Optimal Inlet Temperature Profile Strategies for Decaying Fixed Bed Reactor

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Abstract

Inefficient use of raw materials in most catalytic processes can be attributed mainly to the deactivation of the catalyst in chemical reactors. In order to achieve efficient use of raw materials, this paper addresses mitigation of deactivation through optimization of inlet temperature-time trajectories. The optimization of temperature profiles in reactors is one of the key problems in the synthesis catalytic reactor (Hwang, 2004).

The economics of the catalytic reactor, which is prone to coking, depends on the relative rates of the reactions and deactivation of catalyst. Optimum performance, measured in terms of yield, is achieved by decreasing the inlet temperature with time as the catalyst deactivation rate is more sensitive when compared to the reaction rate. In contrast to this, it is widely believed in industry that increase of inlet temperature with respect to time results in constant performance of the reactors. This results in lower impact on the separation networks. Therefore, two types of objectives in terms of reactor yield have been considered, *a.* maintaining average yield constant through a single operating cycle, which results in increasing inlet temperature profile through time, *b.* optimizing for the maximum overall yield results in decreasing inlet temperature profile through time. Optimization of the operational variables of the catalytic reactors mainly depends on the downstream processing requirements i.e. separation networks.

Simulation of the transformation of methanol into olefins and light gasoline is carried out in an isothermal fixed bed reactor using the reaction and deactivation kinetics from (Gayubo et al., 1996). It is noted that the performance decreases very quickly in the case of the higher temperature, where the rate of deactivation is found slow for the lower temperature. Therefore, it can be concluded that higher inlet temperature maintains higher olefins yield initially but elevated temperature causes very rapid deactivation, which leads to rapid decay in performance. Lower

temperature gives lower yield compared with higher temperature initially but maintains the olefin yield for a longer time, due to lower deactivation rate at lower temperature. Therefore, it is deduced that controlling inlet temperature to be higher in the initial time and decreasing with time on stream maintains higher average olefins yield. This means that the relative kinetics of the reaction and deactivation dictates the performance at given temperature. In overall, optimization of the inlet temperature through lifetime of the catalyst can result in improvement of the performance of the catalytic fixed bed reactor, instead of maintaining it constant.

In this work, average yield is maintained at higher value but decreasing through cycle time. In common practice, performance of the reactor is usually maintained constant or nearly constant to get less impact on down stream but with a cost of product and inefficient use of raw materials. Some more runs are also made keeping constant olefin yield at certain values and inlet temperature profile is optimized through cycle time. In these runs, inlet temperature profile is found increasing for lower value of olefins yield and maintains constant performance through cycle time.

A novel profile generation tool (Choong & Smith, 2004) is used to develop a profile and parameters of profile determine the size and shape of the temperature profile and so the values of the optimizing variables at different time. The resulting dynamic optimization problem is solved using a nonlinear optimization algorithm.

1. Introduction

Catalytic processes are the backbone of chemical, petroleum refining and environmental remediation industries. The development of catalysts and catalytic processes is a multidisciplinary effort involving chemists, chemical engineers and business professionals.

Most of the processes mentioned above face the problem of catalyst deactivation, which deteriorates the performance of the plant. Catalyst deactivation occurs because of coke formation, poison deposition and solid state transformation (sintering). Coke formation results from undesired side reactions and affects the activity through the coverage of active sites and blockage of pores. Poisoning of catalysts involves species present in the feedstock that are either irreversibly adsorbed or modify the active sites by chemical reaction. The poison may also be formed in the reactor from feedstock components or intermediates.

The lack of a reliable mathematical model of catalyst deactivation by coke formation is the main problem in simulating this effect. Kinetic equations for the main reactions are now well established and are being used as an essential tool for process design and simulation. However, kinetic equations representing the process of coke formation and catalyst deactivation are still not well developed. This makes it difficult to optimize the overall system.

In order to understand and quantify the catalyst deactivation by coke deposition, realistic models have been proposed (Gayubo et al., 1994), together with mechanisms that take into account several causes of deactivation simultaneously. The application of these models is limited by problems with the calculation of kinetic parameters.

The performance of the catalyst pellets in different reactors can be significantly improved through optimization of different parameters like inlet in order to maintain the throughput of the plant. Adjustment of inlet temperature allows keeping the overall rate of reaction constant over the plant cycle.

The current work will introduce different strategies of inlet temperature optimization through operating cycle of the reactor to compensate the loss of catalyst activity due to catalyst deactivation.

2. Inlet temperature profile optimization

In practice, inlet temperature of the reactants to the reactor is increased with time to compensate for the loss of catalyst activity. It helps to keep a constant performance of the reactor or reactor network. However, it is often the case that increasing the inlet temperature accelerates deactivation. This depends on the relative kinetics of the main reaction rate and deactivation rate and their dependency on the temperature. Performance can be improved by developing an optimal temperature profile through catalyst life time. In the current work, profile based optimization is used to find the optimum inlet temperature profile.
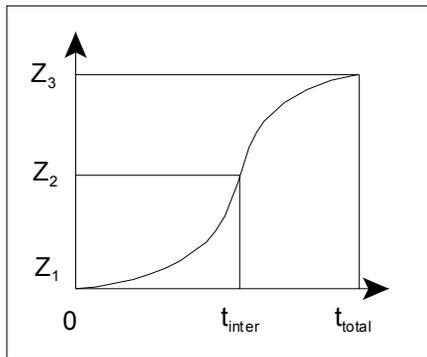
2.1. Profile based optimization

Control variable parameterisation approach was implemented for the optimal operation of various continuous variables in crystallization operations (Choong & Smith, 2004). A novel profile generation tool was used to develop an inlet temperature profile to determine the size and shape of the profile and so the values of the optimizing temperatures at different value of the cycle time. The resulting dynamic optimization problem is solved using a nonlinear optimization algorithm.

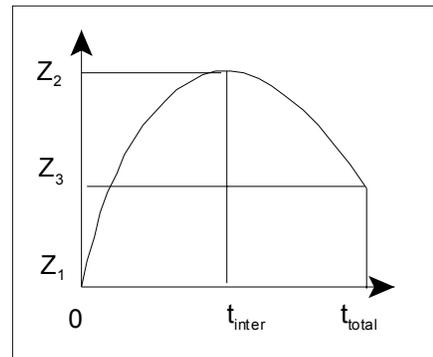### Profile based synthesis

1. Type 1 (exponential curve)

2. Type 2 (asymptotic curve)

$$Z(t) = Z_1 - (Z_1 - Z_2)\left(\frac{t}{t_{total}}\right)^{A_2}$$

$$Z(t) = Z_2 - (Z_2 - Z_1)\left(\frac{t_{total} - t}{t_{total}}\right)^{A_1}$$

(Type 1 + Type 2)

(Type 2 + Type 1)

Figure 2-1 Profile based synthesis

Where,

Z = Profile value at point t

Z_1 = Inlet value

Z_3 = Outlet value

t = Independent variable

A_1 = the power of equation type 2 ($A_1 \geq 1$)

A_2 = the power of equation type 1 ($A_2 \geq 1$)

t_{inter} = the peak location

Z_2 = Intermediate peak point for the curve

t_{total} = final value of independent variable

Fundamentally, profiles are divided in two types Type 1 (exponential) and Type 2 (asymptotic). As shown in Figure 2-1 Combinations of Type 1 and Type 2 profiles generate different kinds of profiles. By changing the profile parameters, various profiles can be generated. More details about profile generation tools are given in (Choong & Smith, 2004).

The optimization of temperature profiles in reactors is one of the key problems in the synthesis catalytic reactors. The objective would be to find a temperature profile for the specified reaction system, which could maximize the yield of one of the products. Many papers dealing with the optimization of temperature profiles have already been published (Grzesik & Skrzypek, 1983); and have dealt with so-called homogeneous or pseudo-homogeneous processes.

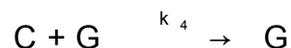## 2.2. Case study 2: Methanol to Olefins (MTO)
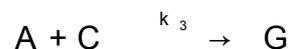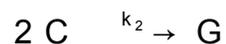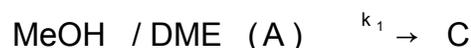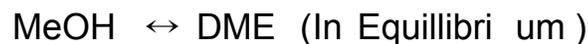
2.2.1. Introduction

Mobil's novel synthetic gasoline process, based on the conversion of Methanol to hydrocarbons over Zeolite catalysts, was the first major new synthetic fuel development since the development of the Fischer-Tropsch Processes. The process is known as the Methanol-to-gasoline (MTG) process. The Methanol-to-Olefins (MTO) process for the synthesis of light Olefins arose from the development of the MTG process, as a supplementary route to the main objective of obtaining synthetic gasoline. Recently, the interest in obtaining light Olefins has been increasing (Gayubo et al., 1996). The catalyst chosen by Mobil for the MTO process was the HZSM-5 Zeolite. In this process, two types of catalyst deactivation occur. The first type is reversible coking of the Zeolite; where the coke is burned off during regeneration, restoring activity. The second type is permanent deactivation of the

Zeolite because of high pressure steam that is produced from the water product due to high processing temperature. This type of deactivation is very slow compared to the first one and highly selective to excessive pressure and temperature.

The conversion of Methanol to light Olefins over a HZSM-5 Zeolite was studied in current work.

2.2.2. Kinetic models for the main reaction and catalytic deactivation

The kinetic scheme used in this work for the MTO process has been adopted from published literature (Gayubo et al., 2003; Gayubo et al., 1996). This kinetic scheme groups the components into lumps and is based on that proposed for the MTG process. Methanol and Dimethyl ether are separately taken in to account because of their different reactivity.

$$MeOH \leftrightarrow DME \ (In \ Equillibri \ um \ )$$

$$MeOH \ / DME \ (A) \ \xrightarrow{k_1} \ C$$

$$2 \ C \ \xrightarrow{k_2} \ G$$

$$A + C \ \xrightarrow{k_3} \ G$$

$$C + G \ \xrightarrow{k_4} \ G$$

… 2.1

Where, $MeOH$, Methanol

  DME, Dimethyl ether

  A, Lump of oxygenate

  C, Lump of Olefins

  G, Gasoline

The net rate equations at zero time on stream for the formation of three of the four components (Methanol, Dimethyl ether and light Olefins) of the kinetic scheme are shown below, where the steps are assumed to be elemental and by expressing the concentration of the components as the mass fractions:

$$-r_{A0} = k_1 X_A + k_3 X_A X_C$$

$$-r_{C0} = k_1 X_A - k_2 X_C^2 - k_3 X_A X_C - k_4 X_G X_C$$

$$-r_{G0} = k_2 X_C^2 + k_3 X_A X_C$$

$$\dots 2.2$$

Where, k_i = rate constant of ith reaction = $k_{i0}\ exp\ [(-E_d/RT)$, h^{-1}

X_i = mass fraction of ith component

r_i = reaction rate of ith component

Kinetic model for catalyst deactivation in the MTO process:

The kinetic modelling of catalyst deactivation in the MTO process includes reversible deactivation by coking at lower temperature. The deactivation model is partially selective as it considers the same catalyst activity, for all the steps of the kinetic scheme. The activity loss by coke deposition is a function of the remaining activity, compositions of the components and the temperature of the reacting medium:

$$r_d = -\frac{da}{dt} = (k_{dA} X_A + k_{dC} X_C + k_{dG} X_G)\, a$$

$$\dots 2.3$$

This equation is based on a previous one for the coke deactivation in the MTG process, that coke deactivation depends on the concentration of all the species present. The values calculated for the kinetic parameters of the deactivation are (Gayubo et al., 2003; Gayubo et al., 1996):

$$k_{dA} = 0.165E9 * exp\left[-\frac{25870}{RT}\right]$$

$$k_{dC} = 0.121E6 * exp\left[-\frac{18930}{RT}\right]$$

$$k_{dG} = 0.603E8 * exp\left[-\frac{26280}{RT}\right]$$

… 2.4

Where,

X_i = mass fraction of ith component

r_d = reaction rate of ith component

k_{di} = rate constant for deactivation, h^{-1}

Simulation of the transformation of methanol into olefins and light gasoline is carried out in an isothermal fixed bed reactor using the reaction and deactivation kinetics. The kinetic models for the main reaction and for the deactivation are adequate in the range between 575 and 650 K.

2.2.3. Model Validation and results

(Gayubo et al., 1996) carried out various experiments in a fixed bed for the same system to show the effects of the deactivation on the performance of the fixed bed reactor. Figure 2-2 shows the olefins fractions in the product at different inlet temperatures and times on stream. Graph **a** in Figure 2-2 presents represents olefin mass fraction in the product stream with time on stream at a constant inlet temperature of 598 K, 0.075 g of catalyst.h / g of methanol of space time for 3.5 hrs. Whereas Graph **b** in Figure 2-2 presents olefin mass fraction in product stream with time on stream at constant inlet temperature 648 K, 0.052 g of catalyst.h / g of methanol of space time for 1.5 hrs.
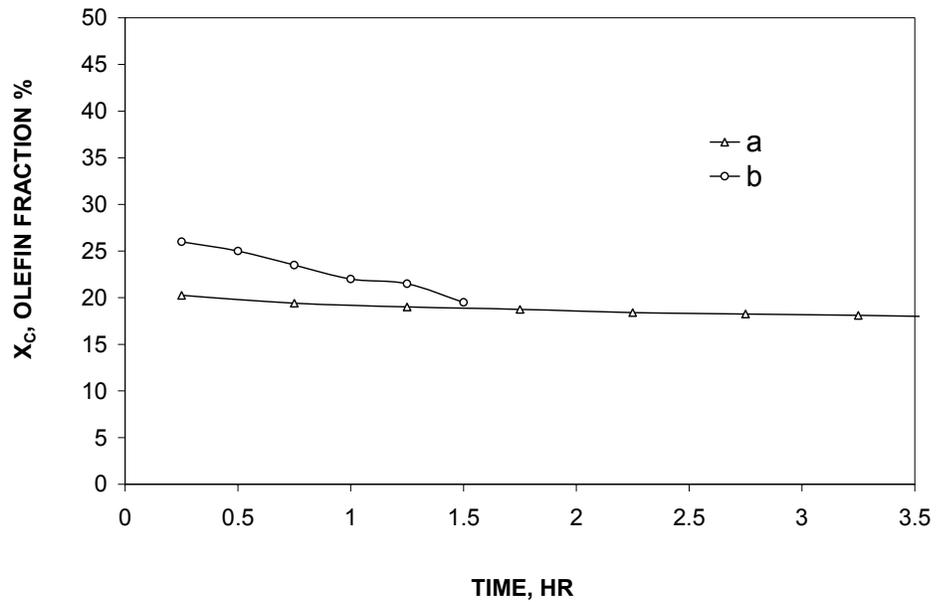
Figure 2-2 Experimental results at 598K and 648 K (Gayubo et al., 1996, 1998)

Figure 2-3 shows a comparison of simulation of the fixed bed reactor with deactivation at various operating conditions compared with the experimental results. The simulation and experimental data are in good agreement.
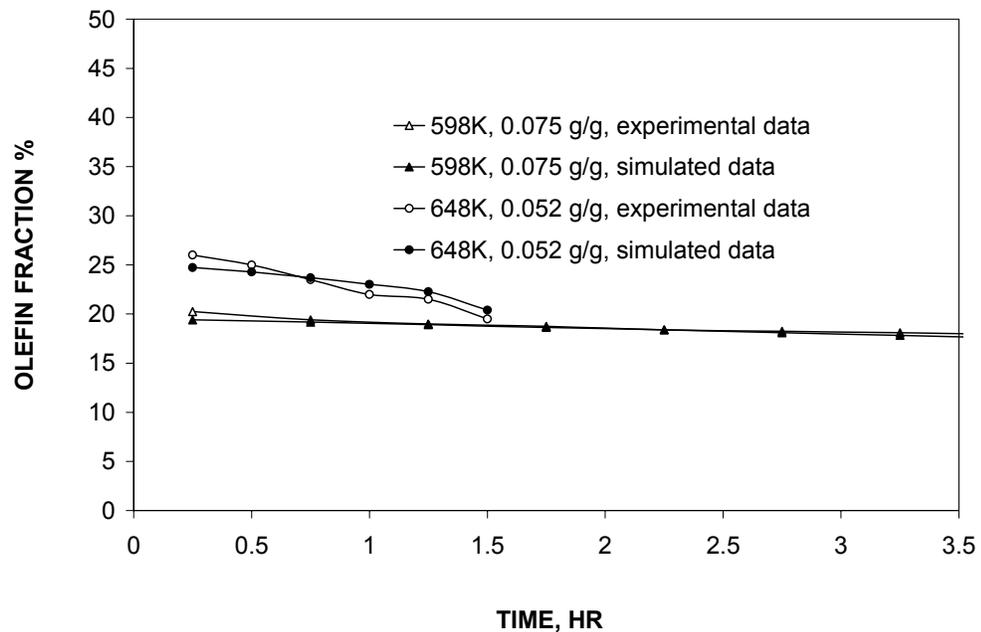

Figure 2-3 Comparison of experimental and simulated results at 598K and 648 K

The good comparison demonstrates the validity of the kinetic model for reaction and deactivation. It is worth noting that the performance decreases very quickly in the case of the higher temperature (648K), where the rate of deactivation is slow for the

lower temperature (598K). Both simulation runs have been carried out for the same time on stream (5.0 hrs) and space time (0.052 g of catalyst.h / g of methanol) to study the effects of inlet temperature. Figure 2-4 shows the effect of the temperature on the fraction of the olefins in the product stream.
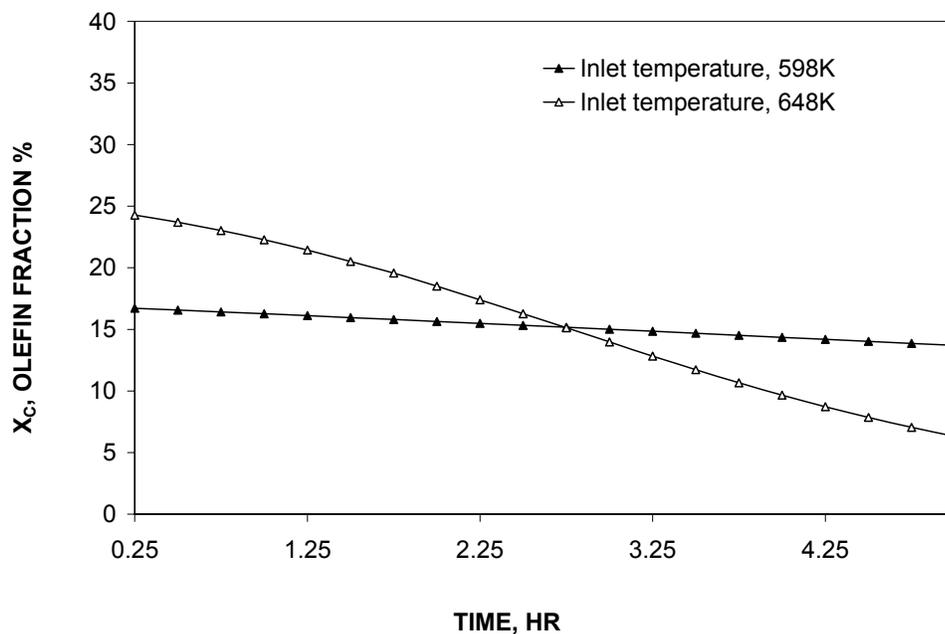

Figure 2-4 Simulated results at different inlet temperature with the same space time

From Figure 2-4, higher inlet temperature maintains higher olefins yield initially but elevated temperature causes very rapid deactivation, which leads to rapid decay in performance. Lower temperature gives lower yield compared with higher temperature initially but maintains the olefin yield for a longer time, due to lower deactivation rate at lower temperature. It can be deduced that controlling inlet temperature to be higher in the initial time and decreasing with time on stream maintains higher average olefins yield. This means that the relative kinetics of the reaction and deactivation dictates the performance at given temperature. Therefore, it is important to optimize inlet temperature through time on stream, instead of maintaining it constant. Figure 2-5 shows the olefins yield fraction at optimized inlet temperature profiles in comparison with constant inlet temperatures at 598K and 648K. The optimized inlet temperature profile is shown in Figure 2-6.
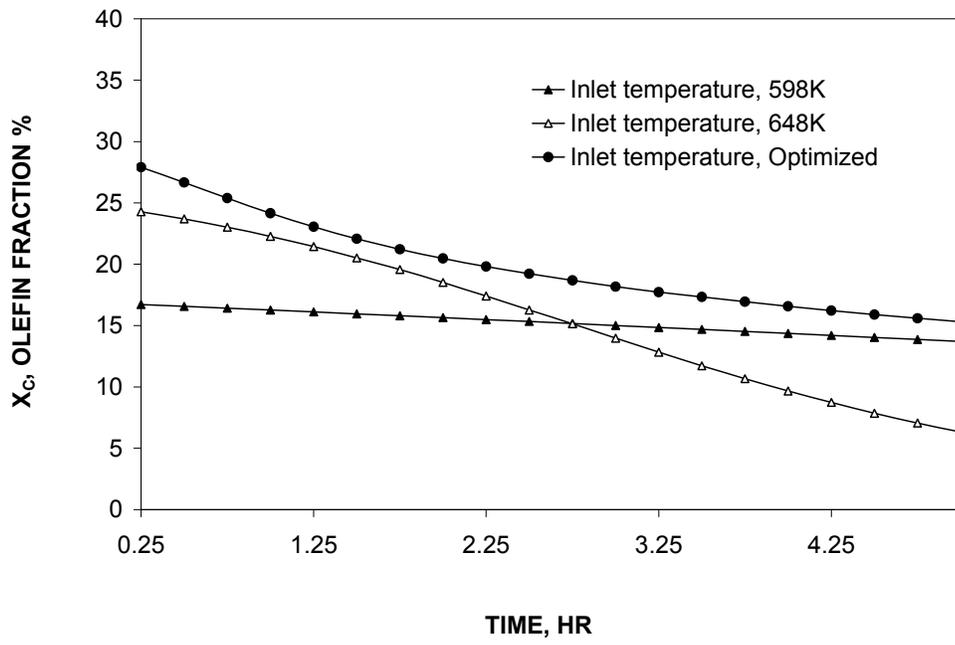
Figure 2-5 Simulated data for optimized inlet temperature profile compared with constant Inlet temperature 598K and 648K
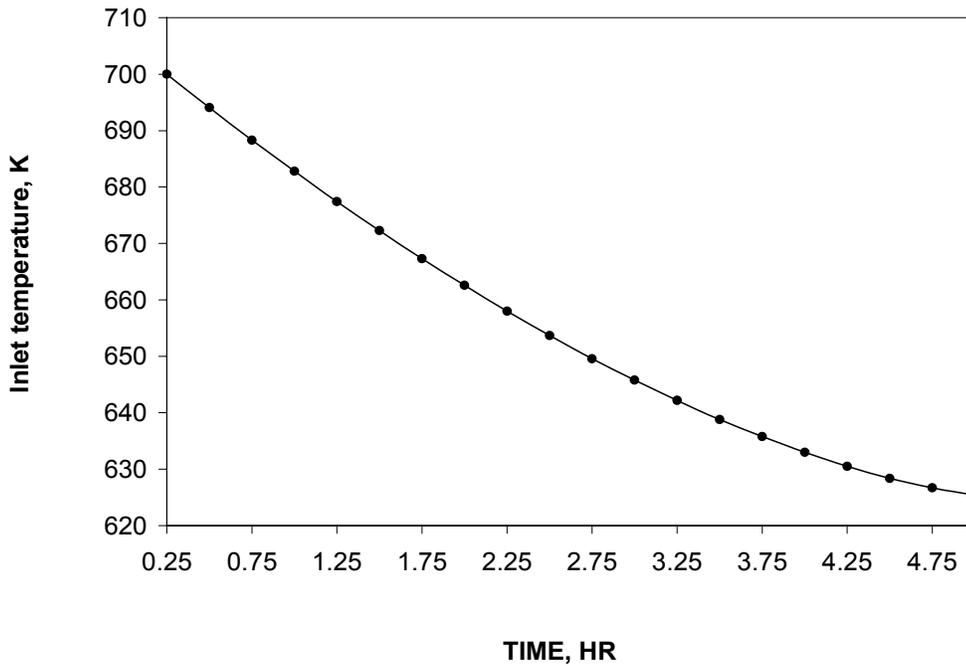

Figure 2-6 Optimized inlet temperature profile through time on stream

The optimized inlet temperature profile tries to maintain the effective reaction rate (reaction rate x catalyst activity) at a higher value, as initial activity is higher, so elevated temperature maintains the higher effective reaction rate (increasing the

reaction rate). Higher temperature causes rapid catalyst activity loss and so it is necessary to control the relative kinetics of the reaction and deactivation through decreasing the inlet temperature with time on stream. Results at different constant temperatures and at optimized temperature are listed in Table 2.1.

Inlet temperature profile	Avg olefin fraction (%)
Constant, 598 K	15.23 %
Constant, 658 K	15.54 %
Optimized through time	19.91 %

Table 2.1 Comparison of the performance at different inlet temperature level

These runs counter to the common industrial practice of increasing temperature through the catalyst life to maintain constant performance. However it should be noted, even though the average yield is maintained higher through cycle, the yield varies through time. This means that the resulting separation problem after the reactor varies through time.

In above runs, average yield is maintained at higher value but decreasing through cycle time. In common practice, performance of the reactor is usually maintained constant or nearly constant to get less impact on down stream but with a cost of product and inefficient use of raw materials. Some more runs are made keeping constant and higher olefin yield at certain values and inlet temperature profile is optimized through cycle time. Olefin yield through cycle time is shown in Figure 2-7 where it is constrained to maintain a constant value.
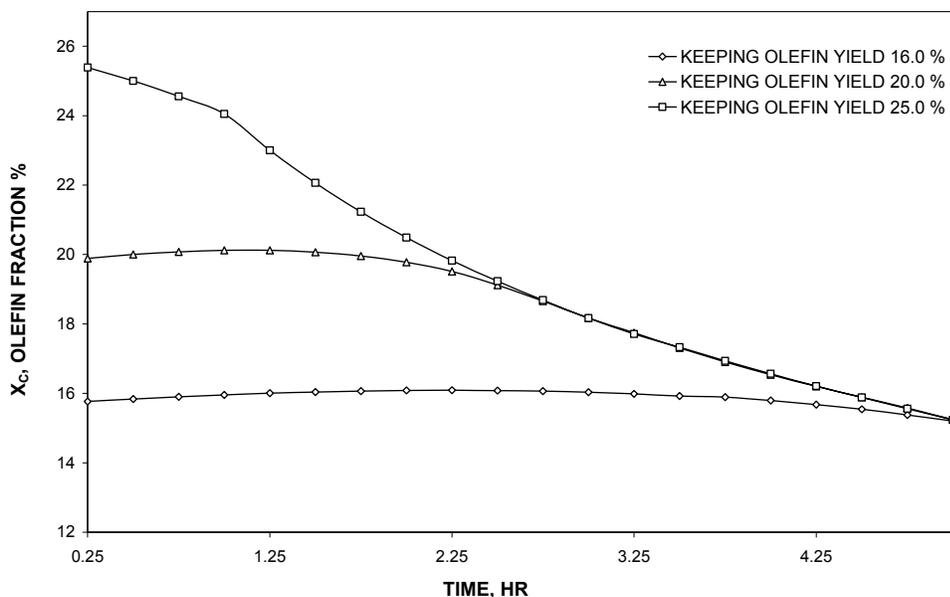
Figure 2-7 Keeping olefin yield constant through cycle at certain values

For lower value of olefin yield (16.0 %), it could maintain the constant value with increasing inlet temperature through cycle time but for the higher value (25.0 %), it could not maintain a constant value because of the rapid loss of the catalyst activity and results out decreasing inlet temperature after increasing for short time. It has come out with increasing profile for short time because of the constraint in olefin yield (25.0 %). It could be decreasing profile if it would have not be constrained and might have come out with higher average yield for that time span as we can see from Figure 2-6, which is an optimized inlet temperature profile for higher average olefin yield without any constraint (Figure 2-5). It has tried to maintain a constant value of olefin yield for 20.0 % for some time (2.25 hr) with increasing inlet temperature in that time period and then it starts decreasing inlet temperature as catalyst activity drops faster due to higher value of temperature. Inlet temperature profiles for various value of olefin yield are shown in Figure 2-8. Simulation run is also made to compare the performance with increasing and decreasing inlet temperature profile. When inlet temperature profile was constrained to be increasing, resulting profile comes with constant temperature profile with olefin yield 15.4 %, where as decreasing profile (Figure 2-6) resulted in olefin yield 19.91 %.
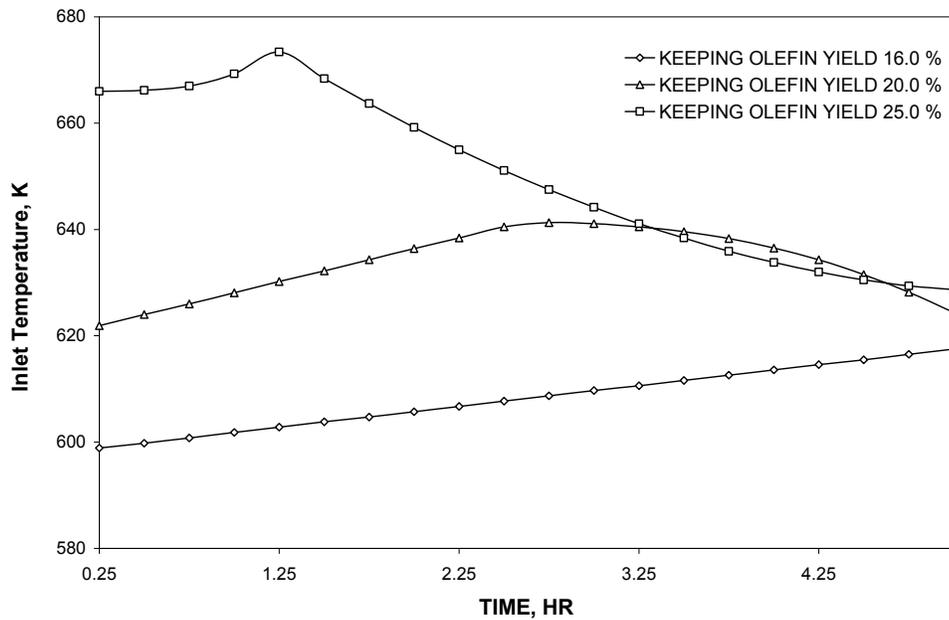
Figure 2-8 Optimized inlet temperature through cycle keeping olefin yield constant

Therefore, it can be concluded that catalyst deactivation is highly sensitive to process temperature as small change in inlet temperature change the catalyst activity in the reactor drastically. Higher value of temperature increases the rate of deactivation so yield could not be maintained constant for longer time and effective cycle time would decrease. Decreasing temperature profile merely gives constant value of yield but maintain higher value of it for longer time. Large change in inlet temperature through cycle may affect the physical and transport properties of the catalyst and reactants and therefore influences the hydrodynamics. It may also lead to significant change in catalyst pellet structure which may tend to sintering. Therefore change in inlet temperature during optimization should be constrained with certain practical value to lessen these effects.

3. Conclusions

Catalyst deactivation takes place in most heterogeneous catalytic reactors and is one of the main causes for the loss of profit in the process industries. Optimization of inlet temperature though operating cycle improves reactor performance significantly by maintaining the optimal ration of main reaction rate and the rate of deactivation.

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