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Multiple objectives application approach to waste minimization*

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Abstract: Besides economics and controllability, waste minimization has now become an objective in designing chemical processes, and usually leads to high costs of investment and operation. An attempt was made to minimize waste discharged from chemical reaction processes during the design and modification process while the operation conditions were also optimized to meet the requirements of technology and economics. Multiobjectives decision nonlinear programming (NLP) was employed to optimize the operation conditions of a chemical reaction process and reduce waste. A modeling language package - SPEEDUP was used to simulate the process. This paper presents a case study of the benzene production process. The flowsheet factors affecting the economics and waste generation were examined. Constraints were imposed to reduce the number of objectives and carry out optimal calculations easily. After comparisons of all possible solutions, best-compromise approach was applied to meet technological requirements and minimize waste.

Key words: Waste minimization, Multiple objectives optimization, Chemical reaction process.
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INTRODUCTION

Economic development eventually leads to the production of a lot of waste products from industrial processes, which had been proved to be the main source of toxic materials in the environment (Nathanson, 1986). Chemical reaction processes generate harmful toxic byproducts that are sometimes difficult to treat even at high cost. Even if factories spend a lot of money to treat the waste products, they often find that those discharged into the environment are not up to the environmental standards imposed by government. Reduction of waste products during industrial processes sometimes increases operation costs greatly. Therefore, the problem was how to reduce waste products during the chemical reaction process but at the same time increase the operation process cost.

In the design of a chemical process, the costs of materials and energy, the wastes amount related to the raw materials, and operation conditions, must all be considered comprehensively. Therefore a multiple objectives approach was employed to simulate such chemical reaction processes, at this strategy can usually help decision-makers to optimize a problem affected by more than one factor (Jeffrey, 1992), which should be considered compressirely in solving the problem. The best solution should be obtained after comparing all solutions. Multiobjective optimization theory enables an analyst to consider several objectives in proper perspective involving the relationships among them (tradeoffs) (Chankong et al., 1983).

In the design and control of distillation columns, multiobjective optimization had already been used to simulate the economic and dynamic performance of heat-integrated distillation columns (Lenhoff et al., 1982). Jacobsen and Skogestad examined design modifications for high-purity distillation columns to improve controllability (Jacobsen et al., 1991). Grassi and Luyben researched the design and control of extractive distillation columns (Grass et al., 1992). Luyben and Floudas examined different control configurations of binary distillation synthesis using the mixed-integer nonlinear opti-

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mization problem approached (Luyben et al., 1994a). Multiple objectives theory had also been employed to examine robustness of three isothermal CSTRs in parallel (Palazoglu et al., 1986), design and control a chemical process (Grossmann et al., 1983), design polymerization reactors (Choi et al., 1983), and optimize design of reactor-separator-recycle system (Luyben et al., 1994b).

In this work, nonlinear programming (NLP) multiobjective simulation was employed to optimize the raw materials ratio, operation condition and control the waste amount of the benzene process. Less generation of waste at not too high operation cost can be achieved under suitable operation conditions. The case study of a benzene production process is used to explain the procedure of optimal simulation.

OPTIMIZATION STEPS

This section, on the steps of multiobjective optimization approach to waste minimization can be summarized in the following four steps:

Step 1: Determine process flowsheet

The process flowsheet can be determined by products and quantity. However, consideration of resource recycling and energy reusing can also change the flowsheet, which must not only conform to technological requirements, but also be most economical.

Step 2: Establish mathematical model

The production process is considered as a system with a set of n subsystems, unit operation, associated with subsystem i, $i = 1, \ldots, n$, with each ith subsystem consisting of input, output, decision, generation, and consumption defined by symbol x_i, p_i, u_i, c_i, and z_i, respectively. If ith subsystem has a set of n_i objective functions, the decision-maker of ith subsystem can be defined as follows:

$$\text{Min} = \begin{vmatrix} f_1^i(x_i, p_i, c_i, z_i, u_i) \\ f_2^i(x_i, p_i, c_i, z_i, u_i) \\ \cdots\cdots \\ f_k^i(x_i, p_i, c_i, z_i, u_i) \end{vmatrix} \qquad (1)$$

subject to

$$z_i = H_i(x_i, p_i, u_i, c_i), \qquad (2)$$

$$g_i(x_i, p_i, u_i, c_i, z_i) \leqslant 0 \qquad (3)$$

$$x_i = \sum_{j=1}^{n} A_{ij} Z_j \qquad (4)$$

where k is the number of objectives of the subproblem. Eqs. (2), (3) and (4) are the constraints model, the feasible region and the couplings between subsystems respectively.

The mathematical models of chemical reaction processes involve mainly materials balance, energy balance, components balance, and kinetics and equilibrium equations. The constraints include the tradeoff among the subsystems (unit operations). The costs of operation and waste generation are the main objectives of optimization.

Step 3: Selection of calculation methods

A commercial software—SPEEDUP was used in our research work to optimized steady-state reaction process on SUN work station (SPEEDUP user manual, 1993), and is an equation-based flowsheeting package designed to simulate processes (in chemical or process engineering environments) as a series of unit operations interconnected by process streams.

Step 4: Analysis of the calculation result to determine the best-compromise solution

After comparing results to determine the constraints and adjusting the processes flowsheet accordingly, the best solution can finally be found. Different flowsheet can be compared by simulation to meet the technological requirements. Fig. 1 shows conclusion through four steps:

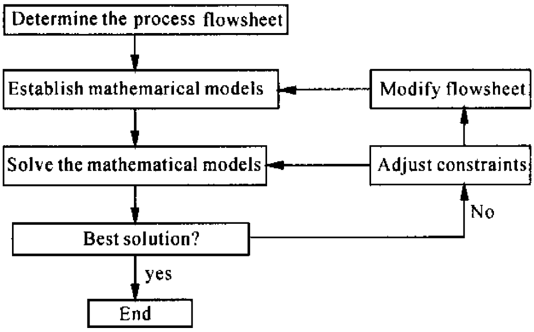

Fig. 1 The optimization procedure

A CASE STUDY

This part presents a case study of multiobjective optimization approach to waste minimization for benzene process.

Flow sheet and benzene process physical data

There are two reaction states (dynamic state and equilibrium state) in the benzene process aimed at producing maximal amount of the required products and minimal amount of useless byproducts. Douglas (1988) showed that less amount of diphenyl produced is related to the flow temperature, feeding reactor used, recycling quantity of H_2 and CH_4, CH_4 content in raw material H_2, etc. All these factors affecting diphenyl generation are discussed as in the following section:

$\text{Toluene} + H_2 \longrightarrow \text{Benzene} + CH_4$

$2\ \text{Benzene} \longrightarrow \text{Diphenyl} + H_2$

The benzene process flow sheet mainly consisted of a continuous steady-state reactor following three separators, a flash and two distillation columns. A mixer and a heat exchanger that were used to mix and recycle raw materials and heat them. A purge following the flash was used to discharge part of the reaction-generated byproducts or raw materials, which did not react completely in the process (Fig. 2).

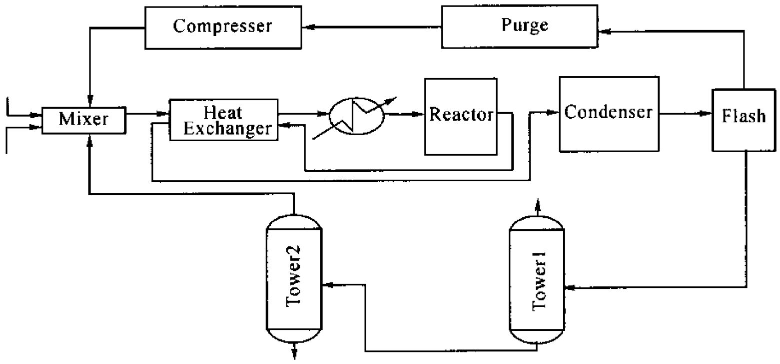

Fig. 2 Flow sheet of benzene process

Toluene and hydrogen with recycle hydrogen and diphenyl entered the mixer followed by a heat exchanger. Heat exchange with the incoming flow from the reactor, the raised feeder contents to the required temperature before they were input into the reactor. When the adiabatic reaction was over, the cooled flow entered a flash, whose light components containing mainly H_2 and CH_4 went into a purge and a part of them were recycled. The heavy components (mainly toluene, benzene and diphenyl) entered two sequential distillation towers for separating products. Benzene was collected as the desired product while toluene was reused for recycling. Diphenyl was the by-product.

The feed data in Table 1 came from Douglas (1988).

Table 1 Physical data for benzene process system

	Toluene	Hydrogen	Methane	Total
F_0(kg•mol/h)	123.8	226.8	11.34*	361.94
T_0(°F)	100	100		
P (psia)	575	575		
Density (kg/m^3)	3.319	0.01588		

* The amount will be determined again after simulation

Mathematical models

1. Process model

This part presents the mathematical model used in NLP multiobjective to optimize benzene steady-state continuous process according to the flowsheet of Fig. 2. It was assumed that there was no reaction and material or heat energy exchange in any pipe, adiabatic condition was assumed.

The main equations of each unit operation are those of materials, components, and energy balance. The following equations make up the mathematical model for each unit of the benzene process (except reactor):

1) Total materials balance

$$F_{in} = F_{out}$$

2) Component balance

$$\sum F_{i\mathrm{in}} x_i = \sum F_{i\mathrm{out}} y_i$$

3) Total energy balance

$$\sum E_{i\mathrm{in}} + \sum E_{i\mathrm{out}} = W$$

There are two reaction states: dynamic state and equilibrium state. It is assumed that the reaction occurred under adiabatic condition; in other words, that no heat energy went into or out of the reactor. Therefore, the mathematical model of the reactor contains one dynamics equation and one equilibrium equation and is expressed as follows:

A. Total material balance

$$F(1)_{\mathrm{in}} - \mathrm{Extent1} = F(1)_{\mathrm{out}}$$

$$F(2)_{\mathrm{in}} - \mathrm{Extent1} + \mathrm{Extent2} = F(2)_{\mathrm{out}}$$

$$F(3)_{\mathrm{in}} + \mathrm{Extent1} - 2^{*}\mathrm{Extent2} = F(3)_{\mathrm{out}}$$

$$F(4)_{\mathrm{in}} + \mathrm{Extent1} = F(4)_{\mathrm{out}}$$

$$F(5)_{\mathrm{in}} + \mathrm{Extent2} = F(5)_{\mathrm{out}}$$

B. Total energy balance

$$E_{\mathrm{in}} + E_{\mathrm{rea}} = E_{\mathrm{out}}$$

C. The kinetics equation of the first step of reaction. Silsby and Sawyer discussed the primary kinetics of benzene reaction (Silisby, 1956).

$$r = -k(T)(H)^{1/2}$$

where $k = 6.3 * 10^{10} \exp[-52000/\mathrm{RT_R}]$ $(\mathrm{mol/L})^{-1/2}(\mathrm{s}^{-1})$

D. The equilibrium equation of the second step of reaction

$$K_e = \frac{[\mathrm{H}][\mathrm{Biphenyl}]}{[\mathrm{Benzene}]^2}$$

Where

E_{in}, E_{out} = Enthalpy of flow in or out units

E_{rea} = Enthalpy of reaction

Extent1, Extent2 = Extents of reaction 1 and 2

F(1), F(2), F(3), F(4), F(5) = Flowrate of toluene, H_2, benzene, CH_4, and diphenyl

F_{in}, F_{out} = Feed flowrate to unit

K_e = Equilibrium constant

r = Kinetics equation

w = The work done outside

x_i, y_i = Inlet and outlet component

The model included 138 variables and 134 equations, so there were 4 degrees of freedom. In this simulation process, six constraints should be imposed in the calculation of these equations.

2. Constraints

As shown in Fig. 2, the generation of diphenyl is connected with the flow temperature feeding reactor, recycling materials amount, and CH_4 percentage of raw material H_2.

Simulation showed that when reaction time and ratio of hydrogen and aromatics at reactor inlet were fixed (30s and 6 respectively), increasing CH_4 percentage of raw material among H_2 led to increasing amount of diphenyl generated (Fig. 3). The percentage of CH_4 changed from 0.0% to 10%, while the amount of diphenyl increased linearly within a narrow range from 5.36 kgmol/h to 5.81 kgmol/h. However, the cost of purge hydrogen is more expensive than the hydrogen contained in methane.

Fig. 4 shows that difference of CH_4 percentage in raw material hydrogen influenced little the temperature in and out of the reactor. Fig. 5 shows that the fraction of purge increases almost linearly with the percentage of CH_4 of raw material of H_2. Fraction of purge is the ratio of the discharge of flows to the sum of discharge and recycling flows. It was shown that CH_4 percentage in raw material hydrogen is hardly connected with the operation conditions of the benzene process, so 5% CH_4 and 95% H_2 was used (as one of the raw materials for simulating the benzene process).

When we changed the temperature of the reactor inlet, the ratio of hydrogen and aromatics, reaction time and fraction varied correspondingly. Fig. 6 shows that diphenyl generation and ratio of hydrogen and aromatics change with different temperature of reactor inlet. It can be concluded that low temperature of reactor inlet will produce small amount of diphenyl. When temperature was as high as to 1350 °F, the amount of diphenyl was increased greatly. The ratio of hydrogen and aromatics also increase with increasing temperature. However, for low reactor inlet temperature the reaction time was too long (Fig. 7). The fraction of purge was constant when temperature ranged from 950 °F to 1350° F. The fraction of purge increased steeply when reactor inlet temperature increased beyond the above temperature range (Fig. 8). The investment in equipment will be influenced by the fraction of purge. High fraction leads to small amount of recycling requiring only low cost small volume capacity reactor.

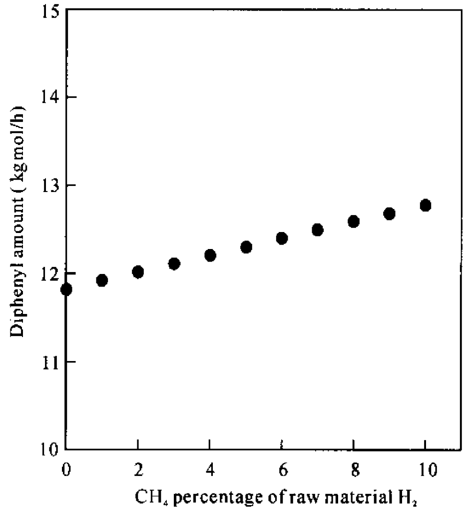

Fig. 3 Diphenyl generation vs CH$_4$ percentage of raw material H$_2$

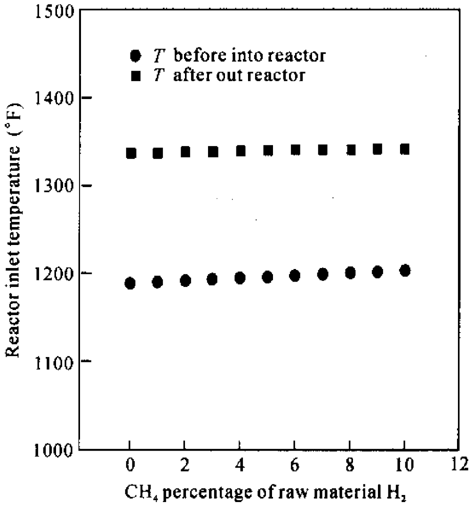

Fig. 4 Reaction temperature vs CH$_4$ percentage of raw material H$_2$

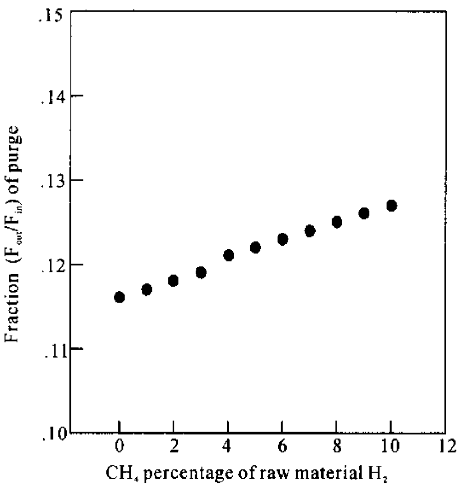

Fig. 5 Fraction of purge vs CH$_4$ percentage of raw material H$_2$

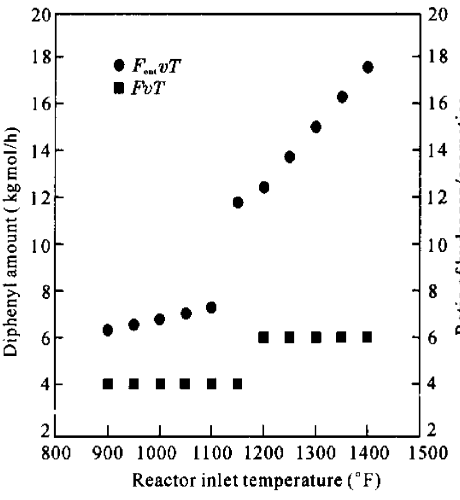

Fig. 6 Diphenyl generation and ratio of hydrogen/aromatics vs. reactor inlet temperature

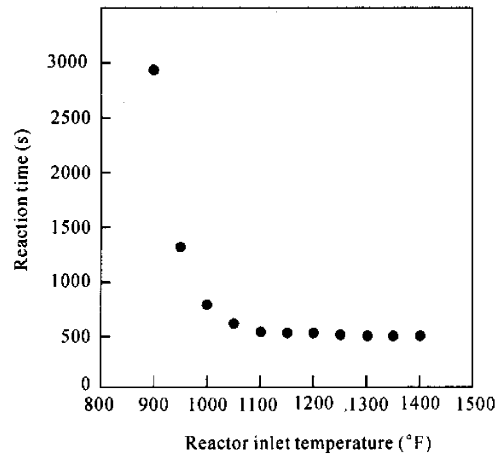

Fig. 7 Reaction time vs reactor inlet temperature

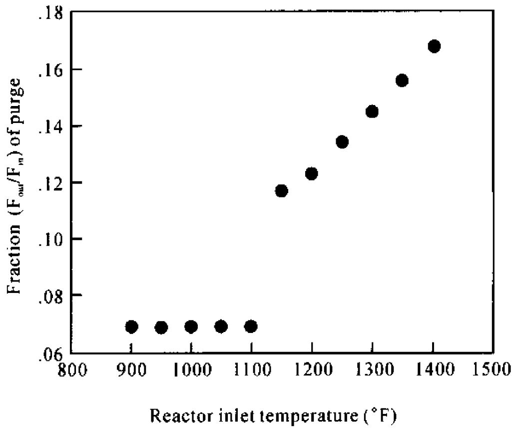

Fig. 8 Fraction of purge vs reactor inlet temperature

The fraction affects not only the reactor cost but also the energy used to heat or cool flows. Fig. 9 shows that the temperature of two flows from the heat exchanger varied with the different fraction of purge. The area of the heat exchanger is fixed. When the fraction of purge increases， the outlet temperature of high temperature flow will decrease and low temperature will increase. Therefore less work will be done to cool the products before they flow into the flash and to heat the raw materials before they go into reactor. The cost of operation will reduce. Increasing fraction of purge will lead to generation of large amount of diphenyl （Fig. 10） and minimize waste proportionally.

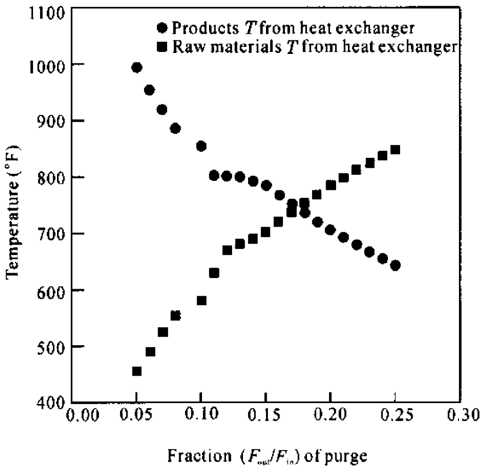

Fig. 9 Heat exchanger outlet temperature vs fraction of purge

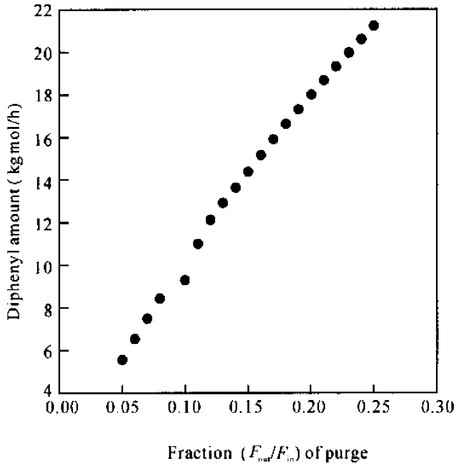

Fig. 10 Diphenyl generation vs fraction of purge

From the above analysis， we can conclude that the factors influencing diphenyl generation are reaction temperature， recycling fraction of purge， and ratio of hydrogen and aromatics. However， the recycling fraction will affect the volume and outlet temperature of heat exchange.

Temperature of reaction leads to great change of reaction time. Therefore，constraints should be select to not only reduce waste generation，but also meet technological and economic requirements. The four constraints chosen were as follows：

950°F < = reactor. temperature< = 1350°F；
4< = reactor. ratio（hydrogen/aromatics）< = 6；
reactor. time< = 60s；
heater_exchanger. T_out2 < = 800°F；

Where T_out2 means the outlet temperature of heat exchanger out from reactor

3 Couplings between subsystems

We assume absence of materials exchange or heat energy exchange during flows through the pipes between any two-unit operations. Moreover，no reaction occurs when flows pass any pipe. Therefore，the outlet material，energy，and components of one unit are the same as those of the inlet of the next unit.

4. Multiobjective optimization results

Table 2 shows the results of multiobjective optimization with waste minimization as one of the objectives.

Table 2 The result of multiobjective optimization

Parameter	Value
Heat_exchanger. *T*_out1（°F）	676
Heat_exchanger. *T*_out1（°F）	800
Reactor. *T*_in（°F）	1144
Reactor. *T*_out（°F）	1279
Reactor. Ratio	6
Reactor. Time（s）	60
Reactor. Diphenyl（kgmol/h）	1.89
Reactor. Benzene（kgmol/h）	124.04
Purge. Fraction	0.102

CONCLUSIONS

In this research，a nonlinear programming multiple objectives optimization method was used to approach waste minimization. A case study，benzene production process，was presented to explain the procedure of optimization of chemical reaction. During simulating calculation，economics and waste minimization are two major objectives of optimization. Economics includes investment and costs of operation. Wise adjustment of raw materials ratio，reaction and purge parameters minimize waste（byproduct diphenyl）generation withnot greatly increasing the costs of operations and investments. The production flowsheet process can be modified easily by simulation to obtain the optimum solution.

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