

# **PACKED BEDS**

## **I-15. Steady State and Dynamic Reactor Models for Coupling Exothermic and Endothermic Reactions**

### **A. Problem Definition and Research Objective**

The summary and the key findings of the thesis on “Steady State and Dynamic Reactor Models for Coupling Exothermic and Endothermic Reactions” are presented in this report. This thesis theoretically investigates the coupling of exothermic and endothermic reactions in the recuperative and in the directly coupled adiabatic reactors using the steady state and transient pseudo-homogeneous plug flow models. The performance of different reactor systems was compared and the preliminary criteria for the selection of the reactors based on the rate of heat generation and the rate of heat consumption are proposed. The coupling of exothermic and endothermic reactions at the catalyst particle level is analyzed using the boundary-element method. Similarly the occurrence of the multiple steady states in the catalyst particle is also examined using the newly developed boundary element combined continuation algorithm. The catalytic partial oxidation of methane to syngas in a short contact time packed bed reactor is studied, as a test system, using the plug flow and axial dispersion heterogeneous models. The finite difference based method of lines approach is used to solve the transient models through out this work and it is found that this approach of solving the partial differential equations is robust, simple to develop and easy to implement in the computer. Some of the specific conclusions are listed below.

### **B. Accomplishments**

The counter-current reactor shows the hot pinch and cold pinch cross-over points in its temperature profiles, for some of the parameters investigated using both 1-D and 2-D models. At these points, both the exothermic and endothermic streams have identical temperatures. The counter-current reactors also exhibit multiple steady states. The hot spot is an issue in the counter-current reactor and the use of inert packing in a portion of the reactor reduces the hot spot, whereas the length of inert packing has to be optimized for the operating conditions. It is also found that the inert packing reduces the magnitude of the cold pinch cross-over point temperature in the counter-current reactor and also the catalyst requirement. In general, it is observed that the counter-current configuration yields higher conversion than the co-current configuration in shorter reactors.

The co-current reactors, generally, result in lower temperature peak on the exothermic side than the counter-current reactor. The magnitude of the temperature peak could be reduced drastically by suitable catalyst activity profiling in the co-current reactors. However, during the transient mode of operation the temperature peaks on the exothermic side exceed the steady state temperature peak. The wrong-way occurs in counter-current and co-current reactors with both increase and decrease in the feed temperature and hence the dynamic studies are essential for the optimization of operating variables in these reactors.

Two dimensional models were used to study the effect of design and operational variables on reducing the temperature peak in the recuperative reactors. It is found that the increase in the distance between the tubes (exothermic side, at constant exothermic stream velocity) or increase in the flow rates of the exothermic streams increase the magnitude of the temperature peak. The radial mixing also plays an important role in determining the magnitude of hot spot and the cases with lower radial Peclet Number favors the uniform transverse temperature distribution resulting in lower temperature peak.

In the direct mode of coupling SIMDCAR (where catalyst favor both the reactions) and SEQDCAR (the reactor has alternate beds of exothermic and endothermic catalyst) were investigated and compared with co-current reactor. It is observed that if  $\beta^c Da^c$  (rate of heat consumption)  $>$   $\beta^h Da^h$  (rate of heat generation), the conversion in the adiabatic reactor is lower than that in the co-current reactor and between the directly coupled adiabatic reactors; SEQDCAR should be used to obtain higher conversion. If  $\beta^c Da^c < \beta^h Da^h$ , then SIMDCAR results in higher conversion with a lower temperature peak compared to the co-current reactor and SEQDCAR. For the case, where  $\beta^h Da^h = \beta^c Da^c$ , the reactors are to be chosen based on the relative magnitudes of the exothermic and endothermic heats of reactions. It is found that as the catalyst particles in SIMDCAR undergo both exothermic and endothermic reactions simultaneously, they exhibit multiple steady states, for some parametric range. The presence of endothermic reaction reduces the range of Thiele Modulus at which the multiple steady states occurs and the multiple steady states were vanished after a critical reactant composition at the catalyst surface.

Exergy analysis of the recuperative and the directly coupled adiabatic reactor show the extra entropic loss (lost work) in the heat exchanger reactor due to the heat transfer across the tube wall between the exothermic and endothermic sides. For most of the cases, the counter current reactor results in a higher exergy loss compared to the co-current or directly coupled adiabatic reactor. The exergy analysis should be combined with other performance parameters such as the exit conversion and the hot spot to obtain a comprehensive understanding of different modes of coupling. The performance (achieved conversion) of the co-current and counter-current reactors is also compared against that of the bench-mark model and this procedure of comparing the performance helps in choosing the suitable reactor for the desired application.

In the case study of catalytic partial oxidation of methane to syngas, investigated using the heterogeneous models, it is found that the packed bed reactor exhibits 'predominantly exothermic' and 'predominantly endothermic' regions. In the region where the exothermic reaction is predominant, the temperature at the catalyst surface is greater than the gas phase temperature and it is otherwise in the region where the endothermic reaction is predominant. It is shown that the increase in the mass velocity of the reactants increases the productivity and the methane conversion slightly in this short contact time reactors but only at the expense of increased pressure drop. The increase in the conversion is due to increase in the temperature peak and/or due to increase in the feed temperature but not due to increase in the transport coefficients, as stated in the literature. The addition of water in the feed reduces the exit temperature / equilibrium temperature but has the potential of increasing the temperature peak within the reactor. The magnitude of the temperature peak in the reactor depends on the methane-to-oxygen ratio and methane-to-steam ratio in the feed.

The dynamic behavior of this process in the short contact time packed bed reactor is also analyzed. The wrong way behavior could result in this process both by decreasing or increasing the feed temperature and/or by the sudden addition of steam to the feed. The wrong way could also result in a cold spot in the reactor, due to the presence of endothermic reactions. It is also found that the rise in the temperature peak, due to wrong way, is limited due to the simultaneous occurrence of the endothermic reforming reactions along with the combustion reactions. For the range of parameters investigated, the wrong-way behavior does not affect the reactor performance or pose any severe challenge to the catalyst used.

### **C. Recommendations for Future Work**

This research provides the foundation for further investigations in this field. The following are to be studied to understand the phenomenon of coupling exothermic and endothermic reactions and to design the efficient reactor:

- i) Various modes of coupling have to be compared using the heterogeneous models accounting for the deactivation of the catalyst. The catalyst used for these systems, especially for exothermic reactions, could deactivate due to sintering etc and its effect on the coupling has to be analyzed.
- ii) Different modes of coupling in the catalyst wall coated reactor (such as in monolith reactor) has to be studied and compared with that of the packed bed reactor.
- iii) Some relevant experiments are to be conducted to confirm the observations reported in this thesis, especially the transient behavior.
- iv) The catalytic partial oxidation of reactors in the radial flow reactors has to be studied. By this approach the short residence time can be achieved with lower pressure drop while maintaining higher productivity. This study will guide us in the scale-up of short contact time reactors.
- v) The packed bed reactor with the distributed oxygen, through appropriate membranes, has to be studied. The distribution of oxygen reduces the magnitude of the hot spot observed in the reactor, as the partial pressure of oxygen at any point in the reactor will be lower compared to the non-distributed case. This also will help in improving the thermal efficiency of the process.

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## I-16. Exergy Analysis and the Reactor Performance

### A. Problem Definition

The thermal efficiency of coupling exothermic and endothermic reactions, in a single reaction space, is a key parameter in comparing the performance of different modes of coupling. The first law of thermodynamics simply guarantees that the total energy (enthalpy) of the system is conserved and it can be transformed to other forms of energy. The decrease in the quality of energy during the transformation is not explained by the first law of thermodynamics. The quality of an energy stream can be defined as the capacity to do useful work with respect to the surrounding / environment. The second law of thermodynamics quantifies the quality of energy streams in terms of entropy losses. Hence, the energy-use and the thermal losses can be effectively determined by combining both the first and the second laws of thermodynamics, by applying the concept of exergy. This work investigates the procedure to calculate the exergy losses in the reactor systems and demonstrate the use of exergy analysis to compare the performance of various modes of coupling. The derivation of stream exergy for chemical and non-chemical systems and the calculation of exergy losses in a process vessel / system are studied.

### B. Research Objectives

The exergy of a stream is defined as the useful energy, thermodynamically available, to perform work (exergy is also termed as ‘availability’). To perform exergy analyses, one needs to know the exergy (available energy) of every material stream participating in a process in addition to the exergy of the heat streams and work. In the absence of kinetic and potential exergy terms, the basic exergy/mol (of a stream) can be defined as,

$$Ex = (H - H_o) - T_o(S - S_o) \quad (1)$$

where  $H_o$  and  $S_o$  are enthalpy and entropy of the stream at reference conditions ( $T_o$ ). The difference between the total exergy entering and leaving the system is the exergy loss. The exergy loss can be used as the parameter to compare the performance of different reactors, at similar conversion level.

The exergy losses, which is also referred to as the Lost Work (LW), can be derived by combining I and II law of thermodynamics and using Eq.1. The lost work is the measure of process inefficiency (which has units of energy) and is given by:

$$LW = T_o \Delta S_{irr} \quad (2)$$

Here,  $\Delta S_{irr}$  is the entropy loss in the system. Lost work tends to zero for reversible process and the magnitude of lost work depends on extent of process irreversibilities like fluid friction, heat transfer due to finite temperature-driving forces, mass transfer due to finite concentration or activity driving forces, mixing of streams at differing conditions of temperature, pressure, concentrations etc.

For chemical systems, the calculation of the exergy of the material streams is an additional challenge. The exergy of material stream can be defined as a summation of three different terms such as exergy due to the chemical term, the physical term and a mixing term and is given as:

$$Ex = Ex_{chem} + Ex_{phys} + \Delta_{mix} Ex \quad (3)$$

The procedure to calculate the individual contributions to the total exergy is prescribed by Hinderink et al. [1].

The exergy analysis is used to compare the thermal losses in different modes of coupling exothermic and endothermic reactions. The detailed procedure to calculate the exergy of material streams in partial oxidation of methane to syngas and the exergy losses observed in the adiabatic reactor system for the above process is also studied.

### C. Accomplishments

This work investigated different types of thermal losses associated with recuperative and directly coupled adiabatic reactors. The exergy loss due to entropy contribution is common to both the modes of coupling. On the other hand, the recuperative or heat exchanger reactor exhibits an additional exergy loss / Lost Work and this is due to heat transfer across the wall between exothermic and endothermic side. Generally, the exothermic side transfer heats to the endothermic side at higher temperature. The endothermic side receives heat from the other side at lower temperature. This results in entropy loss, which results in an additional Lost Work. This extra Lost Work is not present in the adiabatic reactors. The extra Lost Work and Lost Work due to entropy contribution are used to compare the performance of these reactors.

Similarly, the exergy losses in the adiabatic reactor carrying catalytic partial oxidation of methane to syngas are calculated and analyzed. The effects of feed conditions on the exergy losses are also studied. Table 1 shows the exergy losses for the above system for two cases. More detailed information on this work can be found in the doctoral thesis of Ramaswamy [2].

For detailed information and for a copy of the thesis, “Steady State and Dynamic Reactor Models for Coupling Exothermic and Endothermic Reactions”, contact Prof. M.P. Dudukovic at CREL at [dudu@wustl.edu](mailto:dudu@wustl.edu), (314) 935 6021.

**Table 1: Exergy Losses in the Catalytic Partial Oxidation of Methane to Syngas in an Adiabatic Packed Bed Reactor (Pressure : 40 bar, Temperature = 773 K)**

Cases	Feed Conditions (mole %)	Inlet Enthalpy (kJ/g)	Outlet Enthalpy (kJ/g)	Inlet Entropy (kJ/g-K)	Outlet Entropy (kJ/g-K)	Inlet Exergy (kJ/g)	Outlet Exergy (kJ/g)	Exergy Loss (kJ/g)
1	CH <sub>4</sub> : 67 % O <sub>2</sub> : 33 %	-1.549	-1.549	0.00943	0.01549	26.64	25.00	1.64
2	CH <sub>4</sub> : 60 % O <sub>2</sub> : 30 % H <sub>2</sub> O: 10 %	-2.503	-2.503	0.00965	0.01519	24.59	22.93	1.66

### D. References

1. Hinderink, A.P. et al., Exergy analysis with a flow sheeting simulation – I. Theory, calculating exergies of material streams. *Chemical Engineering Science*, 51 (1996), 4693.
2. Ramaswamy, R.C. Steady State and Dynamic Reactor Models for Coupling Exothermic and Endothermic Reactions. D.Sc. Dissertation. Washington University in St. Louis, **May 2006**.