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Communication

Subject: REACTOR OPENING LOSS EMISSIONS CORRELATIONS

VISTA

INTRODUCTION

Current EPA regulations require that PVC Reactor Opening Loss (ROL) emissions be limited to 20 ppm expressed as pounds VCM per million pounds PVC produced (dry weight basis). The regulations specify certain procedures for measuring ROL emissions which are not suitable for the Vista Polymers Inc. ("Vista") in-reactor steam stripping process. Both the Aberdeen, Mississippi and Oklahoma City, Oklahoma Vista plants have operated in the past and continue to operate under equivalencies for measuring ROL emissions. The equivalencies are based on following operating procedures designed to comply with the 20 ppm emissions limit specified in the regulations.

SUMMARY

A research program to study reactor opening loss emissions has recently been completed by Vista. The program was designed to study our current compliance procedures and to develop improved correlations that could be used to quantify emissions. Special sampling and analysis procedures were developed to insure that the reactor opening loss measurements were correct. This proved to be extremely difficult. Many sampling attempts were unsuccessful.

Boiling time during steam stripping was identified as the critical variable controlling ROL emissions. The boiling time is the time period near the end of the steam stripping process when essentially all the VCM has been removed from the reactor and the water in the slurry is boiling vigorously.

Two correlations were developed - one for the two large expansion reactor at Aberdeen, and one for the fourteen standard size reactors at both Aberdeen and Oklahoma City. Both correlations are of the form:

ROL = a exp (-b t)

where: ROL = Reactor Opening Loss, pounds VCM per million pounds PVC produced (Dry weight basis)

t = slurry boiling time, minutes

a and b = Least squares curvefit coefficients of experimental data

The a and b coefficients were generated by linear least squares analysis of forty samples from six reactors in Oklahoma City and forty-one samples from seven reactors in Aberdeen. The exponential curvefit equation gave the best fit of the data of four equation forms studied. The coefficients for the correlations are given in Table I.

Figure 1 shows the ROL and boiling time data and exponential curvefit correlations in graphical form. The graphs in Figure 1 indicate that the correlations are reasonable and yield good fits of the data. The data scatter at very short boiling times emphasizes the difficulty of obtaining good representative samples when concentrations are changing quickly. The data collected is considered to be the best possible representation of reactor opening loss emissions.

The correlations were tested for validity in several ways. Vista utilizes reflux condensers on the reactors to control the polymerization process. The condenser vapor space concentration differs from the reactor vapor space concentration because of the refluxed steam flow. A condenser vapor space sample and a reactor vapor space sample were collected concurrently, emissions from the condenser and the reactor were calculated separately, and the emissions were added to obtain the total ROL emission. The correlations presented in this study are based on the total ROL emission. Correlations were also generated for the condenser vapor space ROL and for the reactor vapor space ROL separately. The exponential time decay b coefficients for the condenser ROL correlation and for the reactor only ROL correlation were essentially the same as the b coefficient obtained when correlating the total ROL emissions. The sum of the a coefficients for the separate condenser and reactor only correlations was similar to the a coefficient for the total ROL emission correlation. When the ROL data for individual reactors was analyzed and correlated with boiling time, the exponential curvefit a and b coefficients obtained were very similar to the composite correlation coefficients. These several separate correlations strongly support the accuracy of the data and the adequacy of the test methods involved.

In conclusion, the research work yields an improved method of quantifying reactor opening loss emissions by correlating the emissions to slurry boiling time. Boiling time, unlike the actual VCM concentration in the reactor vapor space, can be easily monitored. This, the plant operators can use boiling time to insure compliance. These correlations provide an improved equivalency method for determing reactor opening loss emissions for in-reactor stripping operations.

DISCUSSION

The research program consisted of several test runs conducted at both the Oklahoma City plant and the Aberdeen plant. The test runs involved collecting samples of the hot vapors in the reactor and condenser at the end of the steam stripping process before opening the reactor to the atmosphere to transfer the slurry to blend tanks. Previous test runs at Aberdeen, with limited sampling, had indicated that condensable vapor samples from reactors could be collected in heated sample bombs. Additional testing in a controlled environment at research facilities in Ponca City, Oklahoma concluded that determinations of VCM in a low pressure steam atmosphere by gas chromatograph analyses of samples taken in heated gas bombs were accurate. The testing was conducted in a 585 gallon Pfaudler reactor. Known quantities of VCM and water were injected into the reactor. The reactor was then heated to various temperatures and samples were taken using the heated bomb method. A total of 35 hot bomb samples were taken at 12 known VCM concentrations. The concentration of the VCM in the 35 samples as determined by the hot bomb sampling method averaged 115% of the actual concentration in the reactor with a standard deviation of 16 percent. The hot reactor was then cooled and opened to the atmosphere and resampled using EPA Method 106. The VCM concentration as determined by EPA Method 106 averaged 93% of the actual concentration in the reactor with a standard deviation of 12%. Therefore the hot bomb sampling of the hot reactor slightly overstated the reactor VCM concentration in comparison to EPA Method 106, and the analysis variation was comparable. The cooled reactor was also sampled with the hot bomb system at the same time as the EPA Method 106 samples were taken to give a direct comparison between the two methods when sampling similar conditions. The VCM concentration of these bomb samples averaged 89% of the actual concentration in the reactor with a standard deviation of 13 percent. That compares closely to the EPA Method 106 results. The conclusion of this research work was that the heated bomb sampling method is essentially equivalent to EPA Method 106 in both accuracy and precision.

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It has long been recognized that collecting condensable vapor samples for composition analysis is an extremely difficult research task. A large part of the problem is caused by the fact that the vapor being sampled is steam containing very little VCM. Many precautions were taken during the test runs to insure the validity of the samples and the accuracy of the analyses. Special sampling systems were built and special procedures were defined and followed during the test runs. Technical people from the Research and Development Department, the corporate Process Engineering Department, and from the plants collected the samples and data from the reactors, analyzed the samples in the lab, and evaluated the results.

Despite elaborate precautions, a substantial percentage of the attempts to collect samples were unsuccessful. Many times the samples were missed because of polymer plugged or restricted sample nozzles. Occasionally, because of the limited time available near the end of steam stripping, there wasn't enough time to install the sample nozzle insert tubes. Almost invariably a bad sample would cause a high analysis for ROL emissions. This was due to sample condensation caused by steam tracing difficulties, or by VCM evolution from resin entrained into the sample line or from PVC fouling in the sample nozzle. The partial condensation of the steam in the sample artificially inflated the concentration of VCM in the sample. Occasionally, a leaking sample line connection allowed air to enter the sample system while the sample was being collected thus diluting the sample and causing the analysis to come out low. It is clearly not possible to collect representative hot vapor samples for ROL analysis from every batch in a PVC plant. Too many conditions and factors beyond reasonable control can occur that prevent obtaining a sample or that cause a non-representative sample to be caught.

The current in-reactor steam stripping procedures at Aberdeen and Oklahoma City are generally very similar, though some minor differences exist. The steam stripping process consists of a slurry heating period, a hold period, and a cool down period. The heating period involves adding steam directly to the reactor slurry while removing VCM vapors to a recovery system. The process is characterized by a constantly increasing slurry temperature and an essentially constant low vapor space temperature. When most of the VCM is vaporized and recovered, the reactor pressure begins to drop to the vapor pressure of water, and the water in the slurry begins to boil. The vapor space temperature rapidly rises and approaches the slurry temperature. The boiling is maintained for a specified time period. Then cooling water flow to the condenser is started, steam flow to the reactor is stopped, and the slurry is cooled. Then the stripping process is stopped and the slurry is transferred to a slurry blend tank.

Various steam stripping procedures were followed during the test runs to evaluate the effects on ROL of different control parameters. The procedures were selected to evaluate the range of conditions that could reasonably be expected to be experienced in the operation of the plants. Some of the variables investigated included the maximum slurry temperature reached, the time when cooling water flow was started, the time when steam flow was stopped, the final temperature before dump, and a wide range of boiling times. The boiling time is defined as the elapsed time from when the vapor space temperature suddenly increases and approaches the slurry temperature until the time steam stripping is complete. Boiling time was measured from the point where the vapor space temperature reached 160°F to the point where the vapor samples were collected in preheated sample bombs. In special cases where short boiling times were being investigated and high ROL emissions were anticipated, the steam stripping process was restarted after collecting the ROL samples and continued until normal stripping parameters were obtained. The reactor was not opened until after the steam stripping process was completed.

Special ROL sampling procedures and sampling systems were developed and used during the test runs. The sampling system was a specially designed steam traced and insulated hot box containing piping, valves, temperature instruments, and vacuum gauges to allow two samples to be collected in sample bombs simultaneously. The sample bombs were installed vertically in the hot box with sample flow downward to reduce the chances of condensate collecting in the bomb. The top of one sample bomb was connected through a steam traced and insulated sample line to a reactor condenser nozzle. The second bomb was connected through a separate steam traced and insulated sample line to a reactor vapor space nozzle. Special insert tubes were installed in the reactor nozzles just before collecting each sample to reduce interferences caused by resin buildup in the nozzle. Air powered eductors were connected to the sample bomb outlets. The educators were capable of pulling 20 to 22 in. Hg. vacuum using plant process air. The sampling procedure involved establishing flow from the reactor and condenser through the sample bombs to the eductors. The eductor suction valve was then blocked in, temperatures and pressures for the reactor, condenser, and sample bomb were read and recorded, then the bombs blocked in, removed from the hot box, and transported to the lab. The bombs were allowed to cool in the lab to condense the water vapor in the sample. Then the bombs were pressurized with nitrogen to a specified pressure to allow a sample to be analyzed for VCM concentration with a gas chromatograph.

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ROL emissions were calculated based on analyzed sample bomb VCM concentrations, measured reactor vapor space volume, and reactor batch size. The sample bomb concentration was used to calculate the quantity of VCM in the sample bomb. The quantity of VCM in the reactor was then calculated by adjusting the sample bomb quantity for temperature, pressure, and reactor vapor space volume. The vapor space volume was measured by cooling a reactor to ambient temperature after steam stripping, opening the reactor and measuring the slurry level, then adjusting for slurry density at the higher temperature. The accuracy of the vapor volume determinations was checked by adding the volumes of all the materials charged to the reactor and adjusting for the volume change caused by converting VCM to PVC and by removing the unreacted VCM during the steam stripping process.

The Oklahoma City reactor batch size (weight of PVC produced per batch) was determined by dividing the test run period production by the comparable number of batches produced. The Oklahoma City plant produces only one grade of resin. The Aberdeen reactor batch sizes were determined from the reactor VCM charge quantity and the historical conversion factor to PVC for each grade of resin produced.

Many of the parameters measured during the ROL test runs were evaluated to determine their effects of ROL emissions. Boiling time was identified as the most significant variable affecting ROL emissions. The ROL data was evaluated versus boiling time with a linear least squares analysis using four curvefit models: linear, exponential, logarithmic, and power. As discussed in the summary, the exponential model fit the data best.

CONCLUSIONS

The conclusions from this extensive study of reactor opening loss emissions are as follows:

1. Correlations have been developed that relate Reactor Opening Loss to the slurry boiling time during the steam stripping process. The correlations are based on extensive data from both plants and each reactor size. These correlations provide an improved equivalency method for determining reactor opening loss emissions for in-reactor stripping operations.

2. The Aberdeen Expansion reactors must be correlated separately from the other Aberdeen and Oklahoma City reactors because the vapor space volumes and the batch sizes are much larger than the other reactors.

3. The ROL data obtained during the test runs was accurate and represented the actual Reactor Opening Loss emissions. Several separate correlations confirmed the consistency of the data. Previous testing in a controlled environment had concluded that hot bomb sampling and GC analysis yielded results that were comparable with EPA Test Method 106 in both precision and accuracy.

4. Sampling low pressure condensable vapor atmospheres for composition analysis is extremely difficult and is not practical to do on every batch produced in a PVC plant. Too many conditions and factors beyond reasonable control can occur that prevent obtaining a sample or that cause a non-representative sample to be caught.

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Attachments