Austin Chemical Engineering

Austin Publishing Group

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Editorial

Unsteady State Processes in Catalysis: Efficient Way for Energy Savings, Air Pollution Prevention and GHG Mitigation

Sapoundjiev H*

Department of Chemical Engineering, Natural Resources, Canada

***Corresponding author:** Sapoundjiev H, Department of Chemical Engineering, Natural Resources, Canmet Energy, 1615 Lionel Boulet Blvd, P. O. Box 4800, Varennes, Quebec, J3X 1S6, Canada

Received: May 22, 2014; **Accepted:** May 23, 2014; **Published:** May 24, 2014

Editorial

It has been over 40 years since the new area of science called "Forced Unsteady State Processes in Catalysis" has appeared. During these years, significant efforts by many scientists and engineers were made to develop theoretical foundations in this area and to implement these findings in practical catalytic processes. Elsevier recently published a new book [1] in which a comprehensive review – prepared by 21 experts, many of whom are lead scientists and pioneers of the subject–describes the research activities performed in the field of periodic operation of chemical reactors and its translation into engineering applications. This book will assist R&D specialists, research chemists, chemical engineers or process managers in harnessing periodic operations to improve their process plant performance.

In this note, I would like to describe how unsteady state processes operating with a periodic flow reversal are contributing to air pollution prevention and greenhouse gas mitigation.

Periodic flow reversal is fundamentally a heat or mass trapping technique that makes it possible to increase temperatures or accumulate heat in a bed of packing, where the chemical reaction and heat and mass exchange are efficiently integrated. The base of operation of catalytic reactor under flow reversal is described in detail in [1,2]. The main advantage of this technique is that a high temperature plateau is formed at the mid-point of the reactor bed and, often, the difference between the maximum temperature and inlet temperature is much higher than the adiabatic temperature rise. Inter phase heat transfer rates in these packed beds can be quite high so that steep temperature fronts can be achieved for reaction with a low adiabatic rise. This offers an energy efficient operation for large volumes of dilute and cold gases common in air pollution and GHG mitigation.

One example of successful application of the flow reversal reactor is the elimination of SO_2 emissions from non-ferrous metallurgical plants. Smelters from Pb and Zn plants usually emit SO_2 in concentrations ranging from 2.0 to 9.0 vol. %, depending on the cycle of their operations. To treat these gases, multi-bed catalytic reactors with internal heat exchangers are used. At the time of operation, when the smelters emit SO_2 with concentrations below 4.0 vol. %, additional heat is needed to keep the heat balance of the process. This makes the process of SO_2 elimination one that is energy consuming and that involves complex and expensive equipment.

Periodic flow operation with a unique temperature profile along the catalyst bed can solve all above problems for reversible exothermic reactions, such as SO_2 oxidation, allowing high conversion in a single catalyst bed. Another advantage of the reactor with flow reversal operation is that the reactor is not sensible to the time fluctuations of the inlet flow and inlet SO_2concentration. In the catalytic reactor with flow reversal operation, the auto-thermal regime (without adding external heat to the process), can be reached with SO_2 concentrations above 1.0 vol. %. This makes the flow reversal technique an economically viable solution to eliminate SO_2 emissions and prevent acid rains. An example of the industrial application of a flow reversal reactor in the lead-zinc smelter in Plovdiv, Bulgaria, is described in [3]. The reactor operates at a gas flow rate of 20,000–45,000 m^3 (NTP) per hour, with a 1.4–4.8 vol. % inlet SO_2. When the multi-stage classical reactor was replaced by a flow reversal reactor, the heat exchange surface decreased from 6,400m^2 to 330 m^2 and the total capital investments were decreased by a factor of two.

After 10 years of successful operation, the flow reversal reactor at the Plovdiv lead-zinc smelter was incorporated into the first stage of a double conversion–double absorption (DC/DA) acid plant operated in the same factory [4]. The new DC/DA systems offer stable operation even in the presence of inlet SO_2fluctuations. The final SO_2 conversion was over 99% and the tail gas emissions were below 600ppm.

The second successful example off low reversal technology implementation in the industry is the mitigation of the ventilation air methane (VAM) emitted from underground coal mines, as recently reported in [5].

Methane is the second most important anthropogenic greenhouse gas after carbon dioxide. With its GWP (global warming potential) of 21 and its abundant emissions throughout the world, methane is a major component of the greenhouse gas problem. The coal mine industry is responsible for 8% of total methane emissions. The methane emissions resulting from underground coal mining activities are estimated at 26 million tones per year, 70% of which come from coal mine ventilation air (VAM), where methane concentration is below 1.0 % v/v [6].

A great energy potential also resides in lean methane emissions. For example, a flow rate of 100 m^3/s of an air-methane mixture containing 0.5 % v/v of methane can yield almost 18 MW of thermal

Citation: Sapoundjiev H. Unsteady State Processes in Catalysis: Efficient Way for Energy Savings, Air Pollution Prevention and GHG Mitigation. Austin Chem Eng. 2014;1(1): 1001.

energy. This potential is currently not utilized, because no technology has yet to offer satisfactory economic viability for the treatment of these methane gases [7].

The opportunity for heat recovery and greenhouse gas elimination from VAM, using a Catalytic Flow Reversal Reactor (known as a CH4MIN technology) developed by Natural Resources Canada (NRCan), offers an alternative for economically processing large flows of industrial air emissions containing dilute methane (0.1–1.0 %v/v). Process viability results from the CH4MIN's ability to oxidize the dilute methane at the low temperature of 850°C, while recovering up to 90% of the reaction heat as a high-quality (600-800°C) air stream free of NOx. This energy can then be used to meet site-specific thermal energy requirements or converted to electric power, thus avoiding the purchase of energy. The elimination of these methane emissions also benefits global warming prevention [8].

The benefits of the CH4MIN technology were evaluated using a flow rate of 100 m^3/s of coal mine ventilation air at 0.5 %v/v of methane [9]. In the current situation, mine ventilation air is rejected to the atmosphere and greenhouse gas emissions are equivalent to 238,000 tones of CO_2 per year. Gases rejected to the atmosphere contain a large amount (17.9 MW) of potential thermal energy, which is left unutilized. The proposed treatment of this mine ventilation air with the CH4MIN technology provides the following benefits: Heat recovery: 14 $MW_{therm.}$ per year; and reduced greenhouse gas emissions: 208,000 equivalent tones of CO_2 per year.

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Austin Chem Eng - Volume 1 Issue 1 - 2014
ISSN : 2381-8905 | www.austinpublishinggroup.com

Citation: Sapoundjiev H. Unsteady State Processes in Catalysis: Efficient Way for Energy Savings, Air Pollution Prevention and GHG Mitigation. Austin Chem Eng. 2014;1(1): 1001.