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Articles

Kinetics of Highly Selective Catalytic Hydrogenation of 2,3,5-Trimethylbenzoquinone on Raney Nickel Catalyst

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Abstract:

This work focuses on the catalytic hydrogenation of 2,3,5-trimethylbenzoquinone (TMBQ) to 2,3,5-trimethylhydroquinone (TMHQ). Kinetic interpretation has been made by studying the important process parameters using Raney nickel as the catalyst. Thus, at 100% TMBQ conversion level, as high as 100% selectivity to TMHQ was accomplished. Experimentation was performed to acquire the most suitable process conditions from the viewpoint of process research and development.

Introduction

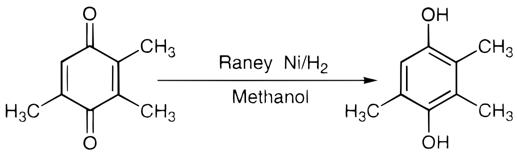
2,3,5-Trimethylhydroquinone (TMHQ) is a precursor for the synthesis of α-tocopherol, commercially known as vitamin E which, besides its anti-sterility effect, presently appears to have an active role in cell aging processes and is employed as an anti-wrinkle agent. TMHQ is prevalently synthesized by hydrogenation of TMBQ over noble metal catalysts.[1−4]

Although the chemistry of the reaction (Scheme 1) has been well-studied, the information pertaining to the kinetics, optimum process conditions, and life of the catalyst are not well documented. This work, therefore, is an attempt to study the kinetics of the reaction as well as to optimize the process conditions from a reaction engineering perspective.

Experimental Section

Materials. TMBQ was prepared in laboratory by air oxidation of 2,3,5-trimethylphenol,[5−8] methanol, and 2-propanol - laboratory reagent grade; Raney nickel and Pd/C - technical grade (Ms. Kalin Industries (India) Ltd, Mumbai).

Scheme 1



Experimental Setup. Hydrogenation of 2,3,5-trimethylbenzoquinone was carried out in a 100 mL Hastelloy autoclave (Parr Instrument Company, U.S.A.). It was equipped with a magnetically driven, six-bladed turbine impeller, an electric heater, two baffles, and a cooling coil. The pressure gauge, pressure release valve, safety head port, sampling valve, and gas inlet were all situated on the top head. The sample port was connected to a condenser to minimize the solvent loss during sampling. Hydrogen gas was supplied from a cylinder. The temperature was measured by a chromium−aluminum thermocouple hemmed in a thermowell and regulated by a temperature indicator−controller.

Experimental Procedure. In a typical experiment, 5 g of 2,3,5-trimethylbenzoquinone, 0.5 g of Raney nickel catalyst, and 50 mL of methanol were charged to the autoclave and were repeatedly purged with hydrogen gas (0.2 MPa) at room temperature. The reaction temperature was maintained at 100 °C by controlling the flow rate of cooling water in the internal coil and the heating rate. The autoclave was pressurized with hydrogen gas to 3.5 MPa, and agitation was initiated. The time of reaction was deemed to be from this instance. A steady pressure was maintained throughout the reaction period. After the stipulated reaction time, the reaction mixture was filtered to remove the catalyst and then distilled under reduced pressure to isolate the product, TMHQ (99.5% purity).

Analysis. Samples of 1−2 mL withdrawn at regular intervals of time were analyzed by HPLC using a MERCK 50983, Lichrospher 100 RP-18 column. The mobile phase used was a methanol− water (65:35) mixture, and the flow rate was maintained at 1 mL/min. The analysis was done at 230 nm. Calibration was done by using standard TMBQ (99.9% purity) and TMHQ (99.7%) samples.

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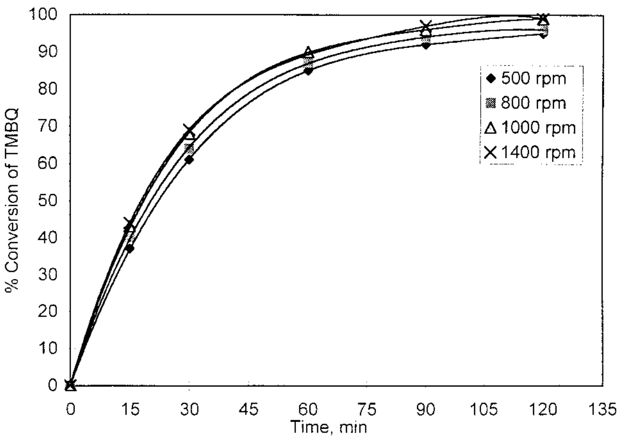

Figure 1. **Effect of speed of agitation on the rate of reaction. Reaction conditions: initial concentration of TMBQ, 10% w/v; catalyst loading, 1% w/v; temperature, 100 °C; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

Results and Discussions

Definitions. ***Overall Conversion.*** The conversion is defined as the ratio of the total moles of the TMBQ reacted to the moles of the TMBQ taken initially in the reaction.

Selectivity. The selectivity with respect to TMHQ is defined as the ratio of the moles of TMBQ reacted for the formation of TMHQ to the moles of TMBQ reacted.

Process Parameter Studies. Different significant process parameters were studied to acquire the most suitable reaction conditions and thus to formulate a kinetic interpretation.

Effect of Speed of Agitation. To ascertain whether the effect of mass transfer is exclusively eliminated, the speed of agitation was varied from 500 to 1400 rpm. There was a significant change in the overall conversion when the agitator speed was increased from 500 to 1000 rpm, indicating the presence of the mass transfer limitation for the diffusion of hydrogen from the gas−liquid interface to the bulk liquid. When the speed of agitation was further increased to 1400 rpm, there was no consequential change in the overall conversion (Figure 1), showing that mass transfer effects were mostly eliminated at or above 1000 rpm and the data represent the true kinetics of the process. Further reactions were studied at 1000 rpm.

Effect of Partial Pressure of Hydrogen. When the hydrogen pressure was increased from 0.2 to 3.5 MPa, it was observed that the % conversion increased (Figure 2). With a further increase in hydrogen pressure to 4.0 MPa there was no change in the conversion level. Therefore,further reactions were performed at the hydrogen partial pressure of 3.5 MPa.

Effect of Initial Concentration of TMBQ and Period of Reaction on the Rate of Hydrogenation. The conversion of TMBQ hardly increased when the initial concentration was varied from 5% w/v to 15% w/v (Figure 3).

With an increase in the reaction period from 15 to 120 min, for a given initial concentration of the reactant, the conversion of TMBQ increased from 43 to 100% (Figure 3).

Effect of Temperature. The reaction temperature was varied from 60 to 110 °C (Figure 4). At 60 °C, the reaction rate was observed to be very slow, and only 22% conversion at 60 min was obtained. With an increase in temperature to 110 °C, the conversion of TMBQ increased to 97% at 60 min.

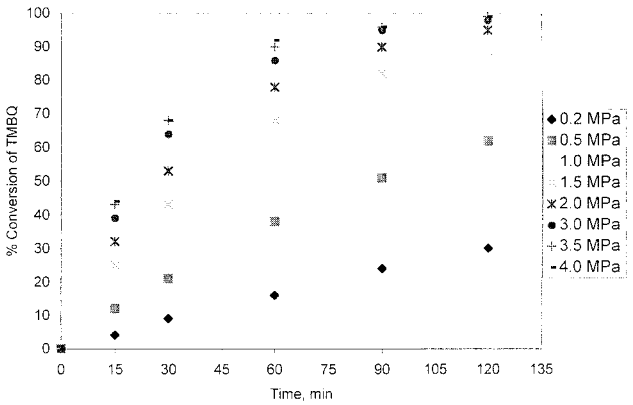

Figure 2. **Effect of hydrogen partial pressure on the rate of reaction. Reaction conditions: initial concentration of TMBQ, 10% w/v; catalyst loading, 1% w/v; temperature, 100 °C; speed of agitation, 1000 rpm; solvent, methanol; reaction volume, 50 mL.**

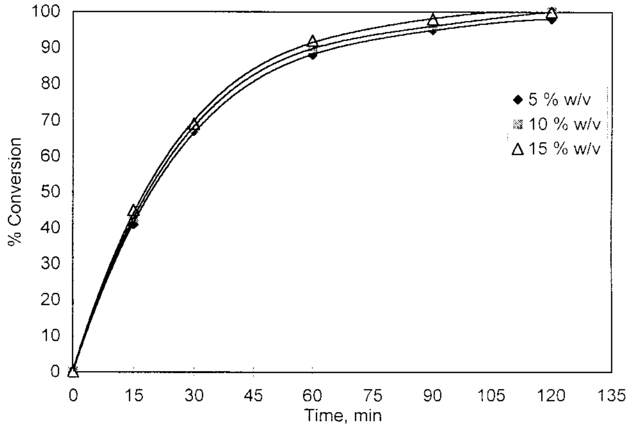

Figure 3. **Effect of initial concentration of TMBQ on the rate of reaction. Reaction conditions: catalyst loading, 1% w/v; temperature, 100 °C; hydrogen partial pressure, 3.5 MPa; speed of agitation, 1000 rpm; solvent, methanol; reaction volume, 50 mL.**

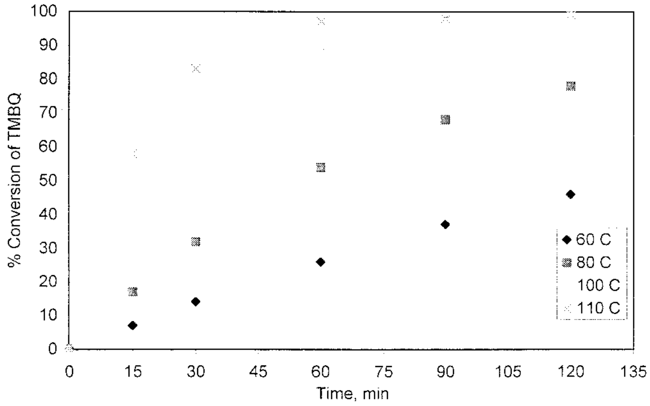

Figure 4. **Effect of temperature on the rate of reaction. Reaction conditions: initial concentration of TMBQ, 10% w/v; catalyst loading, 1% w/v; speed of agitation, 1000 rpm; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

Effect of Catalyst Loading. The catalyst loading expressed as the wt % of catalyst based on the total reaction

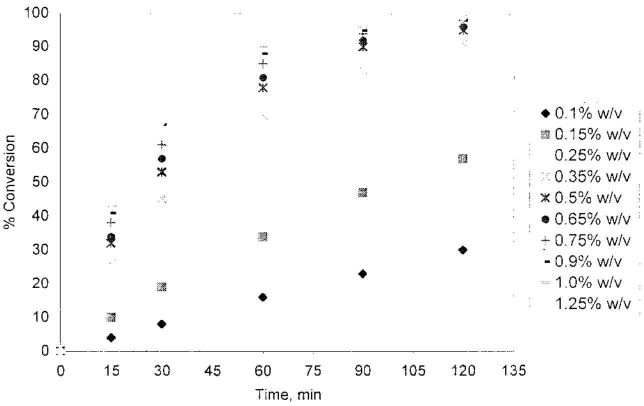

Figure 5. **Effect of catalyst loadings on the rate of hydrogenation. Reaction conditions: initial concentration of TMBQ, 10% w/v; temperature, 100 °C; speed of agitation, 1000 rpm; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

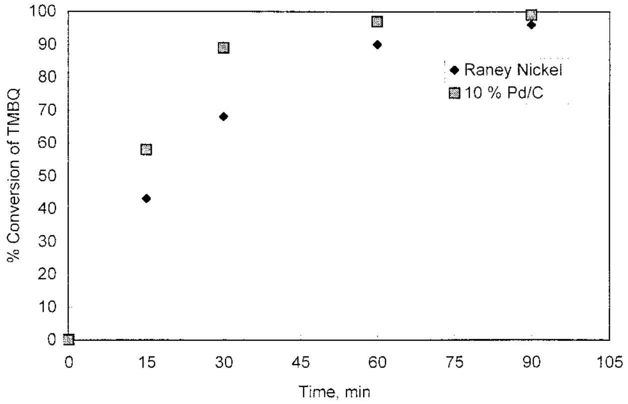

Figure 6. **Effect of different types of catalyst on the rate of reaction. Reaction conditions: initial concentration of TMBQ, 10% w/v; temperature, 100 °C; catalyst loading, 1% w/v; speed of agitation, 1000 rpm; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

volume was varied from 0.1 to 1.25% w/v (Figure 5). The per cent overall conversion increased significantly with the increase in catalyst loading. The selectivity to the desired product remained almost the same.

Effect of Different Types of Catalyst. The different catalysts, Raney nickel and 10% Pd/C, were used for the hydrogenation reaction. From Figure 6, it was observed that in 60 min the conversion was 99% with Pd/C, whereas with Raney nickel 90% conversion was accomplished. Although the rate of hydrogenation with Pd/C was much higher than with Raney nickel, due to the higher cost of Pd/C, Raney nickel was used for practically all of the runs.

Effect of Catalyst Reusability. It was noticed that on reusing the catalyst, the catalyst activity decreased considerably (Table 1). In 60 min, 90% conversion was achieved with the fresh catalyst. After a second use only 71% conversion was obtained. As a solution, to the second time reused catalyst 10% w/w of fresh catalyst was added and used for a subsequent run. Under these conditions, the conversion was almost identical to that of fresh catalyst.

Effect of solvent. Different solvents including methanol, ethanol, and 2-propanol were considered for this reaction. From Table 2, it is seen that any one of these solvents can be used, but methanol is cheaper than the other alcohols; thus, it was worth considering using methanol as the solvent.

Table 1. **Effect of catalyst reusability**[a]

catalyst	% overall conversion	% selectivity
fresh	90	100
first reuse	82	99
second reuse	71	99
second reused catalyst + fresh catalyst (10% w/w of total catalyst loading)	90	100

[a] Reaction conditions: initial concentration of TMBQ, 10% w/v; Raney nickel; 1% w/v; temperature, 100 °C; time, 60 min; hydrogen pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.

Table 2. **Effect of solvent**[a]

solvent	% overall conversion	% selectivity
2-propanol	95	100
ethanol	92	100
methanol	90	100

[a] Reaction conditions: Initial concentration of TMBQ, 10% w/v; catalyst loading, 1% w/v; temperature, 100 °C; time, 60 min; hydrogen pressure, 3.5 MPa; speed of agitation, 1000 rpm; reaction volume, 50 mL.

Table 3. **Material balance on isolation basis**[a]

material	mol of TMBQ accounted for	% accounted for	overall material balance
TMBQ (Input)	0.2	99.9	
TMHQ	0.1936	96.8	96.8
Unaccounted	0.0064	3.2	

[a] Reaction conditions: Initial concentration of TMBQ, 10% w/v; Raney nickel; 1% w/v; temperature, 100 °C; time, 150 min; hydrogen pressure, 3.5 MPa; solvent, methanol; reaction volume, 300 mL.

Material Balance. A complete material balance on isolation basis is given in Table 3. The reaction was performed in a 1 L autoclave. A 96.8% overall mass balance was achieved on TMBQ (99.9% initial purity) under the reaction conditions. The unaccounted material may be due to distillation losses, and there was no residue formations.

Kinetics. The reactions were carried out at a high speed of agitation to eliminate the mass transfer effects. No increase was observed in the conversion level when the hydrogen pressure was increased from 3.5 to 4.0 MPa. This indicates that at or above 3.5 MPa pressure the reaction is insensitive to a further increase in hydrogen pressure.

The rate equation at 3.5 MPa hydrogen partial pressure and a 0.5% w/v catalyst loading can be expressed as

$$\frac{-\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t} = kWP_{\mathrm{H2}}C_{\mathrm{A}} \tag{I}$$

$$-\ln(1 - \mathrm{X_A}) = k_{\mathrm{obs}}t, \quad \text{where } k_{\mathrm{obs}} = kWP_{\mathrm{H2}} \tag{II}$$

It was deduced from the plot of $-\ln(1 - \mathrm{X_A})$ vs t that, for a given initial concentration of the reactant, the reaction is first-order with respect to the TMBQ (Figure 7).

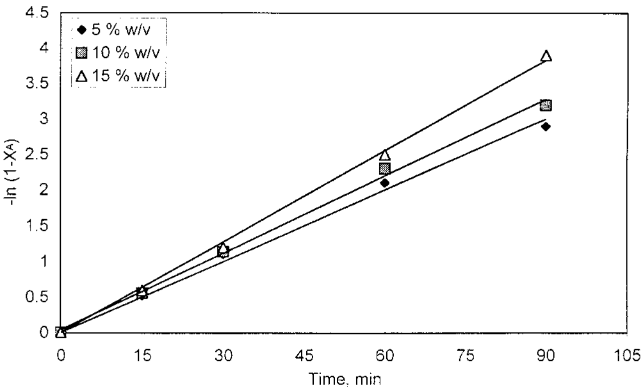

Figure 7. **$-\ln(1 - X_A)$ vs t at different initial concentrations of TMBQ. Reaction conditions: catalyst loading, 1% w/v; temperature, 100 °C; hydrogen partial pressure, 3.5 MPa; speed of agitation, 1000 rpm; solvent, methanol; reaction volume, 50 mL.**

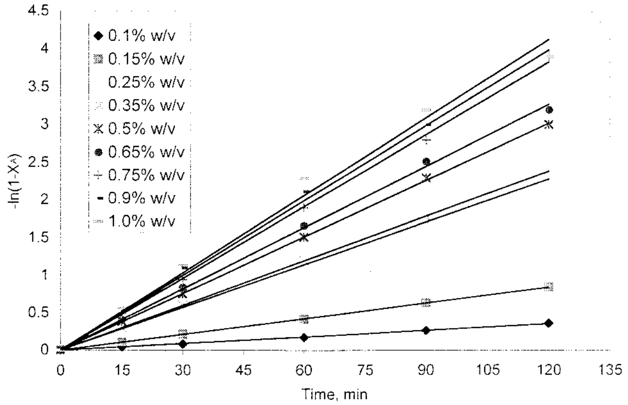

Figure 8. **$-\ln(1 - X_A)$ vs t at different catalyst loadings. Reaction conditions: initial concentration of TMBQ, 10% w/v; temperature, 100 °C; speed of agitation, 1000 rpm; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

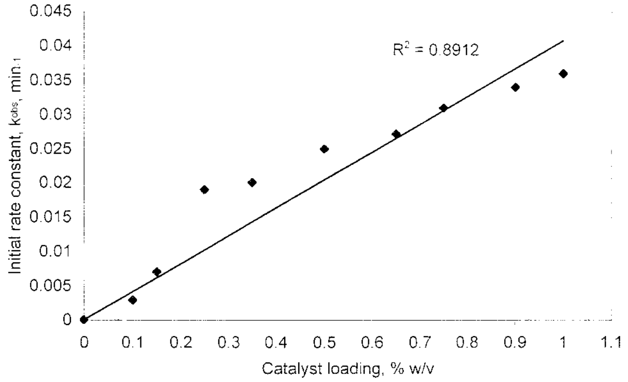

Figure 9. **Initial rate constant vs catalyst loading. Reaction conditions: initial concentration of TMBQ, 10% w/v; temperature, 100 °C; speed of agitation, 1000 rpm; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

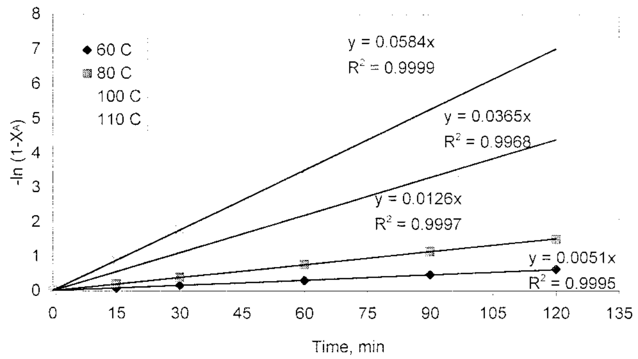

Figure 10. **$-\ln(1 - X_A)$ vs t at different temperatures. Reaction conditions: initial concentration of TMBQ, 10% w/v; speed of agitation, 1000 rpm; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

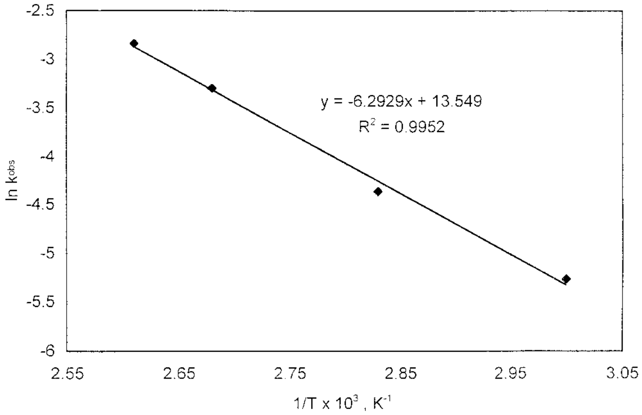

Figure 11. **Arrhenius plot. Reaction conditions: initial concentration of TMBQ, 10% w/v; catalyst loading, 1% w/v; speed of agitation, 1000 rpm; hydrogen partial pressure, 3.5 MPa; solvent, methanol; reaction volume, 50 mL.**

The plot of $-\ln(1 - X_A)$ vs t (Figure 8) at different catalyst loading is plotted. The respective slopes of the line are plotted against corresponding catalyst loading (Figure 9). It was observed that the initial rate increased with the increase in catalyst loading. Since for the physical size of the catalyst used and the conditions employed the role of diffusion of hydrogen from the bulk liquid to the solid is estimated to be unimportant, the data appears to represent the true kinetics of the process at a catalyst loading of 1.0% w/v.

A plot of $-\ln(1 - X_A)$ vs t at different temperature (Figure 10), exhibit a linear relationship. The slope, k_{obs}, when divided by the corresponding hydrogen partial pressure and gram of catalyst at 50 mL reaction size, the rate constant k was found to be 2.9×10^{-4}, 7.2×10^{-4}, 2.08×10^{-3}, and 3.33×10^{-3} min^{-1} MPa^{-1} g-cat^{-1} at 60, 80, 100, and 110 °C, respectively. The energy of activation was found to be 52 kJ/mol from the Arrhenius plot (Figure 11).

Conclusions

The hydrogenation of 2,3,5-trimethyl benzoquinone to the corresponding hydroquinone, using Raney nickel as the catalyst gave 100% selectivity at a conversion ratio of 100%.

At a particular initial concentration of TMBQ, a temperature of 110 °C, and a pressure of 3.5 MPa, the hydrogenation reaction over Raney nickel follows first-order kinetics. A model such as Langmuir–Hinshelwood could explain the kinetic observations more clearly, taking account the adsorption effects on a heterogeneous catalyst.

The catalyst could be reused by adding 10% w/w of fresh catalyst to the spent one to restore its activity under analogous reaction conditions.

Notation

C_A	concentration of TMBQ, mol/L
X_A	fractional conversion of TMBQ
P_{H2}	partial pressure of hydrogen, MPa
k	rate constant, $\min^{-1}$ MPa^{1-} g-cat^{-1}
t	time, min
W	wt of catalyst, g
TMBQ	2,3,5-trimethylbenzoquinone
TMHQ	2,3,5-trimethylhydroquinone

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