

反應器 Hotspot Moderation 의 大規模 實驗

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Large Scale Experiment on Reactor Hotspot Moderation

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要 約

固定層 管型觸媒反應器에 있어서 發熱反應 일때에 過熱로 因하여 hotspot을 形成한다는 사실은 널리 알려져 있고 이 問題는 現場操業에 큰 危險性을 주고있다.

여기서는 反應器내의 hotspot을 避하는 方法을 綜合的으로 檢討하였고, 其中 heat carrier gas 投入法을 集中的으로 研究하여 反應器 hotspot moderation이 可能하다는 것을 大規模장치로 420°C 以上の 溫度에서 實驗하였다.

反應은 p-xylene의 氣相 ammoxidation 으로서 terephthalonitrile을 生産하는特許된 工程이다. 反應 장치는 길이 12ft, 외경 1 inch, salt-jacket식을 사용하였으며 工業用과 거의 같은 크기이므로 scale-up의 問題가 없는 것이 특징이다. 본 실험에서는 heat carrier gas로는 CH₄, C₂H₆, CO₂ 등을 使用 하였으며, 投入量을 決定하였고, hotspot moderation의 工業的 可能性을 明白히 하였다.

Abstract

It is a well known fact that a hotspot formation is inevitable in a fixed-bed tubular catalytic reactor when the reaction is exothermic, and heat generation is excessive; and this is a serious threat to the safety of the commercial operation of such reactors.

Various suggested methods to avoid the reactor hotspot are categorically discussed, and intensive

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investigation is made toward the heat carrier gas injection method to moderate the hotspot. Large scale experimental verification is conducted at temperatures higher than 420°C.

The system under consideration is the patented p-xylene gas phase ammoxidation reaction to produce terephthalonitrile. The experimental unit consists of 12 ft, 1"OD salt-jacketed reactor, very similar to the commercial scale unit and does not require extra scale-up study. The inert heat carrier gases studied were CH₄, CO₂, & C₂H₄, and percent dilution was determined, to demonstrate the commercial feasibility of the hotspot moderation technique.

Introduction

Even though there are many different types of reactors, fixed-bed tubular catalytic reactor is more popular and has future promises.

Some of the advantages are high throughput, low capital investment, high conversion, simple construction, low catalyst cost, and use of standard units while its disadvantages are side reactions and engineering difficulties because of the hotspot formation (*Fig. 10*). Acrylonitrile and terephthalonitrile reactors are subject to such engineering studies.

The problem of hotspot formation is not new and has been a subject of serious research interest during the past 20 years.

At the 1975 Los Angeles AIChE meeting, under the heading of reactor design safety, Jaffee³⁾ explained the hotspots in hydrogenation, Plundo & Carr⁶⁾ described the hotspot experiences in hydrocracking, benzene hydrogenation, and butadiene processes and McCoy⁵⁾ gave hydroprocessing local overheating example. A round table discussion with audience participation has exchanged ideas both from the industry and academic institutions. In spite of the importance, as yet no adequate method of hotspot moderation has been recommended for practice. A systematic review of the methods is vitally needed. So far, whenever the hotspot problem can not be solved, one has to resort to other types of reactors and sacrifice economically. In the present study, the

objective is to overcome the difficulty of the hotspot problem.

Moderation Methods

1. The oldest known method is the semi-continuous cyclic operation. This unit operates between the ranges where the danger is not expected to occur, and if it ever approaches near danger zone, the unit is shut off. The downtime period is not a complete loss because catalyst regeneration can be carried out during this period. Operational hazard and inconveniences can not be avoided.

2. The attempt of direct computer control became natural because of the extensive process computer applications since 1960 for the purpose of safe and economical operation. In spite of over half million dollar investment, measurement and modelling difficulties can not be eliminated completely (*Fig. 3*).

3. It was reported in 1960 that Tompkins²⁾ of Soviet Union has successfully operated a laboratory bench scale "gradientless" reactor. Even though this work was well publicized, people were only intrigued by the word "gradientless". Because of the end effects and narrow reaction temperature zone, commercial possibility was out of question; and it became known ever since as a kinetic study reactor in laboratory (*Fig. 1*).

4. During 1962-1968, Union Carbide¹⁾ operated a high recycle reactor (*Fig. 2*), but the

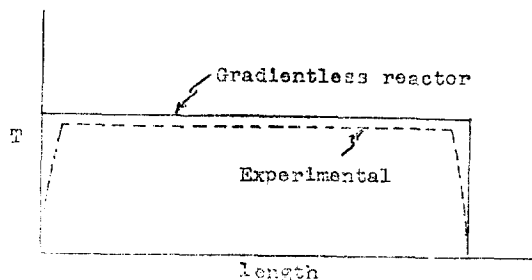


Fig. 1. Tompkin's reactor.

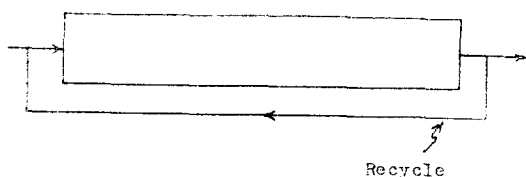


Fig. 2. High-Recycle reactor (Union Carbide).

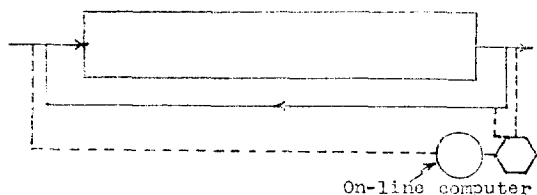


Fig. 3. Computer controlled reactor.

mechanical troubles and operating limitations were excessive. Kuchinski & Squires⁴ have reported that it is difficult for low density gases to reach the high mass velocities necessary to obtain gradientless operation.

5. Local recycle and quench reactor (Fig. 4) was known, but the additional cost and operating difficulties offset any advantages there may be from such reactors. Its temperature profile is shown in Figure 5 and compared with that of fluidized reactor.

6. Use of dummy catalyst and catalyst acti-

vity controlled reactors (Fig. 7) are also reported, but the low conversion and operating difficulties can not be avoided.

7. Surface-coated or fin-tube reactors (Fig. 8) were proposed, but the inherent low gas film-heat transfer coefficient and large pressure drop due to fins, there were very little advantages, and operation was too unreliable. The extent of hotspot moderation was too small compared with the accompanying disadvantages.

8. In the present work, heat carrier gas injection method (Fig. 9) was studied to moderate the hotspot and to provide sufficient safe reaction temperature zone. The details are described in this paper.

A typical pseudo-steady state temperature profile with a reactor hotspot is presented in Figure 10, and upon becoming unstable this system can easily develop into a run-away system as shown in Figure 11. This phenomenon was observed in an unsteady state analog simulation of the reactor dynamics⁷, and was recorded at a short distance away from the reactor entrance. The current objective is to eliminate the difficulties shown in Figures 10 and 11.

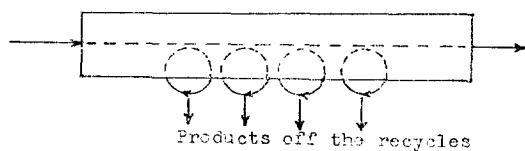


Fig. 4. Local recycle reactor.

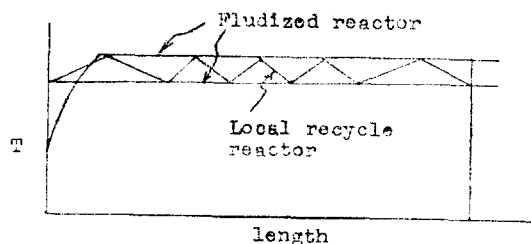


Fig. 5. Manipulated temperature profiles.

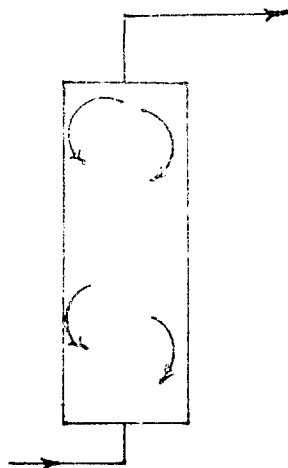


Fig. 6. Fluidized reactor.

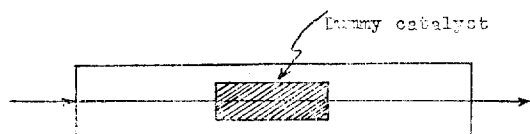


Fig. 7. Reactor with dummy catalyst.

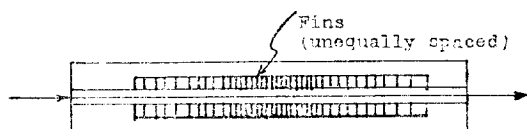


Fig. 8. Fin-tube catalytic reactor.

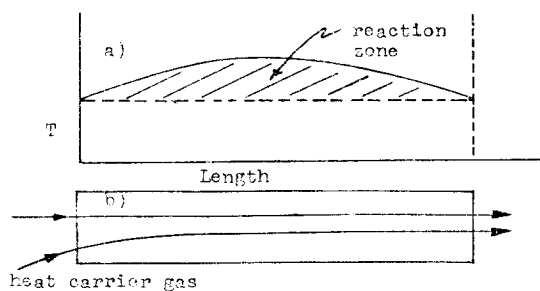


Fig. 9. YOO-Golden TPN reactor.

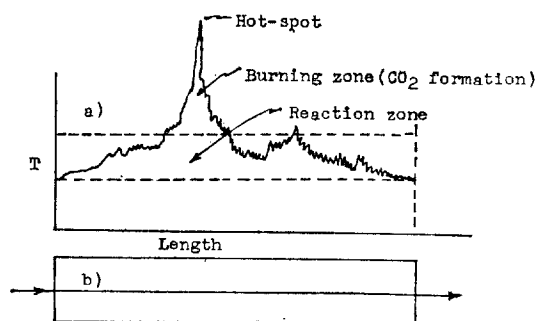


Fig. 10. Typical reactor hot-spot.

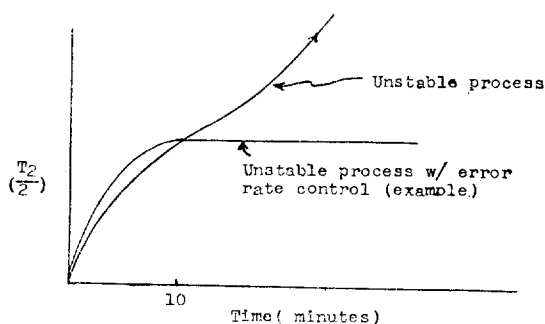


Fig. 11. Temperature control of unstable reactor system.

Experimental Work & Results

The reaction studied in this research was the vapour phase catalytic ammoxidation of *p*-xylene to produce terephthalonitrile⁹⁾ (Fig. 13); terephthalonitrile is an intermediate chemical for polyester fiber. A typical unmoderated feed is *p*-xylene 1%, H₂O 10%, NH₃ 6%, and air 83%, while an example composition of moderated feed is *p*-xylene 1%, H₂O 5%, NH₃ 6%, O₂ 7.1%, CH₄ 20%, N₂ being the balance. *p*-xylene feed was the practical grade of 95% purity, and the remainder 5% consists of *m*-, *o*-xylene, and other aromatics.

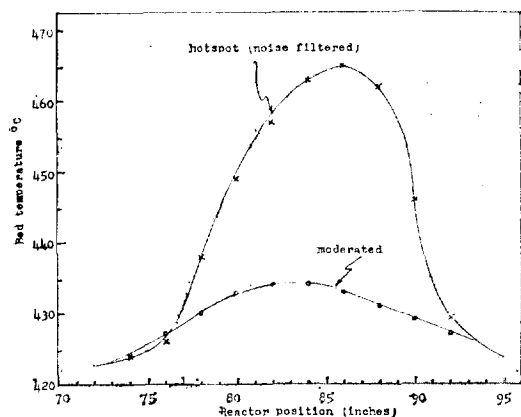
The amount of heat carrier gas injection can vary 5–80% by volume, and the heat capacities can be compared at 427°C: N₂ 7.35 Btu/lb mole °F; CO₂ 11.85; CH₄ 13.88; C₂H₆ 23.72.

The catalyst was 1.28% by weight V₂O₅ and 8.15% Sb₂O₃ impregnated on alumina pellets.

The dark green catalyst was specially prepared for this experiment by using commercially available $\frac{1}{4}$ "-8 mesh Alcoa tabular alumina T-71.

The reactor is a 12 foot, salt-jacketted, carbon steel 1" OD tube, installed with a vapourizer and a preheated at the bottom, and the exit gas departs from the top. The salt bath was kept at all times above 400°C, and the temperature difference between salt bath and the bed temperature varied from 10-115°C along the reactor tube length.

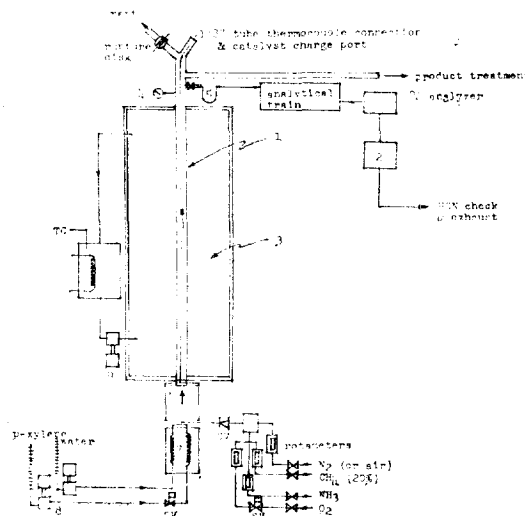
Product was properly treated in an analytical train and vented out to open air after being sufficiently scrubbed. The terephthalonitrile solid product was collected in an air-cooled, ball-joint-



Notes:

1. Catalyst V_2O_5 - Sb_2O_3 on alumina pellets
2. Reactor 1" OD 12ft long
3. Temperature at center, $\frac{1}{8}$ " thermocouple well
4. Feed-1% p-xylene, 21.6% CH_4 , 5% H_2O , 6% NH_3 , 7.1% O_2 , balance N_2
5. Error range: length $\frac{1}{4}$ ", tem. $\frac{1}{4}^\circ C$
6. Dilution w/10% C_2H_6 or 21.6% CH_4 or 31.5% CO_2
7. Slightly above atmospheric pressure
8. Satisfactory conversion & selectivity

Fig. 12. Actual TPN reactor temperature profiles.



1. 12'x1" OD carbon steel reactor, packed w/catalyst pellets
2. Wet test meter
3. Large salt bath, 400°C plus
4. Pressure, atmospheric plus
5. Glass ball-jointed U-tube
6. Preheater
7. Vapourizer
8. Metering pumps
9. Circulating pump

Fig. 13. Sketch of TPN reactor experimental unit.

ted glass U tube as milky white crystals. There were many sampling and analytical difficulties to handle the 3-phase product stream.

Other features of the experimental setup were the provision of a fine screen at the inlet of reactor to load the catalyst from top down, and the installation of a rupture disk at the top even though the operating pressure was slightly above atmospheric, and the installation of $\frac{1}{8}$ " long tube at the center of reactor for a movable thermocouple as the reactor operates at above 420°C. The thermocouple reading error was within $\pm 1/4^\circ C$, $\pm 1/4$ ", and it was considered that there were no end effects in the system.

Operating difficulties of the unit were thought

to be about equivalent to those of commercial unit. Even though there were no particular difficulties encountered, it was tedious to wait for sampling. This is due to the large system time constant to die down. The salt bath was operated continuously 24 hours a day, and it took a long period to take a good sample. There was a slight problem of feed mixing and distribution at the reactor inlet and preheater, but this can be overcome in a well-designed commercial unit. The most difficult part of the experiment was the proper product handling. Ideally, it would seem logical to treat the product in a single gas phase above 420°C, but this became impractical because of analyzer inlet-port plugging and condensation. Thus, one is forced to treat the product in a 3-phase analytical train, which is sufficiently debugged. The solid product was first collected in a ball-jointed *U* tube through a heating-tape-wrapped short sampling tap which terminates at a metal ball joint. The solid product is saturated with condensates and impurities (unreacted *p*-xylene, PTN, IPN, H₂O) and appears wet. The solid-liquid product collected for about $\frac{1}{2}$ -1 hour was analyzed by a separate off-line analyzer for complete details, while the gas was successively treated for NH₃, CO, CO₂, O₂, flowmeter, etc. on-line. The exit gas was occasionally tested for HCN. In general when the conversion is low, a small amount of PTN is produced and when the conversion is high, the solid crystal was nearly pure dinitrile. Upon ammoxidation O₂ and NH₃ concentration diminish, and some NH₃ decomposition was experienced in the vapourizer and preheater section, but this problem can be solved in a commercial unit.

Extreme cautions are necessary to minimize the experimental errors; $\pm 10\%$ error was observed in carbon balance, but this included the errors from 2 feed Lapp pumps, 4 rotameters,

process unsteadiness & noise, sampling tap, *U* tube collector, 4 gas analyzers, wet test meter, etc. One of the best method of error reduction was to lengthen the sampling period. There was no noticable difficulty in moderating the reactor hotspot by the technique. And an excellent hotspot moderation experimental result was obtained as shown in Figure 12, and this is compared with unmoderated result in the same Figure. The conversion was found to be 80-100% with a satisfactory selectivity of 86-83.5%. It was noticed that HCN and CO₂ formation increased with the salt bath temperature level.

Mathematical Prediction

The desire for experimental verification was motivated from the mathematical prediction of the success of the hotspot moderation technique.

The mathematical equations describing the given reaction system are the following three partial differential equations;

$$\frac{k_{ez}}{GC_p} \frac{\partial^2 t}{\partial z^2} + \frac{k_{er}}{GC_p} \left(\frac{1}{r} \frac{\partial t}{\partial r} + \frac{\partial^2 t}{\partial r^2} \right) - \frac{\partial t}{\partial z} - \frac{\Delta H_r r_c \rho_B}{GC_p} = -\frac{\rho_B}{G} \frac{\partial t}{\partial \theta} \quad (1)$$

$$\frac{D_{ez}}{u} \frac{\partial^2 X}{\partial z^2} + \frac{D_{er}}{u} \left(\frac{1}{r} \frac{\partial X}{\partial r} + \frac{\partial^2 X}{\partial r^2} \right) - \frac{\partial X}{\partial z} + \frac{r_c \rho_B}{C_0 u_0} = \frac{\rho_B}{G} \frac{\partial X}{\partial \theta} \quad (2)$$

$$r_c = f(t, X) \quad (3)$$

Upon making a simplified study, neglecting radial gradients $\frac{\partial t}{\partial r} = 0; \frac{\partial X}{\partial r} = 0$ in equations (1) and (2), in the two heat and material balance partial differential equations, it was able to show in principle that the reactor hotspot can be moderated significantly by injecting heat carrier gas of higher heat capacity than that of nitrogen.

In the calculation, actual steady state temperature profile data (similar to Fig. 10) were treated with assumed physical constants to obtain kinetic information, by differentiating and curve

fitting to a 3 constant kinetic rate equation (3). This rate equation was used by coupling, to solve the two simultaneous partial differential equations numerically, to obtain a moderated temperature profile (similar to Fig. 12). This mathematical prediction warranted success in experimental work. Of course, the prediction was off about $\pm 20-30\%$; and this was primarily due to the uncertainties of the physical constants but not due to any serious error in modelling method itself. Since the primary objective of the mathematical study was to predict the general trend of the profile and moderation possibility rather than the exact temperature level, the original expectation had been well fulfilled.

However, from the simplified mathematical study, it was noted that the sensitivity of calculation was high and predicted that a risk would be involved in installing an on-line computer control, which is based 100% on the mathematical study of the process dynamics. Equilibrium conversion was calculated within 5-10% error. Calculations were also made to predict the profiles depending upon the type of inert gas and percent dilution, and some discrepancies were observed because of the fact that the inert gases are not completely inert due to some side reactions, and also accompanying physical constants were not really constants. The heat capacity ratios alone did not give a perfect match of the profiles, but the heat transfer coefficients were considered to be constant. The error introduced due to the inaccurate reaction rate equation are expected to be high, and it is common practice to make on-line model adjustments in a computer control system (1959-1965 IBM-DuPont project).

The details of modelling and simulation are somewhat outside the scope of the present work. Due to the inherent uncertainties, this work was performed for large scale experimental verification, rather than to rely completely on the ma-



thematical model studies.

Conclusions

After reviewing the methods of reactor hotspot moderation, a serious study was undertaken to evaluate the heat carrier gas injection of CH_4 , C_2H_6 , & CO_2 , to moderate the reactor hotspot for the system of gas phase catalytic ammoxidation of p-xylene to terephthalonitrile.

Upon establishing the possibility of success by mathematical prediction, a large scale experimental verification was accomplished in a 12ft, 1" OD, salt-jacketed, fixed-bed tubular catalytic reactor; thus commercial feasibility of hotspot moderation technique has been experimentally demonstrated.

Nomenclature

<i>PTN</i>	p-tolunitrile, (mononitrile)	
<i>TPN</i>	terephthalonitrile	
<i>IPN</i>	isophthalonitriles	
T_2	reactor bed temperature at point 2. above datum	
k_{ez}	effective axial thermal conductivity	
k_{er}	effective radial thermal conductivity	
D_{er}	effective radial diffusivity	
D_{ez}	effective axial diffusivity	
G	mass velocity, lb/ft ² time	
C_p	heat capacity	
z	axial coordinate, ft	
t	temperature	
r	radius	
ΔH_r	heat of reaction, Btu/lb mole	
r_c	reaction rate, lb mole/lb cat time	
ρ_B	bulk density, lb cat/cuft	

θ	time
X	conversion, dimensionless
u	axial gas velocity
C	reactant concentration

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