

Hydrocarbon Oxidation in a Supercritical Fluid Photocatalytic Reactor

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ABSTRACT

This experiment investigated the oxidation of cyclohexane in supercritical carbon dioxide in the presence of titanium dioxide and UV light. An understanding of the oxidation kinetics and catalyst performance was desired. The major findings were that the cyclohexane did oxidize at various rates. The brand new catalyst performed the best. After a catalyst was used for 15 hours the performance drop but then remained constant. The UV light also played an important role in the kinetics. Another major find was that not all the catalyst in the reactor was being used due to the limited UV light coming in from the top of the reactor.

A preliminary rate constant was found for the used catalyst of 7.5×10^{-4} mol of cyclohexane oxidized/ hour * gram of titanium dioxide. There remains studies to be performed to make a justifiable conclusion to was the kinetics are.

INTRODUCTION

Supercritical fluids (SCF's) can become contaminated with small amounts of hydrocarbons. This study centered on supercritical carbon dioxide (scCO₂) charged with small amounts of cyclohexane on the order of 80 parts per million (ppm). The charged scCO₂ was then reacted under UV light in the presence of titanium dioxide (TiO₂) catalyst (see figure 1). The cyclohexane oxidation kinetics were investigated.

Supercritical fluids (SCF's) are fluids in a condition above their critical pressure and critical temperature. Under these conditions the fluids behave as neither a gas nor a liquid but as a combination of both. SCF's exhibit both gas properties in being able to penetrate into things and liquid properties in being able to dissolve materials. This makes them valuable as solvents.

Supercritical fluid solvent properties were first reported nearly one hundred years ago. Since the 1980's there has been a resurfacing interest in their applications (Phasex Corp.). Have you ever had a steaming cup of decaffeinated coffee? Most likely a supercritical fluid removed the caffeine that was once locked away in the coffee grains. Due to their properties SCF's can be used as solvents as in the case of caffeine removal. There are numerous other applications such as extracting hops flavors in brewing, extracting aromas and flavors from spices, waste cleanup, cleaning soil contamination, and cleaning instruments.

The main advantages for extractions with SCF's compared to other solvents are that they are inexpensive, contaminate free, and less costly to dispose (Tissue 1996). Some other advantages of SCF's are that the solvating power and density can be easily adjusted with pressure and temperature. SCF's also exhibit high diffusivities, low

viscosities, and low surface tensions. The most commonly SCF's used today are water and carbon dioxide due to their cost, availability and non-toxicity. Only carbon dioxide (CO₂) was used in this study.

Titanium dioxide (TiO₂) catalyst was another substance used in this study. Titanium dioxide is being researched in many fields today. It can be used in paints to help keep their luster, killing bacteria, on self-cleaning surfaces or as a catalyst for certain reactions. Titanium dioxide is a useful catalyst. When UV light strikes the titanium dioxide "free radicals" are created at the surface. These free radicals can then attack hydrocarbons causing them to eventually oxidize into carbon dioxide and water (Fujishima, 1999). The complete mechanism is still being investigated.

The goal of this study was to gain an understanding of the hydrocarbon oxidation reaction kinetics in scCO₂. These experiments focused on the breakdown of cyclohexane in the scCO₂. Cyclohexane was chosen as a good representative hydrocarbon due to its simplicity. It is necessary to understand the kinetics in order to know design specifications for an industrial applications. Some design specifications would be reactor size, the amount of UV light, the amount of catalyst, and catalyst life. All these must be understood in order to make an efficient functioning reactor.

MATERIALS AND METHODS

All the reactions took place in a supercritical fluid photocatalytic reactor (SCFPR). The reactor was made of a series of metal tubes which connected different components of the entire system (see figure 2). The main components were a reactor chamber, UV lamp (black ray 100 W mercury lamp), pump, flow rate and density

detector (Elite Mirco Motion), hydrocarbon injection port, heater, various valves, and thermocouples. The system was fit to withstand 5000-psia and operations never exceeded 1600 psia. In addition a gas chromatograph (GC) was connected to the SCFPR. It was a HP 5890 series II GC. A computer recorded information from both the GC and the reactor.

The GC was first calibrated using a set of standards for the original four different components. The four components were cyclohexane, hexane, toluene, and benzene. The study focused on cyclohexane. From these calibrations samples were taken from the SCFPR to find cyclohexane concentrations.

All the experiments were run at these standard conditions: 40°C, 1300 psia, 30 g/min flow rate, 0.49 g/ml scCO₂ density,. Four microliters cyclohexane was charged to each experiment in order to get about 80 ppm cyclohexane. The total closed loop reactor system volume was 56 ml. The total reactor chamber volume was 17 ml made of 8 ml free space and 9 ml beads. The beads contained 62 mg of TiO₂ coating. All but two experiments (Aug 2, Aug 3) were initially charged with 150 psia O₂/ CO₂ mixture or 6 times the O₂ needed for complete oxidation

The pump function was to continuously cycle the charged scCO₂ in the loop so the cyclohexane repeatedly passed over the catalyst in the reactor chamber. The reactor chamber is where the oxidation took place. The reactor chamber is a metal block that has a 17-ml chamber with a glass window on either side of the chamber. Titanium dioxide catalyst (Degussa P25) was coated on 3 millimeter glass beads and placed in the chamber (see figure 3). The UV light shined through the glass window onto the catalyst (see figure 4). There was also an Elite Micro Motion unit that measured the density and flow

rate of the scCO₂. The injection port allowed the user to inject the hydrocarbon while the system was pressurized. There were several additional valves and connections, which allowed the user to add and remove the fluids from the reactor. The entire reactor system was enclosed in a Lexan plastic box that blocked UV light and provided a barrier for high pressure components. (see figure 1)

In the experiment procedure the system was first charged with 150 psia 10 % O₂/90% CO₂ gas. This created an excess of 6 times stoichiometric O₂ in the system for complete oxidation. The system was then charged with CO₂ to 1300 psia and allowed to reach to a stable temperature of about 40°C. Fluid density was at 0.49 g/ml. 4 microliters cyclohexane was added to produce about 80 ppm cyclohexane. The system was allowed to circulate so the cyclohexane would be equally distributed throughout the system. The UV lamp was then turned on and left to breakdown the cyclohexane. The GC took samples every 8 to 10 minutes. All the sample results were sent and recorded in the computer. The pump was set about 30 g/min in all the experiments. That meant the fluid would cycle through the reactor loop about 2 times per minute.

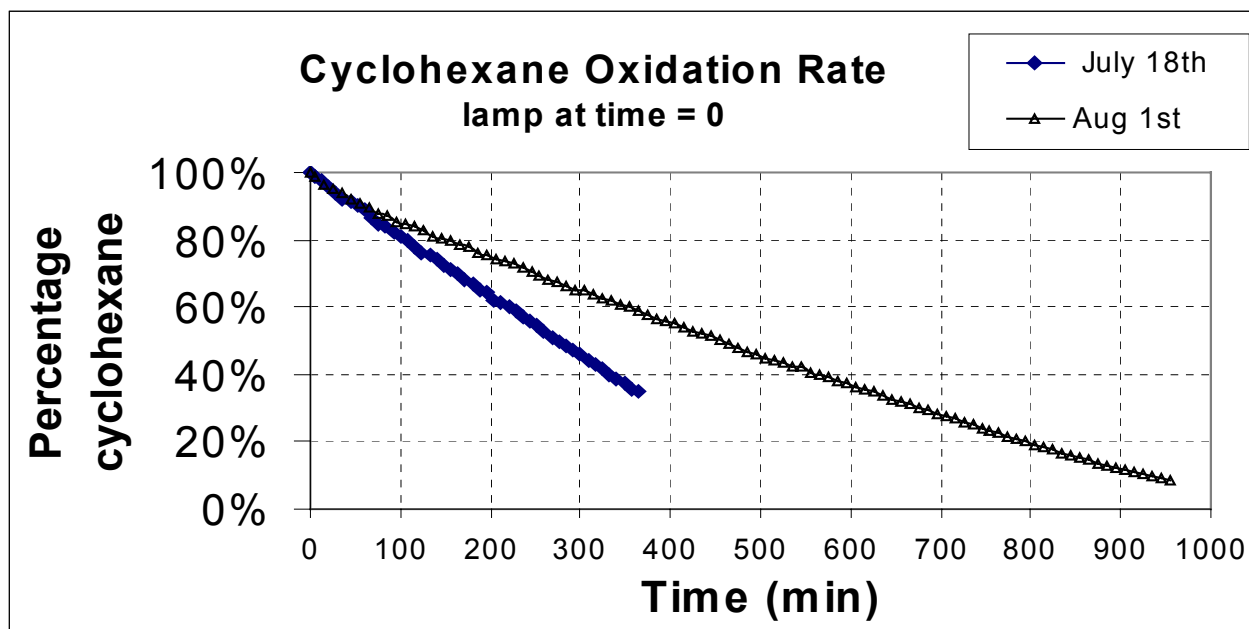
Recharging the catalyst was performed over each weekend. This was accomplished by allowing zero air to flow over the catalyst at a slow rate about 2 ml/sec. The temperature was maintained at 40 °C and the UV lamp was turned on over the catalyst.

Several variations were made from the standard conditions. Some baseline experiments were run with no O₂ initially added. In these experiment no reaction took place. Several experiments (Aug 2, Aug 3) were run where the system was initially charged with 300 psia 10% O₂/ 90% CO₂ for a 12 times the needed O₂ for complete

oxidation. The light position was shifted in the middle of a run on July 27th. The brighter part of the lamp was moved over the reactor window. This caused a significant change in the rate. Once this was discovered the light was kept in the same place for the following experiments. Experiments run on days July 31st through Aug 3rd held the light in the same place. Aug 4th experiment used the cone holder for the lamp. The cone holder is a funnel type holder where the lamp sits on top. The cone is covered in aluminum foil causing more light to funnel into the reactor chamber. In another run on Aug 7th half the beads were removed from the bottom of reactor chamber and replaced with plain glass beads.

Results

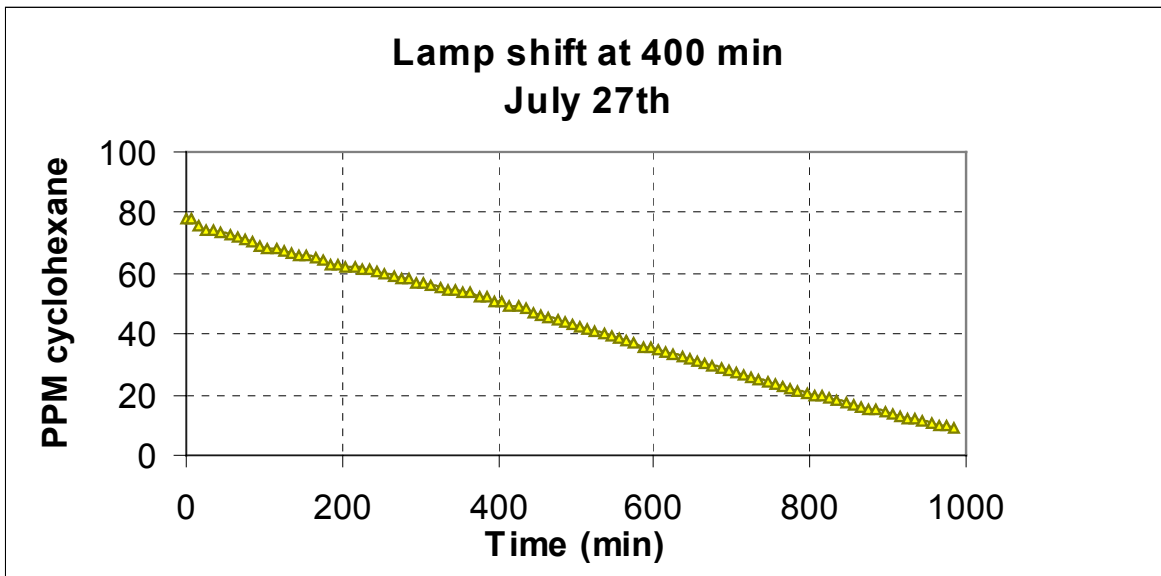
The cyclohexane concentrations decreased over time while in the SCFP reactor. The cyclohexane concentrations decreased near linear until very low concentrations of 20 ppm. The following shows two representative experiments performed on July 18th and Aug 1st using the same catalyst under the same conditions. Experiments started at 80 ppm cyclohexane.



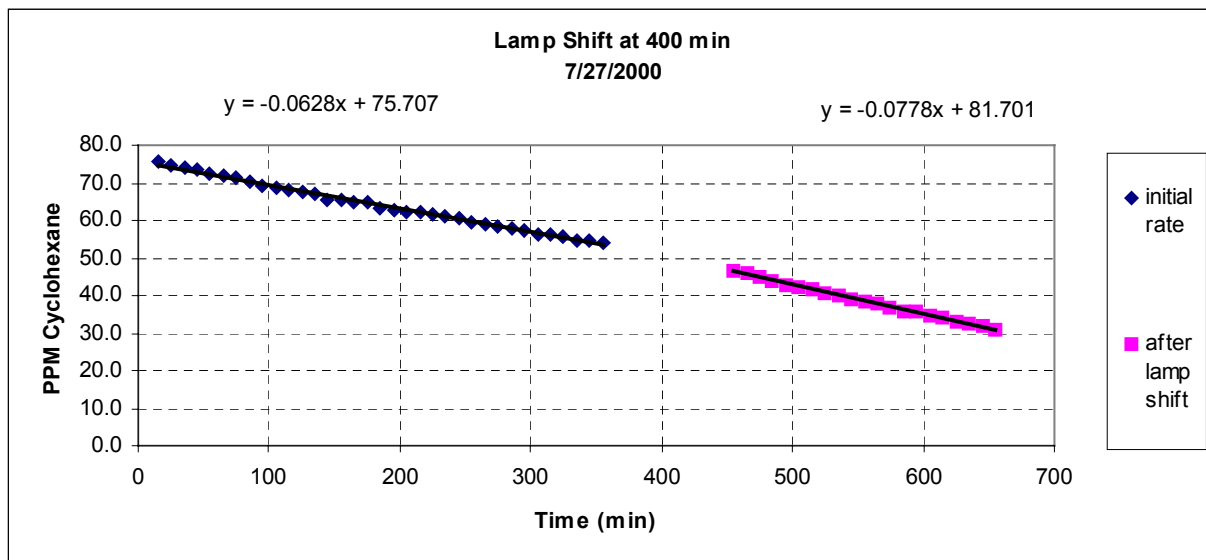
Also shown in the above graph the brand new catalyst (first 15 hrs of use) on July 18th had a higher rate of reaction and never achieved the same rate even after regenerations represented by the Aug 1st line. The original reaction rates seen in the first 15 hrs were not achieved again using the same catalyst under the same conditions.

Furthermore after successive regeneration's seemed to have little effect on reactor performance when using the 6 times O₂ needed for complete oxidation.

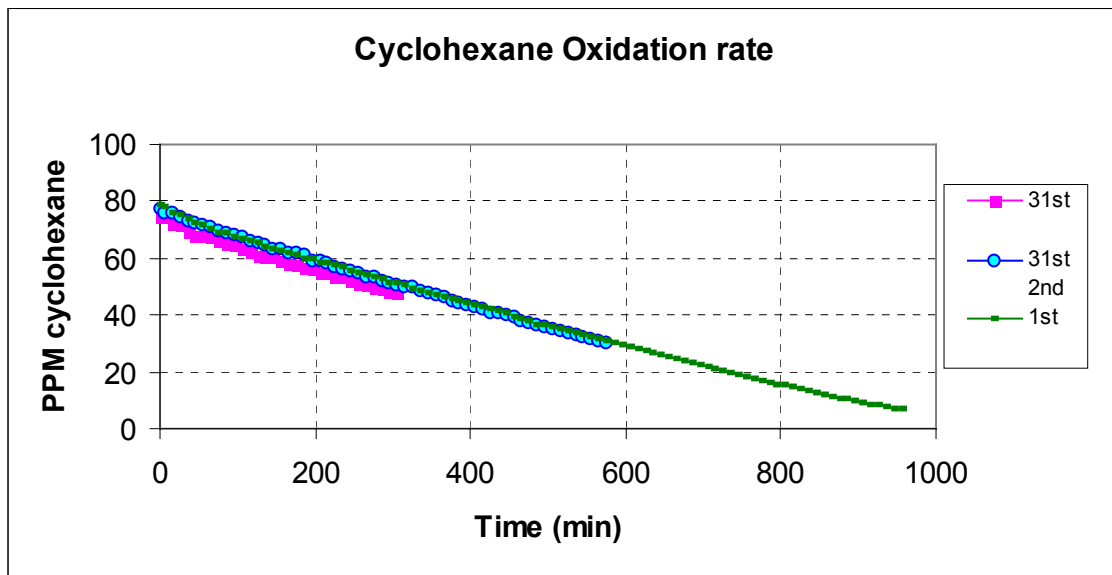
On July 27th the UV lamp was shifted at min 400 of the run. The more intense light was moved over the reactor window. A significant change in the reaction rate occurred.



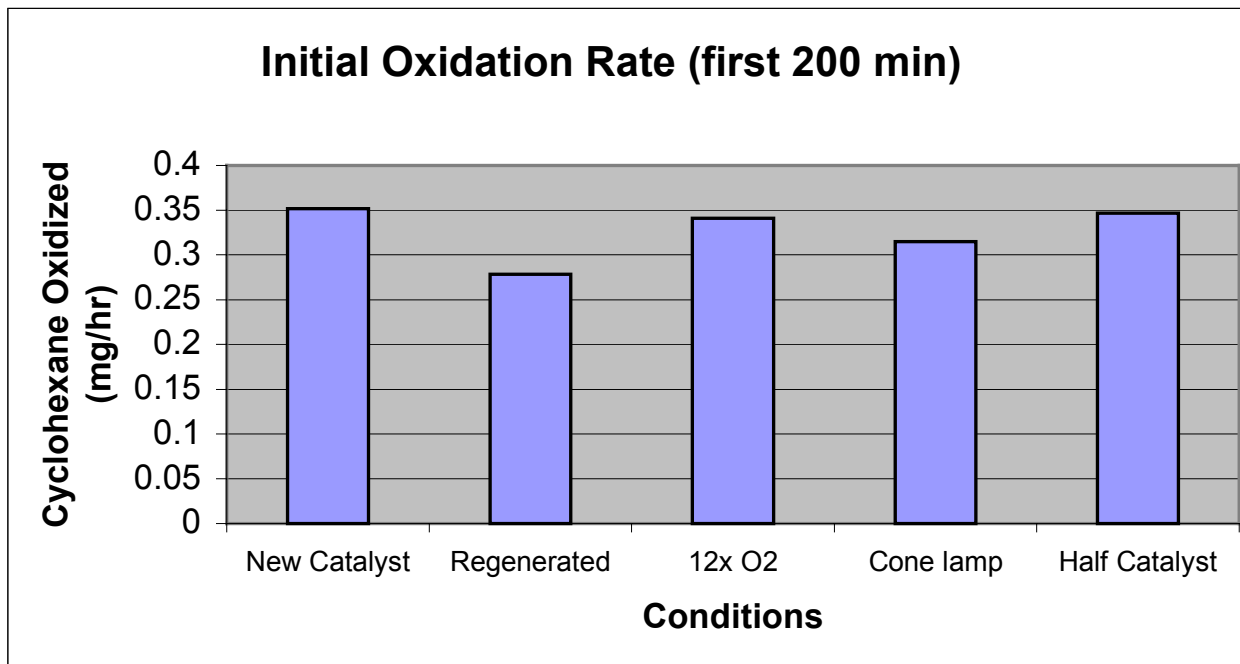
By splitting the graph into two sections the following graph was produced. By shifting the lamp it created a 25% increase in the reaction rate.



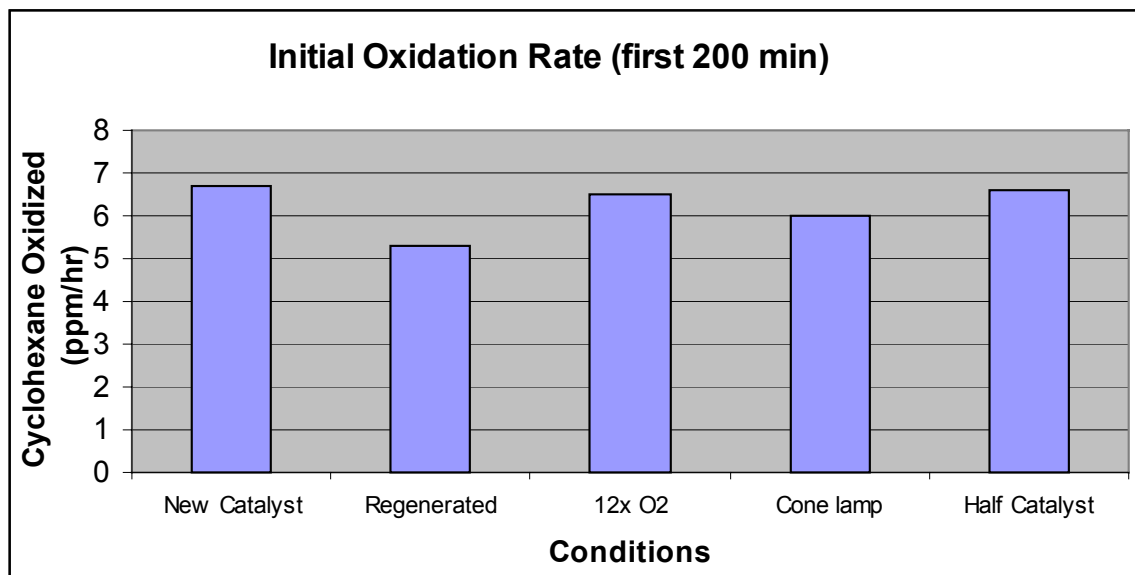
Lamp position was influential in the reaction rate data. Therefore, the following experiments positioned the lamp in an identical place. Standard conditions were used namely 40 °C, 1300 psia, 6 times O₂ level. The 3 experiments showed near identical data. Catalyst performance didn't change over the 33 hours.



The following graphs show a number of experiments. The new catalyst column was the rate when the catalyst was brand new (used for <15 hrs). The regenerated column is after the catalyst had been upwards of 15 hrs to 140 hrs. with regeneration every 40 hrs. The 12x O₂ column is where twice the O₂ or 12 times the needed O₂ for complete oxidation was added at the start of the experiment. The cone lamp column is where the cone holder was used to hold the UV lamp in place of the metal brackets. The half catalyst column is where the beads were removed and plain glass beads were placed in the bottom half of reactor chamber and same beads with the catalyst was placed on the top half. The data was treated as linear data in the first 200 minutes.



Here is another graph showing the same data as the previous graph. The Y axis is in ppm oxidized every hour.



Discussion and Conclusion

First we found that the cyclohexane did oxidize in the scCO₂ with the TiO₂ catalyst and the UV light. The oxidation rate depended on the experimental conditions.

The brand new catalyst did oxidize the cyclohexane at a faster rate than the catalyst that had been used for over 15 hours. Even when the catalyst was regenerated at 40°C with zero air, and UV lamp for 50 hours the catalyst didn't have the same performance. This might be due to the more active sites being inactivated and were not regenerated in the regeneration process. Perhaps a complete regeneration could be achieved at higher temperatures above 40°C.

The regenerations over the weekends didn't seem to have any effect on the reactor performance. Regenerations were performed right before the 24th, 31st, and 7th data. When examining the data before and after regeneration there was no significant change. This would tend to support the fact that the 6 times O₂ needed for complete oxidation was sufficient to keep the catalyst performance constant. The reactions were not deactivating the catalyst because there was enough O₂ present.

The UV light plays an important role in the experiments. On July 27th the lamp was shifted at about 400 min into the run. This caused about a 25% oxidation rate increase. It was noted that at time 400 min the more intense light was directed into the reactor chamber. This was not entirely expected. From the known mechanism it seems that once there is a certain amount of light more light will not make the reaction rate increase. The experiments previous to this date didn't necessarily have the light in the same exact spot on the support brackets. Therefore this limits the data reliability performed on previous dates. The changing reaction rate could be a function of the catalyst or merely a different positioning of the UV lamp. It should also be noted that the lamp was never placed in extremely different locations. The experiments performed afterward were with the UV lamp in the same position except where noted (experiment Aug 4th).

In most design specifications an initial reaction rate is used. Therefore a focus was made over the first 200 minutes. The reactions at this range were nearly linear all giving an R² value of 0.99 or better. This signifies a zero order reaction. A reaction that is independent of the cyclohexane concentration. This is reasonable due to the fact that it is a surface reaction. There are only so many sites available for reactions to occur. The

entire mechanism is not known. It was found that if the entire data set past 200 minutes was plotted it wasn't quite a zero order reaction but between a 0.4 to a 0.6 order reaction. For the initial rates it is reasonable to use the linear data or zero order reaction.

When 12 times the O_2 needed was added to the reactor it did increase the reaction rate for the first 200 minutes. It is important to note that after 200 min the rate decreased and performed similar to the runs where there was only 6 times the O_2 needed. O_2 is part of the reaction and therefore may play a major role in the reaction kinetics. More studies must be done with different O_2 concentrations in order to make a justifiable conclusion.

The cone holder was used in one experiment to see if it would increase the reaction rates. In the one experiment it did increase the rates to some degree. Since only one run was performed it would be necessary to run several more to check the reproducibility. One thing the cone holder does provide is more consistent UV light into the reactor. It is much more difficult to shift the lamp when it is placed on the cone holder.

Using half the catalyst on top and plain glass beads on the bottom had interesting results. It actually outperformed the experiments with all catalyst beads. Again only one run was possible. It would therefore be expedient to run several more experiments. One explanation for this phenomenon is that although the same catalyst was placed back on the top the same top catalyst was not placed back on top. The procedure for changing the catalyst was that the reactor was first emptied by pouring the catalyst coated beads into a container. Then the reactor chamber was filled half way with the plain glass beads. Then the used TiO_2 coated beads were replaced placed on top of the plain beads to fill the

reactor. Some of the TiO_2 could have been essentially “new beads” that were on the bottom and never participated in the first set of experiments.

Setting these further experiments aside a preliminary reaction rate constant can be calculated. Assuming sufficient UV light and all the catalyst was being used at the half catalyst reaction (Aug 7th). There was 31 mg of TiO_2 catalyst. The new catalyst rate was calculated to be $r = 9.4 * 10^{-4}$ mol cyclohexane/(hour * gram TiO_2). For the used catalyst regenerated the rate would be $r = 7.5 * 10^{-4}$ mol cyclohexane / (hr * gram TiO_2). The used catalyst would be most usable. So if you wanted to oxidize 1 gram of cyclohexane in one minute you would need about 956 grams of TiO_2 catalyst or about 1 kilogram. In addition with the same type beads it would require a reactor with a 250 L volume. This is just a preliminary rate of reaction. Nevertheless it illustrates that for large oxidation amounts this is not a practical strategy.

Although a major step in refining the equipment and procedure was achieved there remains more experiments to perform. Further investigations should be made in order to understand the reaction kinetics more completely. A study of the UV light effects should be performed. The cone holder could be used to keep the amount of UV light reaching the reactor consistent. Further studies should also be made to see how much catalyst is actually participating in the reaction. Continued changing the layers of plain glass beads and catalyst-coated beads could be performed.

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Oxidation Reaction

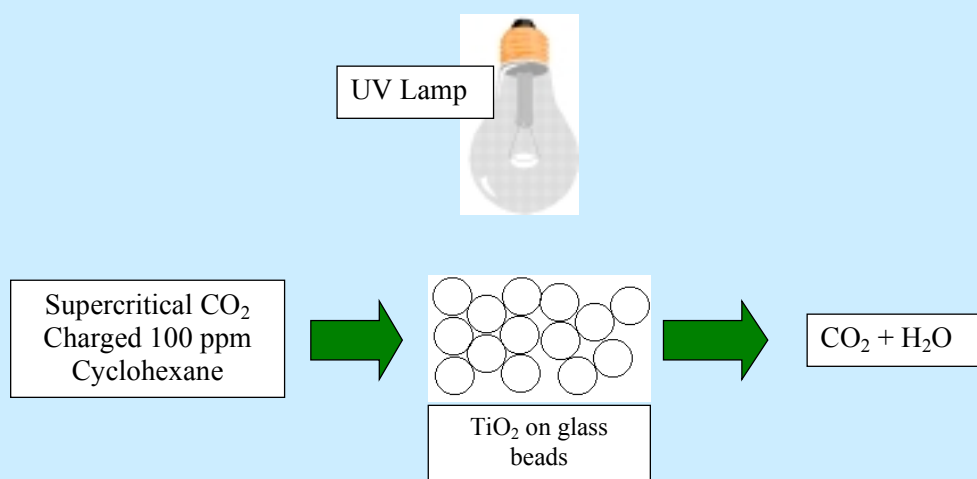


Figure 1.

SCF Reactor

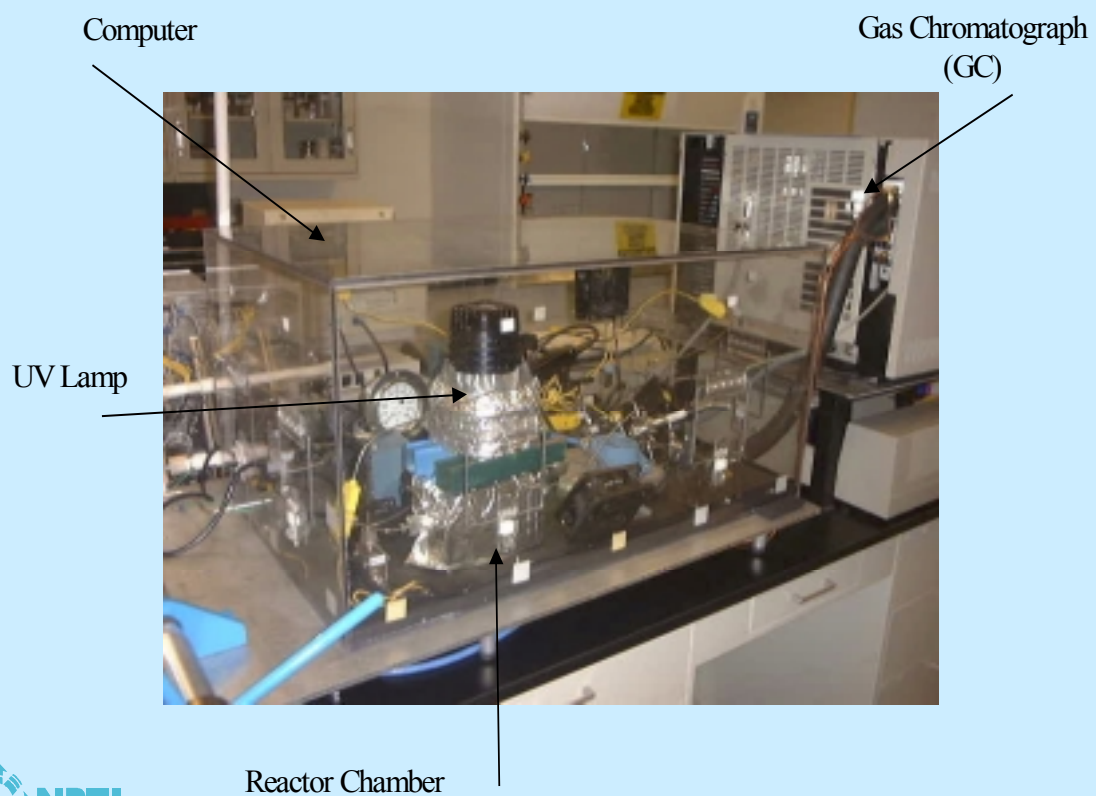


Figure 2.

TiO₂ Catalyst (On 3mm glass beads)



Figure 3.

SCFP Reactor



Figure 4.