Characterizing Combustion Kinetics in a Miniature Thermal Oxidizer

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Introduction

Thermal oxidizers (TOs) are systems that destroy chemical compounds via high temperature oxidation. Some of the key performance criteria for TOs include destruction efficiency, carbon monoxide (CO) emissions, and oxides of nitrogen (NOx) emissions. When designing a TO, selecting the proper residence time and operating temperature have a significant impact on: destruction efficiency, CO emissions, capital costs, and operating costs. For unusual applications, determining the operating temperature and residence time can be difficult without previous experience with the compounds involved. Testing is an obvious solution, but compounds can be toxic, carcinogenic, or mutagenic. To bring into a test facility sufficient quantity of a dangerous compound for a test in a full-size thermal oxidizer can pose too large a risk to personnel and the surrounding community. Waste streams can be simulated in a test facility with simpler and/or less toxic surrogate compounds in some cases but may be very expensive in a full-scale test and there is always a concern about the representativeness of the results. Leveraging prior experience from commercial systems in actual operating environments provides valuable information but field data tends to be limited since the process conditions are not typically varied over a wide range and composition and flow measurements are not always available. The limitations of field data introduces extrapolation uncertainties when applying the data to other systems. Small-scale testing can supply data with much smaller quantities of compounds, making tests with special chemicals feasible from a safety perspective as well as being more cost effective.

Small-Scale Testing

There are some special considerations that must be addressed when applying small-scale test data to full-scale commercial thermal oxidizer systems. Full-scale systems generally have slower mixing rates than a small-scale system. The mixing dynamics couple to the reaction rates in the overall observed burnout rates. Temperature gradients within a thermal oxidizer chamber typically range from 100 to 300°F (post flame) in full scale systems, which also affect the reaction rates and data interpretation. Small-scale test results will not replicate the mixing dynamics of the larger systems, but this can be advantageous when attempting to understand reaction rates separate from the mixing. It should be noted that mixing dynamics in two full-scale systems may be substantially different based on their respective geometries, which complicates the comparison of data between systems. Understanding reaction dynamics and mixing dynamics separately is valuable when attempting to develop models to apply broadly to many systems and process conditions.

CFD Modeling

Computational Fluid Dynamics (CFD) is a powerful tool [1,2] that can be used to quantify mixing rates and couple kinetic rates into those models. Some commercial CFD codes can integrate large reaction mechanisms and/or simpler global kinetics. The multi-species, multi-reaction mechanisms are derived to be more fundamentally consistent with the actual reaction chemistry but require significantly more computational and engineering effort to apply these models. These types of kinetic models are typically applied with reaction modeling parameters (e.g., activation energy, reaction order, etc.) as-is and reactions and species that are "less important" (i.e., less impact on the results) are removed from the mechanism to reduce the computational load. Global reaction rates are much simpler to apply but are only expected to be valid over narrower process conditions. Global reaction modeling is typically applied by tuning reaction constants to match the test results over a range of conditions. Application of either approach should be validated against real data before using with confidence.

Small-Scale TO Test Apparatus

A thermal oxidizer test apparatus designed to study kinetic rates should be built in a manner that allows the composition and temperature of the flue gases to be controlled to conditions closely matching a full-scale thermal oxidizer. John Zink Hamworthy Combustion has recently developed a small-scale thermal oxidizer system designed to study combustion kinetics. The system has a burner that is used to provide heat input and produce bulk flue gases (H_2O, CO_2, N_2, O_2) in concentrations that are very close to the conditions of interest in commercial applications. The hot flame from the burner also produces free radicals that may help initiate combustion of the waste gas, presumably at comparable levels that would be produced in a full-scale system. Temperature gradients and heat losses are difficult to manage with just refractory in such a small system, therefore, the system is equipped with electrical heaters to hold the temperatures in the system at the desired set points. Several sampling points are positioned along the axis of the reactor so that measurements of temperature and concentration can be made along the length (varying residence time). Figures 1 through 3 show photographs of the small-scale thermal oxidizer.

Figure 1 – Small-scale Thermal Oxidizer

Figure 2 - Extractive Sampling

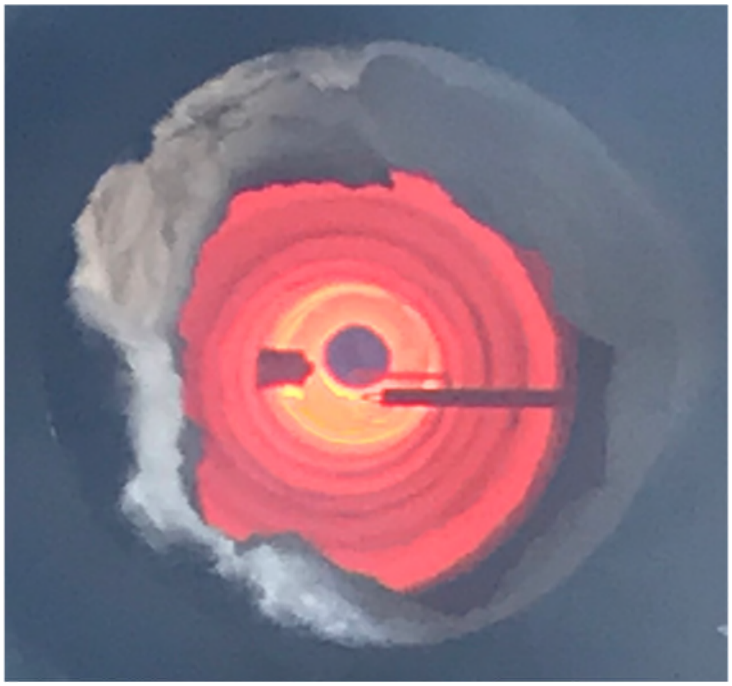

Figure 3 – View through sight glass at base of stack looking back towards the burner

Several researchers have reported CH_4 and CO burnout rates in combustion flue gas and proposed global reaction models based on their results [3-10]. Each study was conducted under specific test conditions, which have some test conditions in common and more that are unique. As a result, each study reports different reaction constants that are best applied only to the conditions under which the experiments were conducted. Many thermal oxidizers are designed to burn trace amounts of waste diluted in large concentrations of inert gases. These types of thermal oxidizers will have bulk flue gas that is more diluted in inert gases (N_2, CO_2) and less concentrated in H_2O (OH radical source) compared to just fuel/air combustion conditions. Generally, CO reaction rates are overpredicted using burnout models developed from test conditions with lower inert gas concentrations in the flue gas.

Example Test Results

Tests were done to study trace combustion reactions in flue gases with bulk gas concentrations typical of thermal oxidizer gases. Two series of tests were conducted where the waste was simulated with natural gas diluted in either N_2 or CO_2. Two relatively low concentrations of natural gas were tested in each inert gas to evaluate the methane concentration dependence on the reaction rates. The tests were also conducted over a range of temperatures to evaluate the temperature dependence of the reaction rates. Figures 4 to 6 show the results for three temperatures of the CO_2-diluted tests while Figures 7 to 9 show the results for three temperatures of N_2-diluted tests.

The test results showed noticeably slower burning in the CO_2-rich atmosphere. To the authors' best understanding, there are no published global kinetic models that discriminate between CO_2 and N_2 dilution in CH_4 and CO oxidation rates. A proprietary 2-step kinetic model accounting for the effects of gas concentration (inert, H_2O, O_2, CO, CH_4) and temperature was developed from the test results for application to thermal oxidizer systems. The lines in each graph correspond to the CH_4 and CO concentrations calculated using this model. Note that a single model applies to all tested conditions.

The miniature thermal oxidizer provides the capability to test compounds that pose too large a risk in large quantities as well as to test non-hazardous compounds to obtain kinetic data independent of mixing. From such data, kinetic models can be generated. These validated kinetic models provide a basis for improved emission prediction tools, better understanding of thermal oxidizer performance to further optimize designs, and can be implemented within CFD models to improve the accuracy of simulations.

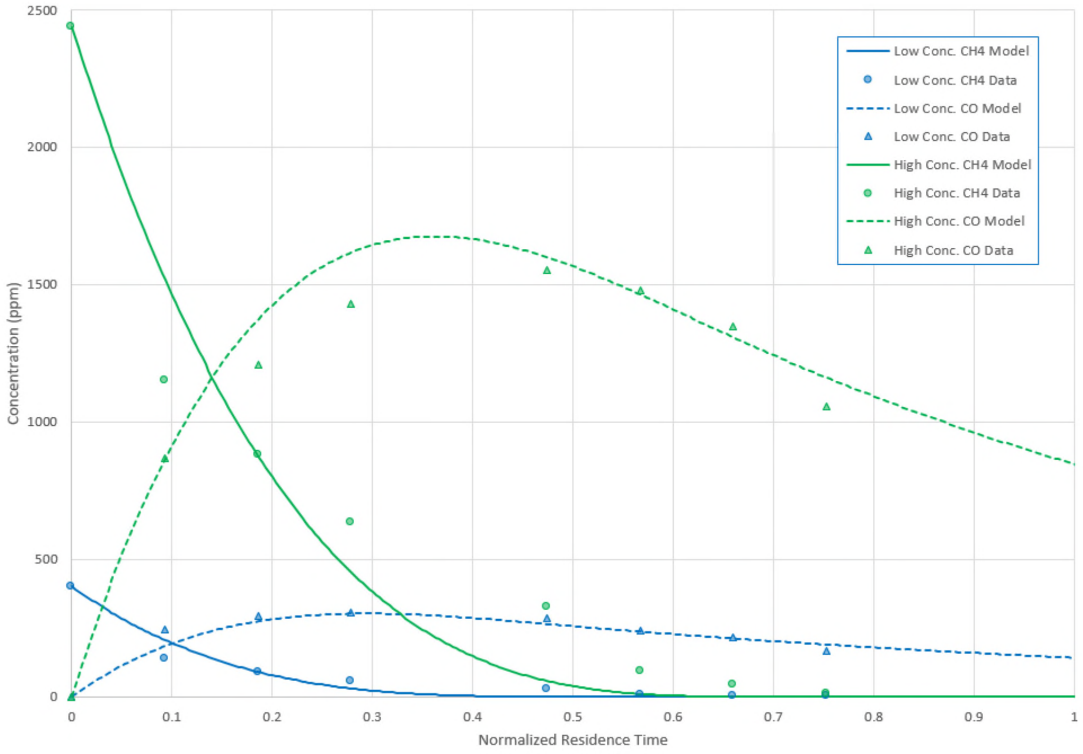

Figure 4 Natural gas in CO2 (reference temperature 1)

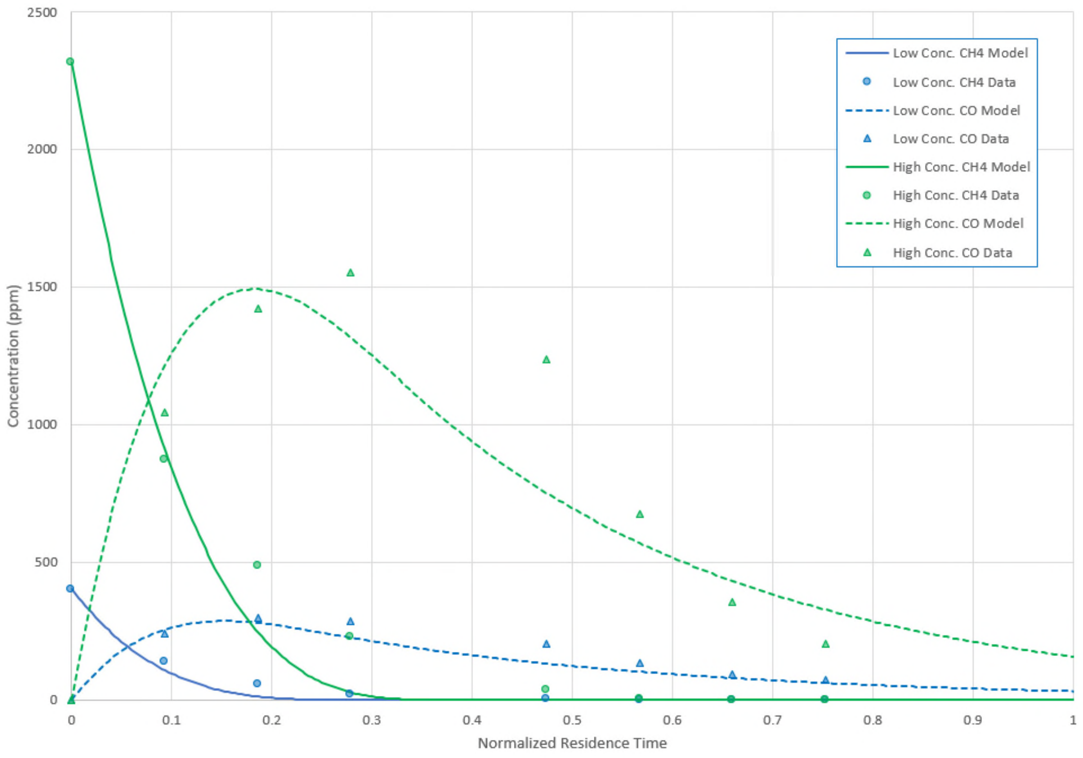

Figure 5 Natural gas in CO2 (reference temperature 1 + 75°F)

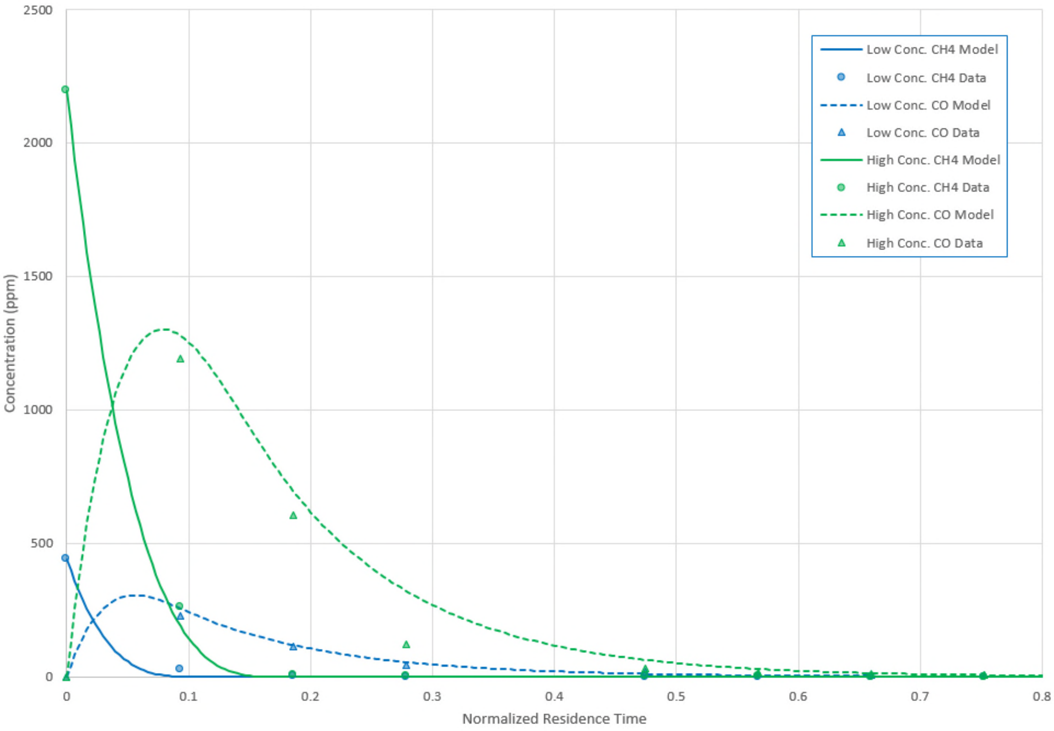

Figure 6 Natural gas in CO2 (reference temperature 1 + 175°F)

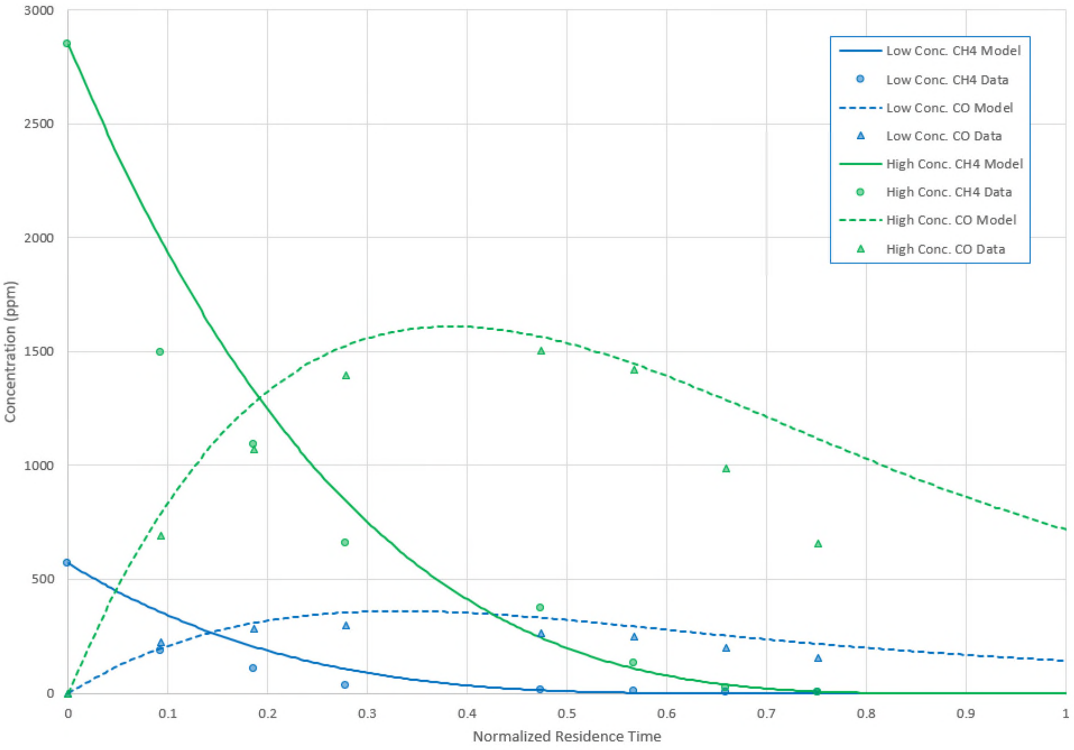

Figure 7 Natural gas in CO2 (reference temperature 2)

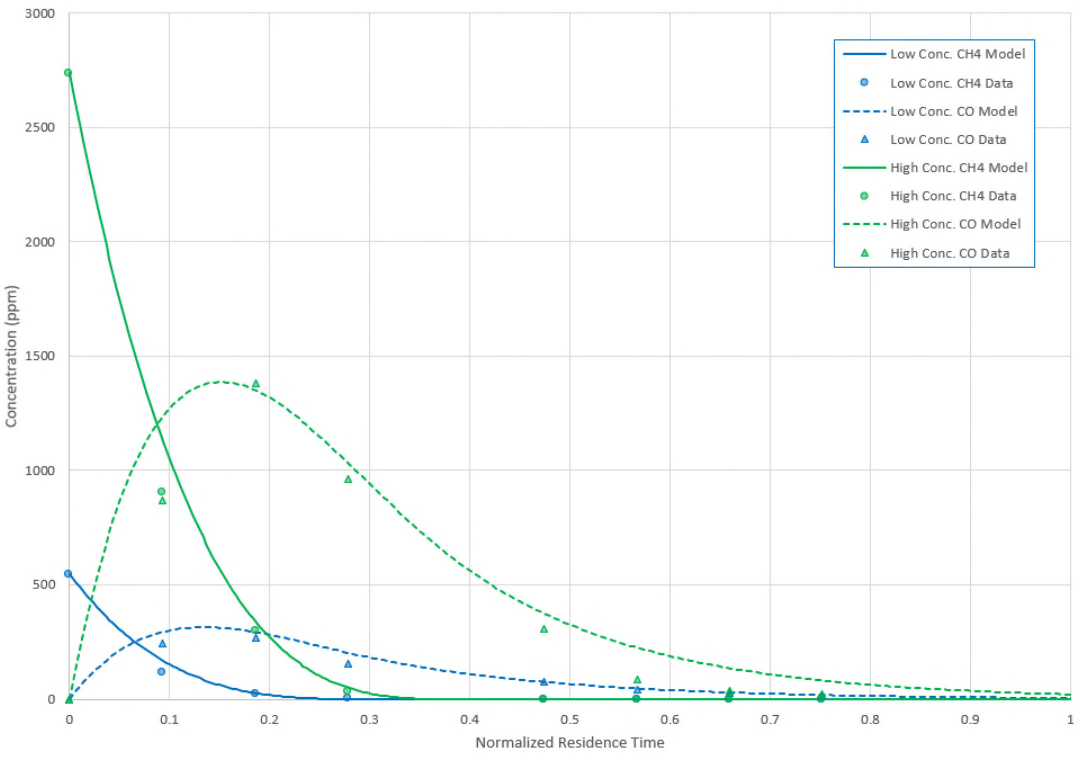

Figure 8 Natural gas in CO2 (reference temperature 2 + 100°F)

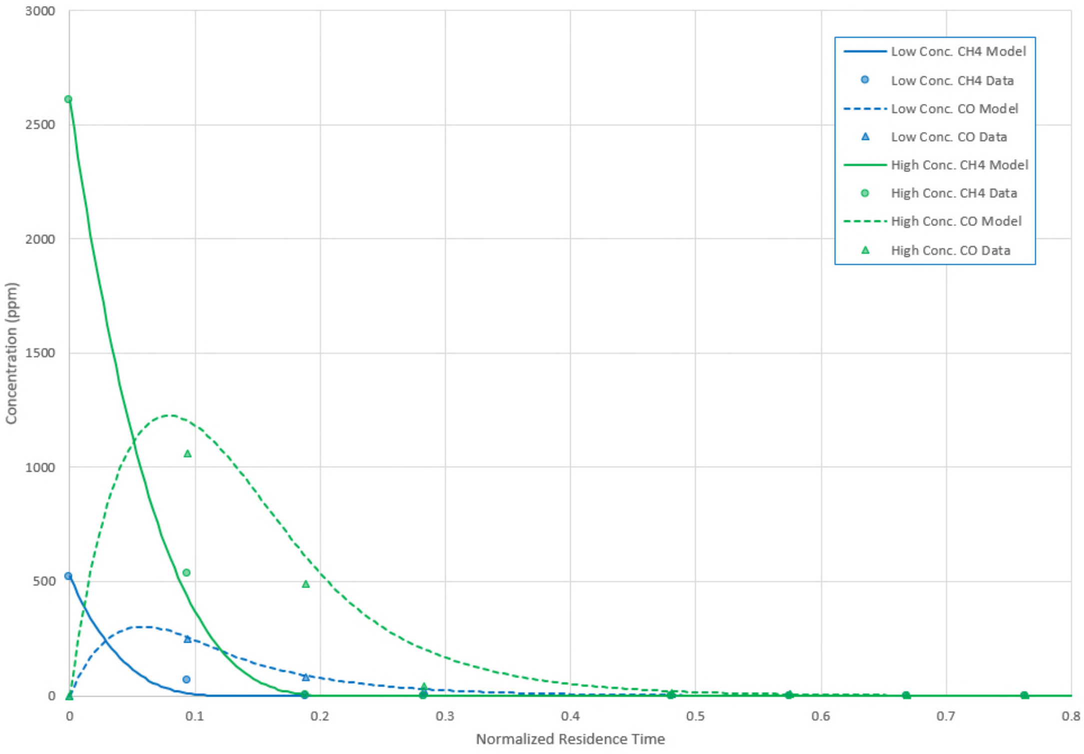

Figure 9 Natural gas in CO2 (reference temperature 2 + 175°F)

Conclusions

Kinetic information is needed to properly design thermal oxidizers, particularly the minimum residence time and temperature in the combustor. Kinetic data are not always readily available for the conditions of interest. They can be difficult to obtain from full-scale TOs operating at different conditions from those of interest. While CFD is a powerful design tool, it requires appropriate kinetic data to generate valid results. A small-scale thermal oxidizer can produce useful kinetic results more quickly and safely and at a reasonable cost compared to full-scale testing. An important benefit of such a tool is the capability of varying the operating conditions to match those that will be encountered in the field. Sensitivity studies can also be conducted to determine how important variables are impacted by, for example, the combustor temperature. That information can be used to determine how much of a safety factor may be needed in the design of the actual TO.

References

1. Baukal, C.E., Gershtein, V.Y., Li, X. *Computational Fluid Dynamics in Industrial Combustion*, CRC Press, Boca Raton, FL, 2000.
2. Lorra, M.A., Chen, S.X. “CFD-Based Combustion Modeling,” in *The John Zink Hamworthy Combustion Handbook*, Vol. 1: Fundamentals, C.E. Baukal (ed.), CRC Press, Boca Raton, FL, 2013.
3. Howard, J. B., Williams, G. C., Fine, H. “Kinetics of Carbon Monoxide Oxidation in Postflame Gases”, Fourteenth Symposium (International) on Combustion, 975 (1973).
4. Dryer, F. L., Glassman, I. “High-temperature Oxidation of CO and CH_4”, Fourteenth Symposium (International) on Combustion, 987 (1973).
5. Yetter, R. A., Dryer, F. L., Rabitz, H. “Complications of One-step Kinetics for Moist CO Oxidation”, Fourteenth Symposium (International) on Combustion, 975 (1973).
6. Dowling, N. I., Huang, M., Clark, P. D. “Chemistry and Kinetics of Claus Tail Gas Incineration – Improving Incinerator Efficiency”, Brimstone 2008 Sulfur Recovery Symposium (2008).
7. Williams, G. C., Hottel, H. C., Morgan, A. C. “The Combustion of Methane in a Jet-Mixed Reactor”, Twelth Symposium (International) on Combustion, 913 (1969).
8. Lee, K. C., Morgan, N., Hanson, J. L., Whipple, G. M. “Revised Model for the Prediction of the Time-Temperature Requirements for Thermal Destruction of Dilute Organic Vapors and its Usage for Predicting Compound Destructibility”, 75th Annual Meeting of the Air Pollution Control Association (1982).
9. Dellinger, B., Torres, J. L., Rubey, W. A., Hall, D. L., Graham, J. L. “Determination of the Thermal Stability of Selected Hazardous Organic Compounds”, Hazardous Waste, 137 (1984).
10. Hottel, H. C., Williams, A., Nerheim, N. M., Schneider, G. R., “Combustion of Carbon Monoxide and Propane”, Tenth Symposium (International) on Combustion, 111 (1965).