# Microwave Heating of Endothermic Catalytic Reactions: Reforming of Methanol

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*In an endothermic reaction, such as methanol-steam reforming, the reaction rate can be limited by the ability to supply heat to the reactor. Heat transfer from the reactor wall normally supplies the required energy in such processes. Drawbacks, such as operating temperature constraints and practical heat-transfer restrictions, limit this practice. In such situations, microwave heating could provide an effective and efficient method for transferring heat to the catalyst. To explore this possibility, the methanol-steam reaction performed by conventional heating and microwave heating was studied. Mathematical modeling was performed for 1-D heat transfer in a single catalyst pellet and for 2-D heat transfer in a tubular packed-bed reactor. The single catalyst pellet model indicated that productivity could increase significantly using microwave heating. The 2-D model showed that microwave heating could minimize radial heat-transfer effects. Conducting the methanol-steam reaction in a microwave-heated reactor experimentally verified the improved productivity.*

## Introduction

Many extremely important industrial reactions are endothermic, that is, they require thermal energy to proceed. Table 1 presents a sampling of industrially significant endothermic catalytically-promoted organic reactions. Limitations in the operation of endothermic catalytic reactors are quite universal: radial heat transfer to a packed bed results in a pronounced temperature profile. For this class of reaction, heat is rapidly consumed in the outer layers, affecting the rate of reaction toward the center of the reactor. There are various reactor designs conventionally used to provide the heat of reaction in these systems. Typical designs use one or more burners outside a tubular reactor (Billings, 1995), reheaters between reactors (Ozokwelu, 1997), diluents to supply sensible heat (Müller, 1989), or combinations of these. Energy requirements and costs can be substantial (Rosen and Scott, 1988). The use of external burners, with the associated fuel and flue-gas handling, adds extra complexity and size that can hinder some applications. Traditional designs also limit the ability to tailor the energy production rate to achieve the desired temperature and conversion profiles, and optimize utilization, although many clever heat-transfer schemes exist. There is motivation for new reactor technology for applications in which reactor size, simplicity, and efficiency are especially important. The ability to uniformly provide heat throughout the catalyst bed via microwave heating is an option worth considering.

Microwave heating may provide advantages over conventional routes for heating heterogeneous catalysts. There have been reports of improved catalytic performance for heterogeneously catalyzed reactions (Ioffe et al., 1995). Ioffe's group proposed that altered reactivity and selectivity for the catalytic reaction of methane over carbon to form acetylene could be attributed to nonisothermal effects. They suggested the catalytically-active phase reached higher temperatures than the surrounding support. To investigate the phenomenon of microwave-enhanced reactivity, an experimental study of the CO oxidation reaction was previously conducted,

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**Table 1. Industrially Significant Endothermic Catalytically Promoted Organic Reactions**

| Reaction | | Use* | Reaction Temp., $K$ | $\Delta H_{ren}$, kJ/mol |
|---|---|---|---|---|
| Steam reforming of natural gas | $CH_4 + H_2O \xrightarrow{NiO} CO + 3H_2$ | Production of synthesis gas | ~1,100 | ~ +225 |
| Dehydrogenation of cyclohexane | $C_6H_{12} \xrightarrow{Pt/Rh/Al_2O_3} C_6H_6 + 3H_2$ | Production of toluene | ~ 775 | ~ +220 |
| Dehydrogenation of methyl cyclohexane | $C_6H_{12} \xrightarrow{Pt/Rh/Al_2O_3} C_6H_6 + 3H_2$ | Production of toluene | ~ 775 | ~ +215 |
| Dehydrogen of *n*-butane | $C_4H_{10} \xrightarrow{Cr_2O_3/Al_2O_3} C_4H_6 + 2H_2$ | Houdry process for producing butadiene | ~ 925 | ~ +250 |
| Dehydrogenation of ethyl benzene | $C_8H_{10} \xrightarrow{Fe_2O_3/K_2O} C_8H_8 + H_2$ | Production of styrene | ~ 875 | ~ +125 |
| Steam reforming of methanol** | $CH_3OH + H_2O \xrightarrow{CuO/ZnO} CO_2 + 3H_2$ | Production of fuel–cell feed | ~ 525 | ~ +60 |

*Reactions are major routes to these products; not necessarily the only industrially-significant routes.
**As yet only potentially important; significance contingent on its use being accepted for generating feed for mobile fuel cells.

comparing microwave with conventional heating (Perry et al., 1997b). There was no observable effect of microwave heating on this reaction; the activation energy and reaction order were unaffected by the mode of heating. A theoretical investigation of the extent of nonisothermal heating of small metal particles (10 nm) was also carried out (Perry et al., 1997a). We concluded that it was not possible to sustain appreciable thermal gradients between the metal particles and support, especially when the metal particles were only a few nanometers in diameter. However, this did not rule out a beneficial impact of microwave heating for an endothermic reaction, whose performance can be limited by the rate of heat transfer. This latter application is explored in this work.

This article provides both analysis and experimental confirmation showing that microwave heating can provide a more uniform temperature profile, allowing the active catalyst surface to be more effectively employed. This has the added advantage of decreasing the required mass of the catalyst bed, making the system more attractive in terms of cost and compactness. The nature and magnitude of thermal gradients within a microwave-heated catalytic reactor have not been extensively studied. Therefore, a major goal of this research has been to gain a better understanding of the thermal gradients through both experiments and theoretical study. First, a theoretical analysis is presented of a single catalyst pellet that establishes the potential benefits of using microwave heating. This is followed by a presentation of the experimental results. A 2-D heat-transfer analysis of the packed-bed reactor aids in interpreting the experimental observations. The results presented here are broadly applicable to any endothermic catalytic reaction.

To examine the effectiveness of the application of microwave energy to endothermic catalytic reactions, the methanol reforming reaction (MRR) was used (Table 1). The MRR is a good candidate for producing $H_2$ to supply proton-exchange membrane fuel cells (Idem and Bakhshi, 1996; Birdsell and Vanderborgh, 1994; Amphlett et al., 1994), which is the currently favored fuel-cell type for automotive use. However, obstacles have arisen in developing mobile fuel processors because of the reforming reactions' severe endothermic nature (Brown, 2001). These difficulties stem from heat-transfer limitations, and affect the size and cost of the unit, partly because of increased catalyst requirements. For the MRR, where the catalyst will not survive temperatures much beyond 600 K, there is a limit to the energy provided via sensible heat in the incoming reactant stream. In such a situation, the ability to provide heat uniformly throughout the catalyst bed, via microwave heating, merits attention. The MRR reaction has been widely studied, and there is a good knowledge base concerning the effects of reaction conditions and catalysts (Peppley et al., 1999). The reaction is endothermic with $\Delta H_{rxn} = +61.57$ kJ/mol at 600 K, and typically uses a CuO/ZnO catalyst at temperatures from 500 to 600 K, at pressures from 0.1 to 0.3 MPa.

## Single Catalyst Pellet Model

The coupled heat- and mass-transfer equations have been numerically solved for a single spherical catalyst pellet subjected to microwave heating

$$\begin{aligned} 0 &= D\frac{1}{r^2}\frac{d}{dr}r^2\frac{dC_M(r)}{dr} + r_{\mathrm{MeOH}}(r) \\ 0 &= k\frac{1}{r^2}\frac{d}{dr}r^2\frac{dT(r)}{dr} + Q_{mw} + Q_{rxn}(r) \end{aligned} \tag{1}$$

In these relationships, $T$ is the temperature, $C_M$ the concentration of methanol, $k$ the thermal conductivity, and $D$ the effective diffusion coefficient. The rate $r_{\mathrm{MeOH}}$ accounts for the consumption of methanol by chemical reaction, $Q_{rxn}$ represents the heat generated by the reaction, and $Q_{mw}$ is the heat generated by microwave energy dissipation. The balanced reaction is $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$. Amphlett et al. (1994) have suggested a first-order rate law for reaction over an alumina/CuO/ZnO catalyst (CCI Inc.'s C18HC)

$$r_{\mathrm{MeOH}} = -\left[1.15\times10^6 + \ln\left(R_{S/M}\right)\ 9.41\times10^5\right] \times \frac{1}{P^{1.46}}\exp\left(-\frac{E_a}{RT}\right)C_M = kC_M \tag{2}$$

$$r_{\mathrm{MeOH}}(r) = -A\exp\left(\frac{-E_a}{RT(r)}\right)C_M(r)$$

$$Q_{rxn}(r) = -\Delta H_{rxn} A \exp\left(\frac{-E_a}{RT(r)}\right) C_M(r) \tag{3}$$

in which $E_a$ is the activation energy, $R$ the gas constant, $A$ the pre-exponential factor, $P$ the total pressure, $R_{s/m}$ the feed steam-to-methanol ratio (molar), and $\Delta H_{rxn}$ the heat of reaction. Under the conditions of interest, $A = 30{,}100\ \mathrm{s}^{-1}$ and $E_a = 84{,}100$ J/(mol K). Combining Eqs. 1 and 3 gives

$$0 = D\frac{1}{r^2}\frac{d}{dr}r^2\frac{dC_M(r)}{dr} - A\exp\left(\frac{-E_a}{R_gT(r)}\right)C_M(r)$$

$$0 = k\frac{1}{r^2}\frac{d}{dr}r^2\frac{dT(r)}{dr} + Q_{mw} - \Delta H_{rxn}A\exp\left(\frac{-E_a}{R_gT(r)}\right)C_M(r) \tag{4}$$

Useful physical insight is gained by making the equations dimensionless. First, introducing the following relationships for the dependent and independent variables, respectively

$$C^*(r^*) = \frac{C_M(r)}{C_s};\quad \Theta(r^*) = \frac{T(r)-T_s}{T_s};\ r^* = \frac{r}{R};\quad (5)$$

gives

$$0 = \frac{1}{r^{*2}}\frac{d}{dr^*}r^{*2}\frac{dC^*(r^*)}{dr^*} - \left\{\frac{AR^2}{D}\exp\left(\frac{-E_a}{R_gT_s[\Theta(r^*)+1]}\right)C^*(r^*)\right\}$$

$$0 = \frac{1}{r^{*2}}\frac{d}{dr^*}r^{*2}\frac{d\Theta(r^*)}{dr^*} + \left[\frac{Q_{mw}R^2}{kT_s}\right] - \left\{\frac{C_s\Delta H_{rxn}R^2A}{kT_s}\exp\left(\frac{-E_a}{R_gT_s[\Theta(r^*)+1]}\right)C^*(r)\right\} \tag{6}$$

The second term in the righthand side of the concentration Eq. 6 is the Thiele Modulus squared ($\phi^2$), and the coefficient of the exponential is called $\phi^{12}$. The third term in the righthand side of the energy equation is the fourth Damköhler Number ($Da_{IV}$). Similarly, the coefficient of the exponential is called $Da_{IV}'$. The second term in the righthand side of the energy equation relates the rate of microwave energy absorption to the rate of energy conduction to the surface of the pellet. This number is defined as the "microwave" number $MW$. Finally, by defining $\gamma$ as $E_a/R_gT_s$, Eq. 6 is

$$0 = \frac{1}{r^{*2}}\frac{d}{dr^*}r^{*2}\frac{dC^*(r^*)}{dr^*} - [\phi^{12}]\exp\left(\frac{-\gamma}{[\Theta(r^*)+1]}\right)C^*(r^*)$$

$$0 = \frac{1}{r^{*2}}\frac{d}{dr^*}r^{*2}\frac{d\Theta(r^*)}{dr^*} + MW - [Da_{IV}']\exp\left(\frac{-\gamma}{[\Theta(r^*)+1]}\right)C^*(r) \tag{7}$$

These equations need four boundary conditions to obtain a unique solution. At $r = 0$, derivatives of both temperature and concentration are zero because of symmetry. The other two conditions are of the first kind at the pellet surface

$$\Theta(r^*=1) = 0 \qquad C^*(r^*=1) = 1 \tag{8}$$

For the numerical approach, we specified the values of the concentration and temperature, together with the values of the derivatives, at $r^* = 0$. As mentioned, the derivatives are zero at $r^* = 0$. However, the concentration and temperature are unknown, and an interative procedure was employed. The Mathematica program (Wolfram, 1988) which applies an adaptive Runge-Kutta routine, was used to obtain the solutions presented here. Sets of possible temperature and concentration values at $r^* = 0$ were tested until the proper boundary conditions at $r^* = 1$ appeared. Brown (1996) gives the data necessary for calculating $\phi^{12}$ and $Da_{IV}'$. For the numerical calculations, $\phi^{12} = 2\times10^8$, $Da_{IV}' = 2.7\times10^7$, and $\gamma = 16.3$. In addition, this work empirically determined that a value of $MW = 0.6$ satisfied the temperature leveling requirement. Figures 1 and 2 show the concentration and temperature behavior for $MW = 0.6$ at a gas phase temperature of 600 K. This temperature was chosen because it represents the upper operating temperature that is typically used for this reaction. In addition, there are other terms to consider in the $MW$ term to show that 0.6 is a reasonable number. This was accomplished by applying the equation to find the specific power ($P/V$ in W/m$^3$) dissipated in a dielectric medium exposed to microwave radiation (Metaxis and Merideth, 1988)

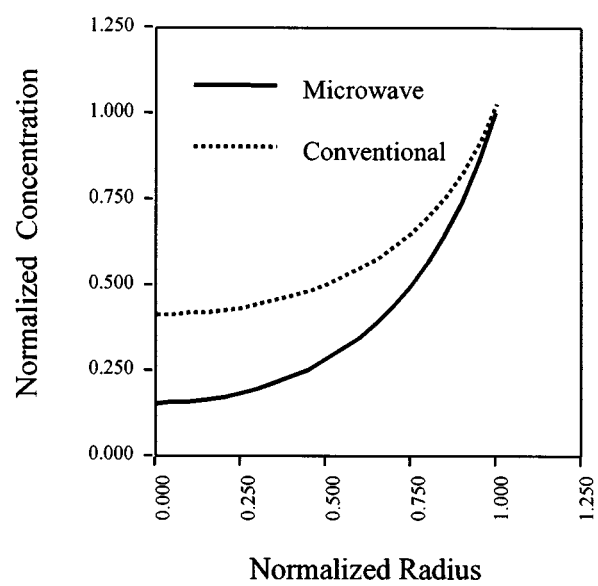


**Figure 1. Numerical solution for methanol concentration from coupled heat- and mass-transfer equations.**

Larger slope for microwave case at pellet boundary indicates a higher overall productivity.

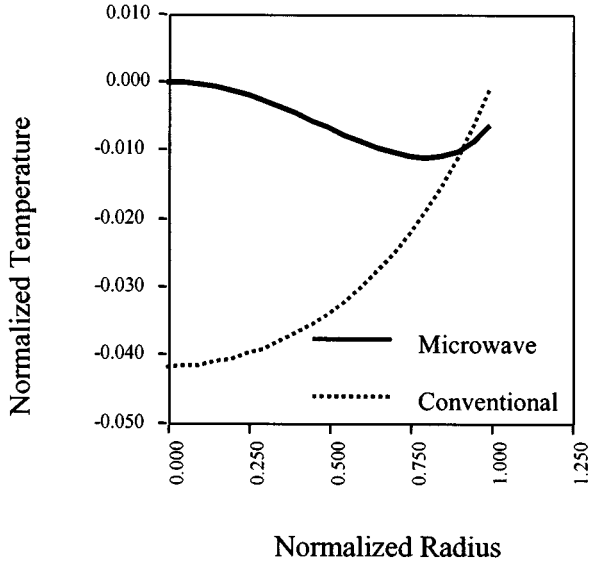


**Figure 2. Numerical solution for temperature from coupled heat- and mass-transfer equations.**

Microwave power was adjusted to make temperature profile as flat as possible.

$$Q_{mw} = \frac{P}{V} = \pi f E^2 \epsilon_0 \epsilon'' \tag{9}$$

An order-of-magnitude estimate for the thermal conductivity is 0.5 W/(m·K) (Hill, 1977), and a typical pellet radius is 3 mm. Using a microwave frequency $f$ of 0.915 GHz and assuming dielectric loss ($\epsilon''$) of 0.001 (approximate dielectric loss of alumina), the required electric field ($E$) is approximately $5 \times 10^5$ V/m.

The total reaction rate was calculated from the mass flux at the boundary of the pellet, directly proportional to the concentration gradient (slope) at this point. Close examination of Figure 1 shows that the slope (flux) is higher for the case where MW = 0.6. This analysis shows a volumetric rate increase of approximately 2. Qualitatively, the phenomenon noted here is general. In an endothermic reaction occurring within a porous catalyst where significant thermal gradients exist, the reaction rate on the microwave-heated catalyst pellet will always exceed the rate in a conventionally-heated system.

## Differential Conversion Reactor Study

The first step toward understanding experimental behavior was to verify that the rate expression provided by Amphlett et al. (1994) could represent the kinetic behavior of this reaction. It was also important to ensure that there was no effect of microwave radiation on the kinetic behavior. The evaluation used a differential isothermal microreactor. Figure 3 shows the experimental reactor. Two boilers provided the methanol vapor and steam for reaction. Regulated power supplies provided heat to a water boiler and a methanol boiler at a rate that generated the desired mass-flow rate. The flow rate as a function of power input was calibrated by condensing the effluent. An additional heater at the exit of the boilers superheated the vapors to avoid condensation in the feed lines, and to avoid condensation of the water vapor upon mixing. The vapor mixture then passed through a final reheater stage that maintained the superheated state and provided the desired reactor inlet temperature. An HP-5890A gas chromatograph measured effluent concentrations to determine conversion in the experiments. The chromatograph used a HayeSep P (Alltech, Deerfield, IL) column, and the feed system described was used for all experiments.

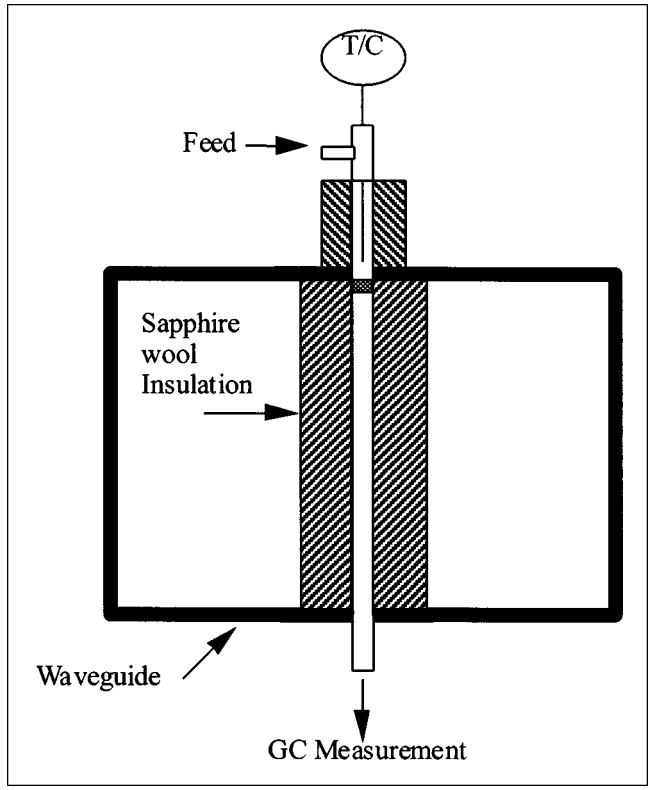


**Figure 3. Reactor configuration used for the differential experiment.**

Heat was supplied to reaction from sensible heat in feedstream. Reaction was run at a fixed temperature with microwaves on or off. For scale, wave-guide, 9.8 × 4.9 in.; tube diameter, 8 mm.

Experiments used 24.4 mg of crushed $Al_2O_3/CuO/ZnO$ catalyst (C18HC, obtained from CCI). The oxides were present in a 40–50/35–40/8–15 ratio, and copper was reduced to active reaction sites *in situ* (Brown, 1996). The small amount of catalyst enabled this work to keep the conversion below 5%. This helped maintain the reactor isothermal without the complications induced by the reaction's endothermic nature. In a differential reactor operating at low conversions with a constant space velocity and catalyst mass, the rate of reaction is directly proportional to conversion. The only variable is temperature, which provides a straightforward method to find the activation energy. The reactant gases, mixed at 1:1 steam-to-methanol ratio (molar), were fed at 8 $cm^3/s$ at STP. All experiments used these feed conditions over a temperature range of 500–600 K. The experiment was repeated for two cases: (1) no applied microwave power, and (2) an electric field strength of $3 \times 10^5$ V/m. Figure 3 shows the detailed

reactor configuration. The experiment was designed so that the sensible heat from the gas stream provided the heat required for the reaction. During both experiments, the region of the quartz tubing containing the catalyst was located inside the microwave cavity, where sapphire wool provided insulation. The small mass of catalyst would not appreciably increase in temperature due to the interaction of the microwaves and the catalyst. Therefore, this experiment tested the effect of exposing the reaction zone to intense microwave radiation.

A calibrated antenna and an HP-8481A power meter provided the means to measure the electric field strength inside the waveguide. The antenna was calibrated using a vector network analyzer such that the free-space electric field strength was determined using the scattering parameters. The antenna occupied the location where the differential mass of catalyst resided during the study of Case 2. A power meter gave the response of the antenna. This measurement guaranteed the existence of microwave energy at the differential-bed location.

These experiments were designed to confirm that the kinetic behavior of the MRR was identical whether heated conventionally or by microwaves, and to justify the use of Eq. 2. Figure 4 shows the Arrhenius plot for this reaction. Analysis of the experimental data revealed a preexponential factor and activation energy of $2.3\times10^4$ $m^3/s/kg$ and 80,500 J/mol, respectively, using a linear least-squares fit. These values are close to the values reported by Amphlett et al. (1994), which were $3.01\times10^4$ $m^3/s/kg$ and 84.1 kJ/mol. Close observation of Figure 4 reveals a slight but consistent curvature, somewhat undermining the first-order assumption. Others have suggested expressions other than first order (Peppley et al., 1999). However, our intent here was to justify the use of the Eq. 2 for modeling purposes and to examine the effect of microwaves on the kinetics of the reaction. The linear fit is adequate for this purpose.

Over the parameter space used for the models and the experiments, the reaction rate comparison for microwave vs. conventional heating revealed virtually indistinguishable results. In addition, the activation energy and pre-exponential values agree very well with those published by Amphlett et al. (1994). Thus, Figure 4 shows that exposure to microwave energy does not affect the MRR reaction over Cu/ZnO catalysts.

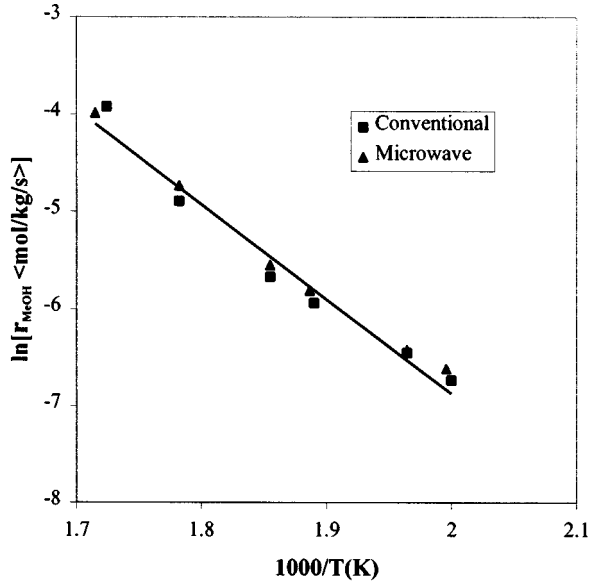


**Figure 4. Arrhenius plot showing reaction rate of methanol over 24.4 mg of catalyst.**

Microwave and conventional reaction rates compared are nearly identical. Activation energy, 80,600 J/mol·K; preexponential factor, $2.3\times10^4$ $m^3/s/kg$.

## 2-D Packed-Bed Experiments

To explore heat-transfer effects, this research performed experiments in an integral packed-bed reactor using crushed catalysts (approximately 100 $\mu$m particle size. The size of the pellets available for the C18HC catalyst precluded using them in this work's small experimental reactors). With this crushed powder, heat transfer was not expected to affect the rate as described in the Single Catalyst Pellet section. As a result, the effectiveness factor of the catalyst in these experiments was assumed to be 1.

For the 2-D case, the experiment used a bed diameter and length sufficiently large that radial and axial temperature gradients would exist in the conventionally-heated case because of wall and inlet heat fluxes. It compared the effect of identical inlet conditions on the performance of the microwave-heated vs. the conventionally-heated reactor. A fixed conversion of 60% determined the input power to each reactor. The power required influenced the exit temperature of the reactors, which reflected the efficiency of each process.

In choosing the radial dimension of this reactor, a Peclet number large enough to warrant the 2-D approximation was required. A tube 4 mm in radius and 15 mm in length satisfied this requirement. Methanol and steam were fed at 8 $cm^3/s$, a molar ratio of 1:1, a temperature of 575 K, and a pressure of 1 atm. These conditions gave a heat-transfer Peclet number ($Pe_H$) of approximately 0.2. This is not a large value, but the reactor model presented in the next section shows that appreciable radial temperature profiles will develop under these circumstances. (The stated number was based on reactor dimensions; alternatively, Peclet numbers are sometimes based on catalyst particle diameter (Carberry, 1976).) The experiment maintained constant inlet conditions and conversion, while a thermocouple measured the exit temperature for the cases where the bed was heated in Case 1, conventionally, and in Case 2, by microwaves.

For Case 1, a wrapped nichrome wire, as shown Figure 5a, supplied the radial heat. For Case 2, the reactor tube was transferred into the waveguide, as shown Figure 5b. In both cases, a thermocouple monitored the inlet temperature at the top of the assembly. Sapphire wool separated the thermocouple from the catalyst bed by approximately 1 cm, as shown in the figures. A second thermocouple measured the exit temperature below the bed in both cases. Again, sapphire wool separated the bed from the thermocouple. For the conventional case, the thermocouple was located just below the bed, placing it just outside the waveguide after transfer to the microwave configuration. A temperature drop occurred in Case 2 because this relocation of the thermocouple placed it slightly outside the insulation. This temperature drop was calibrated

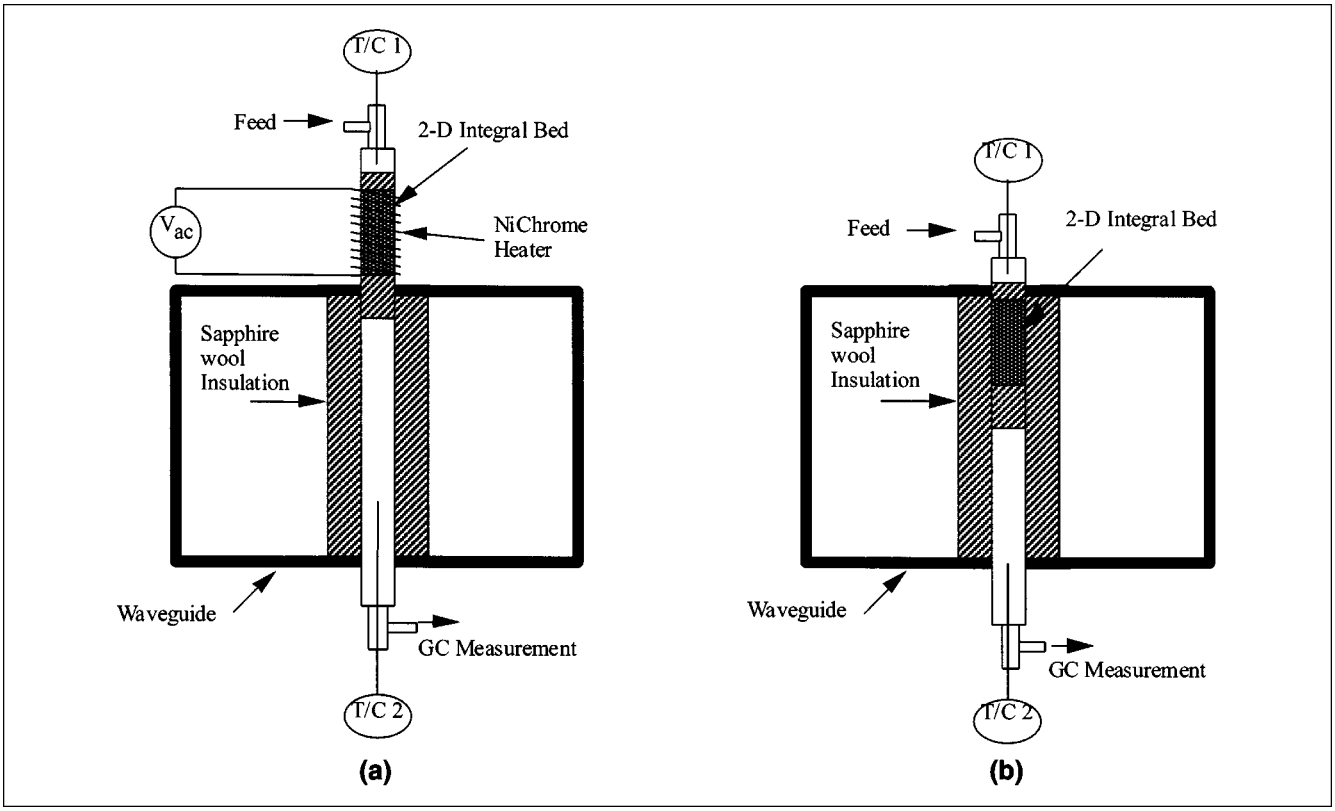


**Figure 5. Reactor configuration for 2-D integral-bed experiment.**

This configuration was heated (a) conventionally by wire wrapping around reactor tube, or (b) by microwaves. Inlet and exit temperatures were measured. For scale, wave-guide, 9.8 × 4.9 in.; tube diameter, 8 mm.

and added to the measured temperature for the microwave case. To generate comparative data, the reactor was run at a constant power input, such that the conversion was nominally 60%. Several GC measurements were made to insure this condition. The exit temperature, which was quite stable, was observed concurrently with the GC acquisitions.

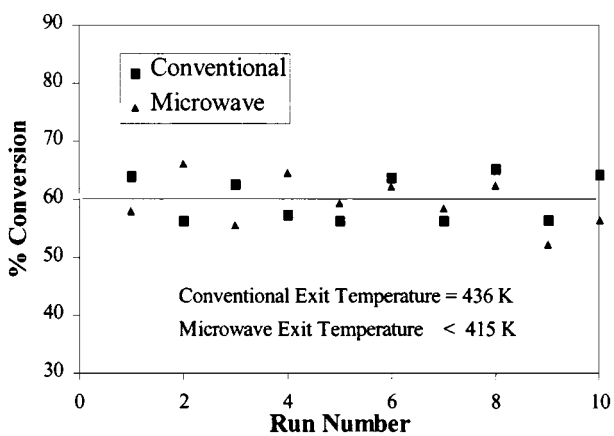


**Figure 6. Ten runs with nominal conversion of 60% for microwave and conventional cases.**

Exit temperature measured in both cases, and found to be less in the microwave case. Result indicates energy required for conversion less for microwave case, as suggested by results of 2-D model.

Figure 6 shows these exit temperatures at 60% conversion and an inlet temperature of 575 K for both the microwave-heated and the conventionally heated case. An exit temperature of > 21°C degrees lower resulted in the microwave case. (The previous paragraph tells how the authors estimated the error incurred by the relocation of the thermocouple relative to the insulation.) The upper error margin for the microwave case is conservatively reported.

An energy balance will show the significance of the lower exit temperature

$$Q_{\text{in}} - Q_{\text{out}} + Q_{mw} = Q_{rxn} \tag{10}$$

for the microwave case, and for the conventional case

$$Q_{\text{in}} - Q_{\text{out}} + Q_{\text{con}} = Q_{rxn} \tag{11}$$

where $Q_{\text{in}}$ is the heat supplied to the reactor by convection, $Q_{\text{out}}$ is the heat leaving the reactor by convection, $Q_{mw}$ is the energy supplied by microwaves, $Q_{\text{con}}$ is the conventionally supplied energy, and $Q_{rxn}$ the heat consumed by the endothermic reaction. Identical conversion in the two cases leads to the identical energy consumption by the two endothermic reactions

$$Q_{\text{in}} - Q_{\text{out},mw} + Q_{mw} = Q_{rxn} = Q_{\text{in}} - Q_{\text{out,con}} + Q_{\text{con}} \quad (12a)$$

The $Q_{\text{in}}$ cancels if the inlet conditions are identical

$$-Q_{\text{out},mw} + Q_{mw} = -Q_{\text{out,con}} + Q_{\text{con}} \quad (12b)$$

The following substitutions are appropriate

$$\begin{aligned} Q_{\text{out,con}} &= \dot{m}C_p T_{\text{out,con}} \\ Q_{\text{out},mw} &= \dot{m}C_p T_{\text{out},mw} \end{aligned} \quad (13)$$

$T_{\text{out},mw}$ and $T_{\text{out,con}}$ are the average exit temperatures. Making these substitutions into the energy balance results in

$$-\dot{m}C_p T_{\text{out},mw} + Q_{mw} = -\dot{m}C_p T_{\text{out,con}} + Q_{\text{con}} \quad (14)$$

$$\dot{m}C_p(T_{\text{out,con}} - T_{\text{out},mw}) = Q_{\text{con}} - Q_{mw} \quad (15)$$

Equation 15 shows that the difference between the exit temperatures in the two reactors, scaled by $\dot{m}C_p$, is a direct indicator of the difference in energy required for each process. The authors observed $T_{\text{out,con}} > T_{\text{out},mw}$, and therefore, results reveal

$$Q_{mw} < Q_{\text{con}} \quad (16)$$

These results support our hypothesis that the homogeneous nature of microwave heating can be beneficial. The following theoretical model supports the observations, and aids understanding the nature of the differences between the two modes of heating.

## 2-D, Nonadiabatic Packed-Bed Model

The mathematical model of a microwave-heated, 2-D tubular packed-bed reactor differs little from a conventionally-heated reactor and many references analyze this latter type. Feyo de Azevado et al. (1990) and Lemcoff et al. (1990) review much of this literature.

This research hypothesizes that the conventional energy required $Q_{con}$ exceeds the microwave energy required $Q_{mw}$ to achieve a given conversion $X$, when all other conditions are identical. To test this hypothesis, a cylindrical system was chosen, where radial heat-transfer effects were not negligible, as a theoretical test platform. Hill (1997) presented a diagram of an identical system. Our model accounts for axial heat and mass transport by convection, radial heat transport by conduction and radial mass transport by diffusion. The model includes an endothermic reaction heat−sink term and the temperature-dependent reactant sink term, making the equations coupled and nonlinear. This complexity precludes an analytical solution, but the general behavior can be illustrated using a numerical approximation. Several simplifications were made to illuminate the fundamental differences between the microwave and conventionally heated reactors. The model was derived subject to the following assumptions:

(1) Axial dispersion is negligible: $D\dfrac{\partial^2 C}{\partial z^2} = \alpha\dfrac{\partial^2 T}{\partial z^2} \approx 0$.

(2) Intra- and interparticle gradients were neglected.

(3) The packed bed was assumed to be pseudohomogeneous in that transport properties, such as an effective thermal conductivity and radial diffusivity, could be applied.

(4) Plug flow.

(5) Negligible pressure drop.

(6) No volume change on reaction.

(7) Constant properties such as gas density and heat capacity.

These assumptions lead to the following equations

$$u_s \rho_g C_p \frac{\partial T}{\partial z} = k\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \rho_B \Delta H_{rxn} r_{\text{MeOH}} + Q_{mw}$$

$$u_s \frac{\partial C}{\partial z} = \epsilon Der\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) + \rho_B r_{\text{MeOH}}, \quad (17)$$

where

$$\begin{aligned} r_{\text{MeOH}} &= -A\exp\left(\frac{-E_a}{RT}\right)C_M \\ C &= C(r,z) \\ T &= T(r,z) \end{aligned} \quad (18)$$

In these equations, $C_M$ is the concentration of methanol, $\rho_B$ the catalyst bed density, $\rho_g$ is the gas density, $k$ is the radial thermal conductivity, $u_s$ is the gas velocity, $C_p$ is the gas heat capacity, and $\epsilon$ is the void fraction of the bed. As with the previous model, $\Delta H_{rxn}$ is the heat of reaction and $Q_{mw}$ is the heat supplied by the microwave. The equations were made dimensionless using the following definitions

$$C^* = \frac{C_M}{C_0}; \quad T^* = \frac{T}{T_0}; \quad r^* \frac{r}{R}; \quad z^* = \frac{z}{L} \quad (19)$$

where $R$ and $L$ are the radius and length of the reactor, respectively. Making the appropriate substitutions and rearranging the physical parameters to make equations dimensionless yields

$$\frac{\partial C^*}{\partial z^*} = \frac{\epsilon D_{er} L}{u_s R^2}\left(\frac{\partial^2 C^*}{\partial r^{*2}} + \frac{1}{r^*}\frac{\partial C^*}{\partial r^*}\right) + \frac{\rho_B r_{\text{MeOH}} L}{u_s C_0}$$

$$\frac{\partial T^*}{\partial z^*} = \frac{Lk}{R^2 u_s \rho_g C_p}\left(\frac{\partial^2 T^*}{\partial r^{*2}} + \frac{1}{r^*}\frac{\partial T^*}{\partial r^*}\right) + \frac{\rho_B \Delta H r_{\text{MeOH}} L}{u_s \rho_g C_p T_0} + \frac{Q_{mw} L}{u_s \rho_g C_p T_0} \quad (20)$$

The dimensionless parameter groupings have familiar definitions

$$\begin{aligned} \frac{\partial C^*}{\partial z^*} &= \frac{1}{Pe_M}\left(\frac{1}{r^*}\frac{\partial}{\partial r^*} r^* \frac{\partial C^*}{\partial r^*}\right) + Da_{\text{I}} \\ \frac{\partial T^*}{\partial z^*} &= \frac{1}{Pe_H}\left(\frac{1}{r^*}\frac{\partial}{\partial r^*} r^* \frac{\partial T^*}{\partial r^*}\right) + Da_{\text{III}} + MW \end{aligned} \quad (21)$$

where the dimensionless ratios are

$$Pe_M = \frac{u_s R^2}{\epsilon D_{er} L}; \quad Pe_H = \frac{R^2 u_s \rho_g C_p}{Lk}$$

$$Da_{\mathrm{I}} = \frac{-\rho_B A \exp\left(\frac{-E_a}{RT}\right) C_M R}{u_s C_0};$$

$$Da_{\mathrm{III}} = \frac{-\rho_B \Delta H_{rxn} A \exp\left(\frac{-E_a}{RT}\right) C_M L}{u_s \rho_g C_p T_0}$$

$$MW = \frac{QmwL}{u_s \rho_g C_p T_0} \tag{22}$$

Again, Eqs. 21 are coupled through $Da_{\mathrm{I}}$ and $Da_{\mathrm{III}}$ terms. In addition, the equations are nonlinear in $T$, and require an interactive solution in the $z$ direction. The boundary conditions are

$$\begin{gathered} C^*(0,r^*) = 1 \\ T^*(0,r^*) = 1 \\ \left.\frac{\partial T^*}{\partial r^*}\right|_{r^*=0} = \left.\frac{\partial C^*}{\partial r^*}\right|_{r^*=0} = 0 \\ \left.\frac{\partial C^*}{\partial r^*}\right|_{r^*=R} = 0 \\ \left.\frac{\partial T^*}{\partial r^*}\right|_{r^*=R} = -\frac{qR}{kT_0} \end{gathered} \tag{23}$$

Hanna and Sandall (1995) recommend using a backward Euler method for cases such as chemical reactions when severe stability requirements exist. Following this recommendation, we used a backward Euler method to solve these equations numerically. This approach uses $T^*$ and $C^*$ information from the j (radial) index to calculate $C^*$s and $T^*$s at the j+1 index (one step further in axial distance). The backward Eular method assumes linear behavior of the variables. However, $T^*$ was imbedded in the nonlinear (exponential) reaction term, and small changes between indices produced large errors. To correct this, a predictor–corrector scheme iterated at each index to modify the reaction temperature ($T^*_{rxn}$) until convergence was achieved. The convergence criterion was

$$10^{-3} > \sqrt{\frac{\sum_{i=1}^{N} \left(T^*_{rxn} - T^*_{i,j+1}\right)^2}{N-2}} \tag{24}$$

Perry's (1998) work presents complete details of the numerical approach for solving this model.

The goal was to determine if the addition of volumetric microwave heating would sufficiently lessen the severity of the radial temperature profiles leading to more efficient reactant conversion. That is, it was necessary to determine that the addition of microwave heating consumes less energy to produce the same conversion. The goal was to discover whether conditions exist that require less energy to induce the same conversion when microwave, rather than conventionally delivered energy, is used. Figures 7–10 show the modeling results that were generated using numerical values given in Table 2. This table also summarizes the "base case" dimensionless parameters used to generate the plots of normalized temperature and methanol concentration (Figures 7 and 8).

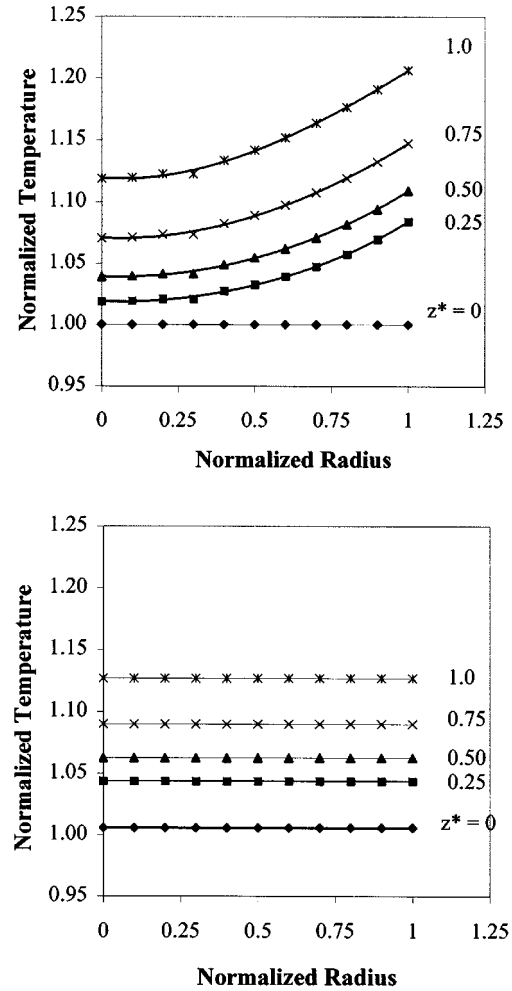


**Figure 7. Temperature profiles from $r^* = 0$ to $R$ (c.l. is to the left) for base case: (top) reactor is heated conventionally; (bottom) by microwaves.**

Conversion is 80% in both cases.

These figures illuminate the marked differences between the two modes of heating. In the conventional case, heat transfer occurs from the walls into the gas stream and through the packed bed. Significant radial profiles will develop if the potential rate of energy consumption by the endothermic reaction exceeds the rate of axial heat transport. The dimensionless parameters in Table 2 characterize these relative rates. $Pe$ (mass or heat) indicates the relative importance of axial convection to radial diffusion. $Da_{\mathrm{I}}$ is the ratio of mass consumption by reaction to the axially-convective transfer of mass. Similarly, $Da_{\mathrm{III}}$ represents the competition of heat consumption by reaction of the axially-conductive heat transfer. Finally, the microwave number is a ratio of heat dissipation by microwaves to the rate of axial heat transfer.

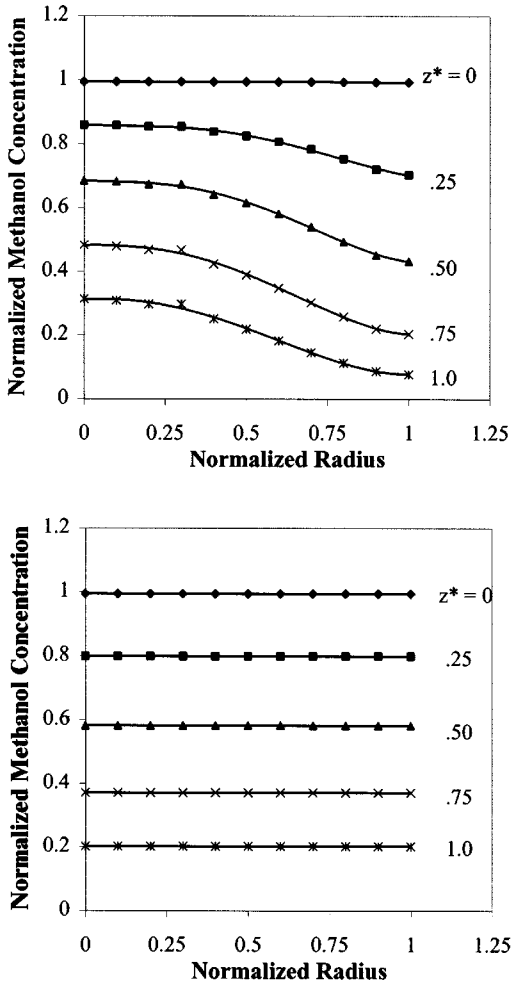


**Figure 8. Concentration profiles from $r^* = 0$ to $R$ (c.l. is to the left) for base case: (top) reactor is heated conventionally; (bottom) by microwaves.**

Conversion is 80% in both cases.

As stated in Table 2, the base case was estimated a $Pe_H$ of 0.2. This value, being an indicator of the relative importance of axial heat transfer vs. radial heat transfer, shows that radial heat transfer was significant. The moderate profiles in Figure 7a reflect this observation. $Da_{\mathrm{III}}$'s magnitude is more difficult to calculate. This parameter varies exponentially with temperature and linearly with concentration; therefore, the value can drastically change throughout the reactor. Radial profiles develop for concentration here as well, because of the elevated temperatures at the walls. When the local rate of reaction at the walls exceeds the radial diffusion rate, the profiles will develop as shown in Figure 8a.

The model for the microwave-heated reactor shows no radial variation for either heat or mass, as shown in Figures 7b and 8b. As suggested by the original hypothesis, injecting heat by microwaves does not rely on conduction or convection. The energy dissipates homogeneously as the chemical reaction consumes it. Axial variations exist because consumption of heat by reaction varies along the reactor length as temperature and concentration change, while energy dissipated from microwave heating remains constant.

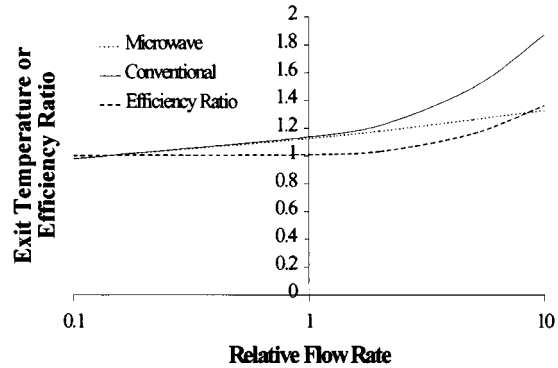


**Figure 9. Trend of exit temperature vs. relative flow rate for both conventional and microwave cases at 80% conversion.**

Temperatures normalized to exit temperature of microwave base case. Ratio of efficiency of the two processes is also indicated.

Figure 9 summarizes the trend for exit temperature vs. flow rates relative to the base case of the microwave model. The microwave exit temperature increases linearly as shown by the dotted line, while the conventional exit temperature increases in a nonlinear fashion. (This linear behavior of the microwave exit temperature must eventually fail as the conversion approaches zero or as the relative flow rate becomes very large. The linear behavior exists merely over the range studied.)

Also in Figure 9, the long-dash line shows the ratio of the microwave efficiency to the conventional efficiency. Efficiency was defined as the ratio of energy required by the reaction to the energy supplied by the source, conventional or microwave

$$\eta = \frac{Q_{rxn}}{Q_s} \tag{25}$$

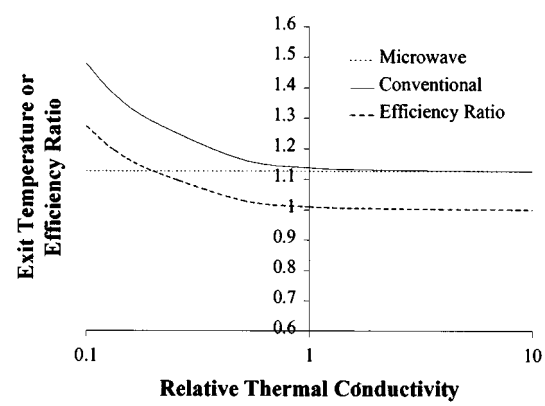


**Figure 10. Trend of exit temperature vs. effective radial thermal conductivity for both conventional and microwave cases.**

Temperatures normalized to exit temperature of microwave base case. The ratio of the efficiency of the two processes is also indicated.

**Table 2. Numerical Values Used in 2-D Model Calculations**

| Parameter | Value | Units | Comments |
|---|---|---|---|
| Eff. thermal conductivity, $k$ | 1.0 | W/(m·K) | (Froment and Bischoff, 1990) |
| Preexponential factor, $A$ | $3.01\times10^5$ | $m^3/(s\cdot kg)$ | (Brown, 1996) |
| Initial concentration, $C_0$ | 12.2 | $mol/m^3$ | 50% molar ratio |
| Initial temperature, $T_0$ | 575 | K | Approaching upper limit for catalyst |
| Catalyst bed density, $\rho_b$ | 1000 | $kg/m^3$ | (Brown, 1996) |
| Gas density, $\rho_g$ | 0.75 | $kg/m^3$ | Estimated using ideal gas law |
| Particle diameter, $d_p$ | $150\times10^{-6}$ | m | Measured |
| Bed radius, $R$ | $4\times10^{-3}$ | m | Known |
| Bed length, $L$ | $15\times10^{-3}$ | m | Known |
| Average gas velocity, $u_s$ | 0.2 | m/s | Measured in experiment |
| Activation energy, $E_a$ | 84,100.0 | J/mol | (Amphlett et al., 1994; Brown, 1996) |
| Heat of reaction, $\Delta H_{rxn}$ | −60,000 | J/mol | (Brown, 1996) |
| Heat capacity, $C_p$ | 35.0 | J/(mol·K) | (Brown, 1996) |
| Mass Peclet no., $Pe_M$ | 23.0 | None | (Froment and Bischoff, 1990) |
| Heat Peclet no., $Pe_H$ | 0.2 | None | Estimated from values in this table |
| Mass Damköhler no., $Da_{\mathrm{I}}$ | $6.3r_{\mathrm{MeOH}}$ | None | Estimated from values in this table |
| Heat Damköhler no., $Da_{\mathrm{III}}$ | $10r_{\mathrm{MeOH}}$ | None | Estimated from values in this table |

Substituting the energy balance from Eq. 11 or 12 for $Q_s = Q_{mw}$ or $Q_{\mathrm{con}}$ gives

$$\eta = \frac{Q_{rxn}}{Q_{rxn}+Q_{\mathrm{out}}-Q_{\mathrm{in}}} = \frac{1}{1+(Q_{\mathrm{out}}-Q_{\mathrm{in}})/Q_{rxn}} = \frac{1}{1+\dfrac{\dot{m}C_pT_0(T^*_{\mathrm{out}}-1)}{\Delta H_{rxn}XC_0\upsilon}} \tag{26}$$

Substituting for the constants and taking the ratio of the microwave efficiency to the conventional efficiency yields

$$\frac{\eta_{mw}}{\eta_{\mathrm{con}}} = \frac{1+0.9(T^*_{\mathrm{out,con}}-1)}{1+0.9(T^*_{\mathrm{out},mw}-1)} \tag{27}$$

This expression was used to calculate the curve labeled "efficiency ratio" in Figure 9. The model demonstrates that the microwave process becomes more efficient as the flow rate increases relative to the base case.

Figure 10 summarizes the trend for exit temperature vs. thermal conductivity relative to the base case of the microwave model. The microwave exit temperature remains constant as shown by the dotted line, because the homogeneous nature of microwave energy does not rely on radial heat transfer. Conversely, the conventional exit temperature increases in a nonlinear fashion. The long-dash line shows the ratio of the microwave efficiency to the conventional efficiency. Equation 27 was also used to calculate the curve labeled "efficiency ratio" in Figure 10.

The model made evident that microwave heating was more efficient than conventional radial heating when applied to a tubular packed-bed flow reactor in which an endothermic reaction occurs. The authors observed increasing relative efficiency for the microwave case as radial heat-transfer demands became more severe (decreasing radial thermal conductivity and increasing flow rates). Any parameter change resulting in an increase in the $Pe_h$ will result in an increased relative efficiency between the two systems. Lastly, MRR is significantly less endothermic than other reforming reactions. For example, Table 1 indicates the endothermic reforming of methane requires 3.75 times the heat input per mol reacted than does the MRR. In such cases, we expect even greater relative efficiency.

## Discussion

Two models of the endothermic MRR have been presented: (1) A 1-D spherical model; (2) A 2-D plug-flow model. Both models were assumed to obey a kinetic expression determined experimentally by Amphlett et al. (1994). The results of Figure 4 show this to be a reasonable assumption. The theoretical 2-D study of the system used several approximations to avoid obscuring basic behavior by the complexity of a multiple parameter rigorous model.

These models assumed spatial uniformity of microwave absorption, both on the micro and macro scale. On the micro scale, the absorption of microwave energy in a catalyst will vary according to the local composition of the material. However, the energy transfer caused by microwave absorption on small length scales is rapid and probably does not lead to a significant temperature rise (Perry et al., 1997a), and, therefore, does not affect the rate of reaction or adsorption and desorption effects. This is confirmed by the comparative kinetic study detailed earlier in this work.

Spatial uniformity of microwave absorption on the macro scale means that the microwave energy density was uniform across the experimental reactor. The microwave energy density forms a sinusoidal distribution in 2-D, and is uniform along the flow axis of the reactor. Evaluation of the energy−density distribution throughout the portion of this wave within the experimental reactor showed a maximum deviation from the average value of 2%. This deviation was judged inconsequential.

The 2-D model assumed a reasonable effective radial diffusion coefficient and a reasonable effective radial thermal conductivity. A more rigorous model might consider transport processes in both the solid and fluid media, but the parameters in such a model remain subject to significant uncertainties. A constant radial effective thermal conductivity was assumed, disregarding the effects of fluid velocity on this parameter. Also, the effects of molar volume change on this

system were disregarded. While these phenomena might affect the behavior, their influence is minor compared with the observed results.

In the single catalyst pellet model, the influence of volume change is unclear. Thus, in this case, the model may over- or underestimate the increase in reaction rate. Finally, in both the 1- and 2-D models, the effect of external gradients, both concentration and temperature were disregarded. Inclusion of these effects will surely influence the behavior of the model. Nevertheless, in spite of simplifying assumptions, these models reveal valuable qualitative information about how microwaves affect endothermic reactions.

Originally, it was hypothesized that a reactor's performance in which radial heat-transfer effects were not negligible would show some form of improvement. The experimental and theoretical results both showed that the exit temperature of the microwave reactor was lower than the exit temperature of the conventional analog. The energy balance resulting in Eq. 16 showed that less energy was required from the source to achieve the same conversion. In addition, the data shown in the Arrhenius plot of Figure 4 demonstrates that the microwaves do not affect the basic reaction mechanism. The sum of this evidence strongly suggests that heat-transfer effects caused this increased efficiency.

In the conventional case, inefficiency arises from the heat leaving the reactor before being consumed by the reaction. More concisely, the low surface area wall heating process preferentially heats the gas oversupplying heat to the reaction. Conversely, the efficiency of the microwave reactor relies on heat dissipation over a high surface area near where the reaction occurs. The microwave process heats the catalyst first, and subsequently heats the gas. This sequence of heat transfer more effectively supplies heat to the reaction.

In this article, the chosen system and conditions result in a $Pe_H$ of 0.2. Figures 9 and 10 show the improvement in relative efficiency when the radial thermal conductivity decreased or the axial flow rate increased. Both parameters influence $Pe_H$ in a linear way, as does the reactor feed rate. The general conclusion is that relative efficiency will increase with increasing $Pe_H$, or as demands on radial heat transfer become more severe. The performance improvement could be dramatic when using microwave energy for more typical reactors.

This is an important conclusion relating to the required size of a catalytic reactor for an endothermic reaction. Reactor size is frequently important in many situations, for example, onboard processors creating a hydrogen-rich feed for an automotive fuel cell. Increases productivity on both the pellet level and on the reactor level decreases the amount of catalyst required. This has positive benefits in terms of cost, weight, size, and energy required for heating.

## Conclusion

Endothermic catalytic reaction systems frequently suffer severely curved temperature and concentration profiles within the reactor, hot spots along reactor walls, and spatial requirements for external heaters. Originally it was hypothesized that the homogeneous nature of microwave energy dissipation could alleviate such heat-transfer difficulties by injecting heat homogeneously into the reactor. To eliminate the possibilities of anomalous reaction behavior in the microwave case, a comparative kinetic study was first conducted. In both the microwave and conventional cases, the kinetics were identical, and in reasonable agreement with values reported in the literature.

The first test of the hypothesis was solving the 1-D, spherical, coupled heat- and mass-transfer equations that represented a single catalyst pellet within which the MRR occurred. The modeling results of the conventionally-heated case were compared with the microwave-heated case. This analysis showed microwaves imposed a fairly uniform temperature profile across the pellet. The resulting overall reaction rate (including intrapellet mass-transfer effects) increased by approximately a factor of 2 over the conventional case at the upper operating temperature of the catalyst.

The 2-D experiment compared the behavior of a tubular flow reactor heated either radially or by microwaves. All other aspects of the two systems were identical. Results of the experiment, in which radial transport effects were not negligible, gave a lower effluent temperature in the microwave case than in the conventional case. A subsequent energy balance showed that the energy supplied by the microwave was less than the energy supplied conventionally (radially) to achieve the same conversion.

The 2-D model solution reveals this result occurs because the microwave reactor essentially eliminated radial heat-transfer effects. Thus, the effect mitigated severely curved temperature and concentration profiles, and hot spots typically found in endothermic reactor designs. This important result supports the authors' original hypothesis.

To conclude, it was found that microwave heating of an endothermic reaction, on the pellet scale and the reactor scale, dissipates the energy homogeneously. It is consumed by the endothermic reaction without the spatial gradients inherent in conductive and convective heat transport.

## Notation

$A$ = preexponential factor
$A$ = surface area, $m^2$
$C$ = concentration, $mol/m^3$
$C^*$ = dimensionless concentration
$C_0$ = initial concentration, $mol/m^3$
$C_0$ = reactor inlet concentration, $mol/m^3$
$C_v, C_p$ = heat capacity, $J/(kg \cdot mol \cdot K)$
$D$ = diffusion coefficient, $m^2/s$
$Da_{\mathrm{I}}$ = mass Damköhler number
$Da_{\mathrm{III}}$ = heat convection Damköhler number
$Da_{\mathrm{IV}}$ = heat conduction Damköhler number
$R$ = reactor or pellet radius, m
$R_g$ = universal gas constant, $J/(kg \cdot mol \cdot K)$
$E$ = electric field, V/m
$E_a$ = activation energy, J/mol
$f$ = electric field frequency, Hz
$\Delta H_{rxn}$ = heat of reaction, J/mol
$i, j$ = mesh indices
$k$ = reaction rate constant, l/s
$k$ = effective thermal conductivity, $W/(m \cdot K)$
$L$ = packed-bed length, m
$M$ = molecular weight, $kg/kg \cdot mol$
$MW$ = dimensionless microwave source term
$N$ = number of radial nodes
$P$ = pressure, $kg/(m \cdot s^2)$
$Pe_H$ = heat Peclet number
$Pe_M$ = mass Peclet number
$q$ = heat flux, $W/m^2$

$Q$ = power, W/m$^3$
$r^*$ = dimensionless radius
$r$ = reaction rate, mol/(kg·s)
$r_{MeOH}$ = rate of methanol consumption by reaction, mol/(kg·s)
$R$ = bed radius
$T$ = average temperature, K
$T$ = temperature, K
$T_0$ = initial temperature, K
$T_0$ = reactor inlet temperature, K
$T^*$ = dimensionless temperature
$u_s$ = average gas velocity, m/s
$X$ = conversion of methanol
$z^*$ = dimensionless axial coordinate

### *Greek letters*

$\alpha$ = thermal diffusivity, m$^2$/s
$\alpha$, $\beta$, $\gamma$ = tridiagonal matrix elements, m$^{-1}$
$\epsilon$ = bed void fraction
$\epsilon''$ = dielectric loss
$\epsilon_0$ = permittivity of free space ($8.8\times10^{-12}$), F/m
$\epsilon_m$ = dielectric permittivity of alumina support
$\eta$ = thermal efficiency
$\kappa$ = parameter for volume change on reaction
$\lambda_e$ = electron mean free path, m
$\lambda_g$ = gas mean free path, m
$\rho_b$ = catalyst-bed density, kg/m$^3$
$\rho_g$ = gas density, kg/m$^3$
$\sigma$ = conductivity, $(\Omega\cdot m)^{-1}$
$\tau$ = relaxation time, s
$\upsilon$ = volumetric flow rate, m$^3$/s
$\upsilon$ = volume fraction of conducting phase
$\Phi$ = general dimensionless dependent variable
$\phi$ = Thiele modulus
$\Psi$ = generalized dimensionless mass or heat flux
$\omega$ = microwave angular frequency, rad/s

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