Catalytic Oxidation Experiment for Chemical Reaction Engineering

Robert P. Hesketh and C. Stewart Slater
Rowan University
Department of Chemical Engineering
201 Mullica Hill Road
Glassboro, NJ 08028
hesketh@rowan.edu

submitted to:
1999 ASEE Annual Conference
Charlotte, NC
June 1999
Chemical Engineering Division
“Revitalizing Traditional ChE Courses” Session 2313

Abstract

This unique catalytic oxidation experiment is used in a traditional chemical reaction engineering course to demonstrate the principles of

i) reaction rate determination,
ii) reactor design,
iii) heterogeneous catalysis,
iv) heat and mass transfer,
v) environmental application of reactors,
vi) and safety in reactor design.

A major advantage of this experiment is that it does not have costly product and reactant disposal problems. The reactants are propane and air and the products are primarily carbon dioxide and water. These gases are easily disposed of using a common vent system. This experiment is also cost effective. It is inexpensive to run, since the primary reactant is propane and air and the energy source is electricity. The construction of the experiment is relatively simple. The reactor is a stainless steel tube with a section of a honeycomb monolith placed inside the reactor. The tube is heated using an electric furnace. The most expensive item is the gas analysis system starting with a relatively low cost on-line FID detector to a more expensive gas chromatograph or FTIR system.

These experiments have been tested by Rowan engineering students and chemical engineering faculty at a unique hands-on industrially integrated NSF workshop on Novel Process Science and Engineering conducted at Rowan University. We believe that reaction engineering comes alive with students conducting innovative experiments in a laboratory setting. Students are able to see the catalyst; measure gas phase concentrations and flowrates; and use these measurements to examine at least 6 principles of reactor design.

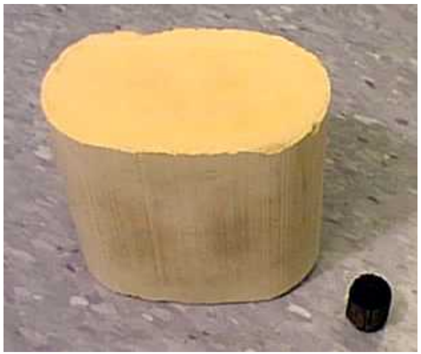

Figure 1: Automotive Catalysts

Introduction

This experiment explores the area of heterogeneous catalysis using the automotive catalytic converter which is the largest market for heterogeneous catalytic reactors. Autocatalysts have been placed in approximately 225 million of the world's 400 million plus automobiles. Nearly everyone with a car less than 10 years old owns a catalytic converter.

A smaller, but growing market is for oxidation catalyst is in the destruction of volatile organic compounds from manufacturing sources. These catalytic reactors are designed using similar principles to the automotive catalysts. Base metals and platinum group metals catalyze the CO oxidation and unburned hydrocarbons as well as reduced NO_x. Large installations have been in place on stationary internal combustion engines, gas turbines. Johnson-Matthey has developed other products such as CONCAT for halogenated hydrocarbon destruction and Honeycat for standby generators and diesel engines working in confined spaces.

Figure 2: Test Catalyst

The catalytic converter was originally introduced to reduce the photochemical smog problems in large cities such as Los Angeles and Tokyo. The automobile was identified as the major producer of smog precursors and a catalytic converter was required. The catalytic converter consists of a honey comb monolith support with a *washcoat* of metals are placed on the surface of the support. A typical monolith is either ceramic or metal and consists of approximately 1 mm square channels 6 inches in length.

The current state-of-the art catalysts is a three-way catalyst in which (1) unburned hydrocarbons and (2) CO are oxidized to CO_2 and H_2O, and NO is reduced to N_2. A brief review of these reactions and reactors is presented by Schmidt (1998). Typical metals used in catalysis are platinum (Pt) and/or Palladium (Pd) to oxidize CO and hydrocarbons and rhodium (Rh) to reduce NO_x. Jacoby (1999) reports that these catalyst are continually being engineered to reduce emissions from cars with cold engines, and meet California's Air standards of low and ultra low emission vehicles. In all new catalyst the reaction rate must be determined. This paper will describe a classic experiment to determine the reaction rate of these catalysts.

Experimental Equipment

In this experiment a small portion of an actual automotive catalyst is used. A typical automotive catalyst is shaped in an ellipse with axes of 5 5/8 and 3 inches. There are 400 square channels per in^2 having a length of 6 inches. The catalyst you will be working with is cylindrical having a diameter of 25 mm length of 30 mm. The average weight (monolith + metal washcoat) is 8.434g. This catalyst is wrapped in a ceramic blanket, used as a gasket, and then placed in a stainless steel tube. A picture of both the full-scale automotive catalyst and the small catalyst are given above.

To obtain rate data the propane concentration and reactor temperature will be varied as shown in Table 1. Note that the temperatures that are used are above the autoignition temperature of propane of 468°C. Why doesn't propane just burn? At room temperature and atmospheric pressure the explosive limits for propane are between 2.3 and 9.5 vol% in air. The concentration of propane we are using in this experiment is around 1000 ppm or 0.1% propane and at these low concentrations it is difficult to burn a hydrocarbon.

The active sites of this Johnson-Matthey catalyst are Palladium. To prepare this catalyst it was aged at 900°C for 12 hours in 10% H_2O and balance nitrogen. The catalyst is contained within a 1.25 Schedule 80 (1.278" ID) 316 stainless steel pipe and is located 8 inches from the top of the reactor. Ceramic fiber blanket is placed between the catalyst walls and the stainless steel tube walls. The ceramic fiber holds the catalyst in place as well as prevents gas from bypassing the catalyst. A 6 inch bed of sand is situated at the bottom of the reactor to both preheat and distribute the gas. The reactor temperature is maintained using a model F79345 Thermolyne split tube furnace from. The furnace has a 12 inch heated zone and is rated for 2880 Watts and a maximum temperature of 1200°C.

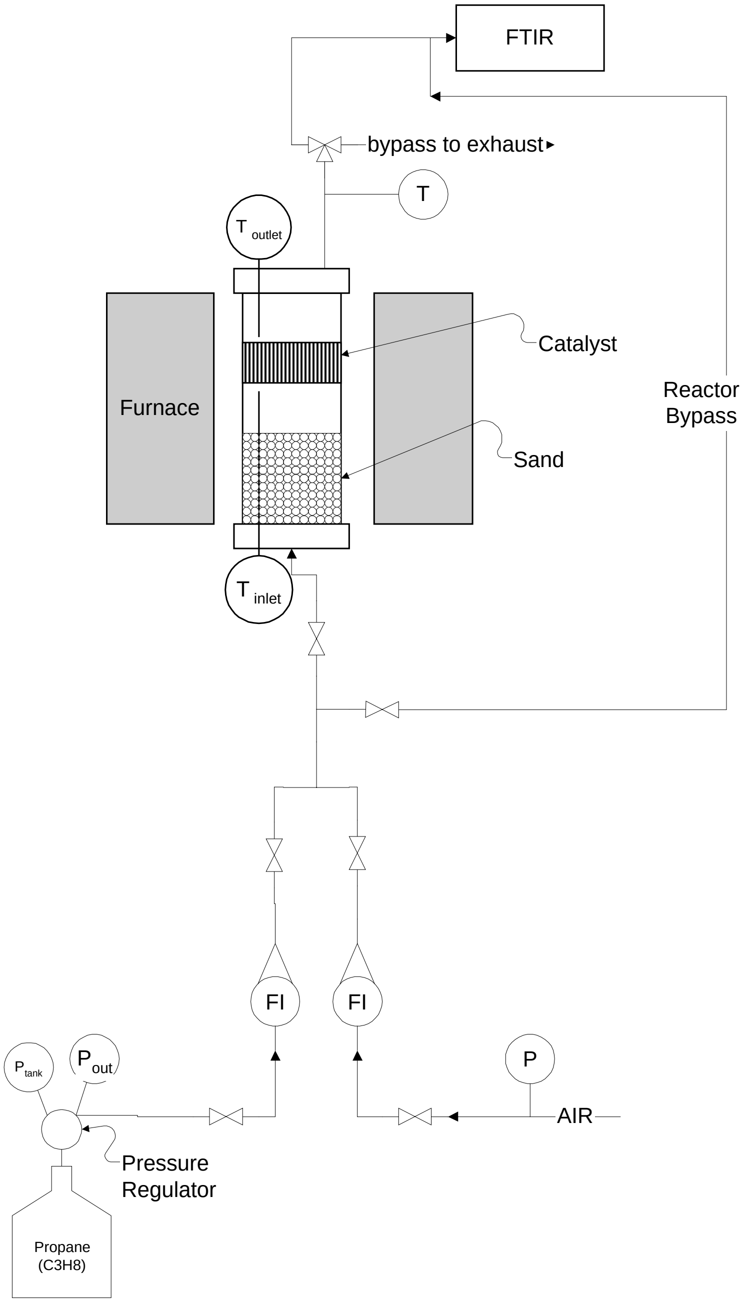

Figure 3: Catalytic Reactor

Propane was obtained from MG Industries and has a purity of 99% propane and is rated chemical pure (CP grade). Air was obtained through the house compressor and regulated from 120 psig to 14 psig.

Gas concentrations are analyzed using a Nicolet Magna-IR® E.S.P. Spectrometer. This spectrometer uses a 2 m gas cell path length with a KBr substrate beamsplitter. In this analysis the spectrometer can detect compounds that have a net dipole moment such as CO_2 or NO, but can not detect compounds with

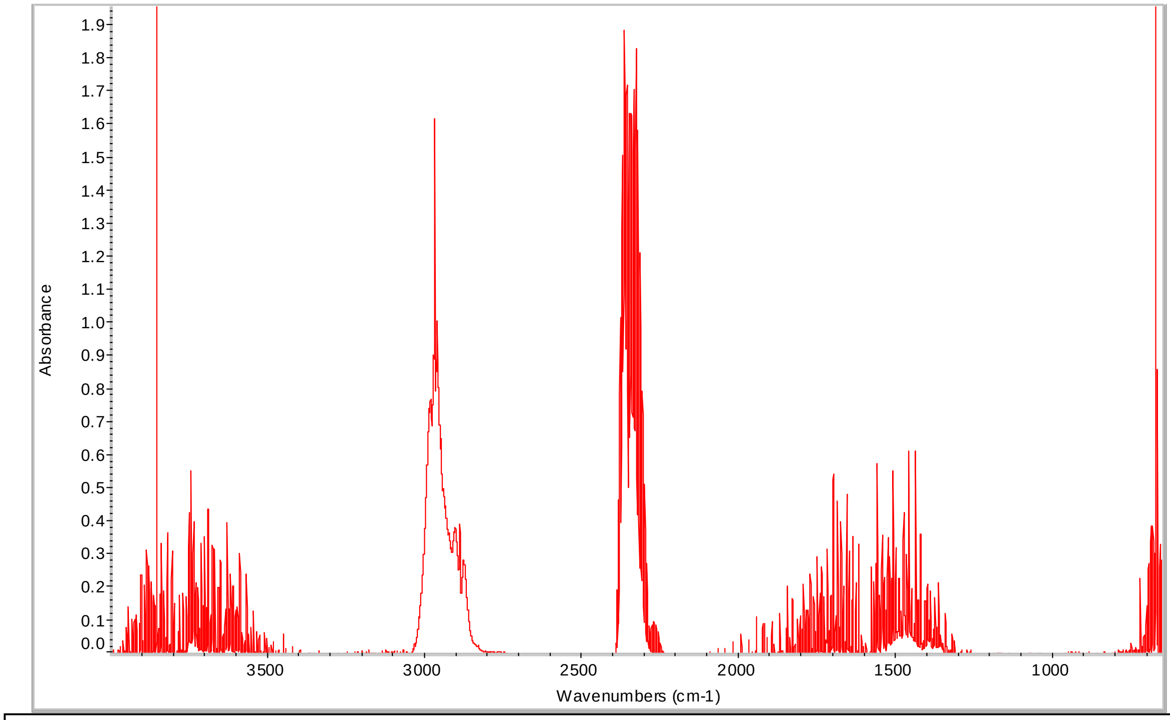

Figure 5: FTIR spectrum a catalytic reactor outlet stream from an inlet stream of 1000 ppm propane in air at a furnace temperature of 500°C.

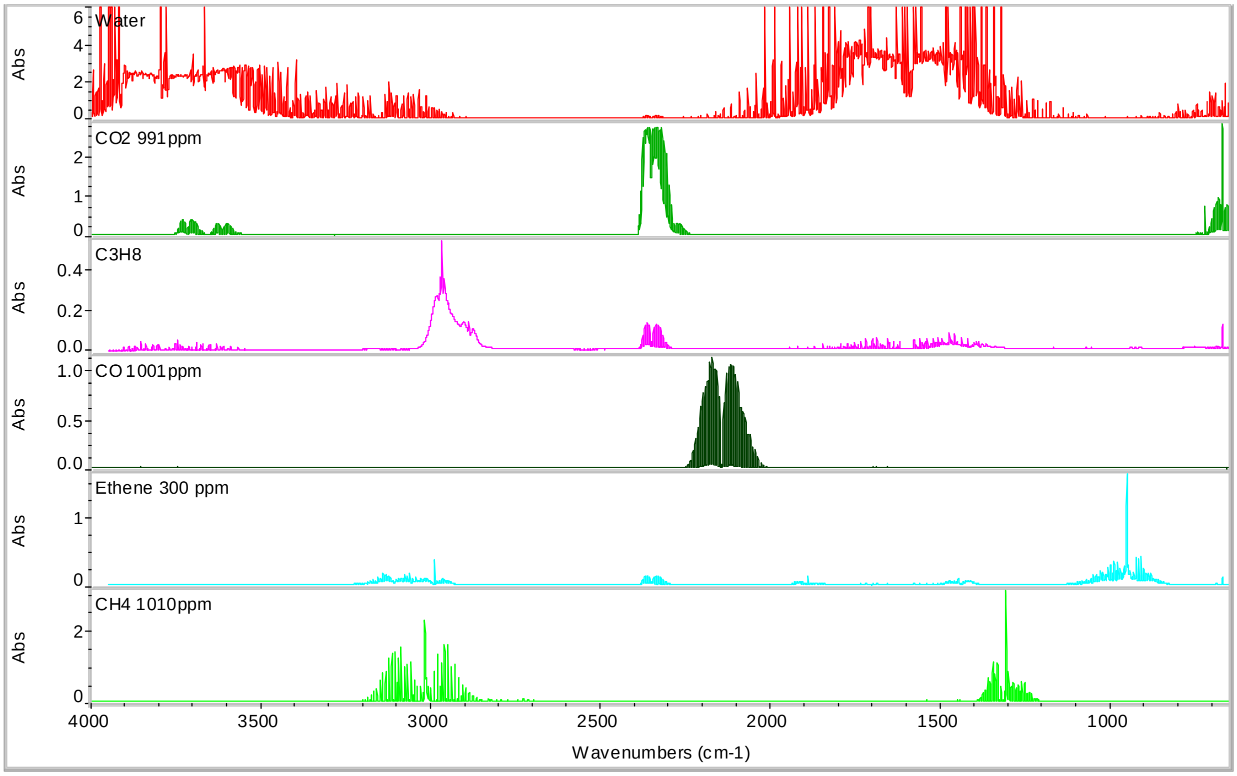

Figure 4: Standard Spectra of Possible Absorbing Compounds

such as O_2 and N_2. In this experiment we will only quantify the concentration of propane. The complete Fourier Transform of a signal from a mixture of 1000 ppm of propane passed through a catalyst sample at a furnace temperature of 500°C is given in Figure 4. Propane is detected primarily from the C-H stretch in the range of 3000 to 2850 cm^{-1}. Figure 4 can be compared with standard spectra shown in Figure 5 to determine if other product gases are present.

Experimental Procedure

In this lab you will determine the reaction rate parameters by varying the inlet concentration of propane and furnace temperature as shown in Table 1. If time is limited, each team can perform several conditions using multiple units or multiple laboratory periods. The results from these laboratories would then be combined for a complete analysis of the rate data. these experiments can be divided into several groups.

Table 1: Suggested Experimental Conditions

Reactor	1	2	3	4	5
Furnace Temperatures °C	400	425	450	475	500

Nominal Propane Concentration, ppm	1600	1400	1200	1000	800
Air Rotameter (mm)	77	77	77	77	77
Propane Rotameter (mm)	64	56	48	40	31

Data Analysis

In this experiment we will assume that the reaction kinetics can be determined from a differential reactor model. In a differential reactor a small amount of catalyst which results in small changes in concentration and temperature. Thus the catalyst can be assumed to be isothermal. At steady-state the mass balance on propane over a small volume of catalyst is:

$$[\text{Molar flowrate of propane in}] - [\text{Molar flowrate of propane out}] + [\text{rate of generation of propane}] = 0$$

Using this $F_{in} - F_{out} + rW = 0$

where

F_{in} molar flowrate of propane into reactor $[=]\,\text{mol/s}$

F_{out} molar flowrate of propane out of reactor $[=]\,\text{mol/s}$

r reaction rate of propane $[=]\,\text{mol/}(\text{g}_{\text{cat}}\text{s})$

W weight of catalyst $[=]\,\text{g}_{\text{cat}}\text{s}$

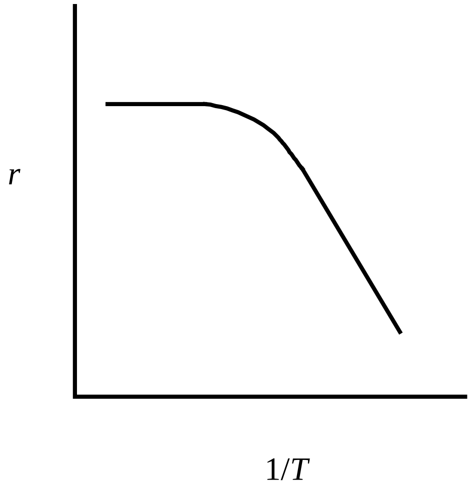

Figure 6: Reaction Limiting Processes

This mass balance is equivalent mathematically to a CSTR. Since there is a change in temperature between gas flowmeters and the outlet of the reactor, then the volume flowrate, Q, of gas increases through the reactor.

$F = CQ$

Another factor, which can be ignored because of small changes in concentration, is the increase in total number of moles going from reactants to roducts. From the ideal gas law the change in flowrate with temperature is

$$Q_{out} = Q_{in}\left(\frac{T_{out}}{T_{in}}\right)$$

Using the above equations the rate of propane destruction is

$$rW = (CQ)_{in} - (CQ)_{out} = Q_{in}\left(C_{in} - C_{out}\left(\frac{T_{out}}{T_{in}}\right)\right)$$

The average concentration within the catalyst is given by

$$\overline{C} = \left(\frac{C_{in} + C_{out}}{2}\right)$$

Since your measurements are being reported in ppm by volume, x, (10,000 ppm = 1%), then

$$C = xC_T = x10^6\left(\frac{P}{RT}\right)$$

In a typical differential reactor model experiment the change of concentration should be less than 10%. In our experiment we will exceed this amount, because we are using an industry standard test catalyst of 30 mm in length. To achieve small changes in concentration would require us to decrease the length of the catalyst.

From the experiments it was determined that the reaction rate order with respect to propane concentration was approximately 1.4. These rates can be compared to reported data of Morooka et al. (1967).

$$r' = kC_{propane}^{1.3}C_{oxygen}^{-1.6}$$

$$with$$

$$k = 10^{6.89}\left(\frac{\mathrm{mol}}{\mathrm{m_{cat}^2\ s}}\right)\exp\left(-\frac{36.3\,\mathrm{kcal/mol}}{1.987\times10^{-3}\,\mathrm{kcal/(mol\ K)}T}\right)$$

Now we need to consider if the reaction rate in the palladium monolith is limited by mass transfer or reaction kinetics. A typical temperature dependence for a reaction controlled by kinetics is:

$$k = \exp\left(-\frac{E_a}{RT}\right)$$

A reaction controlled by external mass transfer is nearly independent of temperature. Thus a plot of $\ln r$, at a constant propane concentration, as a function of $1/T$ would resemble the adjacent graph.

Safety and Environmental Considerations

This experiment is operated in a safe and environmentally responsible manner. All vessels must be rated for pressures greater than the release pressure of the liquefied propane tank. The concentrations of propane in the air stream are representative of hydrocarbons present in the exhaust gases of cars and are converted to CO_2 and water using the catalyst.

Conclusion

These experiments have been run by Rowan engineering students and chemical engineering faculty at a unique hands-on industrially integrated NSF workshop on Novel Process Science and Engineering conducted at Rowan University. We believe that a reaction engineering comes alive with students conducting innovative experiments in a laboratory setting. In addition these experiments are related to a commercially important process: the automotive catalytic converter. Using this experiment students are able to see the catalyst; measure gas phase concentrations and flowrates; and use these measurements to examine at least 6 principles of reactor design.

Acknowledgements:

Special thanks to Chris Bennett, George Quinlan, and Wendy Manning from Johnson Matthey Catalytic Systems Division for donating pretreated catalyst samples and giving advice on reactor fabrication and catalyst operating conditions.

Deep appreciation for the long hours, cut hands and fingers from our team of students and staff in building the catalytic reactor setup. Luke Kline was the lead on constructing the catalytic reactor systems. He was assisted our Head Technician, Mark Showers, and assistance from Tim Francis and Vernon Schwanger.

Equipment Costs and Supplies

Equipment	Vendor	Cost
Split Tube Furnace, multiprogrammable	Model F79345 Thermolyne	$2,825
Propane Flowmeter	03267-00 Cole-Parmer Instrument company	$123
Air Flowmeter	6F-5520-1700 VWR Gilmont Flowmeter	$99
CP Grade Propane, 20 lbs	MG Industries	$120
Propane Regulator	MG Industries	$133
Digital Temperature Indicator	DP116-KC1 Omega Engineering	$195
316 Stainless Steel Pipe Sch 80, 24”	Lincoln Supply	$55
Two 316 Stainless Steel Caps	Lincoln supply	$38
Two Type K Thermocouples, 24”, 1/16 OD	GKQIN-116U-24 Omega Engineering	$63
One Type K Thermocouple,	GKQIN-18U-12 Omega Engineering	$30
Tubing and fittings	Swagelok	$1,200
Nicolet Magnar-IR 560 E.S.P. Spectrometer or NDIR detector (or GC, GC-MS, online FID)	Nicolet	$40,000 or $7,000

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Biographical Information

C. Stewart Slater is Professor and Chair of Chemical Engineering at Rowan University. He received his B.S., M.S. and Ph.D. from Rutgers University. Prior to joining Rowan he was Professor of Chemical Engineering at Manhattan College where he was active in chemical engineering curriculum development and established a laboratory for advanced separation processes with the support of the National Science Foundation and industry. Dr. Slater’s research and teaching interests are in separation and purification technology, laboratory development, and investigating novel processes for interdisciplinary fields such as biotechnology and environmental engineering. He has authored over 70 papers and several book chapters. Dr. Slater has been active in ASEE, having served as Program Chair and Director of the Chemical Engineering Division and has held every office in the DELOS Division. Dr. Slater has received numerous national awards including the 1999 Chester Carlson Award, 1999 and 1998 Joseph J. Martin Award, 1996 George Westinghouse Award, 1992 John Fluke Award, 1992 DELOS Best Paper Award and 1989 Dow Outstanding Young Faculty Award.

Robert Hesketh is Associate Professor of Chemical Engineering at Rowan University. He received his B.S. in 1982 from the University of Illinois and his Ph.D. from the University of Delaware in 1987. After his Ph.D. he conducted research at the University of Cambridge, England. Prior to joining the faculty at Rowan in 1996 he was a faculty member of the University of Tulsa. Robert's research is in the chemistry of gaseous pollutant formation and destruction related to combustion processes. Nitrogen compounds are of particular environmental concern because they are the principal source of NO_X in exhaust gases from many combustion devices. This research is focused on first deriving reaction pathways for combustion of nitrogen contained in fuel and second to use these pathways to reduce NO_X production. Robert employs cooperative learning techniques in his classes. His teaching experience ranges from graduate level courses to 9th grade students in an Engineering Summer Camp funded by the NSF. Robert's dedication to teaching has been rewarded by receiving several educational awards including the 1999 Ray W. Fahien Award, 1998 Dow Outstanding New Faculty Award, the 1999 and 1998 Joseph J. Martin Award, and four teaching awards.