The Degradation of Organic Pollutants Using Supercritical Water

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Abstract

An aqueous phenol solution (9.75E-04 M) was subjected to a constant pressure of 280 bar and various temperatures (550–700ºC) and residence times (12–114 seconds), in a reactor specially designed to withstand these harsh conditions above the the supercritical point of water (T = 374ºC, P = 220 bar). The degradation of phenol was studied as a function of both temperature and residence time. The organic content of the process effluent was examined using three independent procedures – Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and UV-Vis analyses. The general trend for phenol degradation to increase with increased temperature and/or increased residence time was observed in all three analyses. Quantitative results for the COD and TOC analyses are almost identical in terms of percent degradation from the original, untreated solution. Greater than 99% destruction of phenol into non-organic products was observed within the range of temperatures and residence times studied.

Experimental Procedure and Conditions

I) A stock phenol solution of 9.75E-04M was prepared

II) Solution was pumped through specially designed reactor using Shimadzu Model LC-10 Liquid Chromatograph

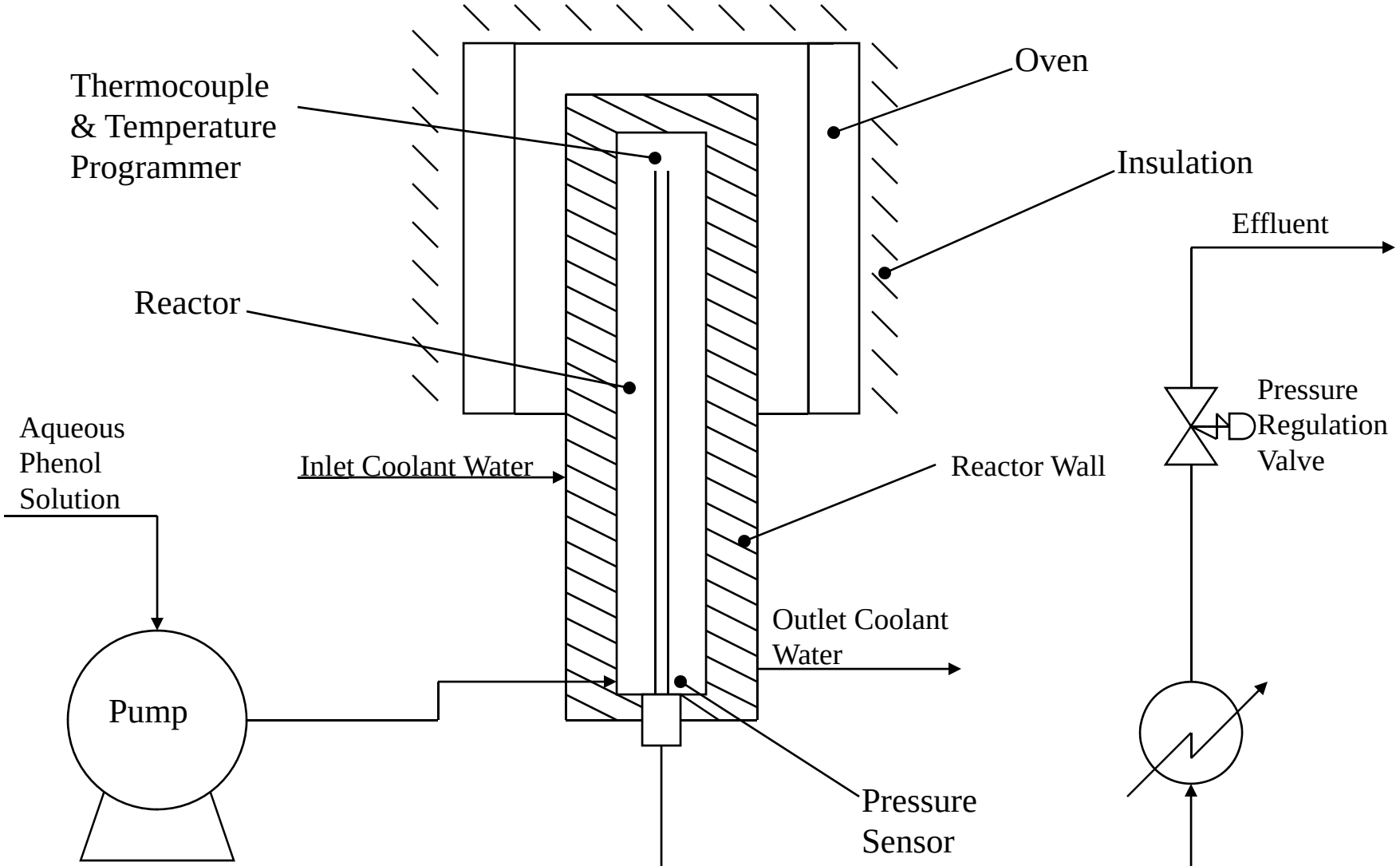
A) Conditions Studied

1) Pressure: 220 bar
2) Temperatures: 550, 600, 650, 700, ^{o}C
3) Reactor Residence Times: 0.2 - 1.9 minutes

III) Reactor effluent was collected and subjected to COD, TOC and UV-Vis analysis to determine phenol degradation

IV) Total time to flush reactor, reach steady state, collect sample: 1-3 hours

Diagram 1: Reactor Apparatus



Maximum Operating Conditions:
Temperature: 850ºC
Pressure: 800 atm

Data Analysis Procedure

I) UV-Vis Analysis - Shimadzu Model 1603 Spectrophotometer

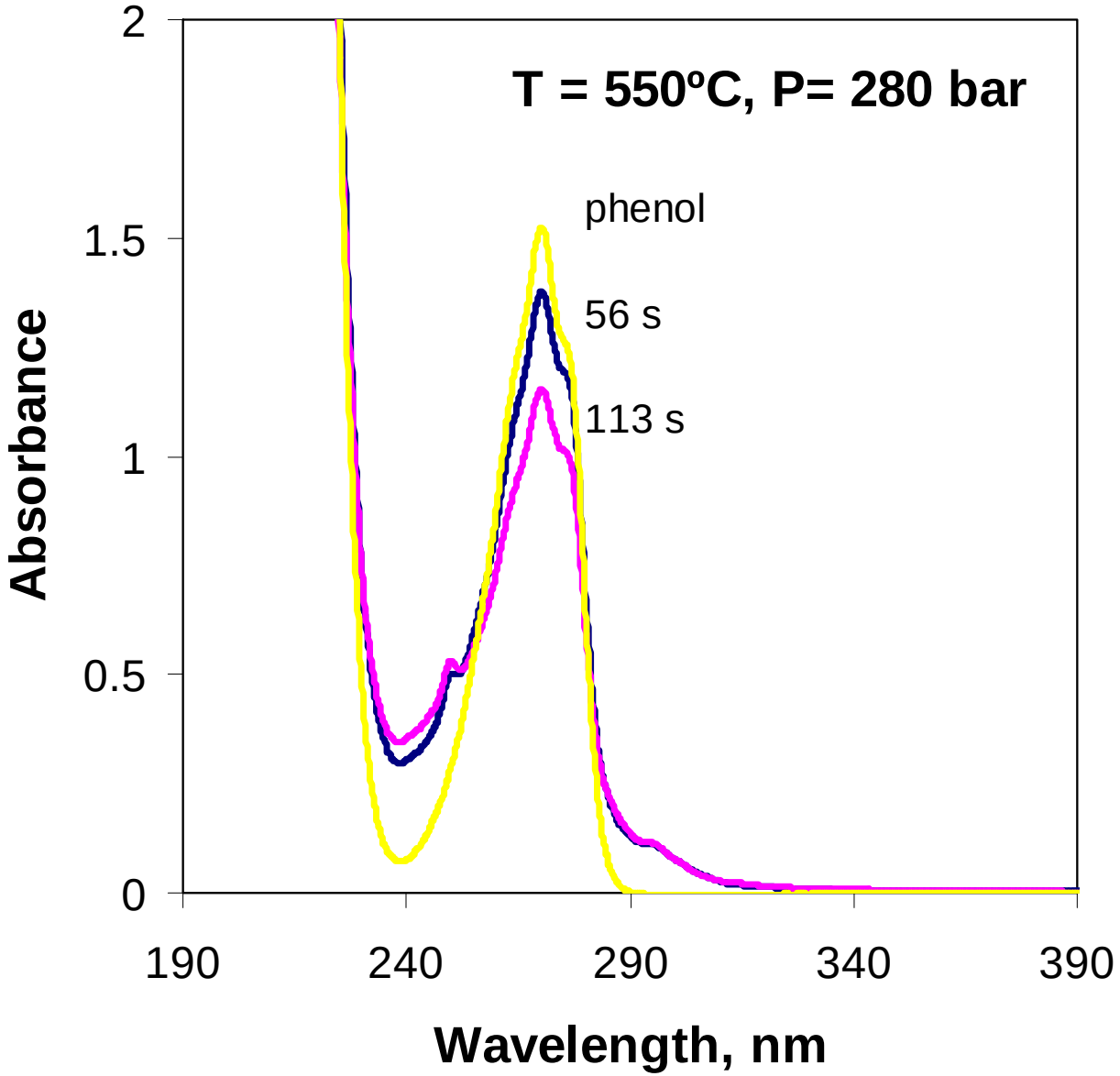
Reactor effluent samples for a given set of operating conditions were measured every 20 minutes until no change in the UV-Vis spectrum was apparent between the current and the previous sample. At this point steady state was assumed and samples collected for TOC and COD analyses

II) Total Organic Carbon (TOC) Analysis

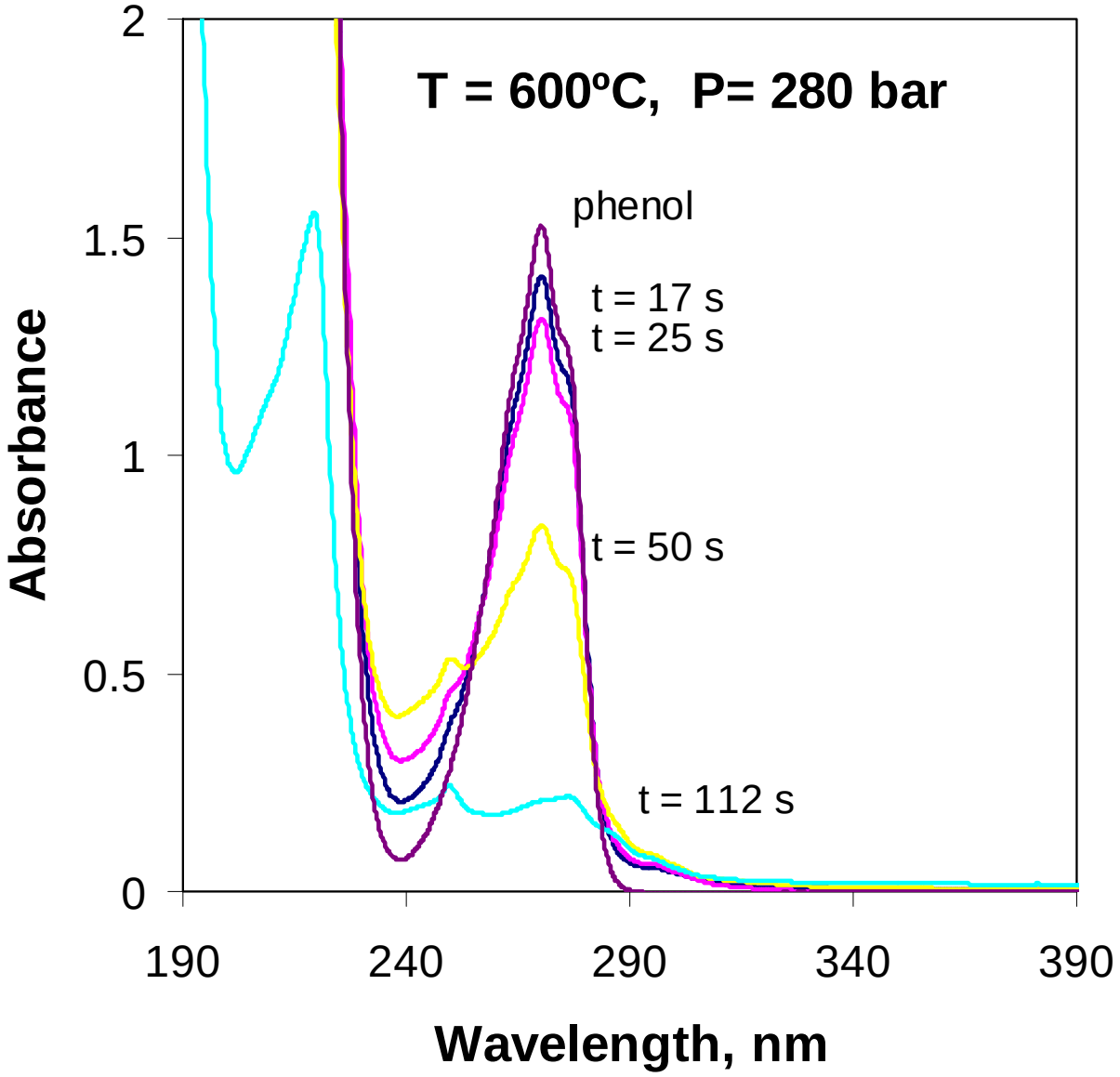
Shimadzu TOC Model 5000-A Analyzer was used

III) Chemical Oxygen Demand (COD) Analysis

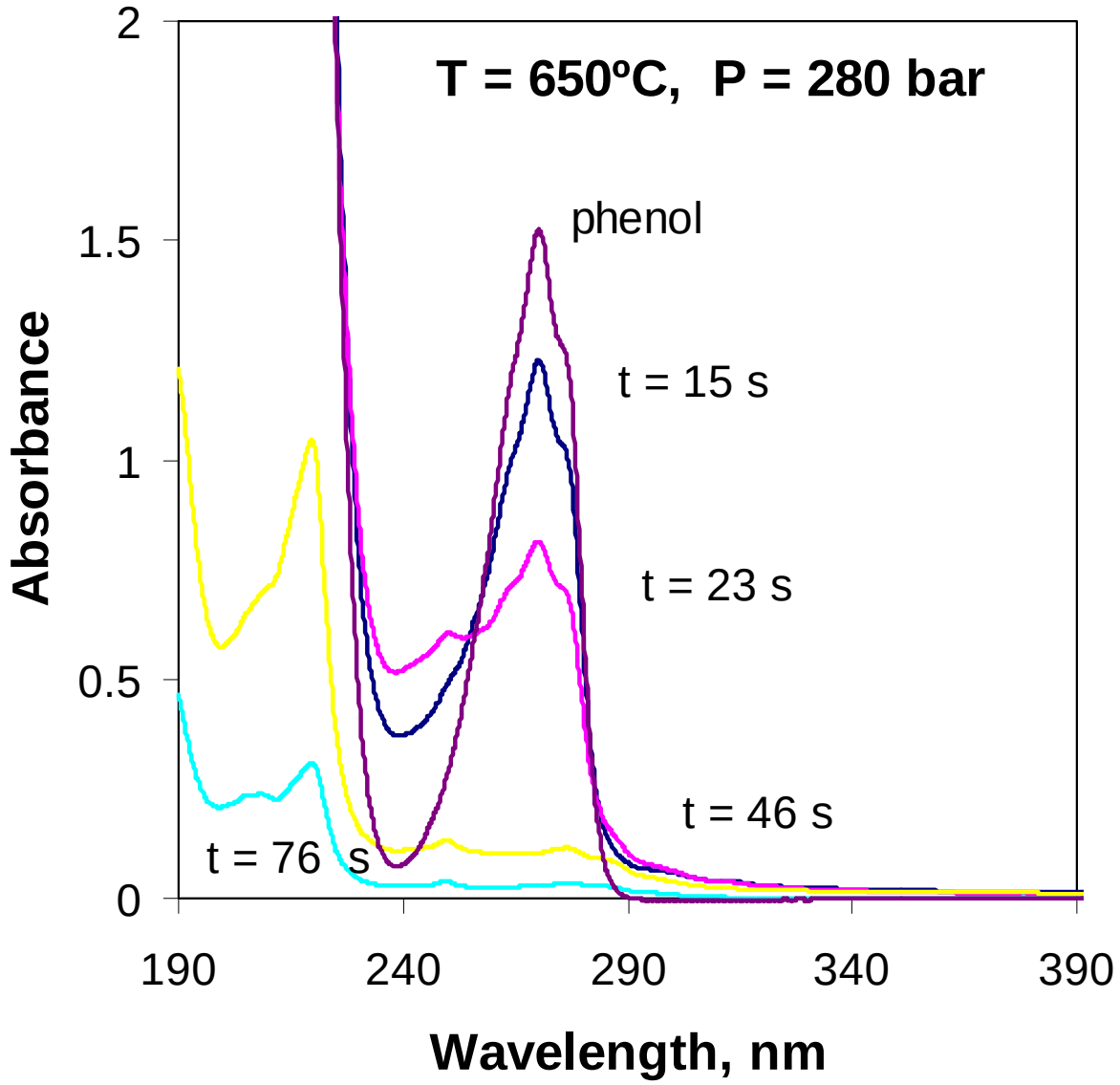
A standardized titration method was used (reference 9)
Titration of sample/potassium dichromate solution with ferrous ammonium sulfate solution to determine COD



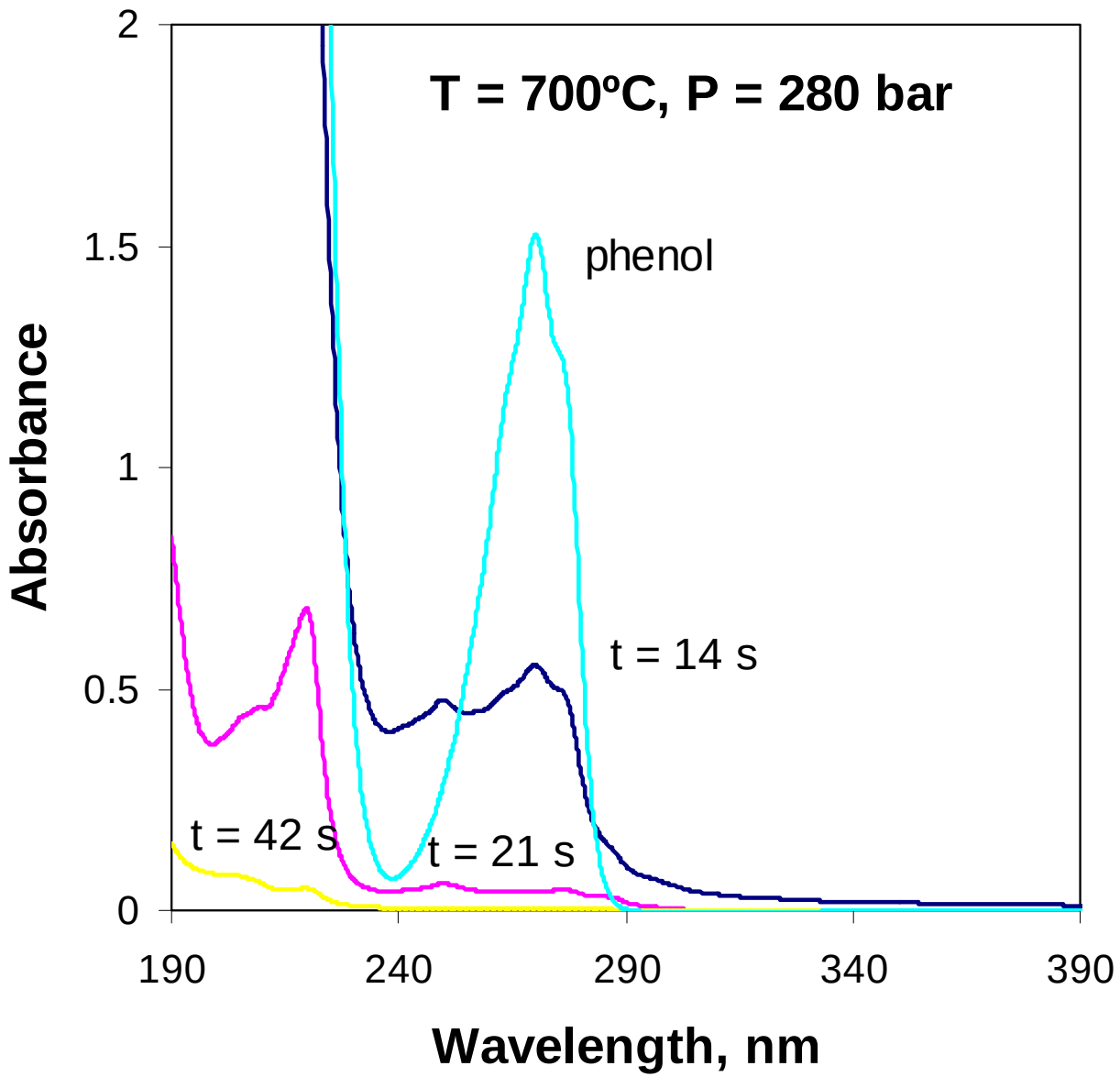
Results: Absorbance at Various Residence Times, 550°C



Results: Absorbance at Various Residence Times, 600°C



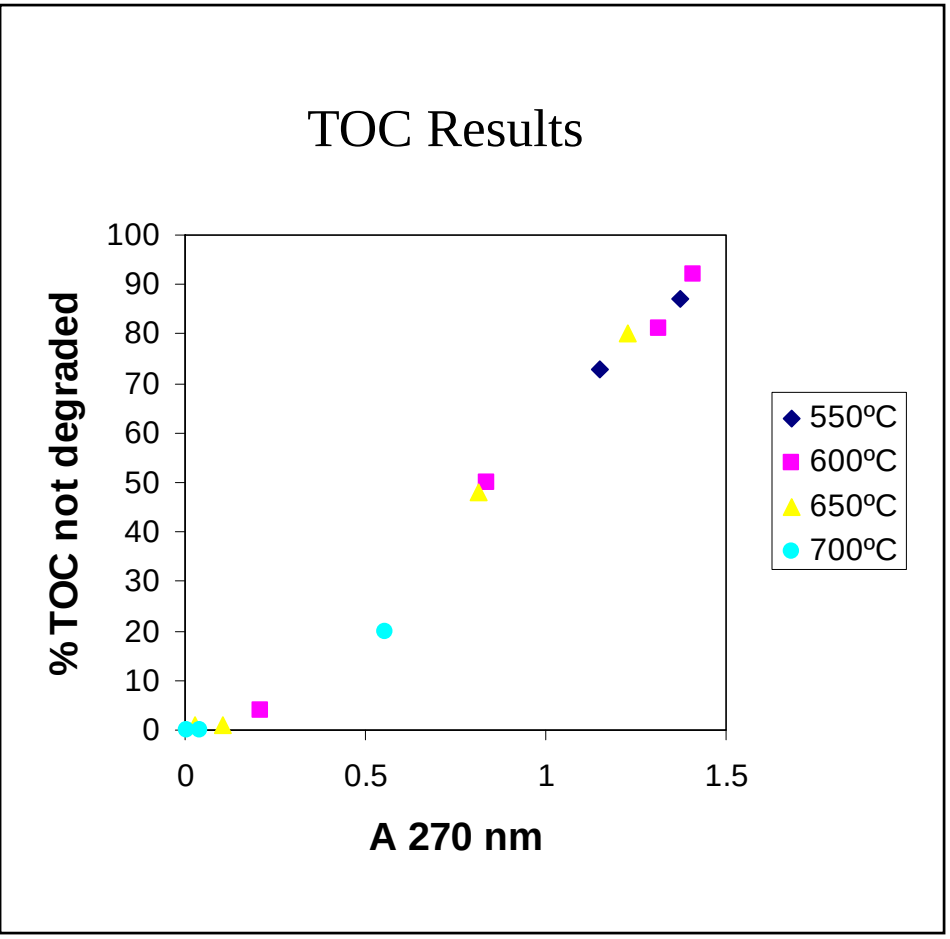
Results: Absorbance at Various Residence Times, 650°C

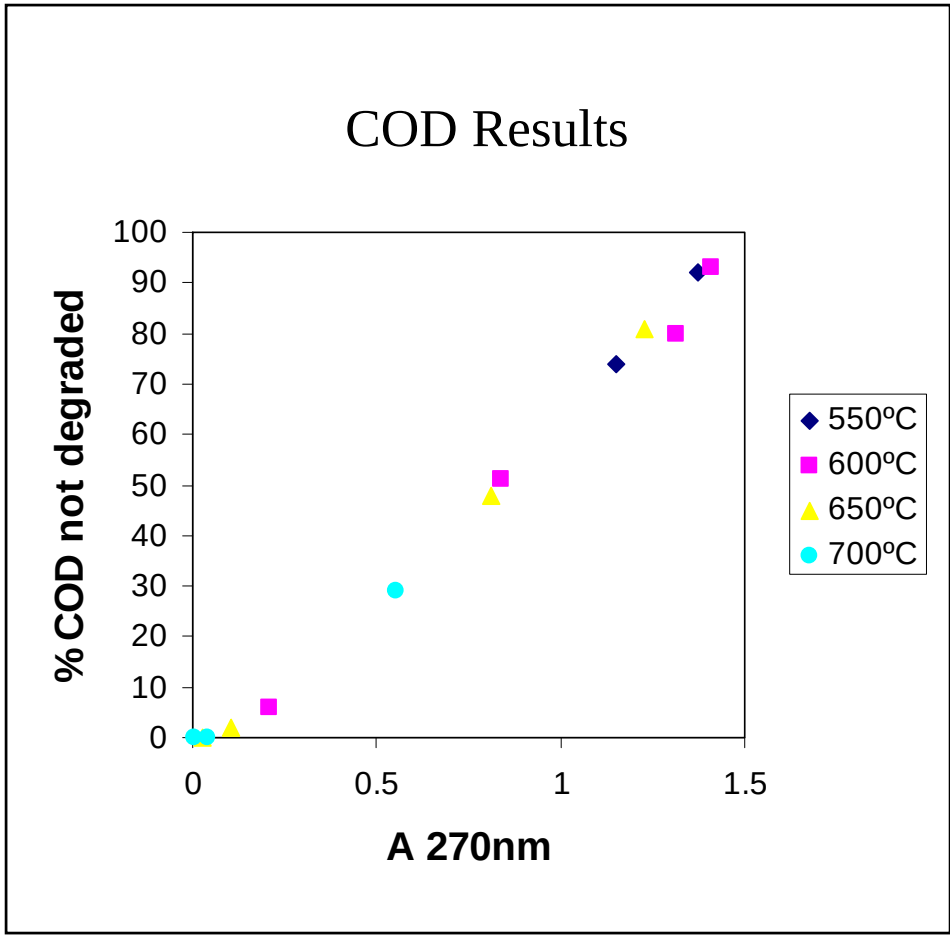


Results: Absorbance at Various Residence Times, 700ºC

Results

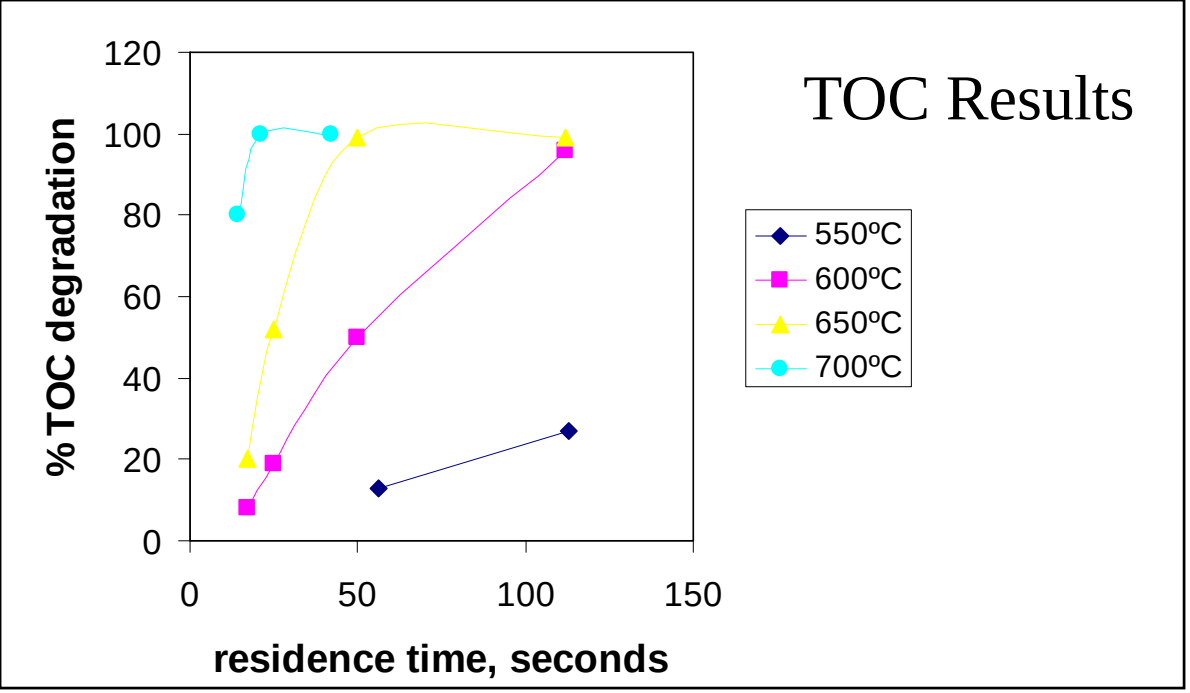
% Organics Not Degraded Vs. UV-Vis Absorption at 270 nm

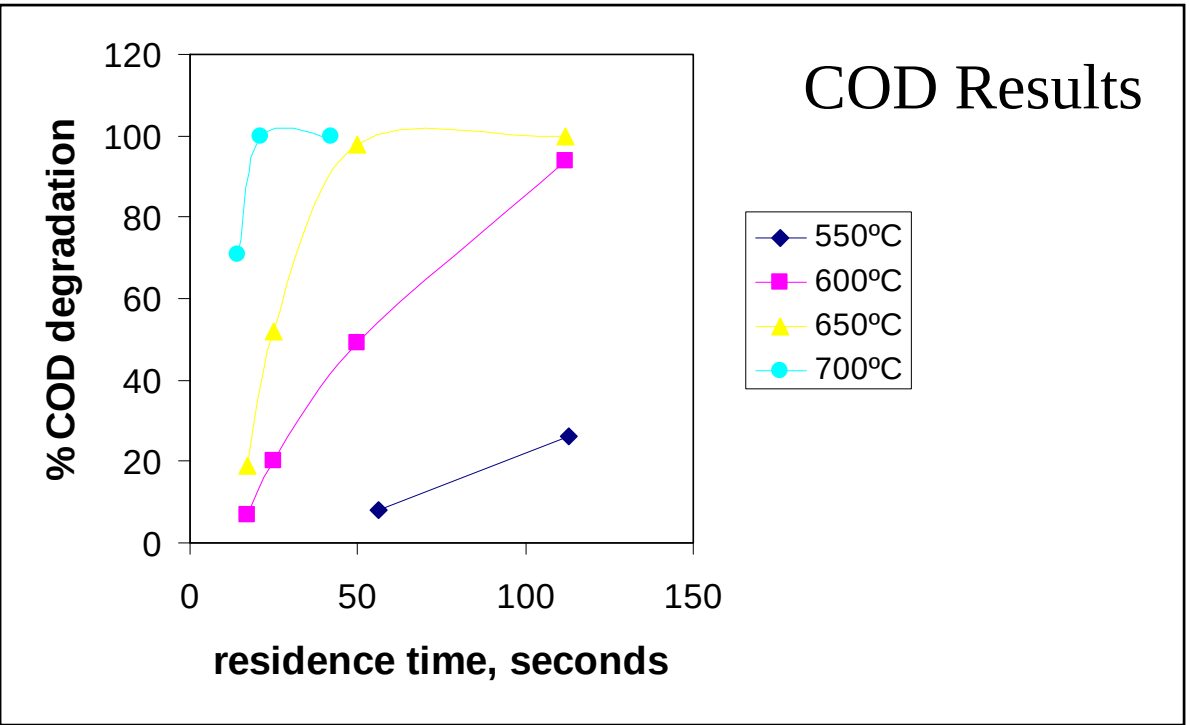




I) Similarity of the COD & TOC Results

II) 1:1 Depletion Ratio Suggests no Organic Products (independent of temperature, residence time, conversion)





Results

Percent Degradation Vs. Residence Time

I) Similarity Between TOC & COD Results

II) 100 % Degradation Achieved at 650ºC, 700ºC (No organic components present)

Conclusions

I) 100% phenol destruction is possible within conditions studied (280 bar, a temperature of no more than 700^{o}C and a residence time of no more than 114 seconds.)

II) Consistency in results based on independent TOC, COD and UV-Vis analyses

II) Results suggest the process produces no organic products (independent of level of degradation, operating conditions).

III) Temperature is more influential than residence time

IV) Further Study?

A) Effectiveness of procedure with other organic pollutants

B) Optimization of temperature and residence time

C) Dependence on pressure, initial phenol concentration

References

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