AUTOMOTIVE CATALYTIC REACTION ENGINEERING EXPERIMENT

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This experiment explores the area of heterogeneous catalysis using the automotive catalytic converter, which is the largest market for heterogeneous catalytic reactors. Since catalysts have been placed in approximately 225 million automobiles, nearly everyone with a car owns a catalytic converter. Students' interest in this experiment is piqued when they realize that their cars use this device every day. This immediate familiarity with the automobile allows students to approach the experiment with a confidence that helps them master the experiment's objectives.

A smaller, but growing, market for oxidation catalysts 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 reduce NO_x. Large installations have been in place on stationary internal combustion engines and gas turbines. For example, 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.

The automotive 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 to rectify the problem. The standard catalytic converter consists of a honeycomb monolith support with a washcoat of metals 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 catalyst is a three-way catalyst in which unburned hydrocarbons and CO are oxidized to CO_2 and H_2O, and NO is reduced to N_2. A brief review of these reactions and reactors has been presented by Schmidt.[1] 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[2] reports that these catalysts are continually being engineered to reduce emissions from cars with cold engines and that they meet California's air standards of low and ultra-low emission vehicles. In all new catalysts, the reaction rate must be determined.

This experiment is an excellent combination of hands-on experiments, advanced analytical instrumentation, reactor modeling, and successful application of a numerical technique.

The temperatures that are used in the following experiment are above the 468°C autoignition temperature of propane. This presents an excellent vehicle for introducing safety concepts such as flammability limits and autoignition temperatures. At room temperature and atmospheric pressure, the flammability limits for propane are between 2.3 and 9.5 vol% in air. The concentration of propane we are using in this experiment is 2625 ppm, or 0.3% propane, and at these low concentrations it is difficult to burn a hydrocarbon.

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Furthermore, the autoignition temperature is defined as the temperature at which spontaneous reaction occurs at stoichiometric propane and air concentrations (4% propane in air).

EXPERIMENTAL EQUIPMENT

Construction of this experiment is relatively simple; a small monolith is sealed inside a stainless steel tube, as shown in Figure 1. This yields a method for measuring gas flowrates, mixing the gases, and measuring the inlet and outlet concentrations.

The experiment can be performed with any catalyst that can oxidize a hydrocarbon, such as Pt or Pd. In this experiment, an actual automotive catalyst, donated by Johnson Matthey, was used. This catalyst can be fabricated using an aqueous Pt solution and buying the corderite monolith from Corning.[3] Alternatively, a used catalytic converter can be purchased from your local junkyard. If the junkyard catalyst has lost its activity, it can be regenerated using an acetic acid leaching process following the method of Angelidis and Papadakis.[4] A typical automotive catalyst has an ellipsoid cross section with axes of 5 5/8 and 3 inches. There are 400 square channels per in^2 having a length of 6 inches. To keep the reactor size small, you will need to cut a cylindrical section out of this monolith with a hacksaw and sand the section into a cylinder. A typical geometry for the cylindrical section has a diameter of 25 mm and a length of 30 mm.

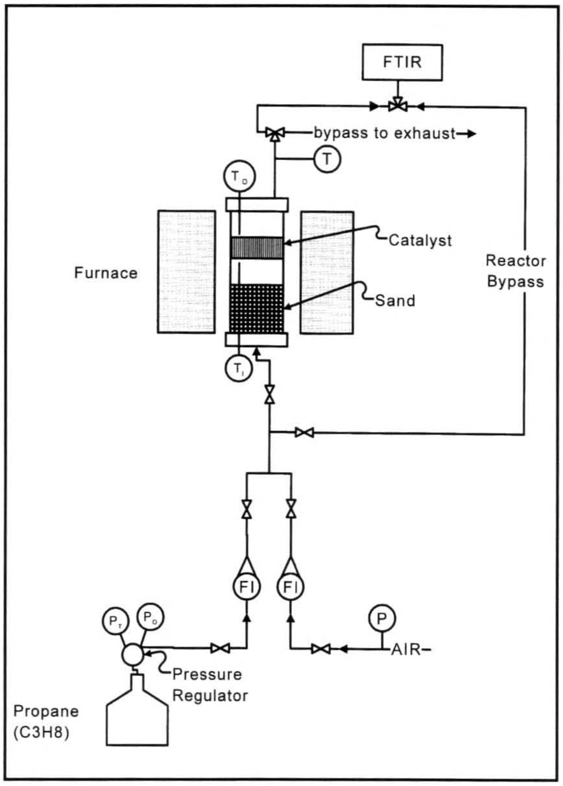

***Figure 1.** Experimental catalytic reactor.*

To prevent gas from bypassing the catalyst, it is wrapped in a 3-mm-thick ceramic fiber blanket or felt. The monolith/felt combination should be carefully inserted into a 1 1/4" Schedule 80 (1.278" ID) 316 stainless steel pipe and gently pushed to 8 inches from the top of the 24" tube. The catalyst is held in place using the friction fit of the ceramic fiber gasket. A flow distributor and gas preheat zone is constructed from blank monoliths or a 6-in bed of washed 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. The furnace has a 12-in heated zone and is rated for 2880 Watts and a maximum temperature of 1200°C. If your budget allows, you can purchase a 3-zone furnace to control the heat loss at the ends of the reactor tube.

The stainless steel tube can be sealed using machined end caps or the more expensive welded flange set. Thermocouples are placed through the top and bottom of the reactor. If threaded end caps are used, the thermocouple fitting must be placed exactly in the center of the tube so that the thermocouple can be inserted approximately 2 mm inside the monolith catalyst channel. The thermocouple end should be touching the channel walls to give the catalyst temperature. The second thermocouple inserted through the opposite end can either be placed in the upstream end of the monolith channel or be shielded and used to measure the entering gas temperature. The external diameter of these thermocouples is dependent on the width of an individual channel and is typically less than 1.16 in.

If a new catalyst is used it should be aged to give a nearly steady-state performance. The catalyst used in this experiment had palladium active sites and was aged at 900°C for 12 hours in 10% H_2O and balance nitrogen. The reaction rates of catalysts are typically reported on a mass, surface area, or active site basis. For commercial catalysts, either the mass or the external surface is known. For example, the catalyst used in this experiment has an average weight (monolith + metal washcoat) of 8.434 g.

Either propane or methane should be used as the hydrocarbon in this study. Propane, for this experiment, was obtained from MG Industries, has a purity of 99% propane, and is rated chemical pure (CP grade). Care must be taken to avoid any catalyst poisons and the standard barbecue propane tank would not be suitable since it contains sulfur compounds to warn the user of gas leaks. Air was obtained through the house compressor and regulated from 120 psig to 14 psig.

Since this experiment uses low concentrations of propane in air, the flowrates must be precisely controlled. The standard method is to use 2-stage regulators and rotameters. The air pressure was controlled using a ControlAir Inc High Precision 100-BA regulator. Propane can be controlled using a MG industries 2-stage regulator. A more user-friendly control scheme would be to use mass flow controllers at a cost of approximately $3,000 for two controllers and a control station.

For this experiment, gas concentrations can be analyzed using a number of analytical instruments, including gas chromatography, online flame ionization detectors, NDIR analyzers, or FTIR spectrometers. At Rowan, we are 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 cannot detect compounds such as O_2 and N_2, as shown in Figure 2. In the basic experiment presented in this paper, only the detection and quantification of propane is required. 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 3. Propane is detected primarily from the C-H stretch in the range of 3000 to 2850 cm^{-1}. Figure 3 can be compared with standard spectra shown in Figure 2 to determine if other product gases are present.

The cost of the experimental apparatus, excluding analytical instrumentation, is approximately $5,000. If new analytical instrumentation is purchased, then the costs of an NDIR gas analyzer, gas chromatograph, or a Nicolet FTIR would cost approximately $7,000, $20,000, or $40,000.

LIGHT-OFF EXPERIMENTS

There are many experiments that can be performed with this reactor configuration, including

- *Examination of light-off curves*
- *Determination of reaction rates using integral-reactor method*
- *Determination of reaction rates using differential-reactor method*

In this paper the results of the light-off experiment will be presented since it is unique to the automotive catalyst industry. The experiment can be integrated easily in the first month of a reaction engineering course in which the basic mole balances for a plug flow reactor have been introduced to the student. It uses the concepts of conversion and the trade-off between the reaction rate and residence time in the reactor. In addition, this experiment can be conducted in approximately 1.5 hours and does not require high-precision quantification.

In cars with catalytic converters, the majority of pollutants are emitted from the car during the start-up period when the catalyst is cold and the required reactions are too slow. This is known in industry as the *cold-start* problem. Various strategies are being employed to eliminate this problem, such as electrically preheating the catalyst and adsorbing and storing the pollutants on a separate bed. The temperature required to activate the car catalyst is commonly referred to as the *light-off* temperature. At this temperature, the net heat released from the reactions is sufficient to maintain the catalyst at temperatures required to obtain high conversions. It is commonly thought that at temperatures below the light-off

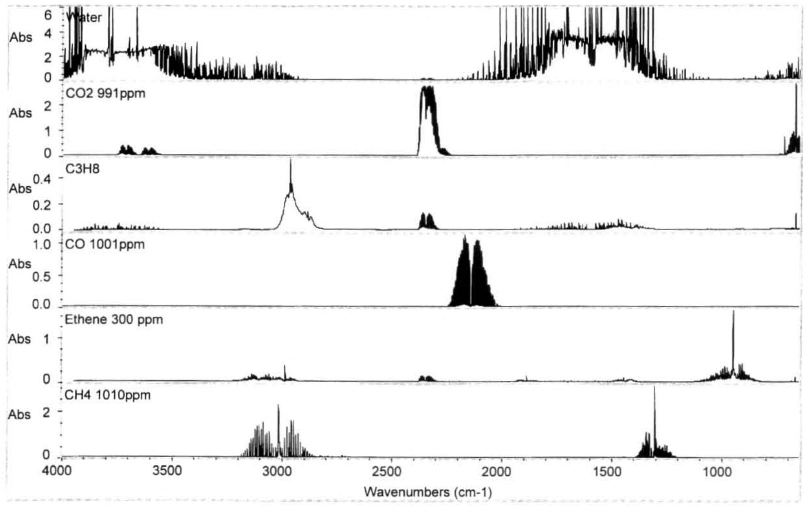

Figure 2. *Standard spectra of possible absorbing compounds from reactor outlet.*

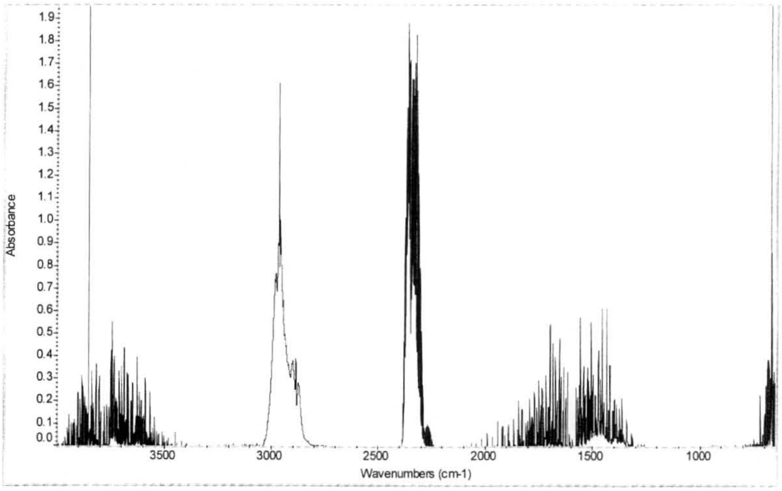

Figure 3. *FTIR spectrum from the reactor outlet stream using an inlet concentration of 1000 ppm propane in air at a furnace temperature of 500°C.*

temperature the catalyst is not removing pollutants, and at temperatures above the light-off temperature the catalyst is working. There are many definitions of the light-off temperature, but the most common is the temperature for which the conversion of a reactant reaches 50%.

Hayes and Kolaczkowski[3] show that this light-off temperature is a function of reactor size and reactor flowrate. This result should be obvious if you have just finished a reactor design course! Assuming a plug-flow model, the mole balance on propane is

$$\frac{dF_{C3H8}}{dW} = r \tag{1}$$

where F_{C3H8} is the molar flowrate of propane, W is the weight of catalyst, and r is the reaction rates with units mole propane/s/kgcat.

Assuming first-order kinetics and a constant flowrate, Q, through the reactor, Eq. (1) can be integrated to give

$$\chi_{C3H8} = 1 - \exp\left(-\frac{kW}{Q}\right) \tag{2}$$

Assuming an Arrhenius reaction rate constant and adjusting for the difference in rotameter flowrate and actual flowrate through the reactor gives

$$\chi_{C3H8} = 1 - \exp\left[-W\frac{A\exp(-E_a / RT)}{Q_0 \frac{T}{T_0}}\right] \tag{3}$$

As the reactor temperature increases, both the reaction rate and conversion increase. At a given temperature, the conversion at high flowrates is less than the conversion at low flowrates. This clearly shows that the light-off temperature is dependent on the volume or geometry of the reactor and the flowrate of gases through the reactor.

The procedure for this experiment is relatively simple. The two flowrates chosen are of 14.5 and 7.76 L/min. The inlet concentration of propane in air is held constant at 2625 ppm. The furnace is initially set to a temperature of 550°C and the gas is analyzed at each flowrate. Next, the furnace temperature is increased by 25°C and samples are again taken at the above two flowrates. If the furnace temperature controller is programmable and an online analyzer is available, then the experiment can be automated following industry practice.

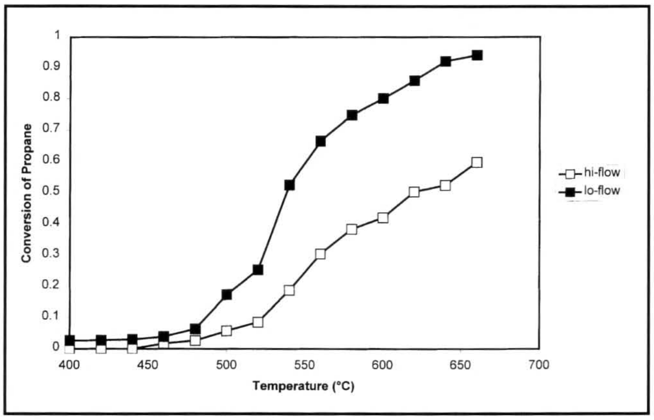

Figure 4. *Results of light-off determination experiment.*

Using this experiment, students are able to see the catalyst, to measure gas-phase concentrations and flowrates, and to model the reactor and find the reaction-rate parameters using a nonlinear regression of the data.

An example of the experimental results is shown in Figure 4. From these results the light-off temperatures at 50% conversion of propane are 620 and 538°C at 14.5 and 7.76 L/min, respectively. These distinctly different curves show that the outlet conversion of propane is a function of the flowrate through the monolith. This confirms that the light-off temperatures quoted in the literature can only be used to compare similar catalysts of equivalent geometry and gas flowrate. Students conducting these experiments will immediately see how they can use a simple reactor model to show the effect of flowrate on outlet conversion. The use of this experiment at an early stage in reactor design courses will help students learn basic concepts in reaction engineering.

DETERMINATION OF REACTION RATE PARAMETERS

A range of reaction rate expressions have been reported in the literature. Morooka, et al.,[5] reported the reaction rate for a palladium catalyst in an atmospheric flow reactor as nearly first order in propane:

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

with

$$k = 10^{6.89}\left(\frac{mol^{1.3}}{m_{cat}^{2} m_{gas}^{0.9} s}\right)\exp\left(-\frac{151.8\,kJ/mol}{8.314\times10^{-3}\,kJ/(mol\,K)T}\right) \tag{4}$$

Recent reaction rate expressions for propane oxidation using commercial monolithic catalysts were reported as first order by Wanke[6] and Bennett, et al.[7] The pre-exponential and activation energy values reported for these first order rates are $A = 3.15\times10^4$ $m^3/(kg\ s)$ and E_a = 89,126 J/mol by Wanke and $A = 2.40\times10^5$ m/s and E_a = 89,791 J/mol by Bennett.

In order for the students to determine the reaction rate parameters, the reaction is assumed to be first order in pro-

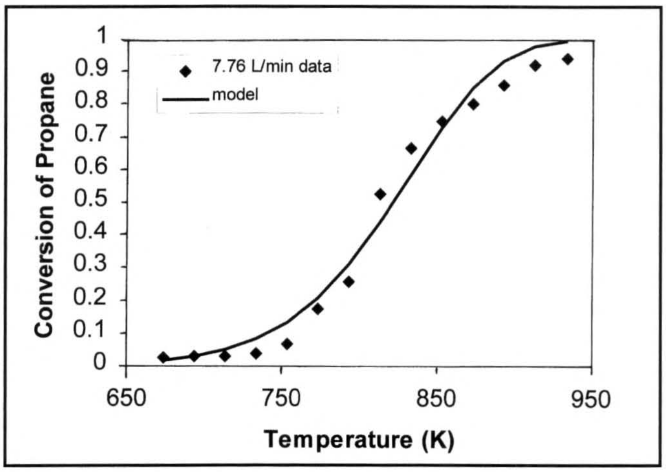

Figure 5. *Comparison of model with experimental light-off curve data.*

pane concentration, which is in agreement with the results of the previous two investigators. Next, the students are asked to perform a nonlinear regression of the data using Eq. (3). With most packages, a good initial guess of the constants is required and an estimate is obtained using Eq. (2). Using a conversion of 0.52 and temperature of 813 K, the value of k is 0.0312. Next, a second value of k is determined and the values of A and E_a are calculated. An alternative method is to use the rate parameters given above as initial starting points. Finally, these values are used as the initial values for the regression of Eq. (3) with the data using the nonlinear regression package in POLYMATH.

The results of a regression of the low flowrate data are shown in Figure 5. The reaction rate parameters from this fit are A = 4.81E+04 $m^3/(kg\ s)$ and E_a = 99,120 J/mol. This value of activation energy is very close to that of both Wanke and Bennett and is a reasonable activation energy. A fit using all of the data results in the reaction rate parameters of A = 2.39E+06 $m^3/(kg\ s)$ and E_a = 124,500 J/mol. This value of activation energy is higher than the values reported by Wanke and Bennett and below the values reported by Mooroka. This discrepancy in the activation energy could be related to a poor flowrate measurement using a rotameter (2% of full scale). Another possibility is that the catalyst reaction rate deviates from first-order kinetics.

This fit of the data with a reactor model enhances the student's connection between the concrete and the abstract. Students perform this simple experiment and observe the peak heights decrease as a function of furnace temperature and increasing flowrate. The peak area is related to the concentration of propane and a conversion is calculated. Finally, the students apply a reactor model to successfully describe the data. This experiment is an excellent combination of hands-on experiments, advanced analytical instrumentation, reactor modeling, and successful application of a numerical technique.

TRADITIONAL REACTION RATE DETERMINATIONS USING DIFFERENTIAL AND INTEGRAL REACTOR MODELS

There are many other experiments that can be performed using this equipment. The most basic in reaction engineering is the integral and the differential reaction-rate determinations. In the differential reaction-rate determination, the total conversion must be kept lower than 15% to obtain good results for an automotive catalyst.[7] In addition, the analytical technique for gas measurement must achieve a resolution of 1%. For the integral reactor, additional catalyst monoliths may need to be added. Using this apparatus, new catalysts can be tested and the experiment can be varied from year to year to minimize copying. Alternatively, a new hydrocarbon could be examined.

The major drawback of the above two reaction rate determinations is that they are time intensive; they require a large number of trials to obtain a reaction rate as a function of temperature. We have found the students quickly grow disinterested in this experiment when they conduct a large number of trials. The light-off experiments are simple since only one inlet concentration is used and the temperature can be ramped automatically.

SAFETY AND ENVIRONMENTAL CONSIDERATIONS

This experiment must be 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 and are well below the flammability limit of 2 mol%. The products of this oxidation are primarily CO_2 and water, which are not harmful and can be vented to an exhaust system. The furnace outlet is hot and students must be prevented from touching it.

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 reaction engineering comes alive when students conduct innovative experiments in a laboratory setting. In addition, these experiments catch the students' interest because they are related to a commercially important process—the automotive catalytic converter. Using this experiment, students are able to see the catalyst, to measure gas-phase concentrations and flowrates, and to model the reactor and find the reaction-rate parameters using a nonlinear regression of the data.

ACKNOWLEDGMENTS

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. Support for the development of this experiment was provided by a grant (DUE-9752789) from the National Science Foundation through the Division for Undergraduate Education and Rowan University.

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ChE *letter to the editor*

Dear Sirs,

We welcome the comments of Baird and Rama Rao[1] on our paper concerning a simple experiment on two-phase film flow[2] and hope that this discussion attracts the readers to this somewhat neglected area in lab courses of fluid mechanics.

Baird and Rama Rao point out that the experiment we described must be performed in tubes with internal diameter greater than 15 mm, for otherwise the bubble velocity will not be given by the simple equation

$$U = 0.345(gD)^{0.5} \qquad (1)$$

It is true that for smaller diameters the effect of surface tension becomes important and Eq. (1) ceases to be valid (if the tube is small enough, the slug will not move as pointed out), but in our paper we also present a general analysis for laminar film flow that makes no use of Eq. (1) (see Eq. (7) in ref. 2). However, if smaller tubes are used, the analysis presented is only approximate since the curvature of the film can no longer be neglected, and Nusselt's analysis is no longer applicable. Figure 1 shows the correct film thickness (calculated for cylindrical film flow[3]) as a function of the approximate film thickness given by Nusselt's analysis (neglecting the film curvature). It can be seen that if the dimensionless film thickness is greater than about 0.2, the errors in film thickness become larger than 10%.

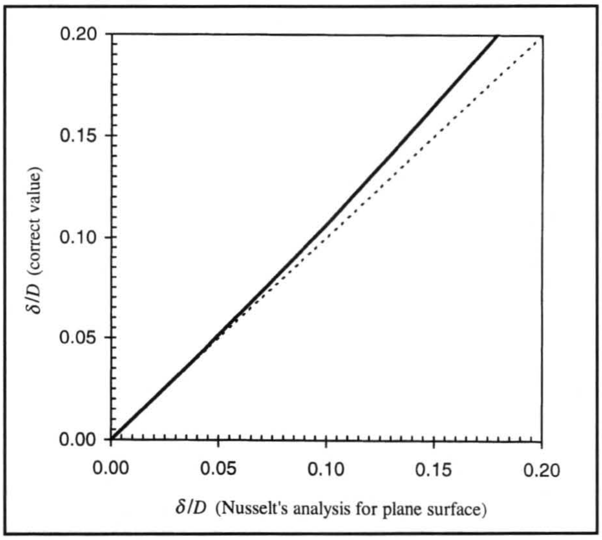

Figure 1- Correct versus approximate film thickness.

In order to minimize possible sources of error, it is suggested that columns with internal diameters in the range of 15-35 mm be used. With larger tube diameters it may be difficult to obtain laminar film flow, unless very viscous solutions are used. Also, one has to use longer columns due to greater velocities of the bubble, and the complexity of the instalation increases.

M.A. Alves, *Teaching Assistant*
A.M. Pinto, *Associate Professor*
J.R. Guedes de Carvalho, *Professor*

University of Porto, Portugal

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