

15-ARPC-01

Development of a model to predict benzene emissions from glycol dehydrators with condensation tanks

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Executive Summary

The oil and gas industry uses glycol dehydrators at many facilities to remove moisture from natural gas streams. The glycol used in these processes also absorbs other components from the gas stream and some of these components are released to the atmosphere during the glycol regeneration process. Benzene, a known carcinogen, is one of these components and there are regulations in place that limit the allowable benzene emissions from glycol dehydrators. One method for reducing benzene emissions from the glycol regeneration vapour stream is to pass the vapour through a condenser tank or some other form of condenser equipment such as a chiller. These condenser devices are allowed by regulations as a control method to reduce benzene emissions as long as the condensing efficiency is measured directly in the field. This efficiency measurement is a costly and dangerous activity as it involves work at height and increased chance of exposure to benzene. There is a need for a simulation method to allow the upstream oil and gas industry and regulators to establish the benzene removal efficiency for these condenser devices without the need for field measurement.

The objective of the project is to develop a software tool (or "Application") which can be used to estimate benzene emissions as a function of various inputs provided by the user, such as the regeneration still vapour composition and conditions, condenser/tank characteristics, and ambient conditions.

The first report, submitted December 31, 2012, described the work done to develop the thermodynamic, heat transfer and ambient mathematical models required for the Application. The report was updated and reissued at later dates. This report summarizes the development work and presents conclusions regarding its application. In summary:

- A survey of Total Capture Tests was completed and compared to simulation models.
- A review of monitoring methods was done in anticipation of potential "enhanced" onsite monitoring to supplement Total Capture Test results.
- A thermodynamic model was developed to predict vapour-liquid-liquid equilibrium of water-hydrocarbon mixtures.
- A heat transfer model was developed for the standard TankSafe brand condenser as well as for a typical above-ground tank.
- An online Application was developed, integrating the thermodynamic and heat transfer models. This Application allows the user to input data related to their facility and predict the benzene emissions reduction performance there.
- An ambient condition "model" was developed to allow for prediction of year-round temperatures and wind speeds in Western Canadian locations. The ambient model was incorporated in the online Application.
- The model was compared and validated to Total Capture tests, as well as multiple field studies. These tests and studies showed that the Condenser Application reliably estimates vent temperatures and benzene emissions reductions in condensers.
- The online Application was made available to PTAC, where it resides at https://condenser.ptac.org.



Background

There is a need for a calculation method to allow the upstream oil and gas industry and regulators to determine benzene levels leaving condenser devices without the need for field measurement.

Ideally, a vapour-liquid-liquid equilibrium ("VLLE flash") calculation using an appropriate equation of state could be used to accurately calculate the amount of benzene in the product phases off a glycol still condenser. In essence, this requires knowledge of the condenser conditions (pressure, temperature) and composition of the still overhead vapour to the condenser. However, in reality, this calculation is complicated by a number of factors:

- **Composition:** The composition of the still overhead vapour is not directly measured and must be calculated. Simulators such as GRI GLYCalc, Aspentech HYSYS, and BR&E ProMax are conventionally used to model the dehydration facility (contactor or low temperature separator as well as glycol regeneration). The simulators are used to calculate facility benzene emissions as required by regulatory agencies such as the Alberta Energy Regulator (AER). The calculated composition of the still overhead vapour will vary according to changes in process conditions as well as which simulator is used.
- **Pressure:** The condenser typically operates close to atmospheric pressure; however a small amount of backpressure in the condenser would have some effect on the flash calculation. Additionally, the elevation of the facility determines the local atmospheric pressure. In principle it should not be difficult to estimate a reasonable condenser pressure.
- **Temperature:** The ambient temperature will vary significantly both on a daily and yearly basis, requiring a calculation which considers this variance.
- It is also known that reboiler firing cycles can result in fluctuating still overhead temperature and composition.
- The temperature to which the overhead vapour will be cooled (the difference between this temperature and the ambient temperature is called the "approach") is a function of the condenser characteristics.
- In principle, the condenser temperature could be measured in the field and used as the basis for the calculation, however:
 - The measurement may not directly correspond to condenser conditions, depending on where the measurement is taken, and especially if a temperature gun is needed to make the measurement.
 - Even if an accurate condenser temperature is measured, one must extrapolate the year-round condenser temperature based on the anticipated ambient temperature variance and performance of the condenser. It could be assumed that the approach remains constant but this would likely introduce significant errors (a linear function which assumes the approach varies with ambient temperature may be sufficient). It would be more accurate to model the performance of the condenser so that the condenser temperature can be predicted for a range of inlet and ambient conditions.



• **Condenser Device**: There are a variety of condensing devices used in industry ranging from simple tanks to engineered condensers. A very common condenser used in Western Canada is the "TankSafe" condenser which is a primary focus of this research. Other less common options include standard aerial coolers, Ruffneck[™] coolers and specific operator configurations. The initial goal is to model TankSafe condensers, standard tanks, as well as the piping connecting the still overhead to the tank/condenser.

It is understood that the ultimate goal was to develop a software application which could be widely applied in industry, incorporating sound engineering principles and underlying calculations, as well as a clear and comprehensive interface. To ensure predictions of benzene reductions in condensers which are as accurate as possible, the software would be validated to accurate field measurements.

Finally, it is important to understand AER's role in accepting calculations of benzene reductions in condensers. The AER has not set a precedent of accepting condenser simulation calculations for establishing benzene removal efficiency in condenser devices (even though the regulations do allow for "supporting engineering calculations"). As mentioned earlier, Total Capture tests are required, which are costly and also prone to error. While the final objective of this project is to develop an application which calculates condenser performance, it was hoped that the AER would ultimately accept the Application. AER has provided feedback at various points throughout the project, particularly in the last few months as it is anticipated that AER will allow the Condenser Application to be applied for Directive 39.

An application which accurately calculates the condenser performance, taking into account all important parameters including condenser type, yearly ambient conditions and process conditions, combined with operator education and ongoing collaboration with AER, can address the requirement for a method which simplifies the evaluation of condenser performance according to the regulations and the intent of AER's Directive 039.

This application was developed and is currently available for use by the AER and Project Team members.

Scope of the Research

Key answers sought in this research stem from the "complicating factors" discussed in the previous section:

How should ambient temperature fluctuations be incorporated in the model? It is noted that GLYCalc provides a methodology and serves as a starting point. Annual ambient temperature profiles can be obtained from a Dominion Land Survey (DLS) location (refer to **Ambient Model**).

A key assumption in the GLYCalc methodology is that the approach is constant, regardless of ambient temperature. Based on data from TankSafe Inc. showing measurements of condenser inlet, condenser outlet and ambient air temperatures, this appears not to be a good assumption. However, it may be sufficient to assume that the approach varies linearly with ambient temperature, an assumption which could be reviewed as part of the research.



A significant part of the research involved developing the model for the condensers. This required that detailed measurements be taken for a number of field units to serve as the basis for developing and/or testing the model. A fundamental (rather than empirical) approach has been taken in developing the models. It is noted that the TankSafe condenser in particular has a somewhat complex baffle arrangement which required the development of a model which could adequately represent the heat transfer characteristics.

A flash calculation was developed. The requirements and methodologies for the equation-ofstate flash calculation are reasonably well-known and component and interaction parameters are available.

The application takes as input the still overhead composition and conditions, then calculates the condenser performance. This requires an accurate estimate of the still overhead vapour composition and conditions. Simulators such as GLYCalc, ProMax and HYSYS can currently be used for this calculation; use of these simulators is accepted by the AER.

The Application has been made available to users as a web-based tool.



Discussion

Survey

A first step was to conduct a "survey" to help determine the scope of the study in terms of the condenser equipment to be studied, as well as to gather previous "Total Capture" (TCT) data.

Specifically, this involved obtaining data from the PTAC 15-ARPC-01 (previously ARPC-03) Condenser Project Technical Committee (PTAC Committee) and other parties. The PTAC Committee is comprised of representatives from PTAC and industry; part of the role of the Committee is to provide technical feedback and input to the project.

The PTAC Committee provided the following initial feedback for the survey:

- The condenser equipment: the scope was determined to include benzene emissions reduction in conventional above ground tanks and TankSafe condensers
- Total Capture data: Total Capture data for a number of facilities was made available by the PTAC Committee members. In addition, a third-party company provided a set of TCT results.

Review of Total Capture Tests

The AER has not in practice accepted simulated results showing the benzene emissions reduction in condenser tanks; more commonly, if companies wish to claim a benzene emissions reduction, they must submit an end of pipe analysis (Total Capture Test) to demonstrate the reduction of benzene in the tank/condenser outlet.

A Total Capture Test (TCT) is performed using a proprietary trailer currently leased by Exova Group Ltd. (the trailer was formerly leased by SGS Canada Inc.). For the Total Capture Test, the condenser inlet (still overhead) and condenser outlet are redirected to the trailer and samples are taken periodically that are later analyzed for composition in a laboratory setting using Gas Chromatography (GC).

In this section, the results of various TCT reports are compared with values calculated by commercial simulation software (AspenTech HYSYS). The format and content of the reported results are quite different for tests performed by SGS Canada Inc. (SGS) and Exova Group Ltd. (Exova), and therefore the comparison is summarized in two sections. The comparison focuses on the benzene reduction in the condenser.

The main conclusions are as follows:

- In general, there is a reasonable match between HYSYS and the Exova/SGS analyses for the benzene concentration (mole or mass %) in the condenser vent.
- The comparison between HYSYS and the Exova/SGS analyses for benzene mass flow in the condenser vent shows significant discrepancies.
- In most cases, a significant reduction in methane mass flowrate between the still overhead and condenser/tank overhead was observed in TCT reports. This finding indicates some problems in the TCT procedures since the vast majority of the methane is expected to remain in the gas phase.



- The mass imbalance of methane seems to indicate a fundamental flaw in the Total Capture Test procedure or equipment (e.g., a leak). In fact, it appears this is an issue that Exova recognized and documented in their reports after acquiring the trailer from SGS (the Exova reports provided much more narrative and details regarding the procedure than the earlier SGS reports).
- The benzene mass rates from the condenser vent were not corrected for this methane loss in the Exova/SGS results. A more accurate estimate of benzene emissions could potentially be determined by using the measured benzene concentration and correcting the mass rates assuming that all methane should be vented (this assumes that benzene is lost in the same proportion as methane).
- 10 out of the 16 reviewed analyses reported stripping gas being used, which is known to significantly reduce the benzene removal efficiency. For these locations in particular, HYSYS predicted much lower benzene removal efficiencies than the Exova/SGS results.
- In all 16 cases, HYSYS gave more conservative results than the Exova/SGS results (i.e., lower benzene removal efficiency).
- Finally, it should be noted that after this analysis was completed, further Exova tests were made available, but were not incorporated in this stage of the analysis. Rather, a more detailed review of the Exova tests are summarized in *Comparison of Total Capture Tests by Exova*.

Total Capture Test Unit Details

The following table provides details regarding the available Total Capture Test data which was available for this analysis.

Unit	Company	Date	Stripping Gas?	Energy Exchange	Flash Tank?
				Pump?	
Unit 1	SGS	2010-06-22	No	Yes	Yes
Unit 2	SGS	2010-06-22	No	Yes	Yes
Unit 3	SGS	2010-07-06	Yes	No	No
Unit 4	SGS	2010-07-07	Yes	Yes	Yes
Unit 5	SGS	2010-07-07	Yes	Yes	No
Unit 6	SGS	2010-07-06	Yes	Yes	No
Unit 7	SGS	2010-07-08	Yes	Yes	No
Unit 8	SGS	2010-08-31	No	No?	No
Unit 9	SGS	2010-09-06	Yes	Yes	Yes
Unit 10	SGS	2010-09-07	Yes	Yes	Yes
Unit 11	Exova	2012-08-16	Yes	No	No
Unit 12	Exova	2011-08-16	No	No	Yes
Unit 13	Exova	2011-06-13	No	No	No
Unit 14	Exova	2012-08-07	Yes	Yes	No
Unit 15	Exova	2011-05-19	No	?	No
Unit 16	Exova	2012-09-12	Yes	Yes	Yes

 Table 1- Total Capture Test Unit Details



Comparison of Total Capture Tests by SGS Canada Inc.

Simulation Setup

The Total Capture Tests by SGS Canada Inc. include the following information useful for the HYSYS simulation:

- flow rate and compositional analysis of vapor, liquid hydrocarbon, and water phase in condenser/tank inlet (still overhead)
- flow rate and compositional analysis of vapor, liquid hydrocarbon, and water phase in condenser/tank outlet
- inlet/outlet temperature

In the SGS Total Capture Test, there is an ambiguous distinction between "Water/Hydrocarbon Phase as Vapor" and "Water/Hydrocarbon Phase as Liquid". These terms are misleading as they convey that both water and hydrocarbons are being measured in the vapor phase as well as in the liquid phase. Figure 1 shows the results as reported by SGS Canada.

Flow Rate	Gas Phase Hydrocarbon Phase Hydrocarbon Phase		Hydrocarbon Phase	Water Phase	Water Phase
	(101.325 & 15℃)	as liquid	as vapour	as liquid	as vapour
(litres/minute)	9.95	<0.01	1.01	0.12	150



Based on analysis of the data it has been concluded that the recovered liquid hydrocarbon and liquid water are simply converted to vapor flow rate based on the density difference of liquid and vapor. Therefore, the following procedure is devised to replicate the reported flow rates in the TCT and thereby obtain an approximate match using the simulation software:

- An inlet vapor stream with given (water-free) composition is theoretically saturated (in HYSYS) with water so that the recovered water matches the SGS reports.
- The reported water and hydrocarbon phases are combined and assumed to be entirely in the vapour phase (setting vapour fraction to 1). This mixture represents the condenser inlet (still vent) "Inlet Composition" in the following figure.
- The composition of the outlet stream is then calculated using the outlet temperature and assuming atmospheric pressure in the tank outlet.

Figure 2 shows how the results are implemented in HYSYS.



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Figure 2 - Implementation of SGS Canada results in HYSYS

Table 2 shows the flow rates of the recovered phases in the still vent as reported by SGS vs. the results obtained from the devised simulation procedure. The simulation results are reasonably close to those of SGS, and strongly justify the validity of the procedure for replicating the reported values measured by SGS Canada using HYSYS simulation software.

Table 2 Comparison	of "I Init Q"	still vont in	SCS and as	implemented in	
			SGS and as	impiementeu i	111010

	As Li	quid	As Vapor		
	SGS	HYSYS	SGS	HYSYS	
Water (L/min)	0.12	0.09	150.0	151.1	
Hydrocarbon (L/min)	<0.01	0.004	1.01	1.006	

Results

Using the established procedure and given analyses, the composition of the condenser/tank outlet was calculated for 10 units, as presented in Table 3. It should be noted that the outlet analyses by SGS shows the presence of air in all cases, indicating that the condenser system was either not fully sealed, or due to air being pulled back into the condenser tank due to reboiler cycling. Therefore, in Table 3 the SGS results were normalized for the presence of air.

Table 3 - Comparison of Tank Vent composition (mol%) in SGS and HYSYS

	Methane		Benzene		Toluene		E-Benzene		Xylenes	
Location	SGS	HYSYS	SGS	HYSYS	SGS	HYSYS	HYSYS	SGS	HYSYS	SGS
Unit 1	25.09	36.24	4.88	4.05	1.70	0.52	0.02	0.00	0.13	0.01
Unit 2	22.76	29.09	4.48	3.25	0.52	0.43	0.00	0.00	0.01	0.01
Unit 3	40.87	39.72	2.24	2.99	0.46	1.04	0.00	0.01	0.02	0.05
Unit 4	17.64	10.66	1.40	6.10	1.81	0.37	0.04	0.00	0.26	0.00
Unit 5	67.91	42.79	0.92	3.51	0.87	1.07	0.04	0.02	0.16	0.06
Unit 6	77.41	77.87	1.28	1.07	2.35	1.24	0.05	0.02	0.36	0.12
Unit 7	71.00	71.65	1.37	1.47	1.02	0.76	0.04	0.06	0.16	0.11
Unit 8	28.58	33.10	2.49	2.53	0.81	0.32	0.01	0.02	0.03	0.01
Unit 9	74.98	68.01	0.90	1.79	0.77	0.72	0.02	0.01	0.15	0.03
Unit 10	57.58	53.42	1.35	2.27	0.41	0.08	0.01	0.00	0.05	0.00



The calculated compositions match reasonably well in 6 out of 10 cases. Where there is not a good match, the HYSYS results are **conservative**; i.e., the calculated HYSYS benzene mole percent is higher, which would result in higher predicted benzene emissions.

The following figure displays the benzene concentration (mole percent) in the condenser outlet for each of the ten SGS Total Capture Tests, as well as the corresponding HYSYS result (i.e., the benzene mol% data from **Table 3**).



Figure 3 – Comparison of benzene concentration – SGS vs. HYSYS

Despite the reasonably good match on concentration for most of the SGS tests, the analysis of the flow rates as given in **Table 4** indicates a very large difference (up to two orders of magnitude) in the reported SGS benzene flow values vs. the benzene flow rates calculated by HYSYS.

To further investigate this large difference, the reported mass flow rate of methane is compared. It is noted that Total Capture testing requires consecutive (as opposed to concurrent) testing of the inlet and outlet streams and so some imbalance in mass flow rate is expected. As can be seen in **Table 4**, in nearly every case, the methane rate in the outlet is significantly lower than the inlet methane rate. This appears to indicate a systemic error somewhere in the Total Capture Testing procedure, since nearly all of the methane from the still overhead should be present in the condenser vent.



	Methane (kg/	e flow rate year)	v rate Benzene flow rate (kg/year))					
	Inlet- SGS	Outlet-SGS	SGS-Inlet*	HYSYS-Inlet*	SGS- Outlet	HYSYS-Outlet	SGS	HYSYS
Location								
Unit 1	737	160	1190	1840	152	798	87.2%	56.6%
Unit 2	623	99	408	464	94	303	77.0%	34.7%
Unit 3**	3886	1723	2050	3336	459	2365	77.6%	29.1%
Unit 4**	94	4	1445	1129	1.5	665	99.9%	41.1%
Unit 5**	15,161	16,579	6395	6241	1087	6228	83.0%	0.2%
Unit 6**	87,611	30,503	5845	6873	2461	6873	57.9%	0.0%
Unit 7**	36,891	6,239	3753	3752	581	3682	84.5%	1.9%
Unit 8	1,135	19	863.4	658	7.86	513	99.1%	22.0%
Unit 9**	103,191	66,769	16897	16842	4193	13178	75.2%	21.8%
Unit 10**	4,139	1,163	4003	2028	268	1697	93.3%	16.3%

Table 4- Flow rates of Benzene and Methane in SGS tests

* the reported benzene inlet mass flow rates do not match since the inlet total volume flow rates were instead matched with the reported values; This difference is negligible in 7 out of 10 cases.

** stripping gas is used at this location

The predicted benzene reduction is significantly different when comparing the HYSYS and SGS results.



Figure 4 - Comparison of benzene % reduction - SGS vs. HYSYS

It is noted that 7 out of the 10 units analyzed here reported stripping gas being used, which would typically result in lower benzene removal efficiencies. Unit 1 and Unit 2 reported no stripping gas; for these units there is a better match between the SGS and HYSYS results (however, Unit 8, which reported no stripping gas, has a poor match).



Comparison of Total Capture Tests by Exova

Simulation Setup

The Exova Total Capture Test (TCT) results did not generally include an extended analysis for the still or tank vents; however, they did report methane, water and BTEX mass content. In some cases, an inlet extended analysis was included in the report.

The extended inlet analysis was needed in order to model the process and generate the full still overhead analysis (these were provided for the SGS tests but not the Exova tests). In addition to the inlet, still vent and tank vent analyses, the Exova reports also include enough process information to develop the HYSYS model, as shown in **Figure 5**.



Figure 5- HYSYS Model of a TEG dehydration plant used for Exova TCT comparison

The reason for modelling the entire process in HYSYS was simply to estimate the composition of C2+ components that were not reported in the Exova Still Overhead and Condenser Outlet summaries. The Methane and BTEX flowrates were specified as reported, and the remainder of the composition was transferred from the full plant model still overhead stream, in order to obtain a full representation of the analysis.

Figure 6 shows the process flow diagram associated with the condenser tank in HYSYS.



Figure 6 - Manipulation of still vent stream to match Exova reports

The tank vent temperature was not provided in the Exova results; however, the ambient temperature was provided, and the condenser vent temperature was then estimated by assuming 10°C as the minimum approach to ambient for the condenser.



Results

Using the described procedure, the calculated outlet composition and reported values are presented in **Table 5**. Similar to the replication done previously of SGS results, the reported compositions agree fairly well in most of the cases when replicating the Exova results via simulation, although there are some significant discrepancies (e.g., Unit 12 and Unit 13).

	Methane Mass %		Benzene Mass %		Toluene Mass %		Ethyl-Benzene Mass %		Xylenes Mass %	
Location	Exova	HYSYS	Exova	HYSYS	Exova	HYSYS	Exova	HYSYS	Exova	HYSYS
Unit 11	38.08	37.00	5.93	6.37	3.11	3.39	0.03	0.03	0.18	0.16
Unit 12	21.73	33.62	3.81	7.46	0.54	5.65	0.02	0.08	0.03	0.57
Unit 13	38.12	40.18	1.78	3.45	0.52	2.31	0.01	0.06	0.05	0.29
Unit 14	53.61	55.9	4.56	4.69	5.06	3.89	0.06	0.03	0.39	0.18
Unit 15	40.04	41.39	4.85	6.09	1.75	2.38	0.02	0.04	0.08	0.18
Unit 16	0.08	0.18	4.03	6.63	1.38	4.85	0.02	0.11	0.16	0.81

Table 5 - Comparison o	f Tank Vent co	pmposition (mass%	6) in Exova and	d HYSYS

The following figure displays the benzene concentration (mole percent) in the condenser outlet for each of the six Exova Total Capture Tests, as well as the corresponding HYSYS result (i.e., the benzene mass% data from **Table 5** converted to mole percent).



Figure 7 - Comparison of benzene concentration - Exova vs. HYSYS

Flow rates of Benzene in the tank vent as shown in **Table 6** below, are in reasonable agreement in 2 out of the 6 cases (Unit 13 and Unit 15). Further analysis of the other four units shows the same problem as with the SGS tests: mass imbalance of methane. For example, "Unit 13" shows that the inlet methane flowrate is 9,373 kg/year, and the outlet methane flowrate is 6,745 kg/year; these



flowrates should be very similar as methane is relatively non-condensable at these pressures and temperatures.

Location	Methane flow rate (kg/year)		Benzene flow rate-	Tank vent (kg/year)	Benzene % reduction	
	Inlet- Exova	Outlet-Exova	Exova	HYSYS	Exova	HYSYS
Unit 11*	81,994	75,424	6,658	7,676	16%	3%
Unit 12	7,884	526	53	1,452	99%	68%
Unit 13	9,373	6,745	315	350	76%	73%
Unit 14*	136,568	35,478	2,015	6,783	76%	18%
Unit 15	35,128	35,128	2,584	2,781	18%	12%
Unit 16*	13,578	10,862	596	1,049	60%	30%

Table 6 - Flow rates of Benzene and Methane in Exova tests

* stripping gas is used at this location

It is further noted that Exova appears to recognize the value of doing the methane balance, as well as the implication of a poor balance, by indicating:

"Balance is provided to evaluate total capture, process stability and control effectiveness. Methane (boiling point -162 °C) is unlikely to be removed by condensation. Significant difference in methane flow rates between tank and still column tests may be due to losses or due to variance in emission rates."

It is our assessment that the difference in methane flow rates is more likely due to losses, rather than emission rate variances, since for all 16 samples there is a bias to having lower methane in the outlet than in the inlet (still overhead). It should also be pointed out that there may be other reasons for the methane imbalance, other than what Exova identified here. For example, some of the error could be attributed to difficulty in accurately measuring low flow rates at atmospheric pressures, precision of the gas meter, and length of test.



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The predicted benzene reduction is shown in the following figure:

Figure 8- Comparison of benzene % reduction – Exova vs. HYSYS

Because of the significant methane imbalance, one further comparison was done as follows:

Exova benzene flow rates were multiplied by a correction factor to account for the discrepancy • between inlet and outlet methane rates and is called 'Exova "corrected" results' in Figure 9 below Refer to the **Ambient Model** section for more details



Figure 9- Comparison of benzene reduction - Exova "corrected" results vs. HYSYS The comparison of results improves significantly when this correction is applied.



Concluding remarks

In this section, a detailed analysis of 16 Total Capture Tests was presented. In general, there is a fair agreement in reported and HYSYS-calculated **compositions** (there was a reasonable match for 12 out of 16 units). However, the **mass flow rates** agree only in a few cases. Analysis of the reported results indicates significant imbalance of methane in the vapor phase, while most of the methane should remain in the vapor phase. This mass imbalance of methane appears to indicate a fundamental flaw in the Total Capture Test procedure or equipment.

In many cases, TCT tests over-predicted the benzene removal due to mass balance issues.

Many analyses had significant amounts of oxygen and nitrogen, which indicates air ingress to the sampling device.



Monitoring Methods

Because of the difficulty in measuring the flowrate and composition of the still overhead and condenser tank vapours, various monitoring methods were reviewed as detailed in this section:

- Total Capture Testing historically condenser emissions have been measured and reported to the AER using Total Capture Testing (Exova, SGS).
- Remote Sensing options refers to utilization at a distance of a device (usually optical) for gathering information about the environment. These methods are being employed in situations where the use of conventional monitoring techniques is difficult or impractical.
- Local monitoring options refers to use of a device to measure information in proximity to the device. Conventional monitoring methods were reviewed, given the high cost associated with remote sensing options.

Total Capture Testing - Procedure

The previous section (*Review of Total Capture Tests*) summarizes a review of previous Total Capture Testing results. Total Capture Testing (TCT) is the sampling method most commonly used in Alberta to estimate benzene emissions (specifically measuring composition and mass flowrate) in still column vent and condenser vapour outlets. SGS and Exova historically offered this testing method.

According to the SGS documentation,

"The still column vent emissions are diverted through a portable process unit designed to condense, collect, measure and sample the various phases in a still column vent stream. The analysis of each phase is performed by Gas Chromatography to determine the Benzene concentration. The results are reported for not only Benzene, but all BTEX components individually from each phase and also combined for a total emission determination."

It is noted that the means of condensing/cooling have varied over time.

Both SGS and Exova claim a number of advantages: [1]

- Measurement of benzene emissions determined directly from the source;
- Continuous sampling over a "longer period of time (hours)";
- Composition and flowrate of each phase (gas, condensate and water) measured;
- Separation of the phases allows representative samples to be taken. Less procedural errors (gas sampling or bag sampling).
- "Better results" for unstable processes.
- Real Time Samples
- Not affected by "Dew-Point Measurement inaccuracies"

The Total Capture Test (TCT) is based on the idea of collecting and stabilizing the emissions in three phases: Water and miscibles, liquid hydrocarbon, and vapor. Each phase is separately analyzed, and the BTEX content of the stream is calculated as the summation of BTEX in these phases. To perform the test, the entire stream flow rate is redirected through "a series of chilled three-phase separators". It is noted that this describes the original SGS configuration, with these vessels (which had coiled tubes inside) situated in the trailer. Later, finned tubed natural



convection radiators were set up outside the trailer to accomplish the condensing/cooling, which is Exova's current setup.

The condensed liquid is collected and analyzed periodically. Noncondensable gas is metered and vented. Chromatography is used at the lab to measure composition of the liquid and vapor phases.

Exova provides the following general methodology (steps 1-3 applicable only to the original chilled separator configuration):

- 1. The vent gas stream is redirected into a baffled primary separator which removes ~95% of the water and some high molecular weight hydrocarbons.
- 2. The gas passes through a secondary separator at ~5°C which removes 99% of the condensable hydrocarbons and the remaining water.
- 3. The tertiary separator is used as protection for the gas meter should the chiller fail.
- 4. Four gas samples are taken at specified intervals during the test and all the liquids are collected.
- 5. Gas analysis is performed on the resulting 4 samples by gas chromatography and the BTEX concentration of each is combined and weighted for amount of gas flowed between samples.
- 6. Liquid samples are combined and the phases (water/hydrocarbon) separated. Hydrocarbon liquid samples are analyzed by gas chromatography and water samples by mass spectrometry.
- 7. The composition of the three phases is recombined gravimetrically and reported in tonnes/year.

Figure 10 shows a typical tie-in of the still column (in the background, with the initially horizontal, then sloping tie-in pipe) to the Tank Safe condenser (blue tank to the right). The condenser (baffled section) sits on top of a tank.



Figure 10 - Tie-in of Still Column Overhead to Tank Vent (Source: Exova)



For the Total Capture Test, it is necessary to collect the still overhead; the following figure shows how the still overhead pipe is temporarily detached from the condenser, which allows all fluids to be routed to the trailer via the yellow tubing.



Figure 11 – Still Overhead fluid collection using TCT Procedure (Source: Exova)



For the Total Capture Test, the tank vent vapour is also collected by connecting to the overhead vent on the condenser, and as before routing all fluids to the trailer for analysis.



Figure 12 – TankSafe Overhead vapour collection using TCT Procedure (Source: Exova)

Total Capture testing has been used for many years and is accepted by the AER for estimating benzene emissions reductions in condensing tanks. However, there are difficulties with this method, as discussed in *Review of Total Capture Tests*.

Comments on Exova Procedure

Exova provided two documents [1] and [2] which summarize the method description and validation for the Total Capture method. Some of the key conclusions are as follows:

- "In 60 tests involving both CTV and SCV [Condenser Tank Vent and Still Column Vent] tests, a mean [non-condensable] balance of 70 % was observed."
- In a comparison of 2008/2009 data, the Glycalc estimate of emissions rate was ALWAYS greater than that measured by TCT.
- In a comparison of 2010-2012 data, 52 of 56 Glycalc estimates of benzene emissions at the still overhead were greater than those measured by TCT.
- During many of the TCT tests, stripping gas was being used. Stripping gas should be turned off if possible; if it is required in the summer, the annual calculation will need to accommodate for



it, as summer efficiency would then be very poor. It is further noted that on several occasions, stripping gas believed to have been turned off was in fact on (due to equipment malfunction in one case and either inadvertent or unauthorised adjustment in another).

- The Exova documentation indicates that a 2 hour interval is sufficient "To be most representative, the test should be long enough to ensure at least one complete exchange of glycol in the reboiler with the exchange rate calculated as circulation rate divided by volume of glycol in the dehydrator. Without such information available, and by default, a minimum two hour test time is used. Scheduling should include at least one hour additional time for tie-in and purging."
- A standard test is performed for two hours with sample collection and readings every 30 minutes. There is an initial purge of 30 minutes (or 2 times system residence time, whichever is less).
- 5 gas samples are collected from the manifold upstream of the meter in a two-hour test (unless there is a situation of limited flow).
- The following figure provides an example of the variability in measured noncondensable flow rate over the course of a two-hour test:



Figure 13 - Exova test - noncondensable flow rate over two-hour test (Source: Exova)

In other examples, the flowrate is much less variable; usually the condenser tank emissions are less than the still column.

• Methanol contamination is identified as being common (more often for EG units). The sensitivity of methanol (which could "contribute significantly to volume of gas phase") to benzene reduction in condensers has not been studied. It is unlikely that methanol amounts would be known, so this is not included in the model.



- The test procedure allows for connection of still column or tank vents from 2" to 4". Still column tie-in is done directly at the vapour vent or where the downpipe is connected to the TankSafe condenser.
- The condenser tank vent test is done first to ensure it is at equilibrium.
- Gas is transported in sample bags (clear Tedlar) or high pressure cylinders. High pressure cylinders were found to collect excess air and therefore Tedlar bags were preferred.
- There is no specific limit for holding time of gas sample, but it is analysed as soon as possible after arrival.
- On site gas meter "totaling gas meter" "C15 175 Roots type rotary meter and MR-8 or MR-12 diaphragm type are available". The meter is verified using a Bell Flow Prover G-22, ± 0.2 % over operating range.
- Dry Gas volume is corrected to standard conditions (15 C & 1 atm), correcting for water partial pressure.
- The validation documents acknowledge the potential significant differences in noncondensables (in particular methane) between the tank and still column tests – "Significant difference in methane flow rates between tank and still column tests may be due to losses or due to variance in emission rates."
- However, variance in emission rates is not a plausible explanation due to condenser outlet methane ALWAYS being less than still vent methane.
- According to the validation document, "Air contamination may be an artifact of sampling, or may be due to air in the dehy / condenser system. Some systems have been found to reverse flow with system cycling. Air can be pulled back into condenser tanks and even back into still column vents. Generally, stable or trending air contents indicate air in the source, while highly variable air or a single high air sample in a set may be an artifact of sampling. Such samples may be disregarded or air corrections applied."
- It is noted that relatively high air contents have been found in SCV tests as well, particularly in configurations involving flash tanks.
- If a leak would explain the "measured methane loss", then sources would include:
 - Tie-in from source (e.g., vent) to TCT apparatus
 - TCT apparatus (tubing, separators)
 - TankSafe tank (vents, leaks, etc.)
 - Pipe connecting still to condenser
 - Losses due to gas sampling
- According to the documentation, "Total capture is assured through the use of Cam lock connections. The system is verified to be free of significant leaks. Losses are assumed negligible and total capture achieved. Samples are protected in transport and storage."
- It is noted that no FLIR camera is used, so the inspection is likely visual/audible. Infrared camera detection of leaks should be considered during TCT testing (this will locate, but not quantify leaks).



Remote Sensing

In the following sections, the applicability and limitations of other monitoring methods are discussed. The methods for measurement of emissions from tanks can be divided into two distinct categories:

- Remote sensing
- Local measurement

Remote sensing methods were initially considered; as a result of this detailed assessment, Process Ecology partnered with Clearstone and sent a proposal to PTAC for measurement of condensing tank emissions. The proposal was submitted; however, the funding was not made available and the tests were not conducted. However, for future reference, a brief description of available technologies is presented here.

The main categories of active optical remote sensing (ORS) technology are:

- Fourier Transform Infrared (FTIR)
- Ultraviolet (UV) and UV-DOAS (Differential Optical Absorption Spectroscopy)
- Tunable Diode Laser
- Differential Absorption Lidar (DIAL)
- Cavity Ring Down Spectroscopy (CRDS)

The estimation methods associated with these technologies are:

- Point Source
- Area Source
- Stationary and Mobile Tracer Correlation
- Vertical Radial Plume (VRPM)
- Solar Occultation Flux (SOF)
- Plane Concentration Flux
- Backward Lagrangian Stochastic (bLS)

ORS technologies measure the concentration of chemicals in an open air path or in contained air samples collected from discrete sampling points. They do this by measuring the interaction of electromagnetic energy (i.e., different wavelengths of light) with the air's components. ORS techniques use the light generated under controlled conditions from one of many sources including heated glow bars for IR light, quartz lamps filled with deuterium or xenon gas, or laser light.

Open-path technologies measure the concentrations of chemicals or particulates across an open path of air. They do this by emitting a concentrated beam of electromagnetic energy into the air and measuring its interactions with the air's components. Open-path technologies provide an average concentration over a line of sight. Point-source applications of these technologies measure the concentration of a confined sample of air drawn into the apparatus from a point or points in air.

There are four major optical sensing approaches:

1. Active- Open-path ORS techniques typically use optical telescopes to transmit and receive energy beams, such as ultraviolet (UV), infrared (IR), or visible wavelength range. A mathematical calculation routine, combined with meteorological data (wind speed, wind direction) collected



during the sampling event, is needed to convert the ORS instrument output (e.g., a path-integrated concentration or a flux measurement) to an emission flux rate (e.g., milligrams per second).

- 2. Passive- Open-path ORS techniques receive light energy from pollutants activated by an external uncontrolled source such as combustion gases (e.g., Passive FTIR radiation) or the sun (e.g., Solar Occultation and mobile DOAS). Open-path techniques use the same technology as active without the need for a controlled source of energy. The PFTIR technique is an example of this technology. The primary difference that must be taken into account between optical remote infrared absorption (e.g., FTIR) and hot gas radiance measurements using PFTIR is the temperature ORS dependence of the FTIR spectral measurements. The results of PFTIR are both temperature and concentration dependent. Knowing the source temperature at the location where the gas concentrations are measured is necessary to quantify the compounds of interest.
- 3. Backscatter- ORS techniques use energy reflected from pollutants after activation from a controlled source of light energy (e.g., Differential Absorption Light Detection and Ranging (DIAL/LIDAR) systems). Open-path optical measurement approaches refer to the use of Light LIDAR technology. DIAL is an application of LIDAR using powerful lasers directed into the atmosphere to measure reflected light energy from aerosols, dust, and gases. The DIAL measurement is achieved by the direct impingement of the laser beam on these materials and its subsequent reflection and scattering. Because the target substances vary in concentration along the axis (optical path) of the transmitted beam, the receiving telescope equipment analyzes the strength of the returning (reflected) beam continually during its reception. The reflected beam strength is reduced from the original transmission strength by a measureable amount that is proportional to the concentration of the target matter.
- 4. Mobile- Measurement methods do not have to be optically based. However, optical technologies have been engineered to be rugged enough to allow stable operation from a moving vehicle. Typically these optical techniques sample the gas into a confined cell while moving along a path to be measured (e.g., cavity ringdown, white cell and FTIR tracer release systems). Unlike stationary monitoring techniques, mobile optical techniques allow the user to move along and between the emission plumes generated by area or fugitive sources.

The predominant measurement applications that use ORS technologies in the open-path mode include line of sight monitoring, Radial Plume Mapping (RPM), and Backward Lagrangian Stochastic (bLS) Modeling.

For large area sources, ORS methods have distinct advantages when compared with traditional single point measurement techniques, such as photo-ionization detectors (PID), PID/flame ionization detectors (FID), various sorbent methods, and flux boxes.

Some of the general ORS advantages are as follows:

- More likely to identify emissions "hot spots" as measurements collected over large area,
- Achieve better spatial and temporal emissions resolution,
- No sample shipping costs,
- Perform direct, measurement-based emission calculations, and
- Represent personal exposure better than fixed point monitoring.



Some general issues that require consideration when ORS methods are used include the following:

- More costly initial sampling instrumentation investment,
- Experienced manpower and higher site preparation cost more to deploy,
- Dependent on weather conditions (e.g., heavy rain, fog, dust), and
- Dependent on chemical interferences (e.g., water, oxygen, O3 and CO2).

FTIR Method

Fourier Transform Infrared (FTIR) Monitoring was proposed as an alternative to Total Capture Testing to obtain reliable field predictions of benzene (and other component) mass flux rates.

According to the EPA Compendium Method TO-16 [3], the method of trace gas monitoring using FT-IR-based, long-path, open-path systems has a number of advantages that are significant over traditional methods. Some of these advantages are related to the path monitoring aspect of this method which, by its very nature, distinguishes the method from point monitoring methods. The main advantages of these systems are the following:

- Integrity of the sample is assured since no sampling actually occurs.
- Multi-gas analysis is possible with a single field spectrum.
- Path-integrated pollutant concentrations are obtained.
- Spatial survey monitoring of industrial facilities is possible if scanning optics are used.
- Coadding of spectra to improve detection capabilities is easily performed.
- Rapid temporal scanning of line-of-sight or multiple lines-of-sight is possible.
- Monitoring of otherwise inaccessible areas is possible.

A proposal and budget was obtained from Rami Hashmonay (Atmosfir), for:

- concentration analysis
- spatial analysis
- flux analysis
- equipment rental

It was noted that Alberta Environment had acquired an OP-FTIR unit, which might have been available for the study. However, at this time, it was concluded that FTIR was not a suitable method for the objectives of the study (including budget).

Airdar

The Technical Committee met with Airdar (Dennis Prince) to review the methodology of Airdar which "delineates plume boundaries and trajectories and tracks the plumes back to the sources - using only measured air concentrations and meteorological data."

Multiple sensors would be set up which draw in air while at the same time measuring wind speed and direction. A 3D plot of wind speed/direction/concentration could be converted to a spatial representation of plumes.



Other methods (e.g., FTIR) rely on emissions passing through a predefined plane. While AirDar is still set up downwind, it is not so reliant on wind speed/direction (and with multiple sensors can be set up for varying wind direction).

For calculation of mass flux, the plume edges are determined (hence some wind shifting is required in order to identify the edges), and some analysis would be needed regarding placement of sensors from source. A minimum wind speed of about 7 km/h is required, however, to pick up a strong characterization of plume above the background noise.

As with the FTIR method, it was concluded that this methodology would not be suitable for the objectives of the study.

Boreal Laser

Boreal Laser, a manufacturer of laser based gas detectors since 1996, was identified as a potential supplier. They identify themselves as a "world-leading supplier of open-path laser gas detection systems for safety and environmental applications."

In the oil and gas industry, Boreal Laser has experience addressing applications such as pipeline leak detection; H2S leak detection in gas facilities, etc., using open-path laser gas detection systems.

Laser-based gas detection utilizes single-line absorption spectroscopy in the near infrared, offering benefits of:

- High resolution
- Excellent selectivity
- Minimum interference from other gases (especially H₂O, CO₂)
- No consumables, and minimum maintenance

Normally the methodology is used to analyze single gases (for a wide range of sources, concentration, etc.), but would not be used for full compositional analysis.



Flow measurement using "local" devices

Due to the expense associated with the aforementioned remote measurement methods (which are considered expensive for this application), local measurement methodologies for the continuous measurement of the flow rate and composition of the still and tank vent were reviewed. The task is difficult as the still vent has the following characteristics:

- Thermodynamically unstable;
- The composition changes with reboiler cycles;
- High temperature (~ 100 C)
- Very high amount of water vapour
- Operating pressure is close to atmospheric
- Pressure drop may not be tolerated

These characteristics make the measurement of the still vent stream a challenging task. In the following sections of the report, viable technologies for measurement of flow rate and gas composition are discussed and their suitability for use in the current application is assessed.

As mentioned earlier, the still vent is theoretically at the dewpoint and prone to condensation; therefore the flow should be measured as close as possible to the regenerator vent. Therefore, the straight pipe requirement of the selected flow measurement device should be as low as possible. Also, the device should be tolerant of very wet gas. These restrictions limit the available options.

According to a technical report prepared by Clearstone [7], the following are test methods considered for making spot checks, or flows from vent and flare headers.

- Insertion flow meters insert velocity probe through valve and gland assembly on top of vent or flare pipe; measure flow velocity at various points across pipe diameter. Thermal anemometers cannot be used in wet gas applications. Pitot tubes can be difficult to maneuver through a valve into the pipe. Micro-tip vane anemometers are most susceptible to fouling.
- End-of-pipe requires safe access to this point and no potential for an unsafe condition to arise. Some types of in-line flow meters (e.g., diaphragm or turbine meters) can be connected directly to the vent opening.
- Tracer Dilution involves injecting a tracer gas at a known rate into the vent or flare header and analyzing samples of gas taken from a suitable downstream location.
- Pulse velocity uses gaseous radioactive tracers.
- Optical Flow meters Uses lasers or LED light; has specific straight pipe requirements.

The Clearstone technical report displays a useful table (Table 2 in [7] – a comparison of gas flow measurement devices). Most of the devices have straight pipe requirements, and most are not suited for wet or dirty fluid. Most types of flow meters are also composition-dependent which means their readings are affected by any changes in the composition of the metered fluid.

Among the reviewed technologies for flow measurement, the following options were identified to be more suitable for use in the current application.



Ultrasonic Flowmeters

Ultrasonic flowmeters operate based on the travel time of an ultrasonic wave between two points, which is affected by the velocity of the fluid. Clamp-on ultrasonic flowmeters in particular provide the benefit of retrofitting the device without impacting the process or introducing a pressure drop; historically, clamp-on flow metering was limited to liquids but current meters work with gases. Ultrasonic flow meters are well suited to extreme fluctuations in temperature and pressure.

It is noted that Clearstone, in their PTAC Study to evaluate emission rates from tanks [17], used an ultrasonic gas flow meter featuring a flow cell and upstream flow straightener to measure vent gas flow rate and temperature.



Figure 14 - Vent Emission Monitoring System (Source: Clearstone)

The mass flow is estimated based on the measured velocity and assumption of a certain velocity profile in the pipe. However, sufficient straight pipe length is required (15 times, according to http://theultrasonicflowmeters.com/, while the Clearstone Guidelines indicate 10-30 diameters upstream and 5-10 diameters downstream). For the GE ultrasonic flowmeter (GC868), the straight pipe requirement is indicated to be 20 diameters upstream and 10 diameters downstream of the pipe for gas/steam services.

The Flexim Flexus G608 [9] ultrasonic flowmeter works for a wide fluid temperature range, from -40 F (-40 C) to 378 F (192 C). The operating temperature of the Transmitter itself is 14-140 F (-10 C to 60 C), which would not be a major concern for condenser efficiency testing unless the measurement is performed in the winter (the GE GC868 operating temperature is -10 to 55 C). The GE GC868 flowmeter works for process temperatures as high as 230 C, and is indicated to be applicable to steam flow. However, the minimum pressure is indicated to be 110 psig. The Flexus G608 indicates



that a minimum "medium" pressure of 290 psia is required for metal pipes, and 15 psia for plastic pipes.

There are other Ultrasonic flowmeters (e.g. GE PanaFlow) that might also be applicable for this application. Typical cost of these devices is estimated to be in the range of \$20,000-\$30,000. In one report [10], the author explains the total cost of the installation and calibration would add up to \$100,000.

In principle, these ultrasonic flowmeters could be used, but there are significant technical and cost challenges.

Thermal Mass Flowmeters

Thermal mass flow meters work based on the heat required to increase the temperature of fluid by certain amount (constant deltaT), available in insertion or inline models. The inline configuration of the device could be used with a less stringent straight pipe requirement than for the ultrasonic meter (8-10 diameters upstream and 3-4 diameters downstream).

Thermal flowmeters have the advantage of providing accurate measurement at lower flow velocities than other "conventional" (e.g., differential pressure) technologies, as well as directly measuring mass flowrate with low pressure drop.

The Fox FT2 flowmeter can be used over a wide temperature range (-40 to 343 C) and requires a minimum velocity of 60 surface feet per minute (SFPM) [11]. According to the Clearstone Guidelines, thermal mass flowmeters are not suitable to be used in wet gas applications.

The Fox FT2 measures gas rate in standard units without the need for temperature or pressure compensation; however, the downside of thermal mass flow meters is the fact that they do require the composition (density) of the gas to determine the mass flow. Because of reboiler cycling, changes would be expected in the composition. According to the Clearstone Guidelines, "for quantitative flow measurement, their use is limited to applications involving a relatively consistent gas composition, similar to that of the reference calibration gas. Otherwise, the meter simply provides an indication of the relative changes in flow rather than an accurate reading of the amount of flow."

Spartan Controls advised against using thermal mass flow meters if the medium being measured is not very consistent.

Turbine Flow Meters

The Calscan Hawk 9500 was specifically reviewed as per request of the committee members. This turbine flow meter is able to work at low pressure and flow rate, and able to measure gas at atmospheric pressure. However, the maximum operating temperature of the valve is 100 C [12].

To prevent water vapour from condensing (detrimental to the performance of this meter), insulation or heaters may need to be installed upstream of the unit. Similar to the thermal mass flowmeter, the reported flow rate would depend on the assumed composition. Straight pipe requirements are 10 diameters upstream and 5 diameters downstream.

Purchase price is \$6,255, or to rent it would be \$1,275/month (vendor-supplied information).



Coriolis flow meters

The device works based on the fact that the amount of deflecting force exerted on tubing with fluid flowing through it depends on the mass flow rate of the fluid. There are many vendors for this type of device, including Emerson and FMC Technologies. These devices are capable of measuring mass flow, volume flow and density. Standard temperatures are -100 to 204 C. Also, according to the Emerson ELITE technical specification, two-phase flow measurement is possible, and there are no requirements for flow conditioning or straight pipe runs. There would be a pressure loss with this flow meter.

Spartan Controls advised that a Micromotion Coriolis meter would be best for mass measurement of two phase or varying density mediums.

The price is indicated to be in the range of \$4,000 - \$5,000. Refer to [13].

Online composition Measurement

The composition of the still overhead and tank vent needs to be measured. The measurement technology:

- should have a high dynamic range as the compositions of compounds of interest vary from 1 ppm to 90%.
- should have a short measuring cycle (cycle should be generally less than 15 min)
- should be tolerant of hot and wet gas
- should be able to detect paraffinic / aromatic hydrocarbons

Gilmer et al [10] has broken down the composition measurement technique to two categories: Online and Offline. There is no clear distinction of these terms; however, it appears that online means a permanent composition measurement solution that requires no regular attendance by the operator. For the offline method, the suggested methods are:

- EPA 18 (a sampling/ collection technique)
- ASTM D-1945 and D-1946 (Standard for Natural/Reformed Gas GC)
- GPA 2261/2177 (For determination of calorific value of fuel gas)
- Multichannel Micro GC: The report indicated two models of these types of GC: Agilent 3000 and CP-4900.

The composition measurement technique should be able to identify all the components in vent gas. Therefore, a unit with a Flame Ionization Detector (FID) cannot be used as it cannot detect water.

MicroGC models

I-GraphX is a MicroGC that uses a Thermal Conductivity Detector (TCD); it could be used for measuring the components without carbon. It has a very short measuring cycle of 30-180 s with sensitivities up to 0.1 ppm, but the maximum operating temperature is only 60 °C [14].

Agilent 3000 is also a Portable MicroGC that operates with high dynamic range and short cycle. The flow can be as high as 90-110 °C, which is higher than I-GraphX but still on the edge for our application [15]. The Chemical and Petroleum Department of University of Calgary has at least one of these units.



Varian CP4900 is shown to successfully measure the Benzene concentration in Natural Gas [16]. This unit seems to be for batch sampling, but it may be possible to modify it to work continuously. The upper temperature limit is 110 °C.

Conclusions

In this section, a detailed review and assessment of monitoring methods is presented.

The Total Capture Test (TCT) and its results were discussed. Currently, Total Capture Tests (TCT) are used in Alberta to estimate the benzene removal efficiency from condensing tanks. Detailed assessment of results indicated reported composition shows a reasonable match to the simulator results; however, there is often a considerable discrepancy in terms of mass flow rates. Often times the issue of reported mass flowrate is directly a result of methane imbalance in the inlet and outlet to the condensing tank. This discrepancy in measured mass flow rates of inlet and outlet leads to an overestimation of reported benzene removal efficiency from condenser tanks. It is noted that the tests performed more recently have improved in terms of methane balance.

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Emission control technologies in dehydration systems

Aromatic hydrocarbons are very soluble in Triethylene Glycol (TEG) and are absorbed in TEG at contactor conditions. Almost all of the absorbed aromatics will then be released in the vapor phase at the top of the regenerator [1].

Aromatic hydrocarbons are not as soluble in Ethylene Glycol (EG), but are still a concern for EG (refrigeration) facilities – they will be absorbed in the EG/Water phase in the low temperature separator, then released in the vapor at the top of the regenerator.

Benzene is considered a hazardous substance and its emission from dehydration units is strictly regulated by the AER and other regulatory agencies, and specifically AER Directive 039. There are three main methods to control BTEX emissions from glycol systems. The first is to combust the BTEX components in a flare or incinerator. The second is to condense the still overhead vent and recover the BTEX in liquid phase. The third approach is to recycle the vent back into the process [2]. There are also other approaches (e.g., routing still overheads to the burner or compressor engine combustion). The following figure shows a typical TEG Dehydration process; the still overhead vent ("WATER VAPOR") is shown.



Figure 15 – TEG Dehydration (Source: GPSA Handbook)

As the focus of this application is the development of a condenser model for dehydration systems, condenser methods are discussed in detail as follows.



Condensers

Due to the difficulty and expense in the operation of combustion systems, condensing is a widely used method for controlling BTEX emission from glycol dehydrators. In the U.S., more than 80% of control devices are condensers [3]. Condensers not only reduce BTEX emissions, they also recover a hydrocarbon liquid phase (in addition to water). Also, the condenser vent could potentially be used as a fuel in the regenerator. There are three major condenser types recognized in the natural gas industry: [1]

- Air-Cooled Condensers: These condensers use ambient air as cooling fluid and can be either forced or natural convection. This approach is used due to its low capital cost and simple design. The condensing temperature will typically be more than 10 °C higher than the ambient air dry temperature. The TankSafe condenser is an air-cooled natural convection condenser (no mechanical fan).
- Glycol-Cooled Condensers: These condensers use the rich glycol from dehydrator as cooling fluid. The condenser outlet temperature would be typically 6-11 °C higher than the ambient temperature. These condensers are not commonly used in Alberta for cooling the still vent overhead.
- Water Quench Condensers: This condenser combines cool water with the still vent. The quench water would be cooled in a separate heat exchanger. However, these condensers are not practical in cold climates.

Alternative condenser process designs such as R-BTEX have been proposed, which would allow for cooling the still vent to sub-ambient temperature; however, it has been rarely implemented in Canada. Due to simple design and ease of operation, most of the condensers in glycol dehydration units are air-cooled condensers. The major condenser vendors specifically designing units for dehydration units include condensers developed by Jatco [4], KWI International [5], and TankSafe [6].

Jatco [4] has developed two major designs for still vent condensing. The first design is a counter-flow shell and tube heat exchanger. The second design features a series of inclined pipes to cool the still overhead by natural convection from ambient air. The typical designs configurations of these condensers are shown in **Figure 16**.

KWI International's condenser is similar to that of the Jatco design shown in **Figure 16**(b). [5]


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TankSafe's condenser design includes two main components: The top section provides the surface for heat transfer and the lower part incorporates two concentric tanks used for storage of the condensate [6]. As the TankSafe condenser is very common in Alberta, the first version of the Condenser Tank Modelling Application is largely focused on the development of a model for this particular design. Other designs could be addressed in later versions of the application, as requested by the PTAC Committee. TankSafe's condenser design is discussed in detail in the Heat Transfer section.

Evaluation of Condenser Performance

Condenser performance can be described in terms of the ratio of condensate to vapor or percentage removal of certain component(s) from the vapor stream. In this case, percentage of benzene removal is referred to as "condensing efficiency" and is used to evaluate the performance of the condenser. The "condensing efficiency" could be either calculated using field measurements or modelled using a computer simulation program. The efficiency depends on process conditions such as presence of a flash tank, glycol pump type, glycol pump rate, stripping (or sparge) gas rate and other operating conditions. The presence of lighter hydrocarbons in particular will reduce the condensing efficiency.

Preliminary findings indicate that the condenser outlet temperature is a good monitoring parameter for "well-designed" condenser systems and can be used to predict control efficiency in combination with a three-phase flash calculation [3]. Therefore, condensing efficiency could be described as a function of outlet temperature. This dependence would differ for different configurations; however, it would have a characteristic "S" shape as shown in **Figure 17**. It should be noted, however, that if the phases are



not well-mixed there may be some departure from equilibrium, and the actual control efficiency will be lower than otherwise calculated.

The current air-cooler model in GRI-GLYCalc requires the user to specify a minimum approach $(T_{Ambient} - T_{condenser outlet})$ for the condenser. However, while this model accounts for ambient temperature changes throughout the year, it assumes a constant minimum approach and would not consider wind velocity or sunlight/shading. The minimum approach depends on the design of the condenser, which is not specified in GLYCalc.



Figure 17- Typical Condensing Efficiency Curve

It is also important to note that the performance of the reboiler will have a significant effect on condenser performance. The reboiler will in practice have firing cycles which means that the reboiler temperature will not be constant. When the reboiler is on, more water is distilled/stripped from the glycol and sent to the condenser. Any field testing needs to be of sufficient length to reduce the transient effects from reboiler cycling.

If the condenser is designed to handle the maximum reboiler load, the condenser exhaust temperature will remain fairly constant. If the condenser is undersized, it will not have the capacity to handle the peak reboiler load, and the condenser temperature may experience significant temperature cycling with the reboiler cycle [3].

Due to the lack of reliable models in commercial software for evaluating condenser performance, the AER requires field testing for evaluation of condenser efficiency (it is noted that many regulatory agencies accept computer modeling that has been validated with field testing [3]). The purpose of this application is to develop a stand-alone program to perform thermodynamic and heat transfer



calculations for well-known condenser configurations to allow for an alternative method to determine condensing efficiency in lieu of the AER requirement for field measurement.

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Thermodynamic Model

This section briefly describes the thermodynamics models and equations used in the developed application to predict equilibrium conditions and compositions of each phase.

A mixture is in thermodynamic equilibrium if the chemical potential of each component is equal in the phases.

$$\mu_i^{\alpha} = \mu_i^{\beta} \tag{1}$$

With manipulation, and based on definition of these properties, this equation can be re-written in terms of equality of fugacities of a component in each phase.

$$f_i^{\alpha} = f_i^{\beta} \tag{2}$$

The problem is thus transformed into the more practical issue of calculation of component fugacity in each phase. Fugacity can be calculated as follows:

$$\ln \frac{f_i}{y_i p} = \frac{1}{RT} \int_V^\infty \left(\frac{\partial p}{\partial n_i} - \frac{RT}{V}\right) dV - \ln Z$$
(3)

The problem has reduced to calculating the integral in Eq. 3. An Equation of State (EOS) provides a mathematical relationship between temperature, pressure and volume of pure compounds or mixtures and therefore could be used to calculate Eq. 3. Over the years, several EOS, especially Cubic EOS, have been proposed to describe properties of certain mixtures. Among those, the Peng-Robinson EOS has been widely used and adopted to describe the pressure-temperature-volume relationship for hydrocarbons and natural gas.

Peng Robinson

In 1976, Peng and Robinson proposed a two-constant equation that improved the liquid density prediction of previously proposed EOS. [1]

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}$$
(4)

where a is an attraction parameter and b is a repulsion parameter. These parameters are calculated based on pure compound properties such as acentric factor, critical pressure and critical temperature.

$$a = 0.45724 \frac{R^2 T_c^2}{p_c} \alpha \tag{5}$$

$$b = 0.07780 \frac{RT_c}{p_c}$$
 (5.a)

$$\alpha = \left[1 + m(1 - \sqrt{T_r})\right]^2 \tag{5.b}$$

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$$m = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2 & \omega \le 0.49 \\ 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 & \omega > 0.49 \end{cases}$$
(5.c)

Equation 4 can be rewritten in terms of compressibility factor (Z).

$$Z^{3} - (1 - B)Z^{2} + (A - 3B^{2} - 2B)Z - (AB - B^{2} - B^{3}) = 0$$
(6)

$$A = \frac{ap}{R^2 T^2} \tag{6.a}$$

$$B = \frac{bp}{RT}$$
(6.b)

Van der Waals mixing rules are used to calculate *a* and *b* for a mixture with composition of *y*.

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} y_{i} y_{j} (1 - k_{ij}) \sqrt{a_{i} a_{j}}$$
(7)

$$b = \sum_{i=1}^{n} y_i b_i \tag{8}$$

where k_{ij} is a binary interaction parameter (BIP) and has been estimated for various binary systems.

Replacing the aforementioned equations and integrating would yield an expression to calculate the component fugacity.

$$\ln \frac{f_i}{y_i P} = \frac{B_i}{B} (Z - 1) - \ln(Z - B) + \frac{A}{2^{1.5}B} (\frac{B_i}{B} - \frac{2}{A} \sum_{i=1}^n y_j A_{ij}) \ln[\frac{Z + (1 + \sqrt{2})B}{Z - (1 - \sqrt{2})B}]$$
(9)

In the two-phase flash calculation, equality of fugacity is the main numerical constraint. Additional relationships are required to estimate the amount and composition of each phase. In this work, the Rachford-Rice iterative procedure is used to obtain component composition and phase fraction. This method involves solving the following equation for F_{ν} (vapor fraction). [2]

$$h(F_{\nu}) = \sum_{i=1}^{N} (y_i - x_i) = \sum_{i=1}^{N} \frac{z_i(K_i - 1)}{1 + F_{\nu}(K_i - 1)} = 0$$
(10)

where $K_i = \frac{y_i}{x_i}$ is the equilibrium ratio and z_i is the mole fraction of component *i* in the feed. As the phase compositions are unknown, K_i is initially estimated using the Wilson equation.

$$K_{i} = \frac{P_{ci}}{P} \exp[5.37(1+\omega_{i})(1-\frac{T_{ci}}{T})]$$
(11)

Using the K-value, Eq. 10 is solved for F_{ν} using Brent's method as suggested by Naji [3]. Component composition in each phase is calculated using Eqs. 12 and 13.



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$$x_i = \frac{z_i}{1 + F_{\nu}(K_i - 1)}$$
(12)

$$y_i = K_i x_i = \frac{K_i z_i}{1 + F_\nu(K_i - 1)}$$
(13)

These compositions are used to calculate the compressibility of the liquid and vapor phases by solving Eq. 6 analytically. Eq. 6 is a cubic polynomial and depending on the coefficients might have three real roots. The acceptable root is the one which leads to the mixture with the lowest Gibbs energy.

$$g_{mixture,L} = \sum_{i=1}^{N} x_i \ln f_{Li}$$
(14)

Using Eq. 9 and compressibility, the component fugacities for the liquid and vapor phases are calculated. If the equality of the fugacity constraint (Eq. 2) is met, the calculation is terminated; otherwise the equilibrium ratio (K_i) is updated using the Successive-Substitution method (SSM) [2].

$$K_{i}^{n+1} = K_{i}^{n} \frac{f_{L_{i}}^{n}}{f_{vi}^{n}}$$
(15)

The calculation continues until $\sum_{i=1}^{\infty} \left[\left(\frac{f_{Li}}{f_{vi}} \right) - 1 \right]^2$ becomes smaller than the specified tolerance. Figure 18 shows the algorithm for this method.

SSM is the safest method for two-phase calculation: however, it becomes slow near the phase boundaries and close to the critical point. Several accelerated methods have been proposed to improve performance of SSM in these conditions. In this study, the General Dominant Eigenvalue Method (GDEM) is used as proposed by Michelsen [2]. In this method, GDEM is used to update Kvalues after five iterations of SSM. The GDEM K-value is given by Eq. 16.

$$\ln K_i^{n+1} = \ln K_i^n + \frac{\Delta u_i^{(n)} - \mu_2 \Delta u_i^{(n-1)}}{1 + \mu_1 + \mu_2}$$
(16)

$$\Delta u_i = \ln\left(\frac{f_{Li}}{f_{vi}}\right) \tag{16.a}$$

$$\mu_1 = \frac{b_{02}b_{12} - b_{01}b_{22}}{b_{11}b_{22} - b_{12}b_{12}}, \mu_2 = \frac{b_{01}b_{12} - b_{02}b_{11}}{b_{11}b_{22} - b_{12}b_{12}}$$
(16.b)

$$b_{jk} = \sum_{i=1}^{N} \Delta u_i^{(n-j)} \Delta u_i^{(n-k)}$$
(16.c)

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Phase Stability

Before performing the flash calculation, it should be determined if two phases do exist. The traditional method of checking the presence of second phase is checking the saturation conditions or performing a flash calculation, which are computationally expensive and not reliable. Michelsen [4] proposed the use of the Gibbs tangent plane criterion to check the stability of a mixture. The idea is to check if splitting the single phase to two phases would lead to lower Gibbs energy of the system. The proposed algorithm is as follows [2]:

- 1. Calculate mixture fugacity, f_{zi}
- 2. Estimate K-values using Wilson correlation (Eq. 11)
- 3. Calculate mole numbers in second-phase. $((Y_i)_V = z_i(K_i)_V)$
- 4. Sum the mole numbers and calculate mole fractions.

$$S_{v} = \sum_{i=1}^{N} (Y_{i})_{V}; \ (y_{i})_{V} = \frac{(Y_{i})_{V}}{S_{v}}$$

- 5. Calculate fugacity of second-phase, f_{Vi}
- 6. Calculate fugacity ratio for SSM, $(R_i)_V = \frac{f_{Zi}}{(f_{vi})_V}$
- 7. Check if $(\sum_{i=1}^{N} (R_i 1)^2 < \varepsilon$
- 8. If convergence is not reached, update K-values using Eq. 15.
- 9. Check if problem is converging to a trivial solution. $\sum_{i=1}^{N} (\ln K_i) < 1E 4$
- 10. If a trivial solution is not indicated, go to step 3.

These steps are for checking if the vapor is present as second phase. The same analysis should be done to check if the liquid is present as the second phase. Note that the equations in steps 4, 6 and 8 would differ for liquid.

The mixture is stable if both tests yield to $S \le 1$ or both tests converge to a trivial solution or if one test converges to trivial solution and the other gives $S \le 1$. Only one test indicating $S \ge 1$ is enough to confirm the presence of the second-phase.

Calculation of liquid fugacity

An equation of state (EOS) could be used to calculate the fugacity of components in two phases, which is referred to as $\phi - \phi$ approach. However, calculating liquid fugacity using EOS is only applicable to ideal solutions, where interaction between components in the liquid phase is negligible [5]. As this application is intended to model the still vent, which is mostly water vapor, this non-ideality should be modelled (given the polar non-ideal nature of water mixtures). To address the presence of hydrogen-bonding and polar molecules in the liquid, liquid fugacity is calculated using Excess Gibbs Energy models. Using these models, the fugacity of liquid is calculated as:

$$f_i^L = \gamma_i x_i f_i^o \tag{17}$$

where γ_i is activity coefficient and f_i^o is fugacity of pure liquid at standard conditions.

$$f_i^o = \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i^L \left(P - P_i^{sat}\right)}{RT}\right]$$
(18)



The exponential term is known as the Poynting factor and is close to unity for most compounds. ϕ_i^{sat} is the fugacity coefficient of the pure compound at saturation conditions. In the current version of the application $f_i^o = P_i^{sat}$, which provides a very good approximation of f_i^o as suggested by Reid et. al [6].

Activity coefficients are calculated using the proposed experimental correlations for Excess Gibbs energy, G_{ex} . In the current application, Non-random two liquid (NRTL) expressions are used to calculate γ_i . NRTL belongs to the local-composition models that are based on the assumption that local composition around a molecule is different from the bulk composition. NRTL is capable of modeling most non-ideal systems including liquid-liquid equilibrium as well as azeotropic systems [7]. The NRTL expression for calculating γ_i in multicomponent mixture is as follows [7, 8]:

$$\ln \gamma_i = \frac{\sum_{j=1}^n x_j \tau_{ji} G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} (\tau_{ij} - \frac{\sum_{m=1}^n x_m \tau_{mj} G_{mj}}{\sum_{k=1}^n x_k G_{kj}})$$
(19)

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{19.a}$$

$$\tau_{ij} = \frac{a_{ij} + b_{ij}T}{RT}$$
(19.b)

where $\alpha_{ij}, a_{ij}, a_{ji}, b_{ij}$, and b_{ji} are five adjustable parameters which are determined experimentally or estimated for binary pairs.

Using activity coefficient models requires the vapor pressure of the pure compound at operating temperature. Vapor pressure is only meaningful below the critical point of the compound, while the still vent includes light hydrocarbons, with critical points below the operating temperature. One could extrapolate the vapor pressure correlation and use the values to calculate the liquid fugacity. However, for the components with very low critical temperature, this solution is not applicable as it yields to unreliable results. For these components, Henry's law is used to calculate the fugacity of the liquid. These components include Methane, Ethane, Hydrogen, Helium, Carbon Dioxide, and Hydrogen Sulfide. Henry's coefficient is calculated using Eq. 20 [7].

$$\ln H_{ij} = A + \frac{B}{T} + C \ln T + DT$$
⁽²⁰⁾

where *A*, *B*, *C*, and *D* are available from the ASPEN HYSYS database.

To estimate $H_{i,mixture}$, the following mixing rule is used [9]:

$$\ln H_{i,mixture} = \frac{\sum_{j=1}^{nc} \ln H_{ij} x_j V_{c,j}^{\frac{2}{3}}}{\sum_{j=1}^{nc} x_j V_{c,j}^{\frac{2}{3}}}$$
(21)

Finally, the liquid fugacity for these components is calculated using Eq. 22.

$$f_i^L = H_{i,mixture} x_i \tag{22}$$



Three-phase flash calculation

Based on the operating conditions and composition of the stream, two distinct liquid phases may exist in equilibrium with a vapor phase. In that case, the first flash calculation would break down the stream into an aqueous phase and mixture of vapor and liquid. Performing the flash calculation on this mixture stream would yield three separate phases and three sets of compositions. Therefore, after the first flash calculation, phase stability analysis is performed on the resulting vapor phase. If the vapor is detected to be unstable, three phase flash calculation would be performed.

The three phase flash calculation is based on a modified version of the Rachford-Rice equation to account for presence of 3 phases.

$$\sum_{i=1}^{N} (y_i - x_i^I) = \sum_{i=1}^{N} \frac{z_i}{F_{L^I} (1 - K_i^I) + F_{L^{II}} \left(\frac{K_i^I}{K_i^{II}} - K_i^I\right) + K_i^I} = 0$$
(23)

$$\sum_{i=1}^{N} (x_{i}^{II} - 1) = \sum_{i=1}^{N} \frac{z_{i} \frac{K_{i}^{I}}{K_{i}^{II}}}{F_{L^{I}} (1 - K_{i}^{I}) + F_{L^{II}} \left(\frac{K_{i}^{I}}{K_{i}^{II}} - K_{i}^{I}\right) + K_{i}^{I}} - 1 = 0$$

$$K_{i}^{I} = \frac{y_{i}}{x_{i}^{I}}$$
(23.a)
$$(23.a)$$

$$K_i^{II} = \frac{y_i}{x_i^{II}} \tag{23.c}$$

The Newton-Raphson method is used to solve these equations.

The following tables show the results of two sample runs of the Process Ecology flash code and its comparison with HYSYS. The results are within 1% of each other. Note that the difference in results is due to difference in pure compound properties between HYSYS and the developed model using Peng-Robinson EOS in liquid and vapour phases.

 Table 7 - Comparison of thermodynamic model with HYSYS (Two-Phase flash)

	Feed	Vapor (Model)	Vapor (HYSYS)	Liquid (model)	Liquid (HYSYS)
Phase fraction		0.1247	0.1243	0.8726	0.8757
Methane	0.1	0.4963	0.4952	0.0422	0.043892
Ethane	0.2	0.3095	0.3101	0.1840	0.1843
Propane	0.3	0.1295	0.1306	0.3249	0.3240
i-Butane	0.4	0.0647	0.0640	0.4489	0.4477
Temperature : -10)C F	Pressure: 1000 kPa	Ig		



	Feed	Vapor (Model)	Vapor (HYSYS)	Liquid (model)	Liquid (HYSYS)	Aqueous (model)	Aqueous (HYSYS)
Phase		0.2085	0.2085	0.0116	0.0115	0	0
fraction							
Methane	0.15	0.7180	0.7186	0.0267	0.0264	0	0
Ethane	0.05	0.2350	0.2351	0.0863	0.0851	0	0
Propane	0.01	0.0441	0.0442	0.0691	0.0680	0	0
Benzene	0.01	0.0026	0.0026	0.8178	0.8203	0	0
Water	0.78	0.0026	0.0029	0	0.0001	1	1
Temperature : -1	0 C	Pressure: 10	00 kPag				

Table 8 - Compar	ison of thermodyn	amic model with HY	YSYS (Three-Phase flash)

The developed thermodynamic model was also validated against Aspen HYSYS using 6 representative still column compositions over the range of expected condenser outlet temperatures.



Figure 19 - Vapor fraction of HYSYS vs. developed thermodynamics model for still vent composition







Figure 20 - Benzene K-factor of HYSYS vs. developed thermodynamics model for still vent composition

Figure 19 and **Figure 20** show that the results of the thermodynamic model are within 2% of HYSYS predictions.

Estimation of mixture properties

The heat transfer model requires properties of the liquid and gas/vapor. These properties include density, thermal conductivity, specific heat capacity, and viscosity. Viscosity of the vapor mixture is calculated using the Reichenberg method [6].

$$\mu_{mV} = \sum_{i=1}^{n} K_i (1+2\sum_{j=1}^{i-1} H_{ij}K_j + \sum_{j=1}^{n} \sum_{j=1}^{n} H_{ij}H_{ik}K_jK_k$$
(24)

$$K_{i} = \frac{y_{i}\mu_{i}}{y_{i} + \mu_{i}\sum_{k=1}^{n} y_{k}H_{ik}[3 + \frac{2M_{k}}{M_{i}}]}$$
(24.a)

$$H_{ij} = \left[\frac{M_i M_j}{32(M_i + M_j)^3}\right]^{0.5} (C_i + C_j)^2 \frac{\left[1 + 0.36T_{rij}(T_{rij} - 1)\right]^{\frac{1}{6}} F_{Rij}}{T_{rij}^{0.5}}$$
(24.b)

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$$C_{i} = \frac{M_{i}^{0.25} T_{ri}^{0.5}}{(\mu_{i} [1 + 0.36T_{ri} (T_{ri} - 1)]^{\frac{1}{6}} F_{Ri})}$$
(24.c)

$$T_{rij} = \frac{T}{\left(T_{ci}T_{cj}\right)^{0.5}}$$
 (24.d)

$$F_{Ri} = \frac{T_{ri}^{3.5} + (10\mu_{ri})^7}{T_{ri}^{3.5}[1 + (10\mu_{ri})^7]}$$
(24.e)

$$\mu_{ri} = 52.46 \frac{\mu^2 P_c}{T_c^2} \tag{24.f}$$

where F_{Rij} is the polar correction and M_i is molecular weight of component i.

Thermal conductivity of the gas mixture is calculated according to the Wassiljewa correlation [6].

$$k_{mV} = \sum_{i=1}^{n} \frac{y_i k_i}{\sum_{j=1}^{n} y_j A_{ij}}$$
(25)

$$A_{ij} = \frac{\left[1 + \left(\frac{k_{tri}}{k_{trj}}\right)^{0.5} \left(\frac{M_i}{M_j}\right)^{0.25}\right]^2}{\left[8\left(1 + \frac{M_i}{M_j}\right)\right]^{0.5}}$$
(25.a)

$$\frac{k_{tri}}{k_{trj}} = \frac{\Gamma_j [\exp(0.0464T_{ri}) - \exp(-0.2412T_{ri})]}{\Gamma_i [\exp(0.0464T_{rj}) - \exp(-0.2412T_{rj})]}$$
(25.b)

$$\Gamma_i = 210 \left(\frac{T_c M^3}{P_c^4}\right)^{\frac{1}{6}}$$
 (25.c)

Thermal conductivity of the liquid is calculated according to the Li correlation [10]

$$k_{mL} = \sum_{i=1}^{n} \sum_{j=1}^{n} \phi_i \phi_j \frac{2k_i k_j}{k_i + k_j}$$
(26)

$$\phi_i = \frac{x_i \rho_{L,i}^{-1}}{\sum_{j=1}^n x_j \rho_{L,j}^{-1}}$$
(26.a)

The viscosity of liquid requires use of group-contribution methods and one of the following methods: Grunberg and Nissan, UNIFAC-Visco, or Teja and Rice. In the current version of the Application, viscosity of the liquid mixture is assumed to be the same as the viscosity of water for the operating temperature [10].

The density of the vapor/gas mixture is calculated using the Peng Robinson EOS. Currently, the density of liquid is also calculated using the Equation of State. Alternatively, liquid density could be



estimated more accurately using proposed correlations. The appropriate correlation would be implemented in the next version of the application.

The heat capacity of the mixture is calculated using a weighted average.

$$C_{p,mixture} = \sum_{i=1}^{n} x_i C_{p_i}$$
(27)

All of the described methods for calculation of mixture properties are interpolative, which means they require properties of the pure compounds. The properties of pure compounds are calculated using correlations and constants given in the DIPPR 801 Database[11].

The correlations are only valid over a range of specified temperature. For instance, the correlation for estimation of thermal conductivity of methane in the liquid phase is only valid for temperatures below the critical point. If the operating temperature is above the critical point of methane, and methane is detected in the liquid phase, the thermal conductivity is assumed to be that of methane at the critical point. The same approach is used to estimate other properties of components outside the range of applicability of the correlation.



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Heat Transfer Model

Pipe

Pipe segment(s) are used to transfer the still vent overhead vapor to the tank or condenser. The pipe would be typically uninsulated to aid the cooling of the vapor; on the other hand, the last section may be insulated to avoid freezing.

In the Application, the user can specify the pipe diameter, and the respective pressure drop and heat loss will be calculated.

Alternatively, if the pipe diameter is not provided, the pipe is designed based on the flow rate and acceptable pressure drop (2 psi / 100 ft). Standard Schedule 40 pipes are used to size the pipe, as shown in the following Table.

Size (Inches)	1/8	1/4	3/8	1/2	3/4	1*	1.25	1.5	2*
External Diameter	0.405	0.45	0.675	0.84	1.05	1.315	1.66	1.9	2.375
Internal Diameter	0.269	0.364	0.493	0.622	0.824	1.049	1.38	1.61	2.067
Size (Inches)	2.5	3*	3.5	4*	5	6*	8	10	12
Size (Inches) External Diameter	2.5 2.875	3 * 3.5	3.5 4	4 * 4.5	5 5.563	6 * 6.625	8 8.625	10 10.75	12 12.75

Table	q	- Sch	nedule	40	nine	sizes
Iable	Э.	- 30	leuule	40	pipe	31203

* Most likely pipe sizes for pipe segment from still vent to condenser. A future version of the Application may limit the pipe selection accordingly.

The pipe pressure drop is calculated using:

$$\Delta P = \frac{f}{2} \frac{L}{D} \rho v^2 \tag{28}$$

where *f* is friction factor coefficient, *L* is pipe length specified by user, *D* is internal diameter of the pipe, ρ is density of the fluid, and *v* is velocity. Friction factor is calculated using the following equation. [1]

$$f = \begin{cases} \frac{64}{Re} & Re < 2320\\ \left(-1.52 \log \left(\frac{\frac{\epsilon}{D}}{7.21}\right)^{1.042} + \left(\frac{2.731}{Re}\right)^{0.9152} \right)^{-2.169} & Re > 2320 \end{cases}$$
(29)

where $Re = \frac{\rho v D}{\mu}$, and ϵ is pipe roughness assumed to be 150 microns. If the user has not specified the pipe size, the smallest pipe where $\frac{\Delta P}{L} < 2 \frac{psi}{100 ft}$ is used. Note that pressure drop is calculated using single-phase flow correlations which might prevail only in the first section of pipe. Using multiphase

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flow correlations in HYSYS and the developed code, the results indicate pressure drop would be very low; therefore, it was decided the single-phase correlations were adequate to calculate pressure drop.

The heat transfer mechanism from the pipe is shown in **Figure 21**. In the model, the user can specify if the pipe is insulated or not. Insulation is assumed to be 2 inches thick.



Figure 21 - Cross-section of pipe

$$Q = U.\pi.D_3.(T_{in} - T_{Amb})$$
(30)

where U is the overall heat transfer coefficient:

$$U = \frac{1}{\frac{D_3}{h_{in}D_1} + \frac{D_3\ln\left(\frac{D_2}{D_1}\right)}{2.k_{pipe}} + \frac{D_3\ln\left(\frac{D_3}{D_2}\right)}{2.k_{Insulation}} + \frac{1}{h_{out}}}$$
(31)

where h_{in} is the heat transfer coefficient for fluid inside the pipe, k_{pipe} is the conductivity of the pipe, $k_{insulation}$ is the conductivity of the insulating layer, and h_{out} is the heat transfer coefficient of ambient air.

The inner heat transfer coefficient h_{in} is calculated using correlations obtained from the literature which are applicable for a range of flow conditions in rough pipe. [2]



$$h_{in} = \begin{cases} 4.364 \frac{k_{fluid}}{D_{in}} & Re < 2320 \\ \frac{\left(\frac{f}{8}\right)(Re - 1000)\Pr}{1 + 12.7\left(\frac{f}{8}\right)^2(Pr^{0.667} - 1)} & \frac{k_{fluid}}{D_{in}} & Re > 2320 \end{cases}$$
(32)

where *f* is friction factor and $Pr = c_p \mu/k$ is the Prandtl number. Currently, the flow is assumed to be fully developed and the effect of the entrance region on heat transfer has been neglected.

Heat loss from an uninsulated surface to air is a combination of loss due to radiation and loss by convection ($h_{out} = h_{Radiation} + h_{wind}$). [3]

$$h_{Radiation} = \frac{0.1713\sigma}{(T_{outsidewall} - T_{ambient})} \left[\left(\frac{T_{outsidewall}}{100} \right)^4 - \left(\frac{T_{Ambient}}{100} \right)^4 \right]$$
(33)

where σ is emissivity of pipe wall which is assumed to be 0.9.

The convective heat transfer coefficient due to wind is calculated as follows:

$$h_{wind} = \frac{0.11C_{p_{air}}G^{0.6}}{D^{0.4}} \tag{34}$$

where $G = \rho_{air}V_{Wind}$ is the mass velocity of the air. If the wind velocity is zero, heat transfer is by natural convection and its coefficient is calculated using the following equation.

$$h_{wind} = \frac{0.27(T_{outsidewall} - T_{Ambient})^{0.25}}{D^{0.25}}$$
(35)

The outside wall temperature of the pipe is unknown. The following equation is used as an initial estimate:

$$T_{outsidewall} = 0.75T_{ambient} + 0.25T_{fluid}$$
(36)

The T_{outsidewall} term is updated using the steady-state assumption of the heat transfer process:

$$Q = UA_{out}(T_{fluid} - T_{Ambient}) = U_{out}A_{out}(T_{outsidewall} - T_{Ambient})$$
(37)

$$T_{outsidewall} = \frac{U}{U_{out}} \left(T_{fluid} - T_{Ambient} \right) + T_{Ambient}$$
(38)

The Brent root-finding algorithm is used to update $T_{outsidewall}$ in each iteration. The iteration is continued until $|T_{outsidewall}^{n+1} - T_{outsidewall}^{n}| < 0.00001$.



Note that all the correlations used in this section are for single phase flow and condensation heat transfer coefficients are not used. The calculated heat loss was compared with that of HYSYS, to ensure this is a reasonable simplification. The following table compares the predicted heat loss and pressure drop from the model and Aspen HYSYS.

	∆ <i>P</i> (psi) (Model)	∆ <i>P</i> (psi) (HYSYS)	Heat loss (BTU/hr) (Model)	Heat loss (BTU/hr) (HYSYS)	$\Delta T(F)(HYSYS)$
Case 1	8.127E-5	1.156E-4	1877	1603	48.5
Case 2	1.30E-5	1.52E-5	3373	3124	49.2

Table 10 - Comparison of heat transfer and pressure drop model in pipe

The results of the developed model are reasonably close to those calculated by HYSYS. Accuracy of the model could be improved by using pipe increments and variable thermal properties of the fluid along the pipe but this is not considered to be necessary.

Heat loss from above-ground storage tank

This section describes a procedure to calculate heat loss from a storage tank as shown in **Figure 22**. The correlations and the methodology used to model the heat loss are taken from the article "Predict Storage-Tank Heat Transfer Precisely." [4].

Individual heat transfer coefficients in this configuration are shown in **Table 11**.

	Dry wall	Wet wall	Roof	Bottom
Inside	h_{VIn}	h_{LIn}	h_{VRoof}	$h_{LBottom}$
Outside	$W_f h_{Air} + h_{Rad}$	$W_f h_{Air} + h_{Rad}$	$W_f h_{Air} + h_{VRad}$	$h_{LGround}$
Wall	k_{metal}/t_{metal}	k_{metal}/t_{metal}	k_{metal}/t_{metal}	k_{metal}/t_{metal}

Table 11 - Individual heat transfer coefficients for storage tank

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Figure 22 - Schematic of vertical storage tank

Heat loss from dry surface is calculated using the following equation:

$$q_{dry} = \left(\frac{1}{\frac{1}{h_{VIn}} + \frac{1}{W_f h_{Air} + h_{Rad}} + \frac{t_{metal}}{k_{metal}}}\right) (\pi D(L - L_w))(T_{Liquid} - T_{Ambient})$$
(39)

The same approach could be used to calculate heat loss from the other surfaces. h_{Rad} is the heat transfer coefficient for radiation and is calculated as described previously. W_f is the wind enhancement factor and is calculated using the following equation:

$$W_f = 0.0659(T_{Fluid} - T_{Ambient})^{0.2441} * V_{wind} + 1$$
(40)

Heat transfer coefficients of surfaces are calculated based on the orientation of the surface and properties of respective fluid.

$$Nu_{roof} = 0.14 (Gr \,\mathrm{Pr})^{0.33} \tag{41}$$

$$Nu_{LBottom} = 0.27 (Gr \text{ Pr})^{0.25}$$
 (42)

Heat transfer coefficient of ground is calculated based on heat conduction for a semi-infinite solid:

$$h_{LGround} = \frac{8k_{Ground}}{\pi D} \tag{43}$$



Heat transfer coefficients for vertical surfaces $(h_{Air}, h_{LIN}, h_{VIn})$ are calculated based on the following sets of equations.

$$Nu = \begin{cases} 0.138Gr^{0.36}(Pr^{0.175} - 0.55) & Gr > 10^9\\ 0.0295Gr^{0.40}Pr^{0.47}(1 + 0.5Pr^{0.67})^{-0.40} & Gr < 10^9 \end{cases}$$
(44)

Outside and inside wall temperature are required for estimation of heat transfer coefficients which are calculated through an iterative process as described in the Pipe section of the Heat Transfer Model.

This method was extended to account for the inlet gas being steadily introduced in the tank vapour space as well as the fact that vapour is leaving the tank. The temperature of the vapor space is therefore unknown, and the following iterative algorithm is used to calculate this temperature:

- 1. Guess an initial temperature based on the inlet and ambient temperature.
- 2. Perform an iterative process to calculate inside/outside wall temperatures.
- 3. Calculate the heat losses using the coefficients obtained in Step 2.
- 4. Calculate the temperature of the vapor space based on the condensation curve and the heat loss calculated in Step 3.
- 5. Calculate the equilibrium condition in outlet temperature and check if the heat balance (Enthalpy In = Enthalpy Out) is met. If the condition is not met, guess a new temperature and redo the calculation from Step 2.



Heat loss from TankSafe condenser

The TankSafe condenser is one of the more common condensers used in Alberta to reduce benzene emissions from still vents in dehydration facilities. The TankSafe design is shown in **Figure 23** and **Figure 24** [5].



Figure 23 – TankSafe Condenser Design – Side View (Source: TankSafe Patent)



Figure 24 - TankSafe Condenser Design - Top View (Source: TankSafe Patent)



It is noted that proprietary drawings were also provided which show baffle dimensions and which formed the basis of the model. The design could be divided into two components: Condensing and Storage.

The Storage component is the lower part of the design and provides the volume for storing condensed water and hydrocarbon. Storage includes two concentric tanks. The outer one is used as a secondary containment and would only be used to prevent a spill if the inner tank failed.

Condensing occurs in the upper part of the TankSafe condenser and in practice its size and design is independent of storage capacity. The condenser consists of 11 baffles, one of which is used as an isolation chamber to prevent heating of the outlet vapor. There is a deflector in each baffle to extend the vapor retention time and ensure maximum contact with the heat transfer area.

The model breaks down the condenser into 10 baffles and calculates heat transfer from each baffle. The modeled configuration is shown in **Figure 25**.

Heat transfer coefficients are calculated based on flow over a flat vertical surface. When the inlet vapor is above its dew point, the following equation set is used to calculate heat transfer coefficients for cooling of the vapor [6].

$Nu_{cooling} = \begin{cases} 0.664 \ Re^{0.5} Pr^{0.33} \\ 0.037 \ Re^{0.8} Pr^{0.33} \end{cases}$	Re < 5E + 5 Re > 5E + 5	(45)
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Figure 25 - Condenser baffle as implemented in model

Each baffle is broken down to two flat vertical surfaces; the width (which considers the presence of a deflector), is important in determining the vapor velocity.

The vapour will condense once it reaches the dew point of the mixture. In this case, condensation heat transfer correlations are used to estimate the heat transfer [2].

$$Nu_{condensation} = \frac{h_L \left(\frac{v_L^2}{g}\right)^{0.33}}{k_L}$$

$$= \begin{cases} 0.943 P_{index}^{-0.25} & P_{index} \le 15.8 \\ \frac{1}{P_{index}} (0.68 P_{index} + 0.89)^{0.82} & 15.8 \le P_{index} \le 2530 \\ \frac{1}{P_{index}} \left[(0.024 P_{index} - 53) P r_L^{0.5} + 89 \right]^{\frac{4}{3}} & P_{index} \ge 2530 \end{cases}$$
(46)

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$$P_{index} = \frac{k_L L (T_{dew} - T_{insidewall})}{\mu_l h_{fg} \left(\frac{\nu_L^2}{g}\right)^{0.33}}$$

where $v_L = \frac{\mu_L}{\rho_L}$ is the kinematic viscosity of the liquid phase, μ_l is the dynamic viscosity of the liquid phase, and h_{fg} is the modified heat of condensation of vapor which is calculated from the following equation.

$$h_{fg} = \Delta H_{condensation} (1 + 0.68Ja)$$

$$Ja = \frac{C_{p_L} (T_{Dew} - T_{Insidewall})}{\Delta H_{condensation}}$$
(47)

Heat transfer coefficients of ambient air, including convection and radiation, are calculated using the previously specified correlations. In this model, wall temperature is calculated using the iterative procedure described in the pipe heat transfer section.

Note that the vertical surfaces in the TankSafe design are curved and the width between the baffle and heat transfer surface at the base of the chamber is different than the width between the baffle and the heat transfer surface at the peak of the chamber. Therefore, the Reynolds number should be calculated using an average value for the velocity.

This model takes into account the effect created by the presence of non-condensable gases in the flow. As pointed out by Valdepeñas et al. [7] and Nahabti [8], the presence of non-condensables in the gas mixture reduces the heat transfer coefficient considerably. For instance, the presence of 1 percent air in steam reduces the heat transfer coefficient by 50%. The non-condensable gas accumulates in the vapor-liquid interface and reduces the heat transfer through two distinct mechanisms:

- The interface introduces a new layer that the gases must diffuse through before reaching the surface
- Accumulation of non-condensable gas in the interface increases the partial pressure of these gases near the interface, which would lead to diffusion of these gases back to the bulk gas.

There are different approaches for modelling this phenomenon. One approach is through the introduction of a "degradation factor" into the correlations. This factor would depend on the mass fraction of non-condensables in the mixture and is calculated experimentally. [8]

$$Nu_{modified} = f(y_{nc})Nu_{condensation}$$
(48)

$$f(y_{nc}) = K(1 - 0.946y_{nc} + 4.989y_{nc}^2 - 4.135y_{nc}^3)(\frac{1 - y_{nc}}{1 + 15.48y_{nc}})$$
(49)

where y_{nc} is the mass fraction of non-condensables in gas mixture and *K* is a correction factor.



These equations are used as they are straightforward and are able to predict the heat transfer reasonably well as shown by Valdepeñas et al. [6]. This approach could be implemented in the model by assuming methane, ethane, nitrogen, helium, hydrogen, hydrogen sulfide, and carbon dioxide are non-condensable.

In the original version of Equation 49, *K* is reported to be 1.0; however, in the developed application, a value of 1.5 is used, since the original value was developed to describe the presence of non-condensables at high pressure steam in fusion reactors, which would overpredict the degradation factor for this application.

However, this approach neglects mass and heat transfer resistance in the presence of more volatile components such as propane that will only condense at lower temperatures. These components will introduce extra heat and mass transfer resistance in the condensing process that should be accounted for. The other complication in modeling the condensation of vapor mixtures is the fact that the process is not isothermal and the condensation range can be large (greater than 100 C). Thus, there are sensible heat effects in both vapor and liquid that should be considered in modeling the process [9]. To address these issues, analytical solutions are approximated using equilibrium and non-equilibrium methods.

An equilibrium method was originally proposed by Silver and extended by Bell and Ghaly as described by Rohsenow et. al [10]. This approach assumes there is a local equilibrium between the vapour and liquid throughout the condenser. The heat transfer coefficient for gas condensation is written as:

$$\frac{1}{h_{effective}} = \frac{1}{h_{condensing film}} + \frac{Z}{h_{gas}}$$
(50)

$$Z = \frac{q_g}{q} = v_f C_{p_g} \frac{\Delta T}{\Delta H}$$
(51)

Where $h_{condensing film}$ is the heat transfer coefficient for condensation and is calculated using Eq. 45. *Z* is the ratio of sensible heat to total heat, and $\frac{\Delta T}{\Delta H}$ is calculated from the condensation curve. The equilibrium condensation curve could be one of the following two types:

- Integral: Condensate and vapour are travelling parallel and are well-mixed along the condensing path.
- Differential: Condensate is removed from the vapour as soon as it is formed.

In the following equation, h_{gas} is the heat transfer coefficient for gas and should be corrected for mass transfer resistance [11].

$$h_{gas} = h_{gas}^* \left(\frac{\phi}{\exp(\phi) - 1} \right)$$
(52)

$$\phi = \frac{\sum_{i=1}^{n} m_c C_{p_{g_i}}}{h_{gas}^*}$$
(52.a)



In this application, the integral condensation curve is calculated for the given mixture after normalizing for non-condensables. Non-condensable components would only be cooled down and their presence is accounted for by using these equations. The dew point and bubble points of the mixture would be calculated using the thermodynamic model and the following criteria:

$$\begin{cases} v_f = 0 & T = T_{Bubble} \\ v_f = 1 & T = T_{dew} \end{cases}$$
(53)

The range between the bubble and dew points is divided into 10 segments and the change in enthalpy calculated based on the heat of condensation and sensible heats of the liquid and vapor phases [9]. Vapor fraction, liquid and vapor phase enthalpies and compositions are calculated in the midpoint of each range.

Knowing the condensation curve, the heat transfer coefficient could be calculated using Eq. 52. The resulting heat loss and condensation curve would be used to calculate the temperature and composition of the mixture after each baffle.

In this application, two distinct liquid phases might exist in equilibrium with each other. In this condition, condensation might occur in the drop-wise regime as the hydrocarbon and aqueous phase are immiscible [10]. Kern [12] has laid out a detailed procedure for rating and designing the condenser in the presence of two immiscible phases. Currently, the developed application neglects the possible effect of the presence of immiscible phases in the condensation regime.

Different approaches for modeling the condenser

There are several approaches to modeling the TankSafe condenser gas/liquid behaviour:

1. Gas and liquid are travelling together in the baffles. In this case, it is assumed that the formed liquid after condensation would remain entrained in the vapor and would be carried with the vapour along the baffles. (Integral condensation) (**Figure 26**: T1 to C^{^m})

2. Gas and liquid would be separated after each baffle. In this case, a new vapor would result from each baffle (along the dew point curve). A new bubble point/condensation curve would be calculated for the new vapour. (**Figure 26**: T1 to A to A' to A'')

3. Condensed liquid would drop out after each stage; however the vapor would remain in equilibrium with the same liquid. This approach is the same as the approach #1 but in this approach the liquid would drop out after each stage.

4. A hybrid approach where some of the liquid would be carried to the next baffle.

The selection of the appropriate criteria for modeling approach would depend on the results from field measurements. In the current version of the application, the second approach is used, assuming liquid is dropped out after each stage of the condenser and a vapor with new composition is sent to the next baffle.



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Ambient Model

RWDI Air Inc. was contracted to create two weather datasets for the ambient data required for the PTAC condenser app. These datasets are:

- Alberta-wide gridded weather dataset based on the AB-MM5 dataset at 12km resolution. This dataset covers all of Alberta as well as a small section of British Columbia and Saskatchewan. **Figure 27** shows the range that this ambient dataset covers.



Figure 27- Ambient data for DLS-based locations

- Gridded-weather data for north-eastern British Columbia. BC data is based on the BC Ministry of Environment (MOE) 5-year WRF dataset at 4 km resolution. This weather dataset covers the section of BC where all the Dehydration and Refrigeration facilities are located. **Figure 28** shows the geographical boundaries of this ambient dataset.



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Figure 28- Ambient data range for North Eastern British Columbia

The ambient data is comprised of monthly averaged values of wind speed and temperature at 2m for 5 years for all the gridpoints. This monthly ambient data along with latitude/longitude and the elevation from sea level were provided in CSV format. The data is now hosted in a database and integrated in the PTAC Condenser Application.

Model validation

Comparison of Benzene removal efficiencies

The Thermodynamic/Mixture property/Heat transfer models described in the last two sections were programmed in C# and the results of the model were compared to Exova Total Capture Tests (TCT) available to Process Ecology. Due to improvements in the test results (relative to SGS), only Exova results were used for validation of the model. **Figure 29** shows the mass imbalance of the Methane difference in the still and condenser vents in the Exova TCT tests over the time. As discussed in **Review of Total Capture Tests** section, the mass balance of methane (still overhead vs. condenser vent) would be regarded as a good indicator of the quality of the TCT, as the methane in the still vent would be expected to remain in the vapor phase and come out in the condenser vent. **Figure 29** shows that with the exception of two recent TCT tests completed in September 2016, the quality of Exova TCT tests (as measured by methane balance) have improved over time.







Figure 29 - Methane balance of Exova TCTs over time

Figure 30 shows the comparison of benzene removal efficiencies as reported by the TCT vs. model output, for the tests which show poor methane balance and therefore would be regarded as poor TCTs. In all these cases, the model predicts a much lower Benzene reduction efficiency. These results indicate that the model could potentially be used to identify problematic total capture tests.





Figure 31 provides the comparison of Benzene reduction efficiency for a set of TCTs where the report indicates that no stripping gas was used; however either the high purity of lean glycol or high methane flow rate in the still vent implies the likelihood of stripping gas use. There are three bars in Figure 31 for each TCT, one showing the efficiency as reported by TCT, one calculated efficiency assuming no stripping gas was used, and one showing the calculated efficiency assuming stripping gas was used. In the latter case, the stripping gas flow rate was adjusted to match the methane flow rate in the still vent as reported by TCT. The results clearly show that with no stripping gas, the model predicts a



higher benzene removal efficiency and adding the stripping gas improves the match to the reported reduction efficiency.



Figure 31 - Comparison of model and TCT Benzene removal efficiency for TCTs with high lean glycol purity

Figure 32 shows comparison of the benzene removal efficiencies for the datasets not included in **Figure 30** and **Figure 31**. The datasets in this graph could be considered as more reliable TCTs. The results clearly show a good match between the model-predicted and TCT-reported benzene removal efficiencies for almost all the datasets. In the plants associated with TCT 10, TCT11, and TCT 25, enhanced condensation equipment such as finned tubes and custom roughneck coolers are reported, which explains the lower benzene removal efficiencies calculated by the model, as the model only accounts for the cooling and condensation in a TankSafe or a generic tank.



Figure 32 - Comparison of benzene removal efficiencies for TCTs not included in Figures 28 and 29



Comparison of condenser vent temperature

In May 2015, Exova started reporting the condenser vent temperature in the TCT report. The reported operating conditions along with the ambient temperature and the wind velocity from the AB-MM5 dataset were used in the model to calculate the condenser vent temperature and compare the results to the reported temperatures. **Figure 33** shows the result of the comparison. The error bars on the TCT-reported values in **Figure 33** identify the reported range for the condenser vent temperature in the TCT report. In general, there is a good agreement between the model and the reported tank vent temperatures especially where smaller fluctuations are reported in the condenser vent temperature.



Figure 33- Comparison of the condenser vent temperature

Condenser vent temperature survey

One of the operating companies in Alberta measured the TankSafe vent temperature at one of their facilities over the course of one month. During this period, the condenser vent temperature, along with the ambient temperature was recorded 3 times per day at 8:00 AM, 12:00 PM, and 4:00 PM. The result of this survey was shared with Process Ecology to help with validation of the condenser model. Process Ecology used the average wind velocity from the closest Environment Canada station during the measurement period, along with the latest gas sample, operating conditions, and the reported ambient temperatures to run the model and compare the measured temperature with the model-predicted condenser vent temperatures.







Figure 34 - Condenser vent temperature survey

Given all the uncertainty in the ambient conditions and operating conditions, the model shows a very good match to the measured condenser vent temperatures.

2015 Site visit

As a part of a model validation effort in 2015, Process Ecology organized a site visit in collaboration with an oil and gas producer. There were two plants in this location, each of them with its own TankSafe condenser. These plants are referred to as Plant 1 and Plant 2 in this report.

Plant 1 included inlet separation, inlet compression, TEG dehydration, glycol regeneration, JT Valve, LTS separator, stabilizer, VRU compression, and sales gas compression.

In this plant, the gas is first dehydrated and then its pressure is reduced (JT expansion). After the JT valve, the stream is sent to an LTS where the hydrocarbon liquid is separated and sent to stabilizer. Stabilizer overheads are recycled to the inlet using a VRU compressor.

This is the configuration of the glycol dehydration/regeneration section in Plant 1:

- Trayed contactor
- Kimray 9015 energy-exchange pump
- No flash tank
- Still vent routed to TankSafe

Throughout the day, various operating data was gathered. In general, the operating data stayed relatively constant through the duration of observations. These are the observations for <u>Plant 1</u>:

 The facility incorporates TEG dehydration followed by a JT valve and LTS. Because the gas is dehydrated before entering the JT process, EG injection is not required, and therefore there is no EG regeneration.



- The still vent outlet temperature was around 70°C, which is an indicator for the presence of a reflux coil. Due to location of the coil, it was not possible to estimate the inlet/outlet temperature using a temperature gun.
- The glycol reboiler was rated at 75 kW. The TankSafe inlet temperature was varying between 60 and 70°C, which is an indicator of reboiler cycling. The change in the TankSafe inlet temperature was observed to occur every 5-10 minutes.
- The first stage of the test (condenser tank vent) was completed at 12:15 PM.
- There was an infrared camera available on-site which was used to observe the tests for possible leaks. In the first day of testing, a leak was found on the still column thief hatch. Operators were asked to fix the leak and the TCT test was stopped. On the second day, the camera was used to look for any additional leaks and no issues were detected.

Table 12 summarizes measurements taken throughout the TCT test in the Plant 1 TankSafe. Some notes on the plant 1 data:

- Gas production rate, contactor temperature, and inlet pressure of Plant 1 were available through the onsite data logger or 'historian'.
- For the duration of the test, the stripping gas flow rate and reboiler temperature were observed to be constant.
- Values recorded after 12:25 PM are for the still column tests, where still vent flow was redirected to TCT apparatus, so no condenser temperature was measured.

Time	Location	Value	Comments
September 24 th	Gas production rate	235-296 E3M3/d	From historian
September 24 th	Contactor Temperature	8 – 32 °C	From historian
September 24 th	Contactor Pressure	3660-4173 kPag	From historian
September 24 th	Stripping gas	2 scfm	Gauge
September 24 th	Reboiler Temperature	190 °C	
10:20 AM	Contactor pressure	4000 kPag	
10:20 AM	Contactor Temperature	24 °C	
10:35 AM	Condenser Inlet	73 °C	Temperature gun
10:35 AM	Glycol pump speed	8 SPM	Strokes
			counted/timed
10:35 AM	TankSafe 1 st baffle outlet	60 °C	Temperature gun
10:45 AM	Condenser Inlet	62 °C	Temperature gun
10:45 AM	TankSafe 1 st baffle outlet	48 °C	Temperature gun
10:45 AM	TankSafe 2 nd baffle	40 °C	Temperature gun
	outlet		_
11:55 AM	Contactor pressure	4100 kPag	Gauge
11:10 AM	Contactor Temperature	25.5 °C	Gauge
11:10 AM	Lean TEG to contactor	37 °C	Temperature gun
11:55 AM	Condenser Inlet	72.5 °C	Temperature gun
11:55 AM	TankSafe 1 st baffle outlet	53 °C	Temperature gun
11:55 AM	TankSafe 2 nd baffle	48 °C	Temperature gun
	outlet		

Table 12- Plant 1 data



September	14,	2020
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11:55 AM	Lean TEG to contactor	36 °C	Temperature gun
11:55 AM	Glycol pump speed	8 SPM	
12:25 PM	Contactor pressure	4100 kPag	Gauge
12:25 PM	Contactor Temperature	29 °C	Gauge
12:25 PM	Glycol pump speed	8 SPM	
12:25 PM	Lean TEG to contactor	37 °C	Temperature gun
1:10 PM	Contactor pressure	4100 kPag	Gauge
1:10 PM	Contactor Temperature	30 °C	Gauge
1:10 PM	Glycol pump speed	8 SPM	
1:10 PM	Lean TEG to contactor	42 °C	Temperature gun

Besides the data shown in **Table 12**, a weather station was used to gather the wind velocity and ambient temperature during the test. **Figure 35** shows these parameters for the duration when the TCT test apparatus was connected to the TankSafe vent. The data acquisition frequency of wind velocity and ambient temperature was set to 20 seconds.



Figure 35- Wind velocity and ambient temperature during Plant 1 condenser test

The TCT report indicates a temperature range of 15-23 °C for the condenser vent. **Table 13** shows the modeling results using ambient conditions for 4 different cases:

- Case 1: Average ambient temperature, average wind velocity
- Case 2: Minimum ambient temperature, maximum wind velocity: Lowest condenser vent temperature
- Case 3: Maximum ambient temperature, average wind velocity: Highest condenser vent temperature


• Case 4: Using the average temperature and wind velocity from nearest Environment Canada (EC) station

Table 13 shows the model prediction reasonably matches the reported TCT results especially when using the average numbers from the nearest Environment Canada (EC) station. The low efficiency of the condenser in this plant is likely due to the use of stripping gas along with the presence of an energy-exchange pump with no flash tank. The high methane content of the still vent would change the thermodynamics of the system so only the aqueous phase is condensed and most of the heavy hydrocarbons remain in the vapor phase.

Case	Ambien	t conditions	Modeling results		
name	Wind Velocity (m/s)	Ambient temperature (°C)	Condenser vent temperature (°C)	Reduction efficiency %	
Case 1	2.2 (AVE.)	12 (AVE.)	22.1	9.13	
Case 2	4.9 (MAX)	9.9 (MIN)	12.1	18.03	
Case 3	2.2 (AVE.)	15.2 (MAX)	23.9	7.8	
Case 4	2.96 (EC- AVE.) 10.2 (EC-AVE.)		18.1	12.4	
Average (Case 1-3)			19.4	11.7	
TCT Results			15-23 C	10.3	

Table 13-	Condenser	model	results
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Plant 2 was comprised of inlet separation, 2 dehydration trains (2A/2B), and sales gas compression. Still vents from plant 2A and 2B were combined and sent to a TankSafe condenser. The TankSafe vapors were then directed to an incinerator. The TCT test on the Plant 2 TankSafe was not completed due to TCT apparatus problems related to high flow rates from the still vent; therefore, a TCT report is not available for this plant. However, a temperature profile of the TankSafe baffles around the condenser tank is documented in **Figure 37**. **Figure 36** shows the TankSafe in Plant 2 with red circles highlighting the approximate regions of temperature measurement across the baffles. Using the available inlet gas analysis, and operating conditions recorded during the site visit, a model was constructed to compare the temperature profile.

Parameter Name	Plant 2A	Plant 2B	
Inlet gas flowrate (e3m3/d)	625	625	
Contactor Temperature (°C)	23	22	
Contactor Pressure (kPag)	4725	4680	
Pump	Electric	Electric	
Circulation Rate (USGPM)	2	2.5	
Reboiler Temperature (°C)	190	190	
Flash Tank	Yes	No	

 Table 14- Operating conditions of Plant 2A/2B



Flash Tank Temperature (°C)	30	NA
Flash Tank Pressure (kPag)	580	NA
Stripping gas used?	No	No

Table 14 summarizes operating conditions used for building the model. Ambient conditions for the day of the test (September 25th, 2015) were obtained from the nearest Environment Canada weather station.



Figure 36- TankSafe in Plant 2 with highlighted measurement points

Figure 37 shows the model prediction vs. the measured value, showing a reasonable match between the model and measured data.



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Figure 37- Comparison of measured and predicted baffle temperature



2020 field visit (Impact of stripping gas use on condenser vent temperature)

A study was completed in 2020 to evaluate the impact of stripping gas use on the condenser vent temperature.

Repsol Oil and Gas Canada Inc. measured the TankSafe vent temperature at their Ferrier (15-16) 03-02-038-06W5 facility over the course of 9 months. During this period, the condenser vent temperature, along with the environment data, was also recorded. The environment data was recorded every hour and the vent temperature was recorded at an interval of 2 to 4 minutes every hour. The result of this survey was shared with Process Ecology to help with validation of the "PTAC Condenser model", which as described in this report incorporates condenser information, environment data, and process conditions to perform thermodynamic and heat transfer calculations.

The goal of this study was to evaluate the impact of stripping gas and glycol circulation rate on the condenser vent temperature to see if the condenser vent temperature could be used as an indication of stripping gas use.

Process Ecology used the environment data, along with the latest gas sample, process conditions, and reported environment data, to run the model and compare the measured temperatures with the model-predicted condenser vent temperatures.

Stripping gas use is known to reduce the benzene reduction efficiency of condenser by:

- Decreasing the hydrocarbon dew point of the still vent due to higher methane fraction
- Reducing the heat transfer efficiency due to:
 - Increased still vent flow rate
 - o Increased fraction of the non-condensable in the still vent

The goal of this study was to evaluate the impact of 1) stripping gas and 2) circulation rate on the condenser vent temperature to see if the condenser vent temperature could be used as a measurable indication of stripping gas use.

This section of the report summarizes the results of the study.



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Repsol generously provided the site (Ferrier 15-16, as shown in the following two figures) for conducting the study.



Figure 38 - Ferrier (15-16) 03-02-038-06W5 facility



Figure 39 - Ferrier (15-16) 03-02-038-06W5 Condenser Vent



The contactor pressure, temperature and flow rate were measured over the course of 9 months, but this study was restricted to the 6 scenarios from March 25, 2020 to April 24, 2020 identified in the following table.

Scenario	Scenario Dat	o Start :e	Scenario End Date		Stripping Gas Flow	Circulation Rate	
1	25-Mar	11:00	30-Mar	10:59	70 SCFH	1.419 L/min	
2	30-Mar	11:00	07-Apr	14:59	0 SCFH	1.703 L/min	
3	07-Apr	15:00	12-Apr	12:44	0 SCFH	1.987 L/min	
4	12-Apr	12:45	13-Apr	12:59	70 SCFH	1.987 L/min	
5	13-Apr	13:00	17-Apr	13:59	70 SCFH	1.703 L/min	
6	17-Apr	14:00	24-Apr	23:58	0 SCFH	1.900 L/min	

Table 15 – Six Dehy Operating Scenarios

The historical process data that was provided was reduced to an hourly interval to make use of the hourly environment data in the calculation of the condenser vent temperature. The following process was used to clean up the data:

- The dehydrator gas flow, temperature and pressure data points were not in sync and did not have time stamps for data points from April 1 to April 12, 2020. Therefore, these 3 variables were brought in sync and a time stamp was assumed based on the frequency of sampling in the previous month.
- The ambient temperature was sampled hourly (877 data points from March 25 to 17 April), whereas the dehy gas flow, temperature and pressure data points (10,000+ data points) were sampled more frequently (every 2 or 4 minutes). The flow rate, temperature and pressure data points were averaged to match them against the 877 ambient temperature data points.

Variable name	Number of data points (March 25 to April 24)			
Gas flow	13,268			
Dehy temperature	11,768			
Dehy pressure	10,281			
Ambient temperature	877			

• Six HYSYS cases corresponding to the six scenarios in **Table 15** were created. The cleaned-up hourly data (temperature, pressure, flowrate) was used as the basis for the HYSYS model.

Note the following with respect to the measured condenser temperature:

- The condenser vent temperature was measured on a more frequent basis and like the other data this was averaged to an hourly basis to compare to the simulation model.
- The condenser temperature was missing at certain points during the test period. If no data points were available to create the hourly averaged data, then the missing data was interpolated.



The following figure displays the ~10,000 data points for the dehydrator process conditions from March 25 to April 24.



Figure 40 – Dehydrator Process Conditions: March 25 to April 24, 2020



During the test, both the contactor pressure and temperature had minimal fluctuations and were about 6,600 kPag and 26 °C, respectively.

Aspen HYSYS cases were created corresponding to the 6 scenarios identified in the previous section. The cleaned-up hourly data (temperature, pressure, flowrate) was used to run the HYSYS model. The calculated HYSYS results were then tabulated on an hourly basis: still vent flow rate, temperature, and composition. The HYSYS results along with the measured ambient conditions (ambient temperature and wind velocity) were then used to run the PTAC Condenser application.

The condenser model was run as described above, and the model closely followed the measured condenser vent temperature data provided.



Figure 41 - Comparison of measured and calculated condenser vent temperature with ambient data







Figure 42 - Condenser Model Vent Temperature - Ambient Temperature

The average values from these measured condenser vent temperatures are reported in Table 17.

Scenario	Scenario F	From	Scenario To		Stripping Gas Rate	Circulation Rate	Average minimum approach
1	25-Mar	11:00	30-Mar	10:59	70 SCFH	1.419 L/min	2.1 °C
2	30-Mar	11:00	7-Apr	14:59	0 SCFH	1.703 L/min	2.8 °C
3	7-Apr	15:00	12-Apr	12:44	0 SCFH	1.987 L/min	2.4 °C
4	12-Apr	12:45	13-Apr	12:59	70 SCFH	1.987 L/min	3.2 °C
5	13-Apr	13:00	17-Apr	13:59	70 SCFH	1.703 L/min	1.9°C
6	17-Apr	14:00	24-Apr	23:58	0 SCFH	1.900 L/min	1.6 °C

Table 17 - Six (6) Dehy Operating Scenarios with average minimum approach

The highest average minimum approach was observed when both the circulation rate and the stripping gas flow rates were increased (Scenario 4). The higher minimum approach in this case could be explained by a higher still vent flow rate going to the condenser. However, as can be seen from the chart and the above table, the difference is small, and when review the six scenarios, no clear correlation between stripping gas use and the minimum approach (and by extension, the condenser vent temperature) was observed.



Table 18 shows the model results for the still vent mass flow rate, methane content of still vent gas, average condenser vent temperature and benzene reduction efficiencies during the testing period:

Stripping gas flow	Circulation rate	Still vent mass flow*	Methane content of still vent*	Avg. cond. vent temp.**	Avg. Benzene red. eff.**			
SCFH	L/min	lb/h	mol%	С	% (mass basis)			
70	1.419	39.61	75.26%	-2.59	18%			
0	1.703	3.13	6.24%	-8.77	94%			
0	1.987	3.51	6.33%	-1.72	92%			
70	1.987	40.33	74.88%	-13.39	30%			
70	1.703	39.92	75.18%	-2.78	19%			
0	1.9	3.38	6.28%	-1.62	92%			
* Calculated from process simulation (in this case, Aspen HYSYS)								
** Calculated from PTAC condenser application								

Table 18 - Aspen HYSYS | PTAC Condenser results

In Table 18, the still vent mass flow rate and methane content were calculated from the process simulation of the dehydrator (using HYSYS), while the condenser vent temperature and benzene reduction efficiencies were predicted from the PTAC condenser application.

The data in Table 18 clearly indicates that when stripping gas was used, the estimated benzene reduction efficiency was significantly reduced (from ~90%+ to ~18-30%). The decrease in the benzene reduction efficiency is directly correlated to the lower hydrocarbon dew point of the still vent due to the much higher methane content.

A key finding from this study is that it showed that the Condenser Application accurately estimated the condenser temperature (as compared to the measured temperature).

Also considering the studies showing a reliable match to benzene emissions reduction (reviewed earlier in this report), these results show that the Condenser Application can be used not just for evaluation studies (as Process Ecology has been doing since developing the PTAC Condenser Application), but also for regulatory purposes.

As noted, there is no clear correlation between stripping gas use and the condenser temperature. However, it should be incumbent on the operator to ensure that accurate information is provided regarding the operation of their dehydration facilities. Government inspection / audit is an appropriate means of ensuring that simulation variables used in the Condenser Application are reflective of what is in the field.



Application development

The *PTAC Condenser Application* (The "Application") is a tool which allows users to estimate the benzene emissions reduction associated with TankSafe condensers and above-ground tanks.

The Application is incorporated in an intuitive web-application. The following steps are followed in order to obtain the results:

Step 1: Input Facility information (name, location, month of operation)

Step 2: Retrieve the ambient data from the database

Step 3: Input Tank type/Pipe details.

Step 4: Input still overhead information (temperature, mass flow rate, composition).

Step 5: Review the data and submit.

Step 6: Print the results (The report can be exported in various formats including PDF, Word, or Excel documents).

In 2018, the following improvements were made to the Application:

- Import/Export capability
- Forgot password functionality
- Adjustment of Condenser App user interface to allow for BC (NTS) lookup
- Adjustment of Condenser App user interface to enable elevation lookup

Application user guide

A detailed user guide is available separately ("PTAC Condenser Application Documentation", *Updated March 2019*). The Application can currently be accessed at https://condenser.ptac.org/.