Condensation and Photolytic Degradation of BTEX from the Oil and Gas Industry

Progress Report, Year 1

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Summary

This report summarizes the activities carried out in the period August 2009-June 2010. Laboratory experiments on toluene and benzene photolysis in waste gas were carried out. The results indicate that up to 2 mg/min of toluene can be degraded with 80 % efficiency with a 40 W lamp. At 7 cents/kWh, this amounts to a $25,000 annual electricity cost to eliminate 1 ton BTEX/year. For benzene, the efficiency at a flow rate of 2 mg/min is about 60 %.

An incomplete but functional simulation model involving 33 reactions and 37 chemical species was developed for benzene photolysis. The results were very similar to the experimental results for toluene but overestimated the benzene efficiencies. When ozone was added as a reagent, the efficiency predicted by the model increased dramatically. If correct, this means that the energy cost of destroying 1 ton of benzene can be reduced to $8,000 per tonne. Given that the benzene degradation efficiency is somewhat less than predicted in the absence of ozone, the cost maybe somewhat above this estimate.

A simple condensation model for BTEX was developed. The model indicates that variability of the feed increases the average condensation efficiency, as hypothesised, but only strong variabilities lead to a pronounced effect.

In Year 2 we plan to continue the experimental work and the model development. The effect of pre-mixing ozone will be given special attention. Condensation modeling will be continued as well. The condensation work will be planned further in consultation with the project manager.

Introduction

The objective of this project is to investigate the effectiveness of condensation and the feasibility of ultraviolet degradation in the destruction of BTEX and other hydrocarbons, as well as H_2S, from waste gas originating from the oil and gas industry. To that effect, the following activities were proposed.

Year 1

In year 1 we proposed to build a laboratory set-up, and test it for the photochemical degradation of benzene, toluene, and xylene under a variety of conditions, and to identify reaction products.

We also proposed to develop simple condensation models, and to do field measurements of the emission of BTEX from glycol dehydration units and their short-term variability.

After one year an evaluation of the data was planned, in order to decide if the results warrant the further development of a photochemical system for the upstream oil and gas industry.

Year 2

In year 2 we proposed to conduct further experiments to improve the efficiency of the process, and to better understand and evaluate the process, like the photolysis of BTEX mixtures, and the pre-mixing of ozone. We also proposed to explore the use of a catalyst to improve the efficiency of the process.

We proposed to develop a reactor model to provide better understanding of the photolytic process.

We proposed to develop sophisticated condensation models, and to combine them with measured time-dependent emission data. The predictions of the models are to be compared with measured efficiencies (third-party data) of an existing condensation system.

Year 3

For year 3 a continuation of some of the activities (photocatalysis, modeling) was anticipated, as well as the study of the photochemical degradation of H_2S streams.

Based on the model, a full scale design of a photochemical system will be made.

The project concludes with reporting, as well as the publication of papers in the open scientific literature.

Accomplishments as of June 2010

Experimental set-up

Preliminary toluene photodegradation experiments were conducted with a borrowed photochemical reactor in batch mode. The reactor was sealed, toluene was added through a septum, and the UV lamp (15 W) was turned on for a set duration. After turning off the lamp, gas samples from the reactor were analyzed by gas chromatography (GC).

The main experiments were conducted with a continuous flow set up. This set up is centered around a UV Sciences (San Diego, CA) photoreactor using a 40 W amalgam UV lamp reactor. The reactor is cylindrical, with the lamp in the axis. The length of the reactor is 56 cm, and the gap between the lamp and the reactor wall is 8.5 mm. The reactor is shown in Figure 1. The reactor has a sensor measuring the UV light intensity at the reactor wall.

Figure 1. Photoreactor

Two air flow streams were generated in parallel using air pumps, and contaminants (toluene as a representative BTEX), as well as water vapour were added by bubbling the parallel air streams through washing bottles containing the contaminant and water. The air flows were controlled with needle valves and measured with rotameters. The air stream containing water and the one containing toluene vapour were then combined in different ratios, creating varying conditions at the reactor inlet. Inlet and outlet toluene concentrations were measured with a gas chromatograph.

Experimental results

A set of preliminary batch experiments was completed in 2009 as proof of concept tests. In these experiments, small concentrations of contaminants were injected in a reactor that utilizes a 15 W ultraviolent (UV) lamp. Toluene was used as a representative volatile organic compound (VOC) due to lower toxicity compared to Benzene. The concentration of toluene was varied between 0.2 and 1.0 g/m^3. After 10 minutes of radiation, 30-65% of the original toluene was degraded.

For the next phase of the project, a continuous flow experiment was designed. This set up utilizes a 40 W Amalgam UV lamp reactor. Contaminants were added to an air stream saturated with water vapour. A larger range of contaminant concentration was tested with the flow-through system. Initial toluene concentrations of 0.3 to 6.1 g/m^3 correspond to 100% to 16% degradation. Figure 2 shows the observed degradation and the steady-state UV intensity values as a function of the mass flow rate of Toluene, at a residence time of 20-60 seconds (flow rate 0.5-1.5 L/min). Degradation efficiencies in excess of 80 % are possible for toluene mass flow rates up to 2 mg/min. This corresponds with an annual degradation of 0.84 kg of toluene with 40 W energy input.

During the experiments the light intensity at the reactor wall was examined. The results are shown in Figure 3. The observed light intensity decreases with increasing flow rate due to the absorption of ultraviolet light by the organic molecules.

Benzene degradation experiments were conducted at a flow rate of 1 L/min. the results are shown in Figure 4. The degradation efficiency is somewhat lower than with toluene: at a mass flow rate of 2 mg/min the degradation efficiency is about 60 %. Light intensities were monitored as well. Those are shown in Figure 5.

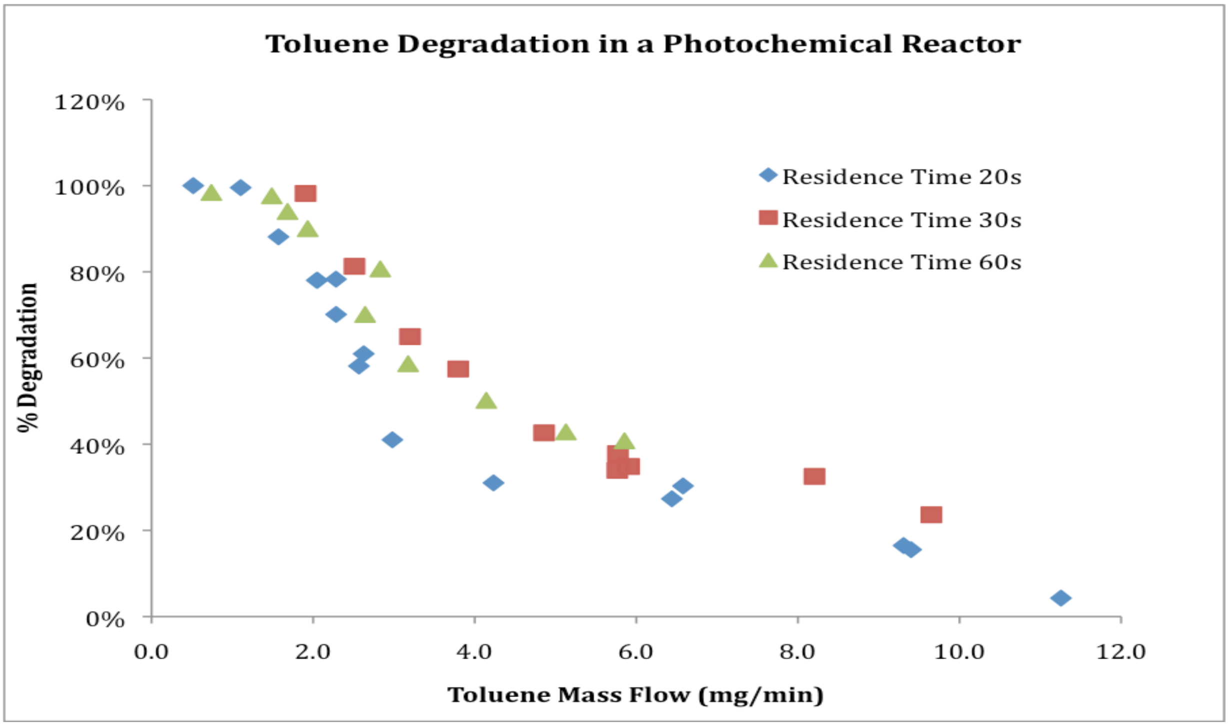

Figure 2. Toluene degradation in a photochemical flow-through reactor containing a 40 W amalgam lamp. Flow rate: 0.5 L/min (residence time 60 s) to 1.5 L/min (residence time 20 s).

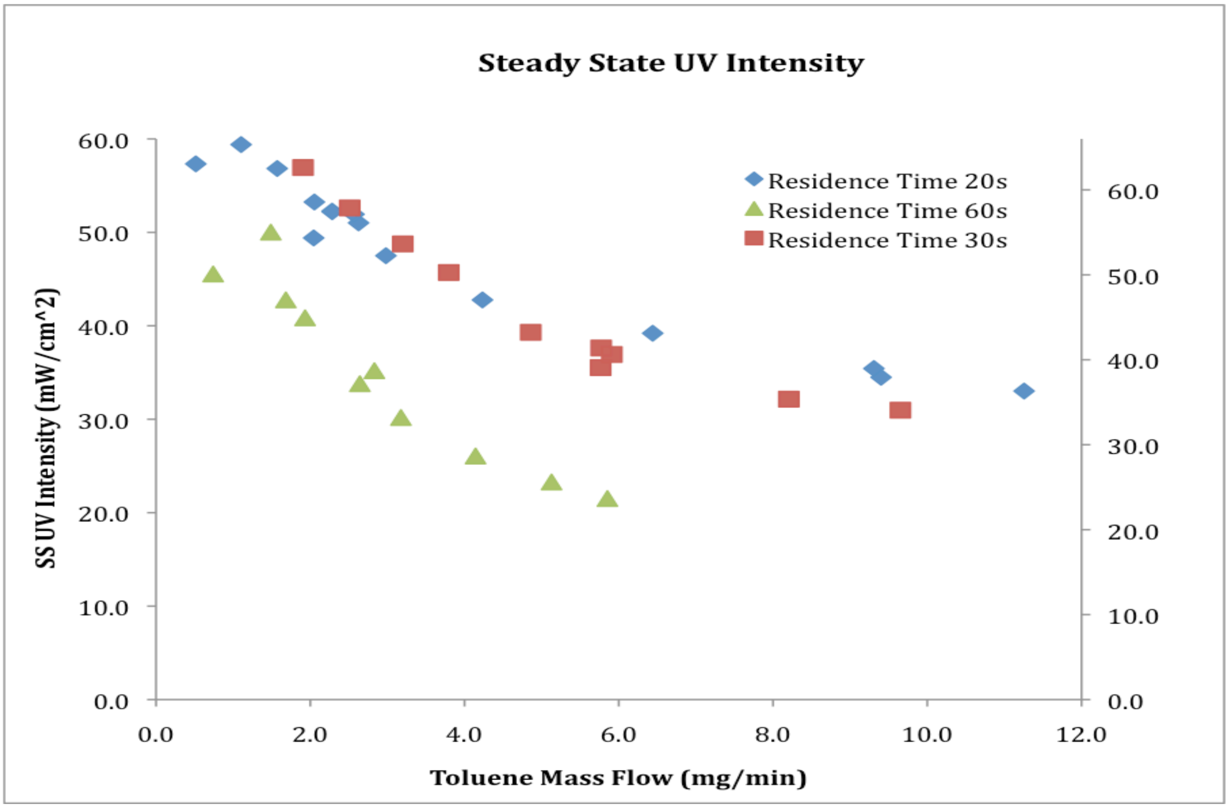

Figure 3. Light intensity at the reactor wall during toluene degradation experiments

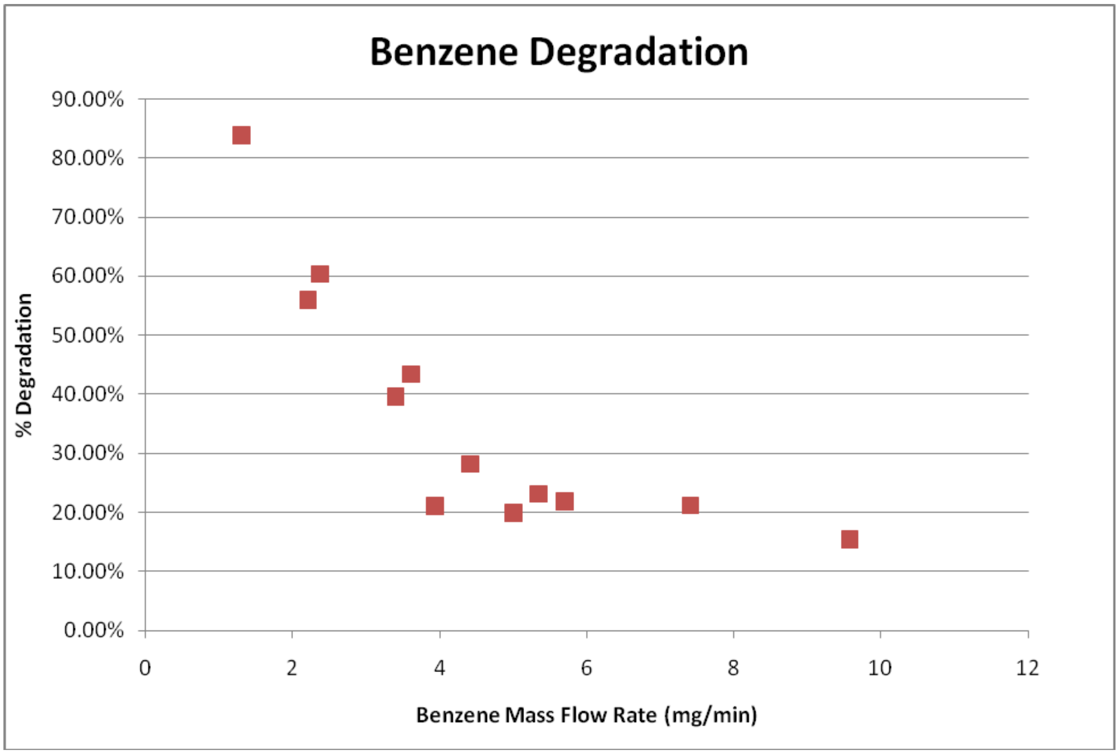

Figure 4. Benzene degradation in a photochemical flow-through reactor containing a 40 W amalgam lamp. Flow rate: 1 L/min

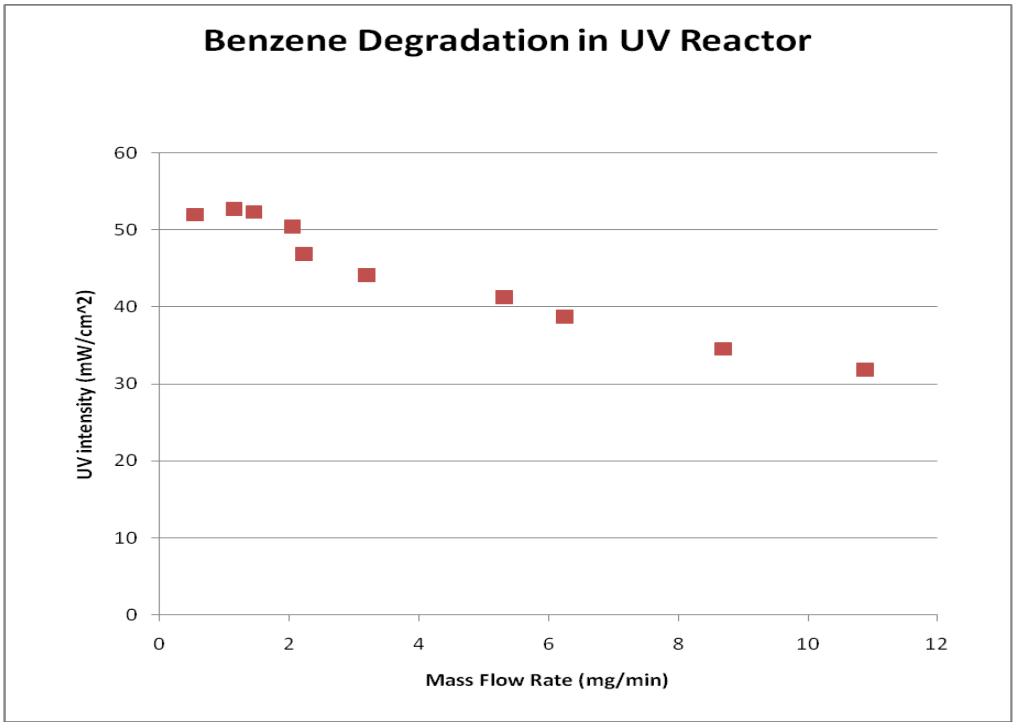

Figure 5. Light intensity at the reactor wall during benzene degradation experiments

Photochemical reactor modeling

A mathematical model for the simulation of the photochemical reactor degrading benzene was developed. The model is still in the development stage, but with 33 reactions involving 37 species, the main degradation pathways are covered (see Appendix). The model assumes a laminar flow velocity profile, which was solved analytically for an annular space. Radial diffusion of all species is included. Pending a better formulation with a different diffusion coefficient for each species, a constant diffusion coefficient of 10^{-5} m^2/s is used. We are still working with a simplified radiation model by assuming that all light is emitted perpendicularly to the lamp. This assumption probably underestimates light intensity towards the reactor entrance, and overestimates light intensity towards the reactor exit, but it is assumed that the model is sufficiently accurate for feasibility studies.

Some results are shown in Figure 6. The conditions are the same as in Figure 1. In spite of the fact that the measured efficiency was not used in any model fitting procedure, the model results compare well with the experimental data, confirming that the model is sufficiently accurate for feasibility studies. At 2 mg/min benzene flow rate, a degradation efficiency of almost 80 % is predicted, which is above the efficiency of the actual reactor with benzene.

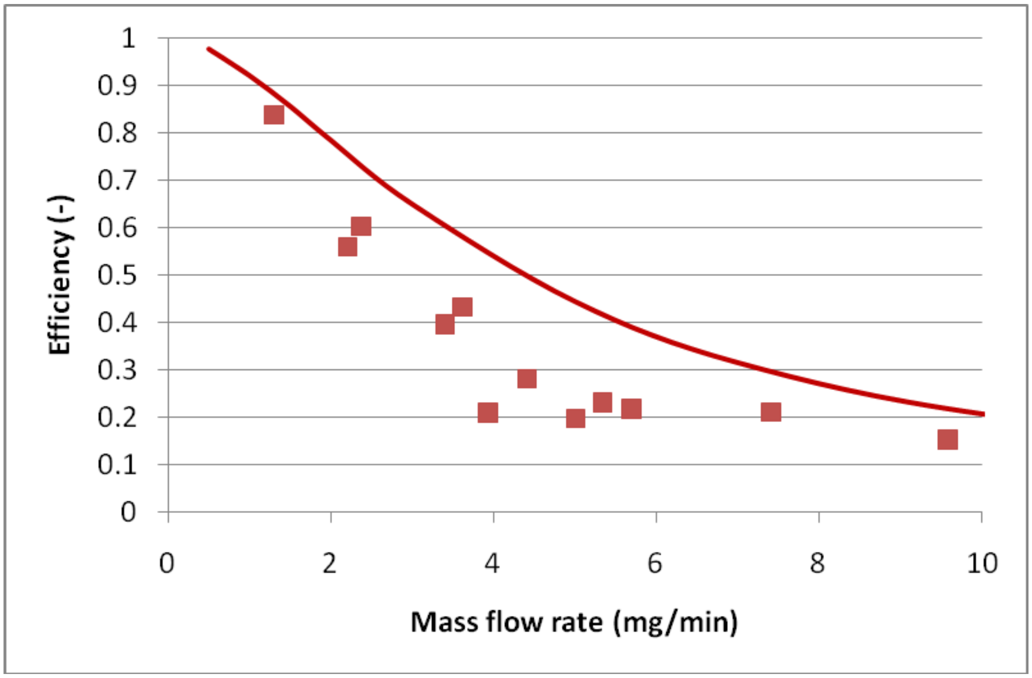

Figure 6. Predicted and measured degradation efficiency versus benzene mass flow rate (40 W amalgam lamp, volumetric flow rate 1 L/min)

Simulations for benzene photolysis with added ozone were conducted as well. The result is shown in Figure 7. The reactor performance roughly triples upon adding 7.5 mg/min of ozone:

up to 6 mg/min of benzene can be treated with 80 % efficiency. This clearly indicates that pre-mixing ozone is a promising improvement of the photochemical process, and we plan to investigate it in more detail during the coming year. Further increases in the added ozone flow rate lead to further increases of the degradation efficiency, but with diminishing returns. The model predicts 80 % efficiency for flow rates up to 12 mg/min when 22.5 mg/min of ozone is added.

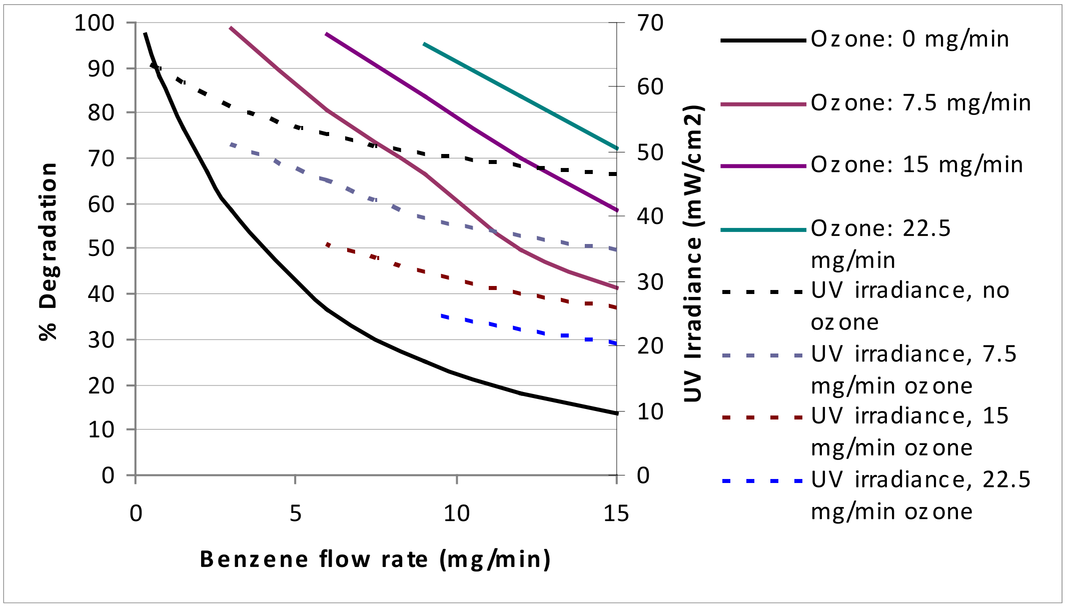

Figure 7. Predicted degradation efficiency and UV irradiance versus benzene mass flow rate, in the absence and presence of ozone (40 W amalgam lamp, volumetric flow rate 1.5 L/min)

Condensation modeling

A simple model for condensation from a vapour mixture containing benzene, toluene, m-xylene (as a representative xylene), water and non-condensables was developed. Some simplifying assumptions were made. Liquid water was assumed to be pure, water in the organic condensed phase was neglected, the organic liquid was assumed to be an ideal solution, vapor-liquid equilibrium was assumed to be reached, and non-steady state conditions was represented by a sequence of steady states.

Figure 4 shows the predicted influence of temperature on the benzene condensation for a vapor flow containing 1 mol/hr benzene, 1 mol/hr toluene, 1 mol/hr xylene, 10 mol/hr water, and 5 mol/hr non-condensables. Temperature is predicted to have a pronounced impact on condensation efficiencies. Considering that temperatures down to 30 °C are realistic most of the time, an efficiency of 70 % is to be expected for the flow considered here.

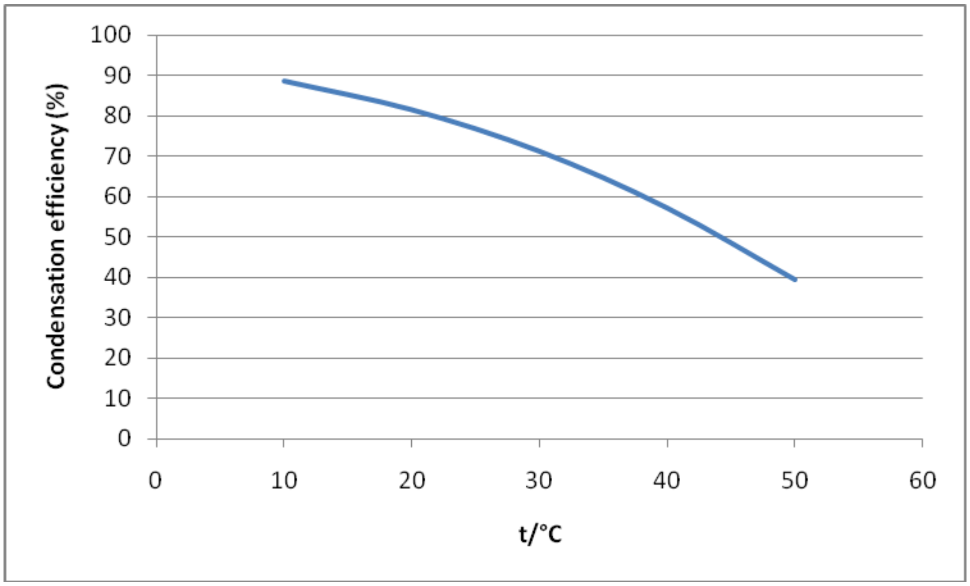

Figure 8. Condensation efficiency versus equilibrium temperature of the following vapour flow: 1 mol/hr benzene, 1 mol/hr toluene, 1 mol/hr xylene, 10 mol/hr water, and 5 mol/hr non-condensables

Next, the impact of non-steady vapour flow was considered. The average conditions are the same as for the steady state example, and a temperature of 40 °C was chosen. The steady state efficiency under those conditions is 57 %. The result is shown in Figure 5. It is found that input variability increases overall condensation efficiency, as hypothesised, but strong flow rate fluctuations are needed to obtain a pronounced effect.

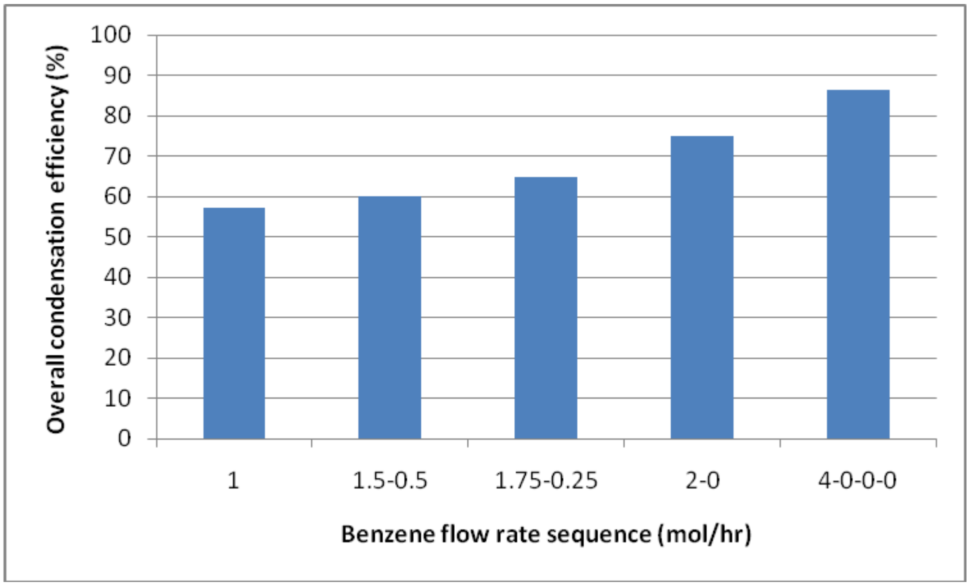

Figure 9. Impact of benzene flow rate sequence on overall benzene condensation efficiency

Discussion and Significance of the Results

Based on the results obtained to date, it is possible to make a tentative estimate of the energy cost of a photochemical benzene removal process. Energy is usually the dominant cost factor in ultraviolet technology, so this is a useful indicator of feasibility of a process. Based on the experimental results obtained to date it is anticipated that a photolytic process with 40 W energy consumption will be able to degrade at least 1 kg of BTEX per year after optimization. This corresponds to about 350 kWh/kg, or 350 MWh per metric tonne. At an electricity cost of 7 cents per kWh, this would amount to roughly $25/kg, or $25,000/year for a process treating a BTEX emission of 1 ton/year.

Adding ozone greatly improves the economy of the process. When the ozone is produced by a plasma ozone generator, the electricity consumption of ozone generation is about 10 kWh/lb ozone. It follows that 22.5 mg/min of ozone can be generated by a 30 W ozone generator. Hence, a combination of a 40 W photolytical reactor and a 30 W ozone generator would destroy over 5 kg of BTEX per year, which brings down the energy cost to 115 kWh/kg, or $8/kg, about a third of the process without the ozone.

The numbers above are still uncertain for a number of reasons. First, more experimental data, with other BTEX are needed to validate the model, and to find optimal conditions for the process. Further, the model needs to be extended with more reactions, a better light field model, and reactions for toluene and the xylenes. Further, photolysis with added ozone needs to be tested experimentally before the model results can be trusted.

The condensation model results provide a baseline for further results. Comparisons with measured condensation efficiencies have not been made yet, but will be made.

Comparison between Planned and Achieved Progress

Based on the plans set out early 2009, Year 1 was to coincide with 2009. Based on those plans, the experimental work is behind schedule, whereas the UV modeling work is ahead of schedule, and the condensation modeling is on schedule. In the 2009 AUPRF application the schedule was revised, accounting for experimental delay and the accelerated modeling work, and postponing BTEX emission field work. Compared with the 2009 AUPRF application the current progress is on schedule.

The experimental work did not proceed as quickly as planned, partly because the photochemical reactor takes much longer to reach steady state conditions than expected. It is assumed that this is due to condensation of reaction products on the lamp, which vaporize as the lamp warms up. As a result, experiments have been limited to toluene and benzene so far, and reaction products have not been analyzed yet.

The modeling work, on the other hand, is ahead of schedule, as modeling work had not been planned for Year 1. So far the modeling results seem much more consistent with experimental data than expected for an incomplete model, and we anticipate that the modeling efforts will reduce the need for experimental data. For instance, without the model, we would not yet have anticipated the strong positive effect of pre-mixing ozone.

As advised by the Project Manager Rosanna Ng, the BTEX field emission measurement work was postponed to Year 2. However, the condensation modeling work was carried out as planned.

Future research Planning

For Year 2 we plan to continue with benzene, toluene, and xylene photolysis experiments, including the determination of the main reaction products and the photolysis of mixtures.

We will also study BTEX photolysis in the presence of added ozone. We are currently investigating the options for the ozone generation system.

The photolysis model will be improved with more reactions, an improved light field model, and by including toluene and xylene.

We will include photocatalysis in the photolysis model. If the model predicts a beneficial effect of photocatalysis, we will test such a set-up experimentally.

We will improve the condensation model by accounting for the non-ideality of the liquid-phase and by modeling the dynamic aspects of the process more explictly.

With respect to field work we will discuss with the Project Manager, as well as others, to determine the best course of action.