

Refereed Proceedings

The 12th International Conference on

Fluidization - New Horizons in Fluidization

Engineering

Engineering Conferences International

Year 2007

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Reactor

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OZONE DECOMPOSITION IN A DOWNER REACTOR

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ABSTRACT

Catalytic ozone decomposition was conducted in an 8.20 m high, 0.09 m inner diameter downer. The ozone concentration profiles were measured under a series of operating conditions. It is found that the ozone distribution in a downer is generally more uniform both axially and laterally than in a riser, and that there exists a relatively significant non-uniform distribution in the entrance acceleration region of the downer. The increase of solid mass flow rate will slightly increase the ozone decomposition. In addition, the acceleration region has a great effect on the reaction.

INTRODUCTION

Although the circulating fluidized bed riser reactor has been used in many catalytic processes due to its improved gas-solids contacting. However, its characteristics such as non-uniform gas and solids flow due to the large amounts of backmixing near the wall region make riser inappropriate for some fast reactions with the intermediate as the desired product. But this can largely be overcome by the gas-solid co-current downflowing fluidized bed (downer reactor). In downers, both gas and solids flow in the direction of gravity. Under such circumstances, backmixing is avoided so that the flow in downer approaches plug flow conditions [1-3]. The advantages of the downer reactor make it a competitive candidate for fast reactions with the intermediate as the desired product, where uniform short contact time is essential to prevent over-reaction and to ensure good selectivity; and for reactions where high solids-to-gas feed ratio is required; and for catalytic reactions with rapid catalysts deactivation [4]. As a result, a large amount of experimental and simulation results of the hydrodynamics of downer reactors have been published in recent years [1, 5-13].

In contrast to the experimental study on the hydrodynamics of the downer reactor, there have been very few studies on heat and mass transfer and reactor performance for downers. Only a few reports in these fields [14-17] can be found, in which different types of dispersion models and correlations are proposed based on different model assumptions. When studying a chemical reactor, chemical reaction

can directly supply information on the reactor performance. Because of the simplicity in reaction kinetics (very close to first-order reaction) and negligible heat effect of reaction due to the low concentration involved, and of a simple and accurate measurement method available, ozone decomposition reaction has been frequently used to investigate the reactor performance [18-21]. In order to improve the understanding of reaction in the downer reactor, the catalytic ozone decomposition with impregnated FCC catalysts was conducted in this study.

EXPERIMENTS

The downer reactor used in this study is schematically shown in Figure 1. The downer column is 8.20 m in height with an inner diameter of 0.09 m. The whole setup is made of plexiglas. Solids are transported upward in the riser, and then separated from the exhaust by two cyclones before returned to a storage tank above the downer column. Solids enter the downer via a butterfly valve, and the main air is introduced at the distribution plate. The gas-solids suspension travels downward along the downer to the end where an elaborately designed fast separator is used to separate particles from the air. Solids separated from the gas are then returned to the riser via an U-valve.

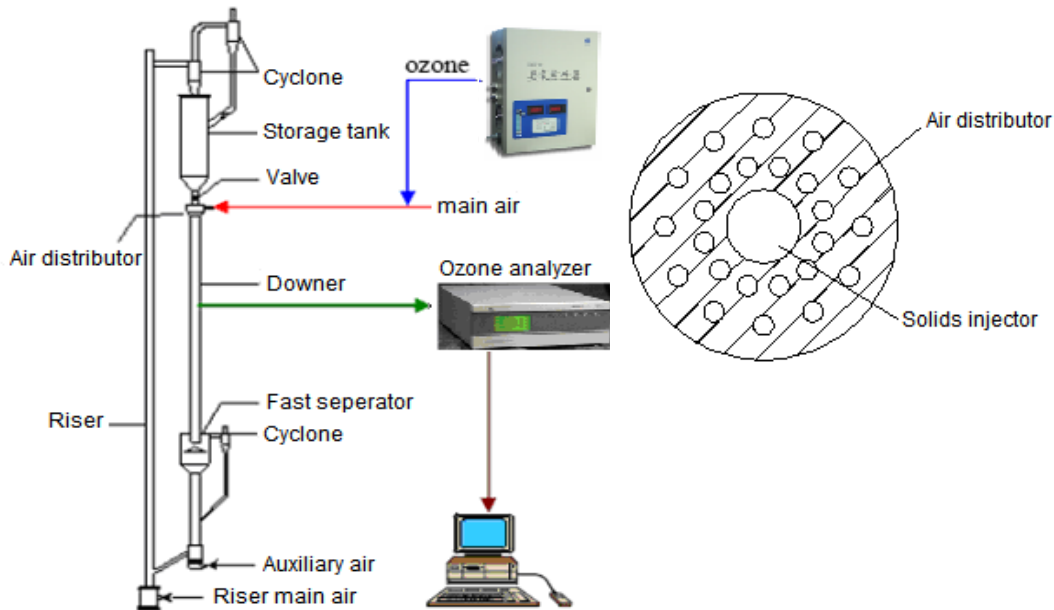


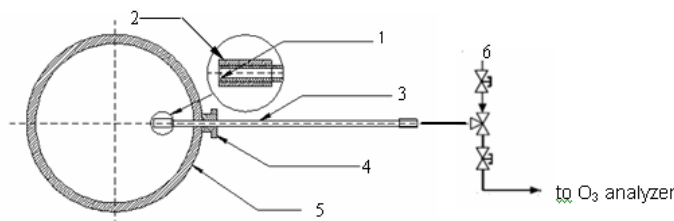
Figure 1. Schematic of the downer reactor and ozone injection and detection system.

Ozone is generated from an ozone generator connected to the main air supply. Corona discharge method is used by this type of generator, with pure oxygen as the source gas in order to eliminate the harmful NO_x formation during the electrical discharge process. Ozone from the ozone generator was completely mixed with the primary air before introduced into the downer from the gas distributor.

The FCC particles were used as bed material. To prepare the ferric impregnated catalyst, the fresh FCC particles were first soaked into a 5% solution of ferric nitrate for 24 hours, then dried and calcined at 475 °C for 2 hours. As a result, desired amount of ferric oxide is introduced into/onto the particles and acts as active component for the decomposition of ozone. The bulk density of the particles

with/without ferric oxide impregnation is 585 kg/m^3 and 755 kg/m^3 , respectively. The apparent particle density of fresh FCC particles is 1400 kg/m^3 . The mean diameter of fresh FCC particles is $72 \mu\text{m}$, and it became $62 \mu\text{m}$ after impregnated with ferric oxide.

Gas samples were continuously drawn from the downer through a sampling system shown in Figure 2. The sampling probes was made of stainless steel, with a length of 135~140 mm and an inner diameter of approximately 2 mm. Undesirable decomposition of ozone was minimized by using silicone and Teflon tubing to connect sampling probe to the ozone analyzer, which is based on the UV adsorption principle.



1- stainless steel screen, 2- cap sleeve, 3- stainless steel probe, 4- external nozzle, 5- downer column, 6- purge air

Figure 2 Sampling system for ozone concentration measurements

The probe was flushed with purge air before each measurement. The measurement was started after a steady state was reached in the downer reaction system, which usually took about 1.5~2.5 hours. Three operating conditions were chosen in the study, as listed in Table 1. The gas flow in the downer is in correspondence with the superficial gas velocity of U_g , and the value of G_s is controlled by the gas flow rate in the riser.

Table 1. Operating conditions

G_s kg/(m ² s)	U_g (m/s)	Gas flow rate in downer (m ³ /hr)
2.36	2.49	57
2.77	2.84	65
3.39	3.06	70

RESULTS AND DISCUSSION

To observe whether there is a large amount of ozone decomposition caused not by the ferric oxide but by the wall of the reactor and the fresh FCC catalyst particle, experiment was firstly conducted with the empty downer column, and then with the un-impregnated fresh FCC particles as bed materials.

Gas was sampled at several radial positions with $r/R = 0, 0.2, 0.3, 0.4, 0.6, 0.8, 0.9$ and 1 , although not all of those radial positions were used in each run. $r/R = 1$ is an approximation because the ozone concentration at this location cannot be obtained reliably when the probe is flushed with the wall. $r/R=1$ thus actually corresponds to $r/R=0.95\sim 0.975$.

Figure 3 shows the radial profiles of the ozone concentration at different axial positions in the empty column. It is seen that there is essentially little decomposition of ozone in the empty column. Thus, the effect of column wall can be neglected.

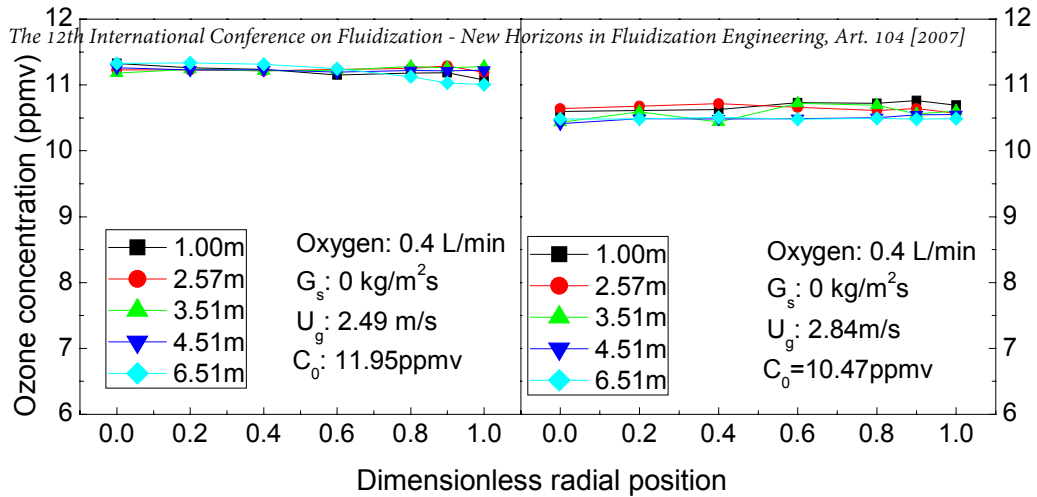


Figure 3 Ozone concentration profiles in the empty column.

Figure 4 shows the reactivity of fresh FCC particles on ozone decomposition. The most noticeable is the large radial gradient in the downer entrance region due to poor mixing and asymmetric distribution of ozone; although the cross-sectional averaged concentration does not change much with the elevation. Compared figure 4 with figure 3, it can be found that with the addition of solid particles to the reactor, the ozone concentration radial profile close to the inlet region of the downer becomes non-uniform, but the difference between the two figures at the fully developed region of the downer are insignificant, the radial profiles of other cross sections in figure 4 are as flat as the profiles in figure 3 (the variation of ozone concentration is limited within 0.4 ppmv in figure 3 and 2ppmv in figure 4).

It is also noted in figure 4 that under the circumstance of initial ozone concentration is 21.7ppmv, the average concentration of all the radial profiles of fully developed region is about 20ppmv. So, the decomposition of ozone caused by the fresh FCC particles could be neglected.

Under the operating conditions given in Table 1, the radial profiles of ozone concentration at different axial positions were measured using ferric oxide impregnated FCC particles. Figure 5 shows typical ozone concentration profiles. It is shown that a sharp decrease of ozone concentration appeared at $r/R = 0.9$ and reached a minimum at $r/R = 1.0$. But at other radial positions the distribution of ozone concentration is as flat as in Figure 4. This sharp drop in concentration did not show up in Figures 3 and 4, and may be associated with the heterogeneous flow structure in downers. In the fully developed region of the downer particles tend to move toward the wall ($r/R = 0.9\sim 1$) and form clusters [22]. In the present study with active catalyst particles, the existence of a densely populated "active clusters" region at $r/R=0.9\sim 1$ increased ozone decomposition, leading to lower ozone concentration near the wall.

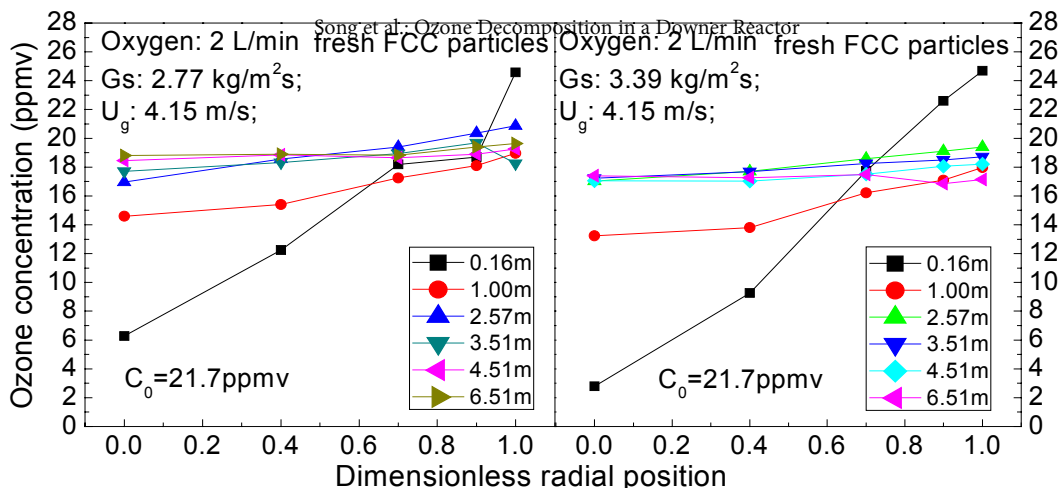


Figure 4 Ozone concentration profiles with fresh FCC particles.

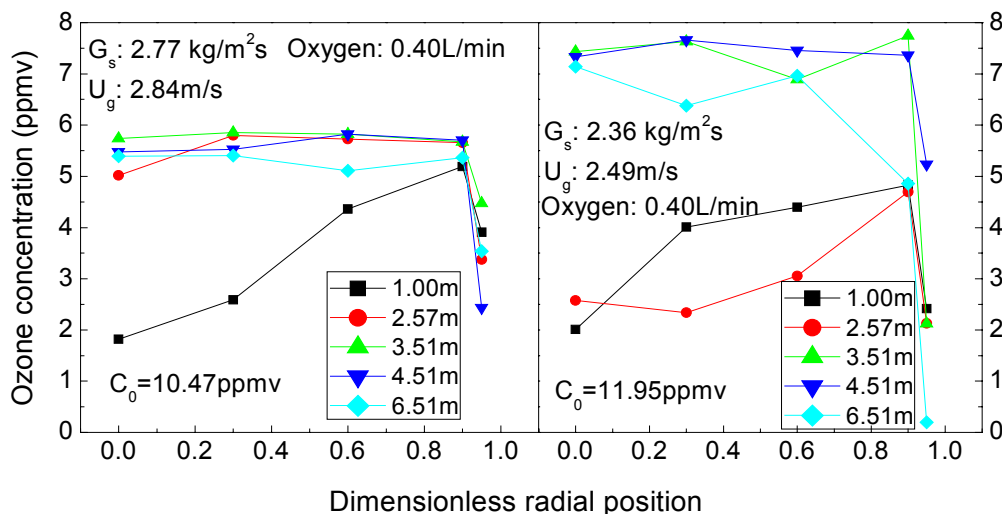


Figure 5 Ozone concentration profiles with impregnated FCC particles.

Results shown in Figures 3 to 5 also suggest that the ferric oxide impregnated catalysts have a prominent contribution to the ozone decomposition. In the empty downer column, the concentration of un-decomposed ozone in the reactor exit was about 10 ppmv, while in the case of impregnated FCC particles, the ozone concentration never exceeded 8 ppmv under similar operating conditions. This is illustrated more clearly in Figure 6 when the ozone concentration in the empty column is directly compared with that loaded with impregnated catalyst particles. Thus, the ozone decomposition in the empty downer can be safely neglected.

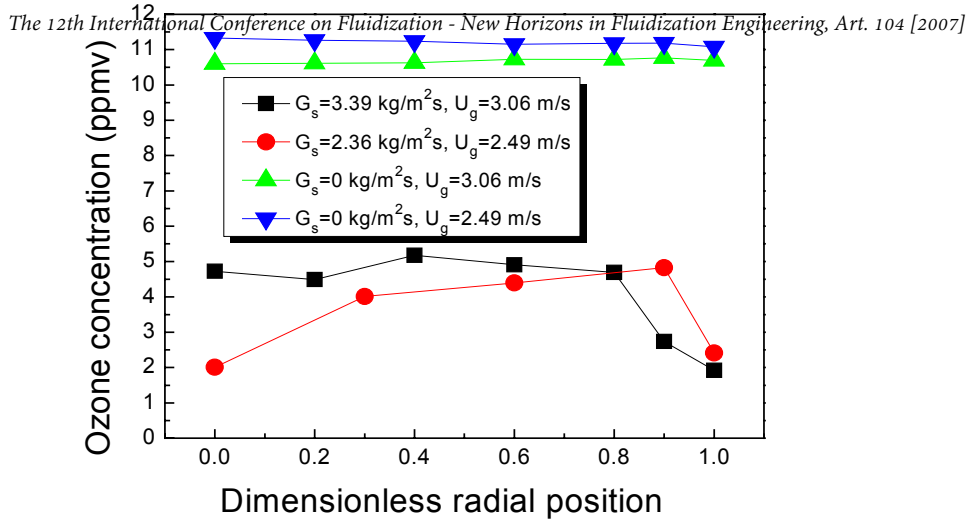


Figure 6 Ozone concentration profiles at the inlet region of the downer ($z=1.00\text{m}$) for both empty column and column loaded with impregnated catalyst particles.

The average concentration of ozone near the inlet part of the downer is often lower than that of fully developed region based on measurement along single radial direction, implying a problem of mass balance. The main reason is the angular non-uniformity of ozone concentration in the downer entrance region. To investigate the angular non-uniformity induced by the solids distribution system (i.e. a jet injection nozzle), the radial ozone profiles along two different directions (A and B) at the same axial position were measured under the same operating condition. The results in the inlet region are shown in Figure 7. It is seen that there is a significant angular

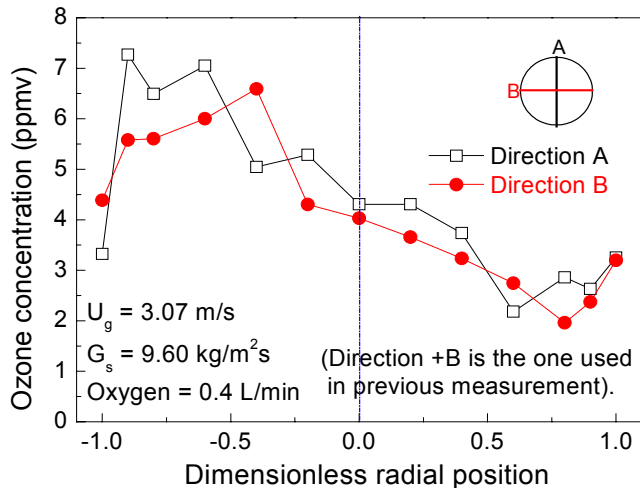


Figure 7. Radial non-uniformity at the inlet region of the downer column

non-uniformity in the inlet region, which could have caused the unreasonable axial ozone concentration distribution if the measurement is only conducted along a single radial direction; but the results from the fully developed region of the downer are still as flat as before, which means that the angular-nonuniformity is insignificant in this region, and the previous measurements are of representative.

The influence of solid mass flow rate on the distribution of ozone concentration was also investigated, with typical results shown in Figure 8. Under the same superficial gas velocity of 2.84 m/s, the ozone conversion increases with increasing solids mass

flow rate, but it increases slowly. There are two reasons for this phenomenon. The first reason is that the increase of the mass flow rate caused an increased catalyst concentration in the reactor, resulting in the increased effective gas/solid contact area for gas/solid mass transfer and reaction. The second reason is that more clusters are formed when the solids concentration increases. Ozone concentration on the surface of catalyst particles within the clusters is usually lower than single particles because the gas/solid mass transfer through the clusters is not as good as that between the dispersed particles and the air. The effective mass transfer rate per volume of particles can be reduced in such a case. The two trends has a compromise with each other when the solids mass flow rate is increased . As a result, the conversion increases, but not very quickly.

It can also be seen from Figure 8 that the total conversion in the downer is about 50.4%. From the gas distributor to the position of 2.7m below the gas distributor, the ozone conversion is about 45.8%, which accounts for most of the total conversion. Similar results are also found under other operating conditions of $U_g=2.84\text{m/s}$ and $G_s=6.58\text{kg}/(\text{m}^2\cdot\text{s})$. This indicates that the reaction is much faster in the acceleration region than in the developed region, possibly due to the higher solids concentration and higher reactant concentration in the inlet region. In other words, the acceleration region is very important to the reactor performance of the whole downer reactor, and the design of gas distributor can play a key role on the downer reactor performance.

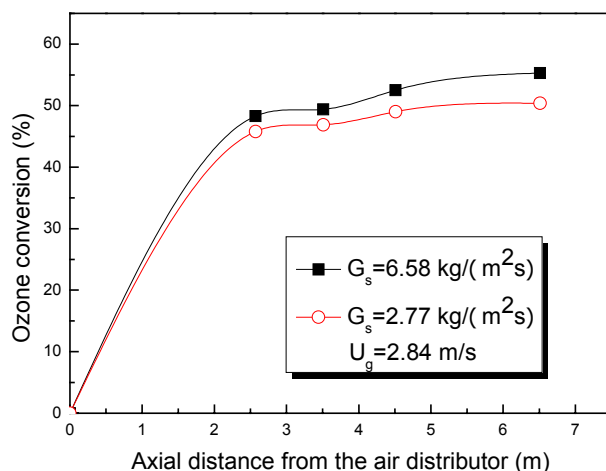


Figure 8. Effect of solids mass flow rate (G_s) on downer performance

CONCLUSION

Ozone decomposition has been used to study the reactor performance of downer reactors. It is found that there exists a significant angular-nonuniformity in the inlet part of the downer, which cannot be observed obviously at other axial positions. The profiles at the fully developed region behaves more flat, except for the position of $r/R=0.9$, where there is a sharp decrease in concentration. This decrease can be attributed to the flow structure of the downer reported in the relative works. At last, calculation shows that most of the ozone was decomposed at the inlet region of the downer, and the conversion at each axial position increases with the increase of G_s , but the increase is not very quick. This can be accounted for the compromise between two trends caused by increasing G_s -- enhancement of gas/solids mass transfer from increase of gas/ solids contact area and the formation of particle clusters in which gas/solids mass transfer is significantly poor.

NOMENCLATURE

The 12th International Conference on Fluidization - New Horizons in Fluidization Engineering, Art. 104 [2007]

U_g = superficial gas velocity (m/s)

G_s = solids mass flux ($\text{kg/m}^2\text{s}$)

r/R = dimensionless radial position (-)

C_0 = mean ozone inlet concentration (ppmv)

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