LEARNING THE FUNDAMENTALS OF KINETICS AND REACTION ENGINEERING

With the Catalytic Oxidation of Methane

Viktor J. Cybulskis, P.E., Andrew D. Smeltz, Yury Zvinevich, Rajamani Gounder, W. Nicholas Delgass, and Fabio H. Ribeiro

School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907-2100 USA

SUPPLEMENTAL INFORMATION

1 Corresponding author. 
E-mail address: fabio@purdue.edu (F.H. Ribeiro).
FIGURES

Figure S1. Design for methane oxidation reactor. Material of construction is borosilicate glass.

Figure S2. Reactor inlet/outlet spacing template, which consists of two, ¼” Swagelok Ultra-Torr fittings held in place with a clamp and separated by a distance of 1-5/8” (C – C).
Figure S3. Additional views of the self-contained laboratory catalytic reactor unit showing: (a) details of furnace controls on bottom, CO₂ product analyzer on top, and recycle gas pump in back; (b) details of gas controls in front and furnace in back.
PLUG FLOW REACTOR (PFR) MODEL WITH WATER INHIBITION

The rate expression for the packed-bed PFR reactor is:

\[ r = q C_{CH_4,0} \frac{dX}{dW} = C_{CH_4,0} \frac{dX}{d\tau}, \text{ for } \tau = \frac{W}{q} \quad \text{(i)} \]

where \( r \) is the rate ((mole CO\(_2\)) (gcat\(^{-1}\)) s\(^{-1}\)); \( q \) is the volumetric flow rate (liters s\(^{-1}\)); \( X \) is the conversion of methane; \( W \) is the mass of catalyst (grams); and \( C_{CH_4,0} \) is the initial concentration of methane (moles liter\(^{-1}\)).

Substitution of the power law rate expression (equation 5) into equation i with \( \alpha = 1, \beta = \gamma = 0, \text{ and } \delta = -1 \), where \( k_{app} \) is the apparent rate constant; \( \alpha, \beta, \gamma, \text{ and } \delta \) are the apparent reaction orders with respect to concentrations of CH\(_4\), O\(_2\), CO\(_2\), and H\(_2\)O, respectively, yields equation ii:

\[ C_{CH_4,0} \frac{dX}{d\tau} = k_{app} C_{CH_4}^{\alpha} C_{H_2O}^{-\delta} \quad \text{(ii)} \]

The solution of the first-order ordinary differential equation for the apparent rate constant with \( C_{CH_4} = C_{CH_4,0} (1 - X) \approx C_{CH_4,0} \) and \( C_{H_2O} = 2C_{CH_4,0} X \) is given as follows:

\[ k_{app} = \frac{X}{\tau} \int_0^X \frac{dX}{C_{CH_4} C_{H_2O}^{-1}} \quad \text{(iii)} \]

\[ = \frac{C_{CH_4,0} X}{\tau} \int_0^{X} \frac{dX}{(2C_{CH_4,0} X)^{-1}} \quad \text{(iv)} \]

\[ = \frac{2C_{CH_4,0} X}{\tau} \int_0^{X} X dX \quad \text{(v)} \]

\[ k_{app} = \frac{C_{CH_4,0}}{\tau} X^2 \quad \text{(vi)} \]
EXPERIMENTAL PROCEDURE

Introduction

In this laboratory experiment you will carry out the methane combustion reaction in PFR, CSTR (i.e. recycle) and batch modes. The objective is to familiarize you with the three ideal reactors we discussed in class. You will measure and compare the reaction rate (moles CO\text{2} produced per gram of catalyst per second) at the same reaction conditions (concentration and temperature) for the three reactors. Pay attention to the detailed mode of operation of each reactor. If the rates of reaction are not the same for the three reactors, discuss why. If you need to make adjustments to the rate as a function of temperature, use an apparent activation energy of 82 kJ mol\textsuperscript{-1}.

Experimental methods

Figure S4 shows a schematic of the methane combustion reactor \((V \approx 0.32 \text{ liters})\). This apparatus is designed to operate in the three main reactor modes: batch, CSTR (i.e. recycle) and PFR. The reactants (CH\text{4}, O\text{2}) are fed from a tank consisting of a mixture of either 1\% or 2.5\% CH\text{4} with balance air. A second tank of N\text{2} provides an inert for varying the CH\text{4} concentration in the reactor. Two rotameters with valves V\text{a} and V\text{b} control the flow rate of each gas (see Figure. S5). V1 is a shut off valve, which can shut off gas to the reactor (required for batch mode). Gas from V1 combines with recycled gas from V2 (if open) and continues to either the reactor or bypasses it depending on the positions of V5 and V6. A pressure relief valve is present to ensure that pressure in the reactor never exceeds 4 – 5 psig. Once the gas passes through the reactor, it can be exhausted via V4 or recycled back to the reactor via a metal bellows gas pump if V3 and V2 are open. The pump is fitted with
a bypass valve, which allows control of the circulation flow rate. The reactor contains ~0.25 gram of a 0.5% Pd/Al₂O₃ catalyst with a thermocouple in direct contact with the catalyst. The clamshell furnace provides the necessary reactor heating and is connected to the temperature controller. The reactor (or catalyst) temperature is displayed on a separate temperature reader. A CO₂ analyzer takes a slipstream of the effluent gas mixture and analyzes the CO₂ concentration by using a nondestructive, IR-based sensor, and then returns the gas to the process stream.

Figure S4: Schematic of the catalytic reaction unit.
Figure S5: Rotameter calibration curves for N₂ and 2.5% CH₄/Air mixture. Gas delivery pressure is 50 psig.

Note: The reaction temperature (operating temperature of the reactor) can be adjusted by adjusting the temperature of the furnace (the set of controls on the left side of the unit). Set this temperature approximately 25 – 35 °C lower than the desired operating temperature. The furnace temperature is typically 25 – 35 °C lower than the reactor temperature because the furnace thermocouple and the thermocouple inside of the reactor are in different locations. The temperature inside of the reactor will be displayed on the temperature readout above and to the right of the ON/OFF switch. Do not attempt to modify the reactor temperature by operating the buttons on this temperature readout. The readout is only a temperature indicator; it is not a temperature controller.
**Procedures**

*Important Notes:*

1) The CO₂ detector will automatically perform a re-zeroing operation every 40 min if the user does not initiate one manually. It does operation by passing the inlet gas through a soda-lime bed, which scrubs any CO₂ from the gas stream before entering the analyzer, and then finally back into the process stream.

In **PFR mode**, the product gases that are analyzed are exhausted immediately with the remaining process gas so the CO₂ detector will not compromise the experimental data if in calibration mode (as opposed to CSTR/batch mode). **If the unit initiates a re-zeroing operation in PFR mode, wait until it is complete and the instrument readout has stabilized before taking a measurement.** Before taking a reading, always re-zero the detector and wait for about 2 minutes after the zeroing procedure has ended so that the reading can stabilize.

In **CSTR and batch modes**, it is necessary to take a more active role to prevent the detector from scrubbing the CO₂ from the circulating process stream. Remember to perform the re-zeroing step before taking any data point in CSTR and/or batch reactor mode. **Re-zeroing can be performed manually by pushing “N” on the keypad to bring up the menu screen. Then, push “1” on the keypad and the unit will re-zero.**

2) When taking measurements, wait for about **5 – 10 minutes** for the system to reach steady state. Then collect the readings for temperature (from reactor temperature...
readout) and corresponding instantaneous CO\textsubscript{2} concentration (from the CO\textsubscript{2} detector, in ppm\textsubscript{v}) for at least \textbf{3 min at 30 s intervals}. Use the average of these readings as your data point to eliminate the problem of instrumental noise.

The furnace, CO\textsubscript{2} detector, and catalyst bed should be warmed up and stabilized before performing the experiments. The furnace thermocouple is typically 25 – 35 °C lower than the reactor thermocouple (since furnace thermocouple and the thermocouple inside the reactor are at different locations and experience different gas flow conditions). You are will measure the rate of reaction in the \textbf{following sequence: PFR, CSTR and Batch modes}.

\textbf{Suggested initial reaction conditions:}

- Furnace temperature: 215 °C
- Reactor temperature: 250±5 °C
- CH\textsubscript{4} feed concentration (CH\textsubscript{4}/air + N\textsubscript{2}): 0.5 – 2%
- Total flow rate (CH\textsubscript{4}/air + N\textsubscript{2}): 70 – 160 ml min\textsuperscript{-1}

\textbf{PFR mode}

In PFR mode, the reactants make a single pass through the catalyst bed before reaching the CO\textsubscript{2} analyzer and the exhaust. Since the goal is to make rate measurements, which then can be analyzed to determine the intrinsic kinetic parameters, the reactor should be operated in the differential conversion regime such that the difference between inlet and outlet concentrations can be directly related to the reaction rate. In the differential regime,
only a few percent (<10%) conversion of methane is obtained. We begin by assuming that
differential conditions can be achieved. However, during the analysis, we will find that
inhibition of the rate by the water product requires a more detailed analysis to obtain the
kinetic parameters. To set up the reactor PFR mode:

1) **Open** valves V1, V4 and **close** valves V2, V3. The recycle pump should be **OFF**.

2) The reactor bypass valves **V5** and **V6** should be set to **reactor**.

3) Adjust Vₐ and V₋ to the desired flow rates and feed composition.

4) The CO₂ detector will report the outlet mixing ratio of CO₂ in ppmv (10,000 ppm corresponds to 1%). Record [CO₂].

5) From the CO₂ concentration, calculate the CH₄ conversion.

6) If the conversion is between **4 – 6%**, **record the reactor temperature**, CH₄/Air, N₂ **flow rate** for at least **3 min at 30 s intervals**. From the data, calculate the rate of the reaction in PFR mode. If the conversion is too high or too low, try to adjust the inlet flow rate (adjusting Vₐ and V₋) or reactor temperature to reach the desired methane conversion (within 4 – 6%).

*Rate of reaction (PFR):*

In the differential regime (*X* < 0.1) with water inhibition ignored, we can assume that the
concentration of reactants throughout the reactor is uniform and therefore the reactor is
essentially a differential slice of a PFR. Therefore, we conveniently calculate the rate of
combustion by using the following:

\[
r = \frac{q\left(C_{CH₄,0} - C_{CH₄}\right)}{W} = \frac{qC_{CO₂}}{W}
\]

(vii)
Laboratory

where $r$ is the rate of methane combustion (($\text{mole CH}_4$) (g$_{\text{cat}}^{-1}$) s$^{-1}$); $C_i$ is the concentration of species $i$ (moles liter$^{-1}$); $q$ is the volumetric flow rate of gas (liters s$^{-1}$); and $W$ is the mass of the catalyst in the reactor (grams).

**Activation energy measurement (PFR):**

7) **Open** valves V1, V4 and **close** valves V2, V3. The recycle pump should be **OFF**.

8) The reactor bypass valves V5 and V6 should be set to **reactor**.

9) Adjust the reactor temperature to the desired value.

10) Adjust $V_a$ and $V_b$ to the desired flow rates and feed composition. Use the same reaction conditions you found to achieve ~ 5% methane conversion.

11) Let the system stabilize until the reactor temperature is within ±1 °C of the desired value.

12) Wait for an additional 3 – 5 minutes for the methane conversion to stabilize and then record [CO$_2$]. This concentration will be the first data point.

Note. When taking measurements, collect the readings for temperature (from reactor temperature readout) and corresponding instantaneous CO$_2$ concentration (from the CO$_2$ detector, in ppm$_v$) for at least **3 min at 30 s intervals**. Use the average of these readings as your data point to eliminate the problem of instrumental noise.

13) Increase the reactor temperature by 10 – 15 °C. Repeat steps 11 and 12 to collect the second data point.

14) Continue to increase the temperature two more times; record the conversion at each temperature. Optimally, a temperature range of 40 – 50 °C should be
covered with 4 data points. You should randomize the temperatures to reduce systematic error. **The methane conversion should be < 10%.** After the reaction temperature and conversion stabilize, record the [CO₂].

15) If time permits, cool the reactor to the starting temperature and measure the rate to obtain an idea of the catalyst stability.

*Methane reaction order measurement (PFR):*

16) Use the same reaction conditions you found to achieve ~ 5% methane conversion. If the conversion is too high (> 10%), increase the total flow rate or decrease the reactor temperature and vice versa if the conversion is too low (< 1%).

17) Allow 5 min for the system to reach steady state, and then record [CO₂]. **The remainder of the experiment must use the same flow rate and reactor temperature.**

18) Incrementally increase or decrease the methane concentration by using the N₂. Wait 5 min and record [CO₂].

19) Repeat step 18 until 2% CH₄ is reached. A total of four (4) CH₄% concentrations should be measured (i.e. CH₄% should be between 0 – 2%).

20) If time permits, repeat the first data point to obtain an idea of the catalyst stability.
Mass transfer limitations – activation energy measurement (PFR):

A common concern in reactor operation is the effect of transport limitations due to external diffusion from the gas to and from the catalyst particle, as well as transport limitations due to internal diffusion throughout the catalyst particle to and from the surface reaction sites within the pores. When the intrinsic reaction rate is faster than the rate of internal or external diffusion, the apparent kinetics calculated from rate measurements will reflect the rate of diffusion, not the rate of reaction for external diffusion limiting and a mixture of diffusion and reaction influence for internal reaction effects.

Measurement of kinetics can indicate the presence of mass transfer limitations. If the measured rate of reaction changes with gas flow rate, then external diffusion is limiting the reaction rate. If the measured rate of reaction changes with catalyst particle size, then internal diffusion is limiting the reaction rate. For example, if a catalyst pellet is crushed into a powder and the reaction rate increases, then the reaction rate on the pelleted catalyst is limited by internal diffusion.

Table S1: Limiting conditions²

<table>
<thead>
<tr>
<th>Limitation</th>
<th>Variation of reaction rate with:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Velocity</td>
<td>Particle size</td>
</tr>
<tr>
<td>External diffusion</td>
<td>$U^{1/2}$</td>
<td>$d_p^{3/2}$</td>
</tr>
<tr>
<td>Internal diffusion</td>
<td>Independent</td>
<td>$d_p^{-1}$</td>
</tr>
<tr>
<td>Surface reaction</td>
<td>Independent</td>
<td>Independent</td>
</tr>
</tbody>
</table>

21) **Open** valves V1, V4 and **close** valves V2, V3. The recycle pump should be **OFF**.

22) The reactor bypass valves V5 and V6 should be set to **reactor**.

23) Adjust the reactor temperature to the desired value.

24) Adjust $V_a$ and $V_b$ to the desired flow rates and feed composition to achieve $\sim 1 \text{ – } 3\%$ methane conversion.

25) Let the system stabilize until the reactor temperature is within $\pm 1 \, ^\circ\text{C}$ of the desired value.

Wait for an additional 3 – 5 minutes for the methane conversion to stabilize and then record [CO$_2$]. This concentration will be the first data point.

26) Increase the reactor temperature by $10 \text{ – } 15 \, ^\circ\text{C}$. Repeat steps 11 and 12 to collect the second data point.

27) Continue to increase the temperature two more times; record the conversion at each temperature. Optimally, a temperature range of $40 \text{ – } 50 \, ^\circ\text{C}$ should be covered with 4 data points. You should randomize the temperatures to reduce systematic error. **The methane conversion should be < 10\%**. After the reaction temperature and conversion stabilize, record the [CO$_2$].

28) If time permits, cool the reactor to the starting temperature and measure the rate to obtain an idea of the catalyst stability.

29) Lastly, exchange data with a group that used a reactor packed with the alternate form of catalyst.
Laboratory

i. Half of the reactors have been loaded with 0.1 g Pd/Al₂O₃ catalyst pellets.

ii. Half of the reactors have been loaded with 0.25 g Pd/Al₂O₃ catalyst powder.

**CSTR mode**

In CSTR (or recycle reactor) mode, the concentration of gases throughout the reactor are approximately the same as in the exhaust. The advantage to running in recycle mode is that we do not have to operate in a differential regime in order to calculate the rate directly from the outlet [CO₂]. However, because the CO₂ detector is calibrated up to 2,000 ppmv, experiments should be designed such that this limit is not reached.

1) **Open** valves V2 and V3. Turn **ON** the circulation pump from the control panel.

2) Check that the reactor bypass valves, V5 and V6, are set to **reactor**.

3) Note that the reactor pressure should not exceed 2 psig (check the pressure gauge). Decrease both flow rates accordingly if this occurs.

4) **Perform the manual “re-zeroing” step for CO₂ detector.**

5) Wait for about 5 minutes and then record [CO₂].

6) From the CO₂ concentration, calculate the CH₄ conversion. The CH₄ conversion you calculate in CSTR mode should be close to what you obtained in the PFR mode.

7) If the conversion is between 4 – 6%, **record the reactor temperature, CH₄/Air, N₂ flow rate** for at least 3 min at 30 s intervals. From the data, calculate the rate of the reaction in CSTR mode. **If the conversion is too high**
or too low, try to adjust the inlet flow rate (via $V_a$ and $V_b$) or reactor temperature to reach the desired methane conversion.

**Rate of reaction (CSTR):**

The rate equation for a CSTR is the same as a PFR in the limit of low conversion:

$$r = \frac{q(C_{\text{CH}_4,0} - C_{\text{CH}_4})}{W} = \frac{qC_{\text{CO}_2}}{W} \quad \text{(viii)}$$

**Activation energy measurement (CSTR):**

8) **Open** valves $V_2$ and $V_3$. Turn **ON** the circulation pump from the control panel.

9) Check that the reactor bypass valves, $V_5$ and $V_6$, are set to **reactor**.

10) Note that the reactor pressure should not exceed 2 psig (check the pressure gauge). Decrease both flow rates accordingly if this occurs.

11) Use the same reaction conditions you found to achieve ~ 5% methane conversion.

12) **Perform the manual “re-zeroing” step for CO$_2$ detector.**

13) Let the system stabilize until the reactor temperature is within ±1 °C of the desired value.

14) Wait for an additional 3 – 5 minutes for the methane conversion to stabilize and then record $[\text{CO}_2]$. This concentration will be the first data point.

Note. When taking measurements, collect the readings for temperature (from reactor temperature readout) and corresponding instantaneous CO$_2$ concentration (from the CO$_2$ detector, in ppmv) for at least **3 min at 30 s intervals**. Use the average of these readings as your data point to eliminate the problem of instrumental noise.
15) Increase the reactor temperature by 10 – 15 °C. Repeat steps 11 and 12 to collect the second data point.

16) Continue to increase the temperature two more times; record the conversion at each temperature. Optimally, a temperature range of 40 – 50 °C should be covered with 4 data points. You should randomize the temperatures to reduce systematic error. **The methane conversion should be < 10%**. After the reaction temperature and conversion stabilize, record the [CO₂].

17) If time permits, cool the reactor to the starting temperature and measure the rate to obtain an idea of the catalyst stability.

*Methane reaction order measurement (CSTR):*

18) Use the same reaction conditions you found to achieve ~ 5% methane conversion. **The remainder of the experiment must use the same flow rate and reactor temperature.**

19) **Open** valves V2 and V3. Turn **ON** the circulation pump from the control panel.

20) Check that the reactor bypass valves, V5 and V6, are set to **reactor**.

21) Note that the reactor pressure should not exceed 2 psig (check the pressure gauge). Decrease both flow rates accordingly if this occurs.

22) **Perform the manual “re-zeroing” step for CO₂ detector.**

23) Allow 5 min for the system to reach steady state, and then record [CO₂].

24) Incrementally increase or decrease the methane concentration by using the N₂. Wait 5 min and record [CO₂].
25) Repeat step 23 until 2% CH₄ is reached. A total of four (4) CH₄% concentrations should be measured (i.e. CH₄% should be between 0 – 2%).

26) If time permits, repeat the first data point to obtain an idea of the catalyst stability.

**Batch mode**

To perform a batch reaction, we first set up the system in the “CSTR mode”, allow the system to come to the “CSTR” steady-state, and then initiate the batch reaction by shutting off the inlet and outlet flow of gas. The concentration of CO₂ is then recorded as a function of time. Once the reaction has reached a CO₂ concentration equivalent to 10% conversion of methane, or ~5 minutes have passed, the reactor is switched back to the PFR mode in the stand-by condition.

1) **Adjust the inlet flow rate (via Vₐ and Vₐ), or reactor temperature to make the methane conversion 0 – 3%**. Record this initial reaction conditions in the reactor: temperature, CH₄/Air flow rate, N₂ flow rate, and [CO₂].

2) **Perform the “re-zeroing” step for CO₂ detector**.

3) **Close valves V₁ and V₄** to initiate the batch reaction. Record [CO₂] at regular intervals (every ~10 – 15 sec) for 4 – 5 minutes.

4) **Open valves V₁ and V₄** to go back to CSTR mode

5) **Turn OFF** the circulation pump from the control panel and close valves V₂ and V₃ to go back to PFR mode.
Rate of reaction (Batch):

The rate equation for a batch system is:

\[ r = \frac{V}{W} \frac{dC_{\text{CO}_2}}{dt} \]  \hspace{1cm} (ix)

where \( V \) is the volume of the reactor (liters).

Measuring the reactor volume (Batch):

In order to determine the reactor volume for equation ix, the system must first be set up in the “CSTR mode”. Allow the system to come to the “CSTR” steady-state, and then initiate the batch reaction by shutting off the inlet and outlet flow of gas. The total conversion of CH\(_4\) is then recorded as a function of time by monitoring the CO\(_2\) concentration. Once the CO\(_2\) concentration reaches a maximum steady-state value, perform the following:

1) **Close** the methane/air mixture valve (\( V_b \)) and **open** the N\(_2\) valve (\( V_a \)).

2) **Open** valves \( V_1 \) and \( V_4 \) to flow N\(_2\) through the reactor in the CSTR mode and record the initial time. Record \([\text{CO}_2]\) at regular intervals (every ~10 – 15 sec) until it reaches zero, or achieves a minimum final, steady-state value.

3) **Record the final time** for the experiment.

The reactor volume can be determined from the dilution of CO\(_2\) by N\(_2\) according to the following equation for a constant volumetric flow \((q = q_0)^3\):

\[ V = q \int_0^\infty [1 - F(t)] \, dt \] \hspace{1cm} (x)

where \( F(t) \) is the fraction of CO\(_2\) that has been in the reactor at time \( t \) or longer.

---

From integration by parts:

\[
\frac{V}{q} = t[1 - F(t)] \bigg|_0^\infty + \int_0^1 t \, dF
\]

(xi)

At \( t = 0 \), \( F(t) = 0 \), and as \( t \to \infty \), \( F(t) \to 1 \). Thus, the volume of the reactor is given by:

\[
V = q \int_0^1 t \, dF
\]

(xii)