# Effect of Gamma Radiation on the Partial Oxidation of Hydrogen

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**The effect of gamma radiation on the partial oxidation of hydrogen was investigated in a stainless steel, tubular flow reactor. Runs were made in and out of a cobalt-60 source which provided a radiation intensity of about 110,000 roentgens per hour. The variables of temperature (330° to 400° C.), hydrogen-to-oxygen mole ratio (1 to 8), residence time (2 to 16 seconds), and pressure (up to 12 atm.) were investigated. The optimum increase in oxygen conversion caused by gamma radiation was about 50% and was obtained for a hydrogen-to-oxygen ratio of 4:1, at a residence time of 2 seconds, a pressure of 1 atm., and at a temperature of about 400° C. Oxygen conversion was greatest for irradiated runs and increased with increasing hydrogen-to-oxygen mole ratio, increasing residence time, and increasing temperature. The oxygen conversion decreased with increasing pressure. However, the rate of reaction increased with pressure at a relatively low order.**

GAMMA radiation, such as that from cobalt-60, has been found to affect significantly some free radical reactions (*1, 5*). Partial oxidation of propane, for example, in a cobalt-60 source resulted in increased rates of reaction plus significant increases in the amounts of oxygenated products obtained (*8*). Combustion studies using a propane flame also indicated more rapid reactions (*4*). Further investigations seem necessary to determine more completely the effects of gamma radiation. One of the problems in partial oxidation studies is the accurate analysis of the large number of products obtained, especially when paraffins are used as fuels. Therefore, a fuel such as hydrogen is of considerable interest. Oxidation of hydrogen would produce as stable products only water and possibly hydrogen peroxide.

The hydrogen-oxygen reaction has been of interest for more than 100 years. There are three distinct explosion limits for a stoichiometric hydrogen-oxygen mixture. These three limits represent a balance between chain initiation, chain propagation, and chain termination reactions (*7, 10, 12*). The surface of the reaction chamber has been found to play a major role (*2, 10, 11*) in the yield of water and hydrogen peroxide. The amount of hydrogen peroxide that is actually found in the exhaust stream of the reactor is often related to the ability of the surface to decompose the peroxide (*6, 10*).

The effect of gamma radiation was tested in this investigation on the partial oxidation of hydrogen. The influence of pressure (up to 12 atm.), temperature, residence time, and reaction ratio were investigated both with and without gamma radiation. Several preliminary runs were also made for the partial oxidation of methane.

## EXPERIMENTAL

The apparatus used in this investigation is shown schematically in Figure 1. Hydrogen, with a purity of 99.8%, and oxygen, of 99.6% purity, were supplied from standard gas cylinders (Figure 1). The hydrogen and oxygen were dried with magnesium perchlorate, metered, mixed, and supplied to the reactor at pressures up to 12 atm. The reactor, which is shown in Figure 2, had an internal diameter of 0.88 inch and a length of 11-$\frac{3}{8}$ inches; it was similar to the one used previously by Liebenthal and coworkers (*8*). The present reactor was, however, constructed of stainless steel, and it was heated by means of heating tapes wrapped around it. A $\frac{1}{8}$-inch inlet line and a $\frac{1}{4}$-inch thermocouple well extended inside to near the bottom of the reactor. The surface-to-volume ratio of the reactor was 2.97 cm.$^{-1}$. The cobalt-60 source used provided a gamma radiation intensity of about 110,000 roentgens per hour inside the reactor. The reactor assembly could be inserted when desired inside the cobalt-60 source for the irradiated runs. The stainless steel connecting line from the reactor to the product receiver was electrically heated to prevent condensation of products. The product receiver was also constructed of stainless steel and had an internal diameter of 0.74 inch and a length of 6 inches. The exit line from the stainless steel product receiver was connected to a Grove back pressure regulating valve, used to maintain a constant pressure in the reactor up to 12 atm.

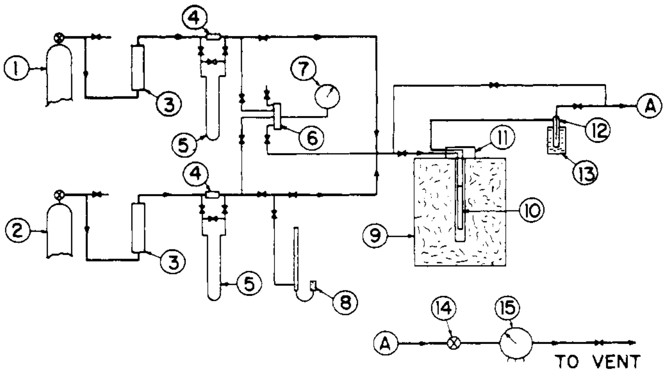

Figure 1. Oxidation apparatus

1. Hydrogen cylinder
2. Oxygen cylinder
3. Gas drier
4. Packed bed for pressure drop
5. Manometer flow meter
6. Manifold
7. Pressure gage
8. Soap bubble flow meter
9. Cobalt-60 pig
10. Reactor
11. Shielding plug
12. Product receiver
13. Dewar flask
14. Pressure reducing valve
15. Wet gas meter

⋈ Valve

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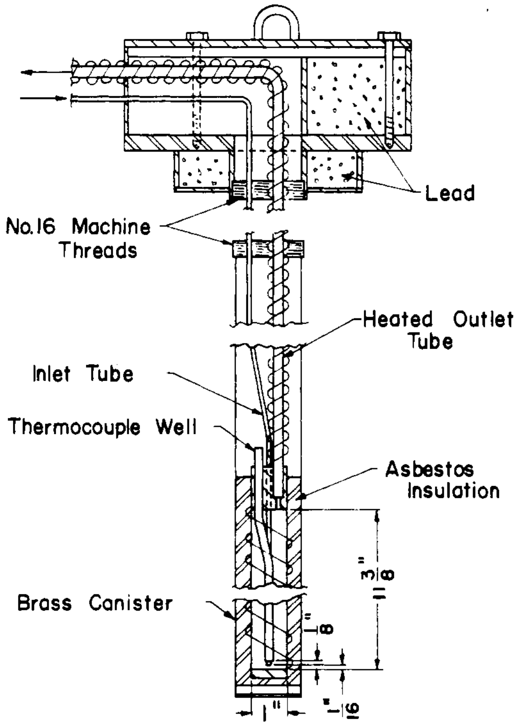

Figure 2. Reactor detail

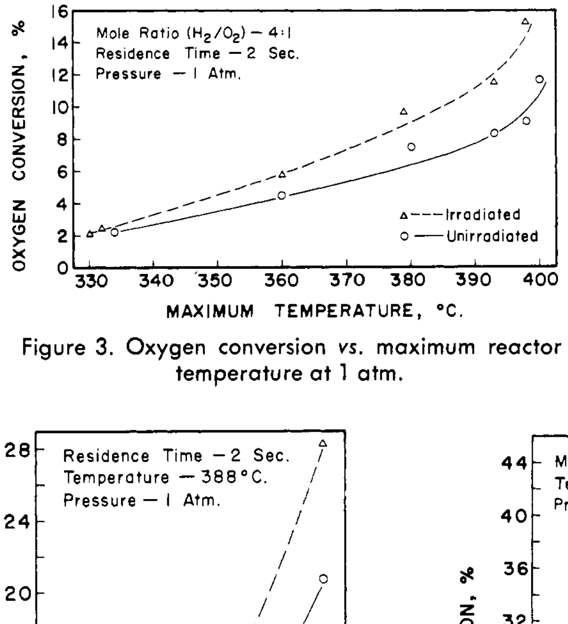

Figure 3. Oxygen conversion *vs.* maximum reactor temperature at 1 atm.

An experimental run was started by initially feeding the desired flow of hydrogen to the system and adjusting the temperature of the reactor to the required level. Then the desired oxygen flow was started. The exothermic nature of the oxidation reaction caused a significant change in the temperature profile of the reactor. If necessary, the power input to the heating tapes around the reactor was adjusted to obtain the desired temperature in the reactor. About a 20-minute period was necessary before the readings of each of the four thermocouples, positioned in a thermocouple well near the axis of the reactor, became relatively constant with respect to time. Then a clean, weighed product receiver was placed in a dry ice-acetone bath and connected to the reactor exit line. The product was then collected for the next 60 to 80 minutes. During this time, temperatures were recorded at intervals of 5 minutes. Immediately after a hydrogen run, the product receiver was weighed, and the liquid product was analyzed for hydrogen peroxide by a standard iodometric method.

## RESULTS

Hydrogen-oxygen runs were made over the following ranges of operating conditions: temperature, 330° to 400° C.; hydrogen-to-oxygen mole ratio, 1 to 8; residence time, 2 to 16 seconds; and pressure, 1 to 12 atm. No hydrogen peroxide was detected in any of the runs.

Preliminary investigations of the partial oxidation of hydrogen indicated that significant rates of reaction occurred only at conditions close to the explosion limit. For a stoichiometric mixture of hydrogen and oxygen at 1 atm. and with a residence time of 2 seconds, the mixture tended to explode at approximately 500° C. Temperature control for atmospheric runs became more difficult as the maximum temperature in the reactor increased above 410° C. Above this point, the temperature tended to increase until an explosion zone was reached—for example, such a trend was beginning in the upper temperature region of Figure 3.

The bottom two thermocouples in the reactor generally indicated a large temperature rise as soon as the reaction was started, but the top two thermocouple readings changed very little. The maximum temperature, which always occurred near the bottom feed section of the reactor (indicated on the thermocouple near the feed point), was used to correlate the results of the hydrogen-oxygen runs. The

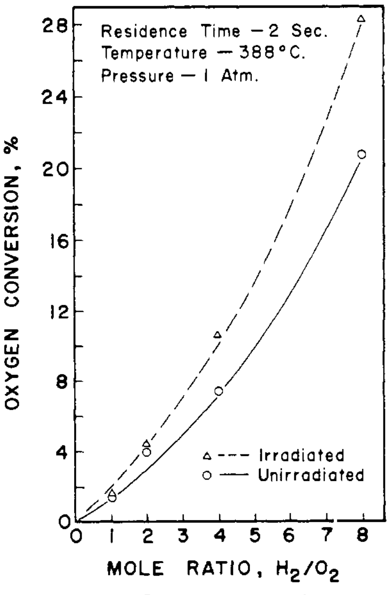

Figure 4. Oxygen conversion *vs.* hydrogen-to-oxygen mole ratio

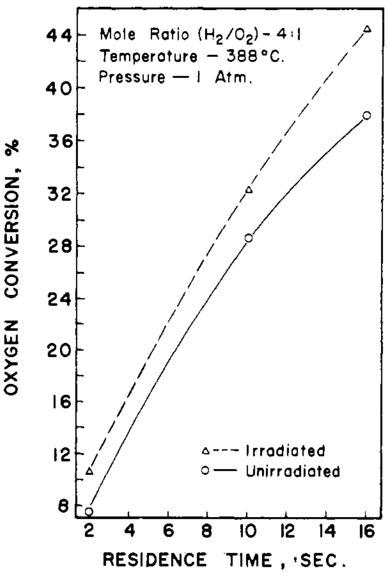

Figure 5. Oxygen conversion *vs.* residence time

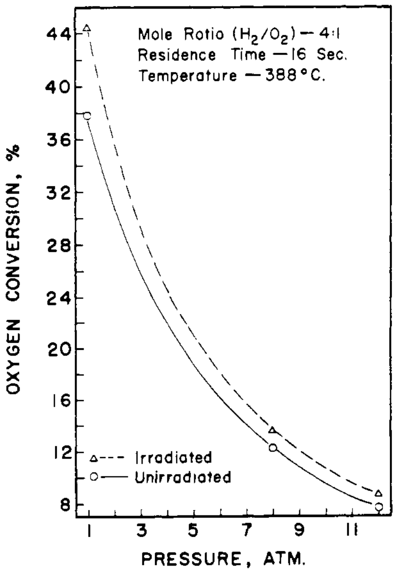

Figure 6. Oxygen conversion *vs.* pressure

temperature values used in the figures are the arithmetical averages of the maximum temperatures recorded during the run. In general, the maximum temperature did not fluctuate more than 10° C. during a run. The maximum temperature for runs made above 390° C., however, sometimes varied as much as 10° to 20° C. as the run progressed.

Heat transfer characteristics of the reactor to the surroundings varied somewhat between runs made in the source to those out of it. This heat transfer was tested by flowing hydrogen or oxygen through the heated reactor, first in the source and later out of the source. The insulation of the stand (used to hold the reactor when it was out of the source) was slightly better than the insulation provided by the cobalt-60 pig. Thus, for a given maximum temperature, the average of the four thermocouple readings in the reactor was slightly higher for a run outside the source than in the gamma source. Presumably then, gamma radiation increased the oxidation conversions even more than was indicated by the present results.

The plots of oxygen conversions *vs.* temperature for a series of irradiated and unirradiated runs are shown in Figure 3. These runs were at 2 seconds residence time, atmospheric pressure, and a 4 to 1 ratio of hydrogen-to-oxygen. The oxygen conversion for both types of runs increased rapidly as 400° C. was approached. The oxygen conversion was about 2% for both the irradiated and unirradiated runs at 330° C. Above 330° C., the two curves are similar in shape with the irradiated runs distinctly higher than the unirradiated ones. The oxygen conversion for the irradiated runs was about 50% greater than for the unirradiated runs at temperatures from 388° to 390° C. The 388° C. temperature was rather easy to maintain whereas at 398° C. the reactor temperature tended to creep up with time. Thirteen days elapsed between some of the experimental runs used in Figure 3, but variations caused by aging of the reactor were not noted.

Other operating variables were investigated at a maximum reactor temperature of 388° C. For these comparisons, results at exactly 388° C. were required since the reaction rate varied greatly with a small change in temperature. Hence, runs were made with maximum temperatures at approximately 380°, 385°, and 392° C., and a smooth curve was then drawn through the three data points to obtain values at 388° C.

The effect of mole ratio, residence time, and pressure on the oxygen conversion is shown in Figures 4, 5, and 6, respectively, at 388° C. In all cases, gamma radiation resulted in significantly higher oxygen conversions. No indication was found of any induction period with respect to time.

Figure 7 shows plots of oxygen conversion *vs.* maximum reactor temperature for runs at 8 atm., a residence time of 16 seconds, and a 4- to 1- hydrogen-to-oxygen ratio. In the higher temperature range of the investigation, the conversions were somewhat greater for the irradiated runs. Several preliminary runs were made using methane as a fuel. The analytical techniques, although quite crude, indicated that radiation increased the degree of oxidation over the ranges of pressures and temperatures previously used for the runs with hydrogen.

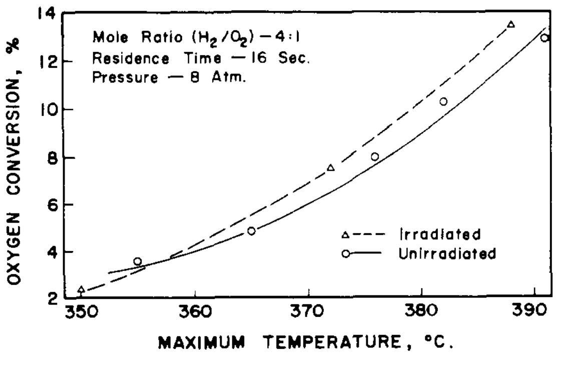

Figure 7. Oxygen conversion *vs.* maximum reactor temperature at 8 atm.

## DISCUSSION OF RESULTS

The present investigation significantly extends the pressure range for the hydrogen-oxygen reaction in a continuous flow reactor. The oxygen conversion decreased with increasing pressure. However, the rate of reaction increased with pressure at a relatively low order, which implies the catalytic surface reactions are the controlling reactions for the reactor used in this investigation. This is predictable for the type of reactor used and with its high surface-to-volume ratio. Sometimes, the reactor surface "ages" as the reactor is used resulting in changes in the over-all reaction rates (*3*). In the present investigation, as in other work (*9*), no "aging" of the reactor was noted.

The reaction rate was increased by gamma radiation, and the data indicate that this was attributed to the surface-catalyzed reactions. Irradiation of an oxygen-hydrogen mixture would be expected to lower the explosive limits. The explosion limit for a 4-to-1 ratio of hydrogen-to-oxygen, at a pressure of 8 atm., and with a residence time of 16 seconds was 450° C. The explosion limits for a stoichiometric hydrogen-oxygen mixture were about 50° C. lower than previously reported (*7*) for a mixture at atmospheric pressure. This also shows the importance of surface in the reaction rate. In this respect, the data of Figure 4 may be significant, since the reaction rate (expressed in moles of oxygen disappearing per second) is about inversely proportional to the partial pressure of oxygen in the mixture.

Hydrogen peroxide is frequently found in the reaction product when the reaction vessels were constructed of glass (*2, 3, 9, 11*). However, when the product trap was over 1 meter from the glass reactor, no hydrogen peroxide was detected in the product (*2*). Hydrogen peroxide also decomposes more rapidly on a metal surface than on glass (*6, 10*). The stainless steel reactor used here and located 80 cm. from the metal product receiver resulted in no hydrogen peroxide.

## CONCLUSIONS

Under the range of operating variables investigated, gamma radiation improved the oxygen conversion up to about 50% as compared to unirradiated runs. The maximum increase of conversion was found for a hydrogen-to-oxygen ratio of 4-to-1, at a residence time of 2 seconds, a pressure of 1 atm., and at a temperature of about 400° C. The oxygen conversions (on a fraction basis) for both irradiated and unirradiated runs increased with increasing hydrogen-to-oxygen mole ratio, increasing residence time, increasing temperature, and lower pressure.

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# Factors That Affect the Potential of the Saturated Corrosive Sublimate (in Ethylenediamine) Electrode

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**The system, Hg/HgCl$_2$ (satd.), LiCl (satd.) in ethylenediamine, after being aged for 24 hours, has a potential reproducible to within ±0.5 mv. and a temperature coefficient of −1.3 mv. per ° C. at room temperature. Introduction of water causes the potential to shift positive, but the effect is less than 3 mv. for not more than 2.5% of water. At 25° C., the apparent potential of the saturated corrosive sublimate electrode (SCSE) with respect to a pH-meter-type (aqueous) saturated calomel electrode is −450 mv. Aging for 2 weeks causes the SCSE to become ~11 mv. negative to a 24-hour SCSE. The difference persists at this value for several days.**

STUDIES in a nonaqueous solvent are sometimes made with the aid of a reference electrode that is essentially a saturated calomel electrode made in the chosen solvent. Although solvents such as methanol (*4*) or acetic acid (*2*) can be used, a calomel electrode prepared with ethylenediamine (EDA) is unsatisfactory because of the reaction between calomel and EDA. In their studies on equilibria in EDA solutions, Bruckenstein and Mukherjee (*3*) introduced the saturated corrosive sublimate electrode (SCSE). This consists of a mercury pool in contact with an EDA solution that is saturated with respect to both mercury (II) chloride and lithium chloride. These workers found that duplicate electrodes agreed in potential to within several tenths of a millivolt. The present work is concerned mainly with the effects of age, temperature, and added water on the potential of the system.

## EXPERIMENTAL

**Chemicals.** EDA, lithium chloride, and mercury(II) chloride, dried as was done previously (*5*), contained, respectively, 0.058, 0.10, and 0.04 gram of water per 100 grams of sample.

**Apparatus.** Each ~80-ml. borosilicate glass half-cell vessel *A* had near the bottom a short side arm pointing upwards at ~45° and terminating in a 10/30 female cone. Twin mercury-pool J-tube electrodes were sealed to the underside of the 29/42 stopper in the mouth of the vessel. Contact to each 5-mm. diameter pool was made by a platinum wire sealed through a septum in the J-tube and brought out through the stopper. The vessels, used only for solutions without added water, were joined by a Λ-shaped junction tube, the ends of which carried 7-mm. diameter fine-porosity glass frits on the ends of 10/30 male cones. Vessel *B*, with two side arms and an additional capped opening near the stopper, was used to carry the saturated (aqueous) calomel electrode or, with J-tube electrodes inserted, for solutions containing added water. When in use, vessel *B* was connected through junction tubes to two type-*A* vessels. Cell assemblies were mounted in a grounded copper box that was almost completely immersed in a thermostat bath. In temperature-difference studies, boxes containing the individual half-cells were placed in adjacent baths. Temperatures were controlled to better than ±0.01° C.

E.m.f. measurements were made through shielded leads to a calibrated Leeds and Northrup Model 7664 pH meter. When necessary, the meter sensitivity was increased to 70 mv. full scale deflection by insertion of Accessory Resistor No. 115077. The (aqueous) saturated calomel electrode was Leeds and Northrup Type 1199–31.

**Procedure.** All operations other than in closed vessels were brief and carried out in dry nitrogen. About 40 ml. of EDA was distilled into each half-cell vessel that contained lithium chloride and mercury(II) chloride in amounts ~10% greater than required to saturate the final solution. When necessary, water was measured in from a microburet. The vessels were then closed and gently agitated at the desired temperature for ~24 hours. The electrodes were inserted, the side arms uncapped, and the junction tube was attached. This tube was filled with EDA saturated at 25.0° C. with both lithium chloride and mercury(II) chloride. A cell used from 24 to 30 hours after insertion of the electrodes is termed a "fresh half-cell."

**Results.** Fresh half-cells prepared from distilled (0.058 gram water per 100 grams of distillate) EDA agreed with one another and with a half-cell of pool diameter ~20 mm. to within 0.5 mv. At 25.0° C., a fresh half-cell was 6.5 ± 0.5 mv. negative to a similar half-cell at 20.0° C. This potential difference remained essentially constant for 1 to 2 days, then slowly increased. After 4 to 5 days, a white film appeared on the mercury in the warmer half-cell. Renewal of all mercury surfaces without changing the solutions or the temperatures caused the potential difference to revert to 6.5 ± 0.5 mv. At 25.0° C., a half-cell aged for 2 weeks was