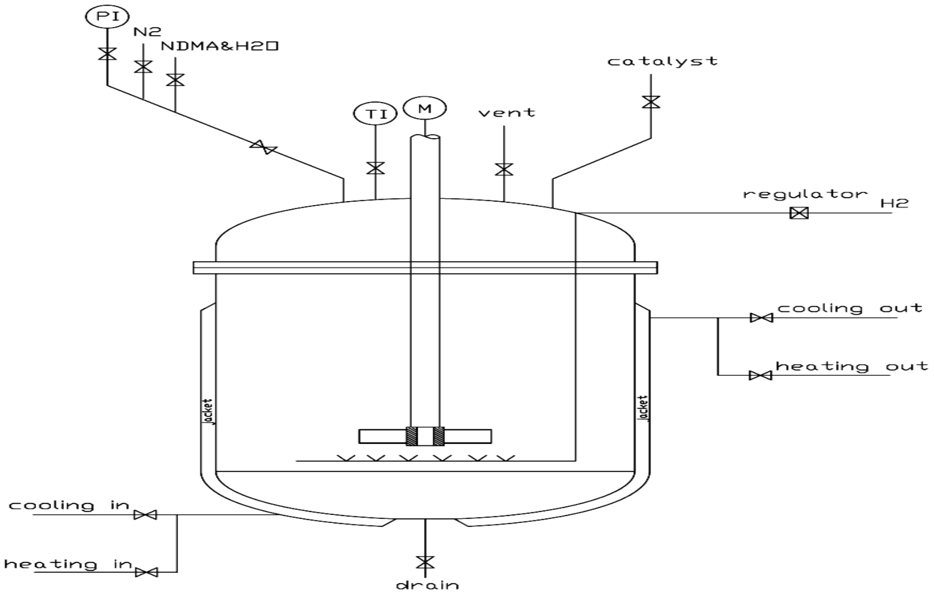


Fig. 1. Schematic of reactor system for production of UDMH from NDMA

3. QUALITITATIVE RESULTS

The above experimental set up was utilized to determine various kinetic data for the system at hand. According to Fig. 2, at a pressure of 7 bar after 8 hours of operation, NDMA conversion of about 7% is achieved. Figure 3 shows that by increasing pressure from 7 to 15 bar, a considerable increase in the NDMA conversion may be obtained. In other words, after 8 hrs the conversion of NDMA reaches to about 99.9%, while the UDMH produced rises to about 95%. A longer hydrogenation period of the NDMA solution (from 8 to 10 hrs) leads to decreasing UDMH product from 95 to 92 %. This effect may be explained by the fact that after the completion of the NDMA reaction, further hydrogenation leads to hydrogenation of N-N bound in UDMH, and in turn, causes the production of DMA, NH_3 and N_2. This finding is consistent with the conclusion of Thatcher, *et al*. [12]. In spite of the desirable effect of pressure on NDMA conversion, these authors were not able to use pressures higher than 15 bar due to constraints on sealing the reactor for such operating conditions. Therefore, other parameters such as reactor temperature and NDMA concentration at a pressure of 15 bar were changed instead. Moreover, in hydrogenation reactions, initially as the pressure of hydrogen rises, the rate of reaction is increased toward a maximum, and then reaches a plateau with further increase in hydrogen concentration. This may be due to the point that at low pressures, hydrogen and other components could be chemisorbed on the catalyst surface having some free active sites available. But as the hydrogen pressure builds up, the rate would increases until all surface sites are occupied by hydrogen and further increase in hydrogen pressure would only marginally affect the hydrogenation rate [14]. Figure 4 shows the effect of hydrogen pressure on the yield of acethyl hydrazine in catalytic reductive alkylation of this material on a 5% Pd/C catalyst [15]. This figure shows that pressures above 15 bar have no significant effect on the yield of the desired product. Comparison of Figs. 3 and 5 shows that by increasing NDMA concentration from 40 to 70%wt not only causes the reaction time to increase, but also leads to a decrease of NDMA conversion, and consequently, lowering the UDMH product. This observation may be explained by the low concentration of water needed in the reaction medium to extract the produced UDMH from the catalyst and prevent its contact with the solid. Therefore, produced UDMH on the catalyst will be converted to undesired DMA product. This result is consistent with the findings of Smith *et al*. [7]. Figure 6 shows that at a high concentration of NDMA, temperature increase leads to higher NDMA conversion while reducing the reaction time. Figure 7 shows four test experiments carried out for global comparison of variable effects on NDMA conversion and UDMH, DMA impurity production. From this comparison it is realized that test No.2, which has the higher pressure, lower temperature and NDMA concentration, achieves the highest NDMA conversion and UDMH production. At this test run the DMA concentration is the lowest as well. Figure 8 comprises the rate of production of UDMH and DMA impurity. According to this figure, by increasing the NDMA solution from 40 to 70 wt%, not only does the reaction time increase, but the rate of production of UDMH decreases. By increasing the solution temperature from 40 to 70°C in 70 wt% solution the rate of production of UDMH increases, but the rate of production of DMA impurity increases accordingly. Figure 9 shows the selectivity and yield of UDMH in comparison to undesired DMA impurity. Here, the selectivity of UDMH is defined as the ratio of UDMH to undesired DMA product and UDMH yield is set to be the ratio of UDMH produced to that of the stiochiometric UDMH value. According to Fig. 9a at 40°C and 40 wt%, NDMA solution yields of greater than 0.91 and selectivities of 10.9 to 17.3 are achieved. By increasing the NDMA concentration to 70 wt%, the yield of UDMH falls within the range of 0.6 to 0.74, while selectivity falls in the range of 1.48 to 3.2. By increasing the temperature from 40 to 70 °C at this 70 wt% concentration, the yield of UDMH falls in the range of 0.72 to 0.81 and the related selectivity is from 2.6 to 4.4. By comparison of Figs. 9a to 9c it is seen that by increasing the temperature, the rate of UDMH production increases, however, the rate of DMA impurity production is also enhanced. Furthermore, by increasing the concentration of NDMA the yield of UDMH is lowered. Figure 10 shows the yield of UDMH versus NDMA solution concentration. This figure shows that at an NDMA solution of more than 50 wt%, the yield of UDMH falls below 0.89 and the best NDMA concentration for the purpose at hand is between 40 to 50 wt%. Figure 11 describes the UDMH yield versus reaction temperature. This figure shows that at temperatures above 50°C the UDMH yield falls to 0.91. According to this figure, the best temperature range is 40 to 50°C and it should be maintained below 50 ° C to have a yield of more than 0.9. Moreover, since the boiling point of the UDMH is 63.9°C, it is better to keep the temperature below 60°C.

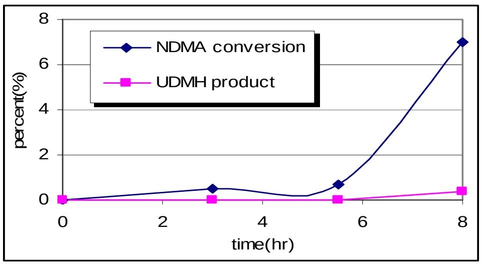


Fig. 2. Amount of the NDMA conversion and UDMH product (%) as a function of time (P=7 bar, T=40 °C, 40 wt% NDMA feed solution)

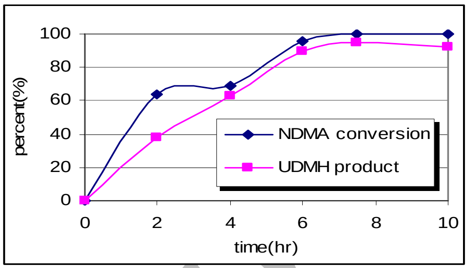


Fig. 3. Amount of the NDMA conversion and UDMH product (%) as a function of time(P=15 bar, T=40 °C, 40 wt% NDMA feed solution)

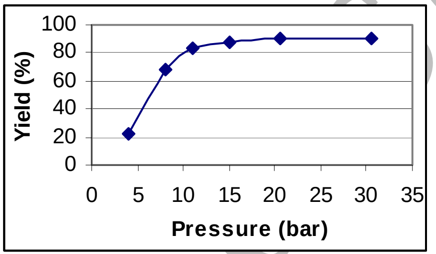


Fig. 4. Effect of hydrogen pressure on yield of catalytic reductive alkylation of acethyl hydrazine on 5% Pd/C catalyst [15]

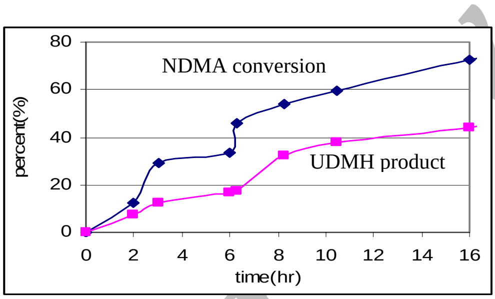


Fig. 5. Amount of the NDMA conversion UDMH product (%) as a function of time (P=15 bar, T=40 °C, 70 wt% NDMA feed solution)

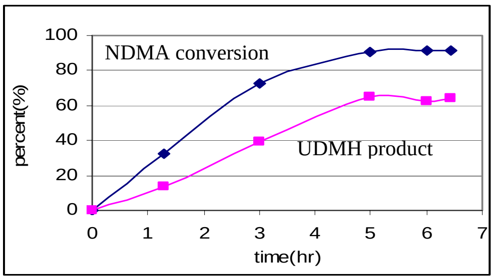
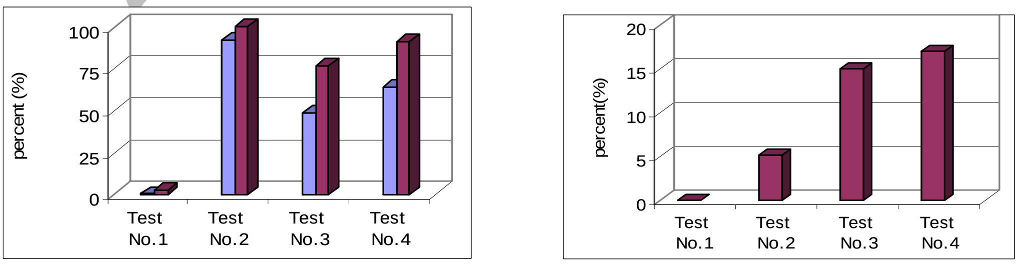


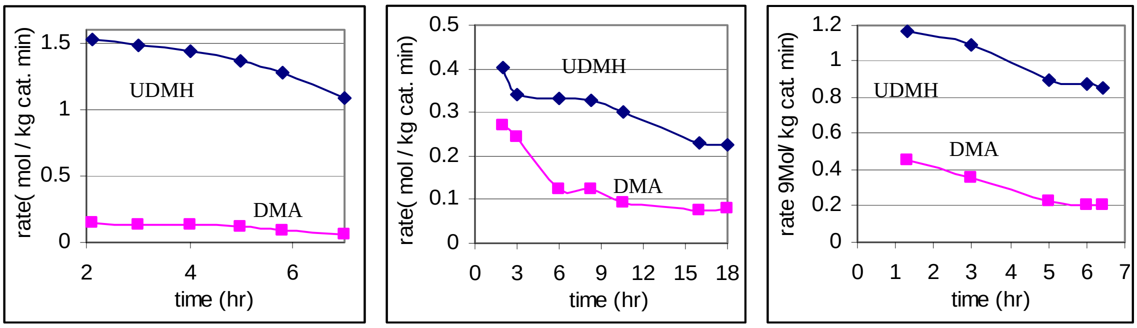
Fig. 6. Amount of the NDMA conversion and UDMH product (%) as a function of time (P=15 bar, T=70 °C, 70 wt% NDMA feed solution)



(a) (b)

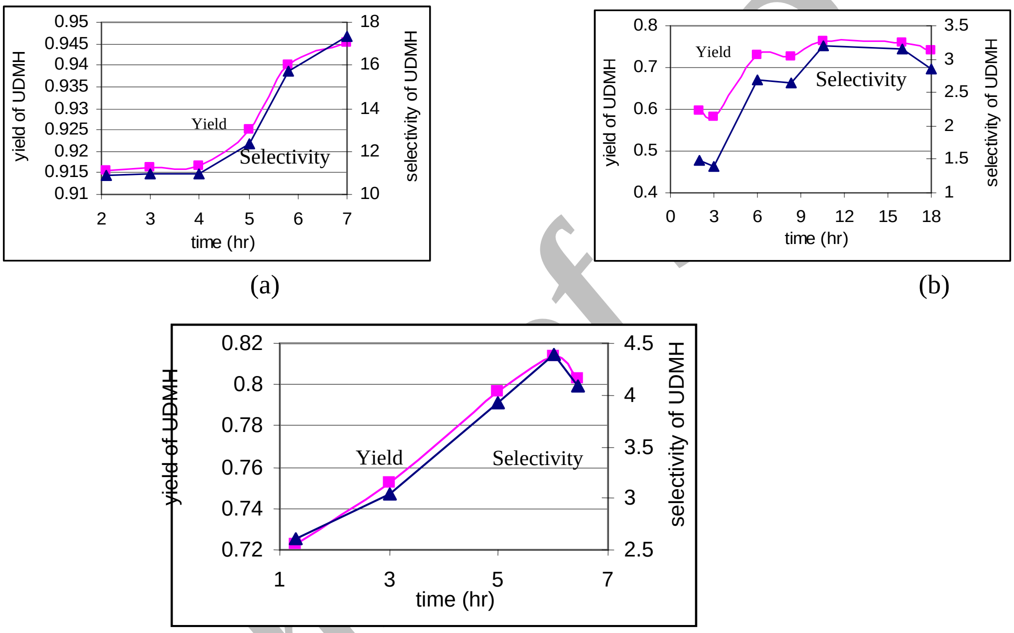
Fig. 7.a) Amount of the UDMH production and NDMA conversion (%) (Left to right) for test No.1 to 4, b) Amount of the DMA impurity production (%) (Left to right) for test No.1 to 4

Test No.1: T=40°C, P=7 bar, 40 wt% NDMA , Test No.2: T=40°C, P=15 bar, 40 wt% NDMA
Test No.3: T=40°C, P=15 bar, 70 wt% DMA , Test No.4: T=70°C, P=15 bar, 70 wt% NDMA



(a) (b) (c)

Fig. 8. Rate of production of UDMH and DMA versus time a) P=15 bar, T=40 °C, 40 wt% NDMA feed solution, b) P=15 bar, T=40 °C, 70 wt% NDMA feed solution, c) P=15 bar, T=70 °C, 70wt % NDMA feed solution



(a) (b)

(c)

Fig. 9. Yield and selectivity of UDMH product as a function of time, a) P=15 bar, T=40 °C, 40 wt% NDMA feed solution, b) P=15 bar, T=40 °C, 70 wt% NDMA feed solution, c) P=15 bar, T=70 °C, 70wt % NDMA feed solution

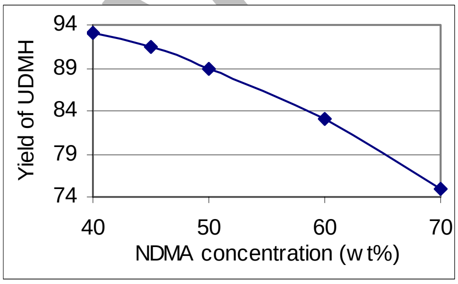


Fig. 10. Yield of UDMH vs. NDMA concentration (P=15bar, T=40°C)

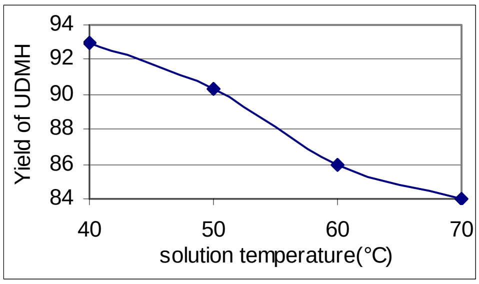


Fig. 11. Yield of UDMH vs. solution temperature (P=15 bar, 40 wt% NDMA feed solution)

4. MODEL FOR HYDROGENATION KINETICS

Hydrogenation reaction was described by a Langmuire-Hinshelwood(LH) type reaction mechanism. As hydrogen molecules are much smaller than the organic ones, some interstitial adsorption sites are available for hydrogen molecules. Therefore, the adsorption behavior can be regarded as noncompetitive [16]. Rapid reversible adsorption is assumed for hydrogen and other species and surface reaction is presumed to control the overall hydrogenation rate. A critical step in obtaining reliable quantitative kinetics is to ensure the absence of all transport limitations including external and internal heat and mass transfer effects, as well as the rate of hydrogen transfer from the gas phase to the liquid phase. Other works have addressed transport limitations for reactions in porous catalysts [17, 18]. In general, temperature gradients arising from heat transfer limitation are not as prevalent under liquid-phase reaction conditions compared to the vapor phase because heat capacities and thermal conductivities of the liquid are an order of magnitude compared to those of the gas phase [19]. The external gas-liquid mass transfer resistance are negligible because of high agitation speed, and thus, a high degree of mixing [14,19,20]. The intraparticle and liquid-solid mass transfer resistance can also be neglected, since the catalyst particle size used was less than 80 μm [14]. By considering average values of 0.4 and 3 for porosity and tortuosity, respectively [18], the Weisz-Prater criterion [21], $\phi < 1$, that shows no pore diffusion resistance is also implied. Moreover, the following assumptions have been utilized in this work:

i) Catalyst dispersion in liquid is uniform and

ii) No temperature or pressure gradient in gas and liquid phase exists.

The proposed hydrogenation mechanism for UDMH production is as follows: [22-24]

$$(CH_3)_2NNO + 2H_2 \longrightarrow (CH_3)_2NNH_2 + H_2O$$

$$H2 + 2\theta_* \rightleftarrows 2\theta_H \qquad K_H = \frac{\theta_H^2}{\theta_*^2 C_{H2}} \tag{1}$$

$$NDMA + \theta_{**} \rightleftarrows \theta_{NDMA} \qquad K_{NDMA} = \frac{\theta_{NDMA}}{\theta_{**} C_{NDMA}} \tag{2}$$

$$\theta_H + \theta_{NDMA} \xrightarrow{k1} \theta_{UDMH} + \theta_{H2O} \qquad r_{UDMH} = k_1 \theta_{NDMA} \theta_H \tag{3}$$

$$\theta_{UDMH} \rightleftarrows \theta_{**} + UDMH \qquad K_{UDMH} = \frac{\theta_{UDMH}}{\theta_{**} C_{UDMH}} \tag{4}$$

$$\theta_{H2O} \rightleftarrows \theta_{**} + H2O \qquad K_{H2O} = \frac{\theta_{H2O}}{\theta_{**} C_{H2O}} \tag{5}$$

On the other hand the site balance is as shown below

$$\theta_* + \theta_H = 1 \qquad \text{and} \qquad \theta_{**} + \theta_{NDMA} + \theta_{UDMH} + \theta_{H2O} = 1$$

From Eq. (1) it is seen

$$K_H = \frac{\theta_H^2}{\theta_*^2 C_{H2}} \longrightarrow \theta_H = \theta_* (C_{H2} K_H)^{0.5} \text{ and with } \theta_* + \theta_H = 1$$

one obtains

$$\theta_H = \frac{(C_{H2} K_H)^{0.5}}{1 + (C_{H2} K_H)^{0.5}} \tag{6}$$

From Eqs. (2), (4) and (5) it is concluded that

$$K_{NDMA} = \frac{\theta_{NDMA}}{\theta_{**}C_{NDMA}} \longrightarrow \theta_{NDMA} = C_{NDMA}K_{NDMA}\theta_{**} \tag{7}$$

$$K_{UDMH} = \frac{\theta_{UDMH}}{\theta_{\bullet\bullet}C_{UDMH}} \longrightarrow \theta_{NDMA} = C_{NDMA}K_{NDMA}\theta_{**} \tag{8}$$

$$K_{H20} = \frac{\theta_{H20}}{\theta_{\bullet\bullet}C_{H20}} \longrightarrow \theta_{NDMA} = C_{NDMA}K_{NDMA}\theta_{**} \tag{9}$$

Combining these equations with the site balance equation of $\theta_{**} + \theta_{NDMA} + \theta_{UDMH} + \theta_{H2O} = 1$; one determines

$$\theta_{**} = \frac{1}{1 + K_{NDMA}C_{NDMA} + K_{H2o}C_{H2O} + K_{UDMH}C_{UDMH}} \tag{10}$$

From Eqs. (3) and (7) the UDMH production rate is found to be

$$r_{UDMH} = k_1\theta_{NDMA}\theta_H = k_1(C_{NDMA}K_{NDMA}\theta_{**})\theta_H$$

Combining this equation with Eqs. (6) and (10) one obtains

$$r_{UDMH} = \frac{k_1K_{NDMA}C_{NDMA}}{(1 + K_{NDMA}C_{NDMA} + K_{H2o}C_{H2O} + K_{UDMH}C_{UDMH})} \cdot \frac{(K_HC_{H2})^{0.5}}{(1 + (K_HC_{H2})^{0.5})} \tag{11}$$

Since the hydrogenation reaction takes place at a constant pressure in a semi batch reactor we may assume that hydrogen concentration in liquid phase is constant, and therefore neglect the K_HC_{H2} term in the related rate equation. Moreover, it is assumed that $K_{UDMH}C_{UDMH} < 1$. In other words, products formed on the catalyst are quickly desorbed. Implementing these assumptions, the rate equation is simplified to:

$$r_{UDMH} = \frac{k_1K_{NDMA}C_{NDMA}}{(1 + K_{NDMA}C_{NDMA} + K_{H2o}C_{H2O})} \tag{12}$$

For DMA production via reactions (2) and (3) with a similar procedure and assumptions it may be shown that

$$\text{(CH3)2NNO + 3H2} \longrightarrow (CH_3)_2NH + NH_3 + H_2O$$

$$(CH_3)_2NNO + 1.5\,H_2 \longrightarrow (CH_3)_2NH + 0.5N_2 + H_2O$$

$$r_{DMA} = \frac{(k_2 + k_3)K_{NDMA}C_{NDMA}}{(1 + K_{NDMA}C_{NDMA} + K_{H2O}C_{H2O})} = \frac{k'_2K_{NDMA}C_{NDMA}}{(1 + K_{NDMA}C_{NDMA} + K_{H2O}C_{H2O})} \tag{13}$$

Now that the kinetic equations are developed, one may use the experimental results to determine the reaction rate parameters. This is down in the following section.

5. PARAMETER ESTIMATION

For the optimum conditions of reaction (reaction temperature of 40°C and 40 wt% NDMA solution) which have resulted in the best yield of UDMH product, the parameters of rate equations of UDMH and DMA (i.e., Eqs. (12) and (13); respectively) were determined. For the temperature range of 40 to 55 °C, the activation energies of these two reactions have been determined. The temperature dependency of the rate constants was described by the Arrhenius equation. Adsorption equilibrium constants, K_i, were assumed independent of temperature. Usually the temperature dependency of K_i is described with Van't Hoff law. However, the heat of adsorption is known to decrease as the surface coverage is increased, as originally reported by Temkin[25] and experimentally confirmed by Babernics *et al*. [26]. The concentration and surface coverages are typically large in the liquid phase, and the effect of temperature on adsorption was, therefore, assumed to be negligible in the temperature interval studied [27, 28].

The objective function was the sum of squares of the relative errors between the experimental and calculated reaction rate of UDMH and DMA as follows:

$$RSS = \sum_i \left(\frac{r_{i,\exp} - r_{i,calc}}{r_{i,\exp}}\right)^2 \tag{14}$$

Minimization was carried out with the non linear regression method of Nelder and Mead [29].
The calculated optimized kinetic and adsorption constants are as follows:

Table 1. LH rate equation parameters

Parameters	Value (Eq. (12))	Value (Eq. (13))
k_1	1.59	-----
k'_2	-----	0.17
K_{NDMA}	9.21	3.375
K_{H2O}	0.0193	0.0367
RSS %	5.76	23.37

If the $K_{H2O}C_{H2O}$ term is neglected in the rate equation, one obtains:

$$r_{UDMH} = \frac{k_1 K_{NDMA} C_{NDMA}}{1 + K_{NDMA} C_{NDMA}} \tag{15}$$

$$r_{DMA} = \frac{k'_2 K_{NDMA} C_{NDMA}}{1 + K_{NDMA} C_{NDMA}} \tag{16}$$

These rate equations are derived from the Eley- Rideal mechanism. In this mechanism it is assumed that reaction takes place between the molecules of the liquid phase (NDMA) that have not adsorbed yet and adsorbed dissolved hydrogen molecules. The proposed mechanism may be presented as follows [22]:

$$\tfrac{1}{2}\,\mathrm{H2\ (aq.)} + \theta_* \rightleftarrows \theta_H$$

$$\theta_H + \mathrm{NDMA\ (aq.)} \longrightarrow \mathrm{NDMA.H} + \theta_*$$

$$\mathrm{NDMA.H} \longrightarrow \mathrm{intermediates + H2} \xrightarrow{\mathrm{Fast}} \mathrm{UDMH + H2O\ (desired\ product)}$$

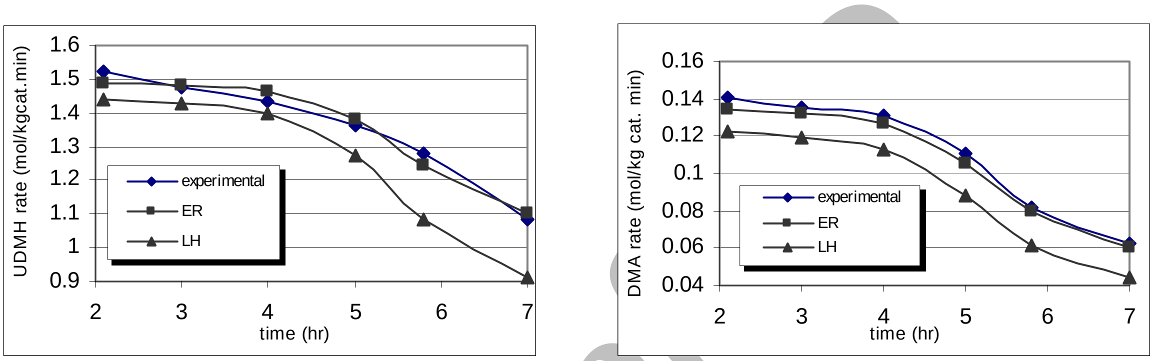
$$\mathrm{NDMA.H} \longrightarrow \mathrm{intermediates + H2} \xrightarrow{\mathrm{Fast}} \mathrm{DMA + H2O\ \ (undesired\ product)}$$

By the similar assumptions for deriving the LH rate equation, one obtains the rate equation of forms (12) and (13), above, for UDMH and DMA. Ghanbari Pakdehi has utilized this mechanism and concluded that the rate equation is the same as Eq. (15), while investigating the liquid phase hydrogenation in the reductive alkylation of actethydrazine [15]. According to these rate Eqs. (15, 16), and using the Nelder and Mead method as mentioned before, the rate equation parameters are estimated as follows:

Table 2. ER rate equation parameters

Parameters	Value (Eq. (15))	Value (Eq. (16))
k_1	1.58	-----
k'_2	-----	0.175
K_{NDMA}	9.14	2.161
RSS %	0.22	0.066

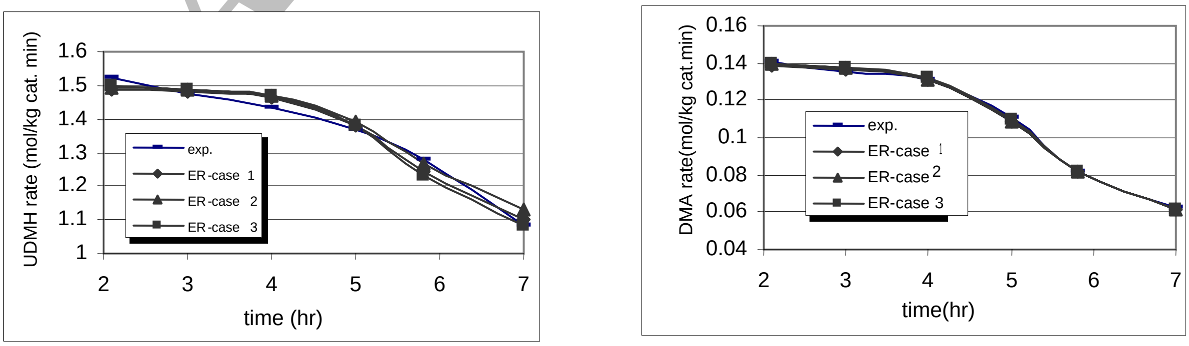
Figure 12 displays the estimated rates of UDMH and DMA with the estimated rates of Eley-Rideal(ER) and Langmuir-Hinshelwood (LH) rates versus reaction time. From this figure it is seen that the ER rate equation does fit the experimental data much better than the LH rate equation for both UDMH and DMA. For this reason, the ER rate model has been selected for both materials.



(a) (b)

Fig. 12: Comparison of experimental with Eley- Rideal(ER), and Langmuir –Hinshelwood(LH) rate equations vs. reaction time at P=15 bar, T=40°C , 40 wt% NDMA feed solution, (a):for UDMH and (b): for DMA rates.

In order to tune the model with experimental data, three cases, namely, 1, 2 and 3 are considered. Case 1 utilizes all six reproducible experimental data points obtained in this work to fit the model. Case 2 represents fitting with four of these data points selected randomly, omitting the second and sixth one. Finally, Case 3 represents tuning with four other random points omitting the second and fifth data points. Figure 13 shows a comparison among the estimated rates of UDMH and DMA for all these three cases and the experimental data. According to these figures, the maximum deviations from the experimental data for cases 2 and 3 are about 4.5 and 3.6% for the UDMH, while they are 1.7 and 1.8 % for the DMA rate. Furthermore, the maximum deviations from the experimental data in Case 1 are 2.8% and 1.6% for the UDMH and DMA rates, respectively.



(a) (b)

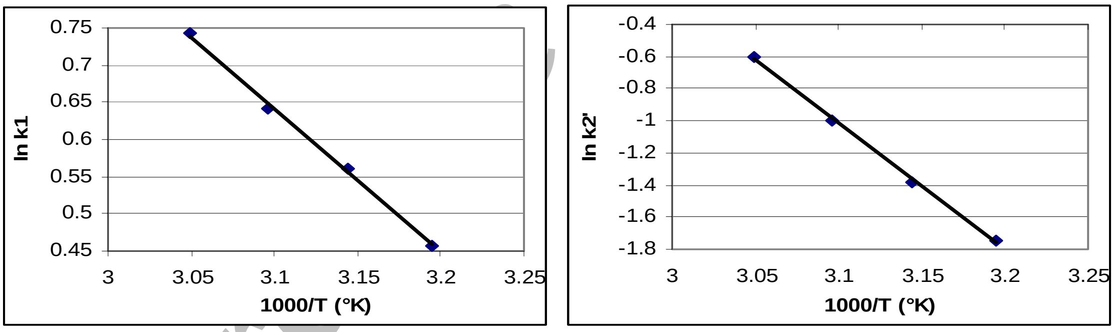
Fig. 13. Comparison of experimental with Eley- Rideal(ER) rate equations for Cases 1, 2 and 3 vs. reaction time at P=15 bar, T=40°C , 40 wt% NDMA feed solution,(a):for UDMH and (b): for DMA rates

Table 3 provides kinetic parameters for the rate equations of UDMH and DMA for all three cases explained above. According to this table, the tabulated kinetic parameters for the DMA rate are very close for all three cases having very low RSS percent, between 0.07 to 0.08%. On the other hand, for the UDMH rate, it is seen that the k_1 parameter resulted for all three cases are in very good agreement with one another, while the adsorption constant, K_{NDMA}, varies among Cases 1, 2 and 3, leading to an RSS percent between 0.22% to 0.37%. These results are indicative of the appropriateness of the ER model chosen in this work for the estimation of the kinetic rates for UDMH and DMA.

Table 3. Comparison of UDMH and DMA rate parameters based upon the ER model for Cases 1, 2 and 3

	UDMH equation rate parameters value (Eq. (15))			DMA equation rate parameters Value (Eq. (16))		
Parameters	ER-Case1	ER-Case2	ER-Case3	ER-Case1	ER-Case2	ER-Case3
k_1	1.58	1.578	1.5995	-------	-------	-------
k'_2	-------	-------	-------	0.175	0.177	0.178
K_{NDMA}	9.14	10.037	8.325	2.161	2.103	2.099
RSS%	0.224	0.371	0.248	0.066	0.0778	0.0796

Ultimately, through comparison of the above three cases, it is determined that Case 1 has the best rate estimation for UDMH and DMA rates. Thus, the activation energies of rate constants for this model have been estimated for this case. Figure 14 shows the temperature dependency of reaction rate constants of UDMH and DMA reactions in the optimum temperature range of 40 to 55 °C. From this figure, the activation energies of these two reactions are determined to be 15.97, 64.98 kJ/mol, respectively.



(a) (b)

Fig. 14. Temperature dependency of UDMH and DMA rate constants (k_1 and $k_2^{'}$) at P=15 bar and 40 wt% NDMA feed solution,(a): dependence of k_1 and (b): dependence of $k_2^{'}$

6. CONCLUSIONS

In this research catalytic hydrogenation of NDMA to UDMH on a 5%Pd/C catalyst was carried out. Experiments showed that the purity of NDMA feed solution are very important in hydrogenation. Even very low impurities in this solution will cause no conversion of this material due to catalysis poisoning. Another important issue is that greater hydrogenation of the UDMH product after reaction completion leads to the hydrogenation of N-N bound of UDMH which produces impurities such as DMA, and in turn, results in lower yields of UDMH product. The optimum conditions of reaction to give high yields of UDMH product was determined to be at a pressure of 15 bar being limited (in this work) by the tolerance of the equipment utilized. Of course, after occupation of all surface sites, further increments of hydrogen pressure have no significant effect on the hydrogenation rate [14, 15]. Furthermore, an NDMA concentration of 40 to 50 wt% and temperature of 40°C to 50°C are needed at this optimum. Higher temperatures lead to hydrogenolysis of the N-N bound of UDMH, production of DMA, and light impurities (NH_3, N_2), thus, a low yield of UDMH product is obtained. Higher concentrations of NDMA lead to lower amounts of water in the reaction medium. This low concentration of water may not extract the produced UDMH from the aqueous catalysis medium, thus preventing its contact with the catalyst. Therefore, the produced UDMH will convert to undesired impurities on the catalyst, resulting in low yields of this product.

A kinetic model based on the general form of the Eley-Rideal was selected due to its good prediction of UDMH and DMA production rates in comparison to the Langmuir-Hinshelwood rate equation. Ultimately, under optimum conditions determined in this work, the reaction rate parameters for the UDMH and DMA, as well as related activation energies were determined. These latest parameters were found to be 15.97 and 64.98 kJ/mol, respectively.

NOMENCLATURE

C_i	concentration of component i(NDMA,UDMH,H_2O,H_2), mol/m^3
k_i	rate constant of reaction i(UDMH,NDMA), mol / (kg cat. min)
K_i	adsorption equilibrium constant of component i(NDMA,UDMH,H_2O,H_2), m^3/mol
r_i	reaction rate of component i(UDMH ,DMA), mol / (kg cat. min)
RSS	residual sum of squares (objective function of equation 14)

Greek Letters

θ_*	fraction of vacant sites of gas phase on the catalyst
θ_{**}	faction of vacant sites of liquid phase on the catalyst
θ_i	fraction of the surface sites of component i(NDMA,UDMH,H_2O,H_2) on the catalyst

REFERENCES

1. Schmidt, E. W. (2001). *Hydrazine and its derivatives, preparation, properties and applications*. John Wiley and sons. Inc, New York, N.Y.
2. Bhute, R. S. (1988). Manufacture and industrial applications of unsymmetrical dimethyl hydrazine. Man-Made Textiles in India.
3. Olin Mathieson Chemical Corporation. (1958). Eng. Pat. 801534.
4. Kreisler, A. V., Schonwald, K. & Siebeneicher, H. (1958). Ger. Pat. 1037464.
5. Klager, K., Willson, E. M. & Helmcamp, G. K. (1960). *Industrial & Eng. Chem.* , *52*(2), 119.
6. Klager, K. & *et.al.* (1962). *Ind. Eng. Chem. Prod. Res. Dev., 1*, 117.
7. Smith,G. W. & Thatcher, D. N. (1962). *I&EC Product Research and Development, 1*(2).
8. Gaskins, E. & Bugalos, E. J. (1964). U.S. Pat. 313 3120.
9. Tindall, J. B. & Haute, T. (1964). U.S. Pat. 31530, 5.
10. Feldman, J. & Frampton, O. D. & *et .al*. (1964). U.S. Pat. 3129263.
11. Moore, W. P. & Pickens, D. P. & *et.al*. (1965). U.S. Pat. 3169993.
12. Thatcher, *et, al*. (1977). U.S. Pat. 4038321.
13. Levering, D. R. & Mavry, L. G. (1958). Eng. Pat. 797483.
14. Telkar, M. M., Rode, C. V., Rane, V. H., Jaganathan, R. & Chaudhari, R. V. (2001). Selective hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol: roles of ammonia, catalyst pretreatment and kinetic studies. *Applied Catalysis a: General, 216*,13-22.

15. Ghanbari Pakdehi, S. (2005). Catalytic reductive alkylation of acethylhydrazine. Ph. D. Thesis, Chemical Enginering College, Tehran University.
16. Aumo, J., Warna, J., Salmi, T. & Murzin, D. M. (2005). Interaction of kinetics and diffusion in complex catalytic three-phase reactions: activity and selectivity in citral hydrogenation. *Chemical Engineering Science*, accepted for publication.
17. Carberry, J. J. (1976). *Chemical and catalytic engineering*. McGraw-Hill,New York.
18. Satterfield, C. (1970). *Mass transfer in heterogeneous catalysis*. MIT press, Cambridge , MA.
19. Singh, U. K. (2001). Vannince, M. A. (2001). Kinetics of liquid-phase hydrogenation reaction over supported metal catalysts –a review. *App. Cat. , A: General, 213*, 1-24.
20. Rautnen, P. A., Aittama, A. & Krause, A. O. I. (2000). Solvent effect in liquid-phase hydrogenation of Toluene. *Ind. Eng. Chem. Res.,39*, 4032-4039.
21. Weisz, P. & Prater, C. (1954). Interpretation of measurements in experimental catalysis. *Adv. Catal., 6*, 143.
22. Smith, J. M. (1981). *Chemical engineering kinetics*. 3rd edition, McGraw-Hill.
23. Holland, C. D. & Anthony, R. G. (1989). *Fundamentals of chemical reaction engineering*. 2nd edition.
24. Lylykangas, M. S. (2004). Kinetic modeling of liquid phase hydrogenation reactions. *Ph.D. Thesis, Helsinki University of Technology*.
25. Temkin, M. I. (1979). The kinetics of some industrial heterogeneous catalytic reactions. *Adv. Cat., 28*,173.
26. Babernics, L., Tetenyi, P. & Kertesz, L. (1974). Investigation of the adsorption of benzene and cyclohexane on some transition metals and their oxides. *Z. Phys. Chem., 89*, 237.
27. Lylykangas, M. S., Rautanen, P. A. & Krause, A. O. I. (2002). Liquid–phase hydrogenation kinetics of multicomponent aromatic mixtures on Ni/Al2O3. *Ind. Eng. Chem. Res., 41*, 5632-5639.
28. Lylykangas, M. S, Rautanen, P. A. & Krause, A. O. I. (2003). Liquid-phase hydrogenation kinetics of iso octane on Ni/Al2O3. *AICHE Journal, 49*(6).
29. Nelder, J. A. & Mead, R. (1962). A simples method for function minimization. *The Computer Journal*, *7*, 308-313.