Effect of Feed Configuration on n-Butane to Maleic Anhydride Yield: From Lab Scale to Commercial

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Introduction

Maleic anhydride is produced commercially by the partial oxidation of n-butane over vanadium phosphorous oxide (VPO) catalyst in both fixed bed and fluidized bed reactors. DuPont commercialized a Circulating Fluidized Bed (CFB) process whereby VPO catalyst was oxidized by air in a regenerator and the oxidized catalyst was transferred to a transport bed reactor (riser) where it was reduced in an n-butane rich feed stream. This configuration may achieve higher yields and superior economics due to the higher n-butane concentrations resulting in a concentrated product stream and the possibility of operating at very large scale [1-2].

Studies show that maleic anhydride selectivity decreases by increasing n-butane concentration in the feed [2-3]. Furthermore, at high n-butane concentrations (5-10%), incremental increases in hydrocarbon in the feed may lead to a decrease in maleic production due to a greater than proportionate drop in selectivity. Direct feeding of gas phase oxygen into the reactor maintains the catalyst in a higher oxidation state and can prevent excessive catalyst reduction together with increased selectivity. However, feeding oxygen through multiple spargers at high temperatures to a concentrated n-butane stream is complicated due to combustion at the nozzle and thermal excursions at the reactor exit. The feed configuration of both the oxygen and n-butane are critical parameters to achieve high product yield. In this paper, we present rare commercial data in which pure oxygen was fed through 2400 nozzles into a transport fluid bed. Maleic yield decreases as the oxygen is fed higher up the reactor. This trend was confirmed in a small scale fluid bed and demonstrated that both conversion and selectivity were sensitive to the separation distance between n-butane and oxygen: the highest yields were achieved when they were fed together from the grid.

Experimental

We measured maleic yield and n-butane conversion over VPO catalyst in a 3½ inch fluidized bed in which the n-butane and the oxygen enter the bed separately through a grid and a ¼ inch sparger. We tested various feed configurations and separation distance between the grid and sparger: n-butane/inert to the sparger air through the grid; air to the sparger and n-butane/inert through the grid; co-feed of all gases to the sparger; and, co-feed of all gases to the grid. We also reviewed the DuPont Asturias plant data in which a recycle gas stream containing as much as 10 vol% n-butane was fed through a grid and oxygen was introduced through three multi-point spargers locate at 0.5 m, 1.8 m and 5.5 m above the grid. A similar configuration was tested in a pilot plant with as much as 20 vol% n-butane in the recycle gas fed through a multi-point candelabra pipe distributor.

Results and Discussion

Our studies on lab scale fluidized bed showed that maleic anhydride yield is sensitive to feed sparger configuration: The maleic anhydride selectivity and n-butane conversion increase as the distance between n-butane and oxygen feed in the bed decreases, as shown in Figure 1. The highest yield was achieved by co-feeding n-butane with oxygen at high n-butane concentrations. Higher yields observed could be due to longer gas residence times or lower mass transfer limitation against diffusing reactants when feeds are close together. Maintaining the oxidation state of the catalyst at higher levels when oxygen is co-fed might also explain the higher yields.

In the Asturias commercial plant, the production rate increased by 15% when oxygen was transferred from the middle sparger (at a height of 1.8 m) to the lower sparger as shown in Figure 2. Both maleic anhydride selectivity and n-butane conversion increased. The same oxygen concentration at the reactor exit was maintained to prevent thermal excursions. Our observations suggest that a higher maleic yield was obtainable only by increasing the co-fed oxygen in the recycle gas to the riser.

Significance

This work describes commercial design principles of co-feeding oxygen through spargers into fluid bed reactors and in particular CFBs. The immediate application is for selective oxidation but the principle is valid for any system concerning separate feed of reactants to fluidized beds.

References