A Study of Coolant Temperature in an Industrial Reactor for O-Xylene Oxidation

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Phthalic anhydride is obtained through a vapor-phase air oxidation of o-xylene and/or naphthalene (Wainwright and Foster, 1979). In principle, this process is realized in multitube reactors. Some side reactions are associated with the main reaction (Wainwright and Hoffman, 1976) such as significant generation of heat, which is removed by using molten salt as a coolant. For the production of large quantities of phthalic anhydride, high-capacity reactor units are used. The large size of the reactor, however, causes nonuniform distributions of the velocity and temperature of the coolant, the latter of which can lead to a decrease in the performance of the whole unit.

The purpose of this article is to study experimentally, the influence of the coolant temperature on both the reactor performance and the composition of the output products.

Experimental

The experiments were carried out on an industrial reactor, containing about 9,000 contact tubes, 3,500 mm in length and 25 mm inner diameter. The amount of the coolant (molten salt $NaNO_2/KNO_3$) was 72,000 kg. The coolant and the reactant mixture flowed countercurrently. A vanadia-titania catalyst was used, the particles of which are porcelain spheres, 6 mm in diameter, covered by a 0.2 mm layer of the catalyst. The height and the density of the bed were 2,800 mm and 1,500 kg/m^3. The temperature of the bed was measured in nine contact tubes, divided in three triplets along the reactor radius at an angle of 120°. In each triplet there was one tube near the steam generator, one in the middle of the bundle, and one near the reactor shell. A 3,000 mm, mobile thermocouple Ni-CrNi was mounted coaxially (in jacket) in each of the tubes mentioned. The temperature was then measured along the whole length of the bed (Figures 2–4), derived at any given position from the arithmetic means of the bed temperatures in the tubes where the thermocouples are mounted. Eight other mobile thermocouples measuring the coolant temperature were placed in specific locations in the shell side, from which the coolant temperature for a given position along the bed was likewise derived, (Figures 1–4). The temperature was measured with an accuracy of 1.5°C.

Analysis of o-xylene and of the products, phthalic anhydride, benzoic acid, o-toluic acid, and phthalide was done on a gas-chromatograph PERKIN-ELMER 8,500. The oxygen contents were measured by an oxygen analyzer BETA-TEST-OM 200, while the contents of maleic anhydride were determined polarographically. The coolant temperature was varied in the interval 360–400°C.

Results and Discussion

The maintenance of a constant coolant temperature is a major concern in the realization of high exothermic processes in a fixed bed (Suter, 1972).

Temperature profiles in the bed and in the coolant after three months work by the catalyst are shown in Figure 1. It can be seen that the coolant temperature rises along the reactor length. The temperature gradient was 4–5°C, while the maximal coolant temperature was about 40 cm before the hot spot in the bed. The hot spot temperature of the profile, K_9 (contact tube in the reactor periphery) was about 15–16°C higher than that of the profile, K_1 (contact tube near the steam generator). The higher bed temperature in the periphery is due to the lower gas flowrate and coolant velocity there.

When we changed the coolant velocity, a temperature gradient of about 12°C occurred in the coolant, and the position of the hot spot changed too, Figure 2. The hot spot moved to the reactor inlet, but regardless of the high temperature gradient in the coolant, its value did not increase. The selectivity to phthalic anhydride did not drop, while the amount of the side products remained low. Moreover, the amount of the main undesired product, phthalide, decreased to zero, Table 1. At the same time, control of the bed temperature was not difficult. All of these facts enabled us to increase the inlet o-xylene concentration by 5%. The hot spot temperature raised by about 11°C (not shown in Figure 2).

We also made experiments with a catalyst used for 35 months

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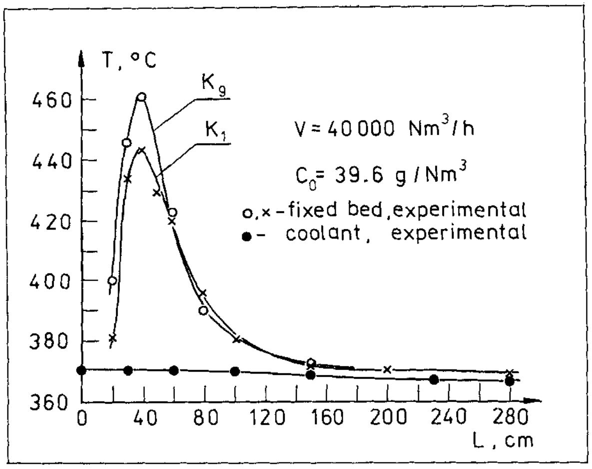

Figure 1. Temperatures in the fixed bed and coolant.

under industrial conditions, obtaining the temperature profiles shown in Figure 3. A gradient of about 22°C was observed in the coolant. Regardless of the high temperature gradient, the maximum bed temperature remained comparatively low, and far from the limiting value of about 500°C. It can be seen that the gradient mentioned did not cause a decrease in the selectivity. The higher amount of side products was a result of the catalyst deactivation in the front portion of the reactor (Pirkle and Wachs, 1986, 1987; Nikolov et al., 1987).

As our industrial experience has shown, to a certain degree the increase of the coolant temperature improves the quality of the raw phthalic anhydride (the contents of phthalide must be not more than 0.1%). But when the coolant temperature was raised by about 3°C, (V = 40,000 Nm³/h, C_O = 40.2 g/Nm³) the selectivity decreased by about 1.5%, while phthalide increased (not shown in Figure 3 or Table 1). Phase changes, probably due to the comparatively high temperature, will occur in the front zone (the first 60–80 cm of the bed in most deactivated catalysts) of a catalyst which is used for long periods under industrial conditions. It is our opinion that these changes result in lower selectivity, as was observed.

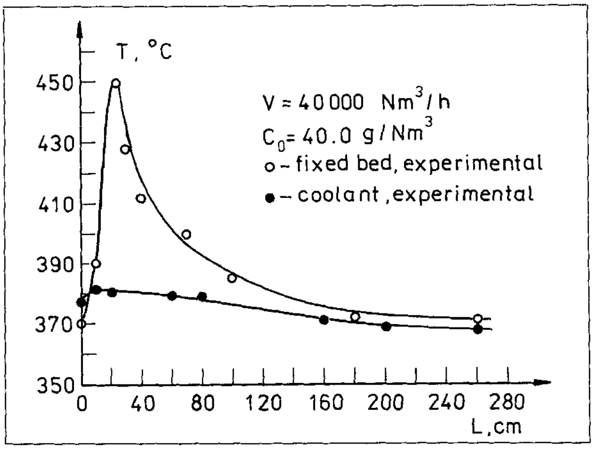

Figure 2. Temperatures in the fixed bed and coolant.

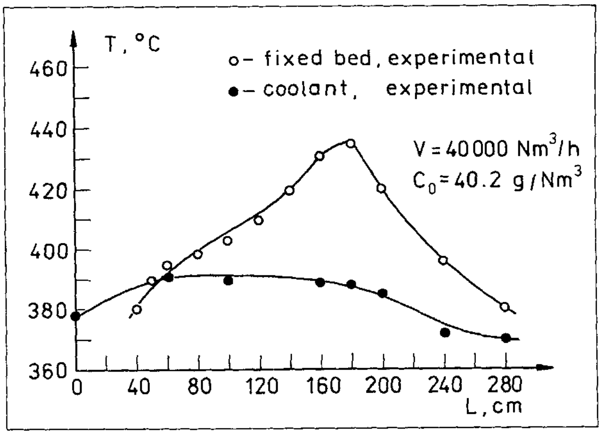

Figure 3. Temperatures in the fixed bed and coolant.

In order to keep the selectivity above 73%, we increased the temperature in the non-deactivated catalyst only (the bed zone from 1.5 to 2.8 m). The temperature rise was achieved by changing the direction of the coolant motion from counter-current to co-current with respect to gas stream. Technically, this operation was realized quite easily. It is important to note that our experimental results (discussed below) confirm the results published in the original paper of Degnan and Wei (1979). These authors have shown, theoretically, that if the coolant and the reactant mixture flow countercurrently, the reactor performance improves due to the establishment of a relatively uniform temperature profile in the bed.

The bed profile, obtained by changing the coolant motion, is shown in Figure 4. It illustrates that the temperature regime is practically quasi-adiabatic, namely that the hot spot is near the reactor outlet. Regardless of the high coolant temperature, a smooth rise of the bed temperature to about 432°C was observed. The selectivity was 0.3% higher compared to the case shown in Figure 3, while the phthalide contents decreased three times. It seems that the improved reactor performance is associated with the higher degree of utilization of the last 50–60 cm

Table 1. Experimental Results*

Ref. to Fig.	*X*	Yield *PA*	Yield *MA*	Yield *BA*	Yield *PH*	Yield *OTA*	T_{hs} *CL*	T_{hs} *FB*	l_{hs} *CL*	l_{hs} *FB*	ΔT_c	*t*
No	%	%	%	%	%	%	°C	°C	cm	cm	°C	months
1	99.8	73.15	4.8	0.56	0.05	0.09	371	461 (K_9)	0	40	5	3
2	99.8	73.20	4.5	0.47	0.00	0.07	381	451	6	25	12	6
3	99.8	73.10	2.4	0.82	0.25	0.29	392	436	60	180	22	35
4	99.8	73.40	2.6	0.44	0.08	0.11	399	432	280	220	7	36

*Data illustrated in Figures 1–4, and chemicals "yielded" defined in notation section

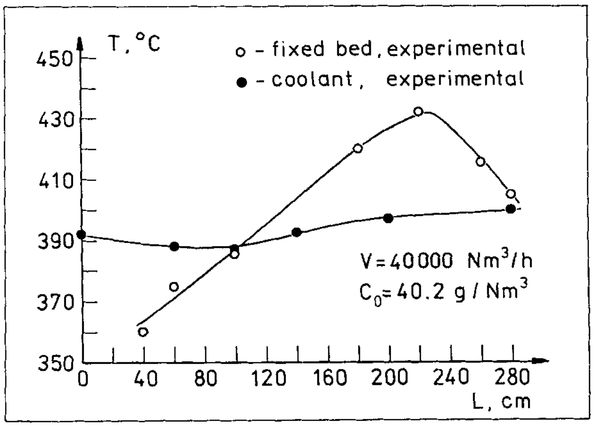

Figure 4. Quasiadiabatic temperatures in the fixed bed and temperatures in the coolant.

of the bed. In fact, the experiments reported in Figure 4 are in good agreement with the conclusions of De Lasa (1983), who also showed that the quasiadiabatic temperature regime is better than the traditional one.

As was pointed out, the quasi-adiabatic regime is achieved quite easily, with no additional expenses for diluting the catalyst with inerts, as Caldwell and Calderbank (1969) suggested there might be. Besides this, such a regime improves the reactor performance in the case of operation with a spent catalyst, a factor of special importance to industry, which may use a catalyst for three years.

Notation

C_O = inlet o-xylene concentration, g/N m^3
L = length of catalyst bed, cm
l_{hs} = location of the hot spot or maximal temperature in the coolant measured from the top of the bed, cm
T = temperature of bed or coolant, °C
T_{hs} = hot spot in bed or maximal temperature of coolant, °C
ΔT_c = temperature gradient in coolant, °C
t = time of use of catalyst, months
V = reactant mixture flow rate, N m^3/h
X = conversion of o-xylene, mol %
CL = coolant
FB = fixed bed
BA = benzoic acid
MA = maleic anhydride
OTA = o-toluic acid
PA = phthalic anhydride
PH = phthalide

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