CHEMICAL REACTOR DESIGN FOR PROCESS PLANTS

Volume Two: Case Studies and Design Data

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CASE STUDY 104

Toluene Dealkylation

THIS STUDY illustrates a case where pilot-plant data already indicate the temperature range for practical rates. Design calculations are made in this range in order to select a design basis.

Problem Statement

Design a noncatalytic reactor for producing 82,000 gal/day (25,000 lb/hr) of benzene by thermal hydrodealkylation of toluene. Hydrogen is available from another unit at 600 psig and 80°F. Toluene feed will normally be essentially pure but can be contaminated with paraffinic hydrocarbons at times.

Chemistry

A number of possible reactions are reported in addition to the primary reaction (1).

$$C_6H_5CH_3 + H_2 \rightleftharpoons C_6H_6 + CH_4$$

These include hydrogenation of benzene and toluene to cycloparaffins, hydrocracking of paraffins, and reaction of benzene and toluene to various diphenyls.

A free-radical mechanism has been suggested (2).

$$\begin{aligned} H_2 &\rightleftharpoons 2H\cdot \\ H\cdot + C_6H_5CH_3 &\longrightarrow CH_4 + C_6H_5\cdot \\ H\cdot + C_6H_5CH_3 &\longrightarrow C_6H_6 + CH_3\cdot \\ CH_3\cdot + H_2 &\longrightarrow CH_4 + H\cdot \end{aligned}$$

$$C_6H_5\cdot + H_2 \longrightarrow C_6H_6 + H\cdot$$
$$C_6H_5\cdot + C_6H_6 \longrightarrow C_{12}H_{10} + H\cdot$$
$$C_6H_5\cdot + C_6H_5CH_3 \longrightarrow C_{12}H_{10} + CH_3\cdot$$
$$C_6H_5\cdot + CH_4 \longrightarrow C_6H_5CH_3 + H\cdot$$

Saturated hydrocarbons if present are thermodynamically favored to hydrocrack to CH_4 and those of C_6 and above do so very rapidly with high heat effects. Success of the process depends on preventing hydrogenation of benzene to cyclohexane and high heat effects of hydrocracking which could occur with saturated impurities or cyclohexane produced in the reactor. Cyclohexane if not hydrocracked will contaminate the benzene product because of its close boiling point to benzene (1).

Thermodynamics

Heats of reaction for the main reaction and heat capacity data are plotted in Fig. CS-4.1 and CS-4.2 and heats of reaction at 800°K for several overall reactions are tabulated in Table CS-4.1. Equilibrium constraints for major overall reactions are plotted in Fig. CS-4.3. Clearly, temperatures above 800°F are required to prevent hydrogenation of toluene and benzene. Although the heat of reaction of toluene dealkylation is modest, much larger heat effects accompany hydrocracking of cyclohexane or saturated hydrocarbons. It is known that these hydrocracking reactions are very fast.

Because of the low value of the equilibrium constants for the side reactions, high temperatures should not encourage forming excessive amounts of diphenyl, methyl diphenyl, and dimethyl diphenyl, and the equilibrium amounts can be reduced by increasing the hydrogen partial pressure (3,4).

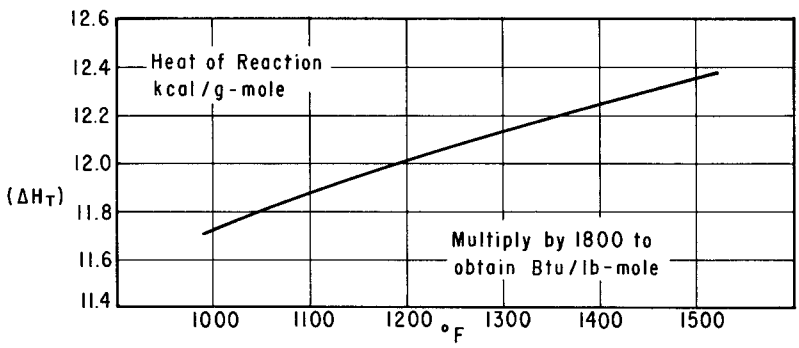
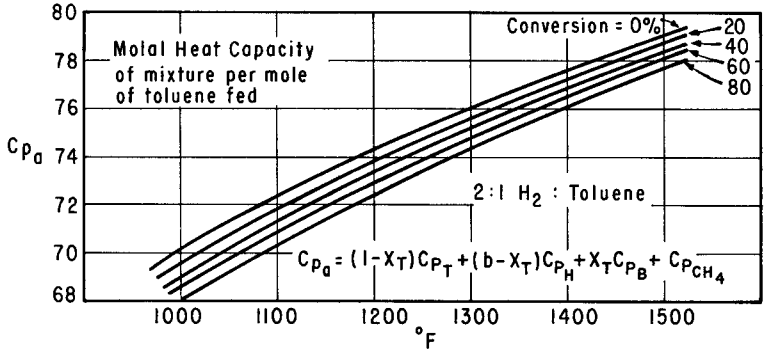


Fig. CS-4.1 Heat of reaction for toluene dealkylation.



For other H_2 : toluene ratios (b) add (7.2)(b-2) to values of C_{P_a} read.

Fig. CS-4.2 Heat capacity for toluene dealkylation.

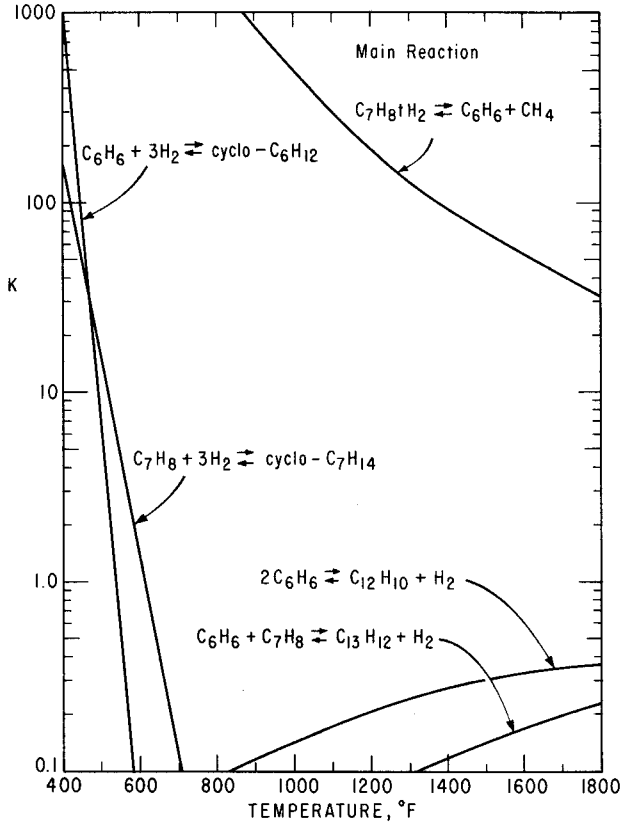


Fig. CS-4.3 Equilibrium constants for various reactions in toluene dealkylation.

Table CS-4.1 Heats of Reaction of Typical Overall Reactions

	ΔH 800°K kcal/g mole
1. $C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$	−11.71
2. $C_6H_6 + 3H_2 \rightleftarrows$ cyclo C_6H_{12}	−52.70
3. Cyclo $C_6H_{12} + 6H_2 \rightarrow 6CH_4$	−87.75
4. $nC_6H_{14} + 5H_2 \rightarrow 6CH_4$	−76.66
5. $CH_4 \rightarrow C + 2H_2$	+22.82

Although the equilibrium constant for the main reaction declines with increasing temperature, its value is such that benzene is still strongly favored at the highest practical temperatures.

The gases behave ideally as determined by pseudocritical calculations. Both fugacity coefficients and compressibilities have values of unity.

Kinetics

The first several steps of the free-radical mechanism can be rationalized in an empirical form for the disappearance of toluene (1,5).

$$(-r_{To}) = (k_{c_1} + k_{c_2})[H\cdot][C_7H_8]$$

$$K_1 = \frac{[H\cdot]^2}{[H_2]} \qquad \text{or} \qquad [H\cdot] = [H_2]^{0.5}[K_1]^{0.5}$$

Thus

$$(-r_{To}) = k_c C_{To} C_{H_2}{}^{0.5}, \frac{\text{(lb moles toluene)}}{(\text{ft}^3)(\text{sec})}$$

where C_{To} is the concentration of toluene and C_{H_2} is the concentration of H_2.

Rate data in the range of commercial interest yield the following (6):

$$k_c = 7.18 \times 10^{11} e^{-98.100/\boldsymbol{R}'T}, (\text{ft}^3)^{0.5}/(\text{lb mole})^{0.5}(\text{sec})$$

or

$$k_p = \frac{k_c}{(\boldsymbol{R}T)^{1.5}}, (\text{lb mole})/(\text{atm})^{1.5}(\text{ft}^3)(\text{sec}) \qquad \text{(CS-4.1)}$$

$$(-r_{To}) = k_p P_{To} P_{H_2}{}^{0.5}$$

$$\boldsymbol{R}' = 1.987$$

$$\boldsymbol{R} = 0.73, (\text{ft}^3)(\text{atm})/(\text{lb mole})(°\text{R})$$

$$T = °\text{R}$$

Rate equations for the side reactions have not been reported, but pilot-plant results at 1300°F and 600 psig indicate that equilibrium is attained for the various diphenyls. The total amount of by-products formed is inversely proportional to the H_2-to-toluene ratios (7). Selectivity to benzene is 98% at conversions up to 75% and H_2-to-toluene ratios of at least 2 : 1 (3,4).

Because of the apparent equilibrium for diphenyls, it will be advantageous to recycle diphenyls to reduce the net consumption of toluene and benzene to these side-reaction products.

Reactor Type

Since the adiabatic factor and heat generation potential are modest (see Table 6.4), an adiabatic reactor will be selected. Because of the possibility of paraffinic contamination, however, inlets should be installed along the reactor for quenching temperature excursions caused by hydrocracking of paraffins. A plug-flow reactor will require the smallest volume.

Operating Conditions

Pressure, temperature, and conversions are selected on the basis of thermodynamic and kinetic data together with pilot-plant data.

Pressure

Equilibrium conversions of the major reactions are unaffected by pressure, but pressure will increase the rate and reduce equipment size. Since the hydrogen is available at 600 psig, a pressure of 50 psi less, for furnace and other ΔP ahead of the reactor, will be selected (550 psig).

Conversion and H_2*-to-Toluene*

A conversion of 75%, 98% selectivity, and a H_2-to-toluene ratio (*b*) of 2 are selected as consistent with pilot-plant data.

Temperature

Pilot-plant data (3,4) suggest operating temperatures in the range of 1150–1350°F. This range can be investigated. In this range with hydrogen present carbon steel and most low and intermediate alloy steels cannot be used (See Fig. B.1, Appendix B). A refractory-lined reactor should be specified with an inner protective liner of stainless steel. A maximum design temperature of 1500°F will thus be set with something in the neighborhood of 1400°F being a normal operating limit.

Reactor Design

In the temperature range of interest the energy balance based on Figs. CS-4.2 and CS-4.3 is well represented as follows:

$$\Delta T = \frac{(-\Delta H_{To})(\Delta X_{To})}{c_{p_a}} \approx \frac{(12.08)(1800)\Delta X_{To}}{74.5}$$

$$\Delta T \approx 292 X_{To} \qquad \text{(CS-4.2)}$$

Toluene Balance

$$\frac{dV}{F_{To}} = \frac{dX_{To}}{k_p P^{1.5}\left(\dfrac{1 - X_{To}}{1 + b}\right)\left(\dfrac{b - X_{To}}{1 + b}\right)^{0.5}} \qquad \text{(CS-4.3)}$$

where b is H_2-to-toluene ratio, X_{To} is the conversion of toluene, F_{To} is the feed rate of toluene, lb moles/sec.

$$F_{To} = \frac{25{,}000 \text{ lb/hr}}{(3600)(78)(0.98)(0.75)} = 0.121 \text{ lb moles/sec @ } 75\% \text{ conversion}$$

For rapid estimates on this system analytically integrate Eq. CS-4.3 using k_p evaluated at $(1/T) = \frac{1}{2}[(1/T_0) + (1/T_e)]$.

Since for 75% conversion $\Delta T = (292)(0.75) = 219$, the maximum inlet design temperature should be $1400 - 219 = 1181$ or approximately 1200°F. Cases at 1150 and 1200°F were calculated and are summarized in Table CS-4.2. With reference to this table it is seen that pressure fluctuations do not have much effect. It is not practical to use L/D values of 100, for the length would be too great. Since the 3 ft–0 in. ID size allows more room for installing and repairing refractory lining, it will be selected.

Table CS-4.2 Summary Dealkylation of Toluene

Inlet Conditions		Outlet	Volume	Total Length	
Temp. °F	Press. psig	Temp. °F	cu ft	2 ft diam.	3 ft diam.
1. 1150	550	1369	608	195	86
2. 1200	550	1418	275	88	39
3. 1150	575	1369	569	181	80

H_2-to-Toluene = 2. Conversion = 75%. Based on numerical solution of the simultaneous balances for mass and heat with the latter in terms of $c_p = f(T, X_{To})$.

Because of low values of L/D some longitudinal dispersion will occur. Hence select Case 1 at 1150°F inlet. This will allow adequate flexibility for raising temperature, if necessary, to meet production requirements.

Final Design

Two vertical reactors, 3 ft–0 in. ID × 43 ft connected in series and lined with refractory with protective type 347 stainless-steel inner liner. Outside shell shall be a low alloy steel for protection against leaks in refractory. Paint with heat sensitive paint, and insulate outside portion only where personnel protection requires. Install quench inlets along length at 5 ft, 10 ft, and 30 ft, respectively of each.

Pressure Drop

The pressure drop in the reactor sections will be negligible, based on Fig. 10.3 on p. 424[1], and a Reynolds number in the turbulent region of

$$N_{Re} = \frac{(6.3)(41{,}818)}{(36)(0.03)} = 243{,}938$$

Hydrogen recycle compressor operating costs will thus be minimized.

Estimate of Effect of Dispersion on Conversion

N_{Re} is in turbulent region. Thus $(N_{Pe})_a = 4$. As an approximation use effective $L/D = 43/3 \approx 14$.

From Eq. 10.35, p. 486[1],

$$(X_A)_{plug} - (X_A)_{actual} = \frac{1}{(N_{Pe})_a}\frac{D}{L}\frac{V}{F_A}(-r_A)_{plug} \ln \frac{(-r_A)_{plug}}{(-r_A)_{0plug}}$$

$$\Delta X_A = \left(\frac{1}{4}\right)\left(\frac{1}{14}\right)\left(\frac{608}{0.121}\right)(3.59 \times 10^{-4}) \ln \frac{3.59 \times 10^{-4}}{5.527 \times 10^{-5}}$$

$$\Delta X_A = 0.06, \qquad \text{negligible.}$$

REFERENCES

1. G. F. Asselin, in *Advances Petroleum Chemistry and Refining*, Vol. 9, Interscience, New York, 1964, pp. 47–97.
2. G. J. F. Stigntjes, H. Voetter, E. F. Roelofsen, and J. J. Verstappen, *Erdol Kohle*, **14**, 1011 (1961).

3. S. Feigelman, L. M. Lehman, F. Aristoff, and P. M. Pitts, *Hydrocarbon Process*, **44** (12), 147 (1965).
4. M. J. Fowle and P. M. Pitts, *Chem. Eng. Prog.*, **58** (4), 37 (1962).
5. R. I. Silsby and E. W. Sawyer, *J. Appl. Chem.*, **6**, 347 (1956).
6. S. E. Shull and A. N. Hixon, *Ind. Eng. Chem. Process Des. Develop.*, **5**, 147 (1966).
7. C. C. Zimmerman and R. York, *Ind. Eng. Chem. Process Des. Develop.*, **3**, 255 (1964).