Membranes, Molecules and the Science of Permeation

Though refueling vapor emissions have captured the attention of manufacturers and regulators alike, what about evaporative emissions? Tedmund (Ted) P. Tiberi has some information on the magnitude of evaporative emissions at retail service stations and new equipment to combat them.

Can escaping vapors be recaptured with new technology?
A significant issue in the saga of ORVR/Stage II refueling vapor recovery concerns the creation of additional storage tank evaporative vapor emissions. This is especially true when ORVR vehicles are refueled at facilities equipped with some Stage II vacuum assist systems (see Joe Totten's article, "Effectiveness of Refueling Vapor Recovery Still Up In The Air," page 16). In the article below, Ted Tiberi of ARID Technologies presents the results of ARID's studies showing that evaporative vapor emissions are generated from storage tanks in significant volumes. The studies show that this is true regardless of whether, and what kind of, ORVR and Stage II systems are involved at the refueling facility. He also discusses a solution to this problem: the technology of a membrane-type vent processor that separates hydrocarbons from the vented vapor and returns them to the storage tank. The information and views in this article are those of the author. Your comments are invited.

The term "vehicle refueling vapors" refers to the vapors displaced from the vehicle fuel tank during refueling. Storage tank evaporative vapors, on the other hand, are vapors that are created as gasoline undergoes a change from liquid phase to vapor phase. This change must occur to re-establish an equilibrium vapor concentration in the space above the liquid in fixed roof storage tanks (USTs or ASTs).

The vapor space concentration is driven below natural levels by the ingestion of lean vapors or air into the storage tank during vehicle refueling. If the natural equilibrium vapor concentration is momentarily reduced, liquid gasoline will evaporate until the equilibrium concentration level is re-attained.

One gallon of liquid gasoline will expand to approximately 520 gallons of vapor at 40 percent hydrocarbon concentration. Therefore, storage tank pressure will increase rapidly as relatively small amounts of liquid evaporate. This increased pressure can result in vapor emissions from pressure/vacuum relief valves or through any leaks in the vapor piping.

What goes in must come out

Any refueling scenario, with or without ORVR or Stage II systems, which introduces lean vapors or air into gasoline storage tanks will result in the creation of evaporative vapors, as discussed above. The subsequent emission of the evaporative vapors compromises the overall efficiency of whatever vapor recovery systems are used. The four possible refueling scenarios are as follows:

• No ORVR and no Stage II (uncontrolled stations). In this scenario, refueling will contribute to significant liquid evaporation as atmospheric air is ingested into the storage tank via the vapor vent or breaches in the vapor piping. The air will enter at a volume equivalent to the volume of liquid dispensed, and upon re-equilibration, this air will generate significant emissions.

• Stage II only (no ORVR). In this scenario, atmospheric air and hydrocarbon vapors enter the storage tank when gasoline is pumped to the automobile. Some typical vacuum-assisted systems obtain high collection efficiencies at the expense of introducing excess air into storage tanks. For example, if 10 gallons of liquid gasoline are pumped to an automobile, the vapor volume returned to the storage tanks may range from 11 to 25 gallons. This excess air/vapor volume will quickly increase storage tank pressure.

• ORVR only (No Stage II). While the ORVR system may capture the refueling vapors as designed, atmospheric air will enter the storage tank as described in the first scenario above (uncontrolled stations).

• ORVR and Stage II. As the ORVR system captures vapors displaced from the automobile fuel tank, the storage tanks will be back-filled with atmospheric air.

Where vacuum-assisted Stage II systems are employed, the storage tanks will be backfilled with atmospheric air at a volume greater than the volume of liquid dispensed. In these cases, the combination of excess gaseous volume and extremely low hydrocarbon concentration will result in rapid storage tank pressurization and subsequent emissions.

These emissions come through either the vent pipes (vent emissions) or leaks in the vapor piping (fugitive emissions). If the vacuum-assisted systems are disabled during refueling of ORVR-equipped vehicles, the resulting storage tank evaporative losses will be equivalent to those generated at uncontrolled dispensing facilities. This must be the case, since the air ingestion volume will be equal to the volume of liquid dispensed.

If balance Stage II systems are used, the storage tank evaporative losses will be equivalent to those generated at uncontrolled stations. This, again, is because the air ingestion volume will equal the volume of liquid dispensed.

In summary, no matter what the scenario, the space vacated by pumping gasoline out of the storage tank is replaced by air or hydrocarbons that are equivalent at least to the volume of liquid displaced. In some cases involving Stage II systems and ORVR, the volume of air ingested is greater than the volume of liquid displaced.

Measuring evaporative vapor emissions

Using its “evaporative loss model,” ARID has estimated the magnitude of the evaporative vapor emissions and associated reductions in the overall efficiency of vapor recovery under each of four possible refueling scenarios described above. These estimates are shown in Table 1, below.

The key inputs in the model are gasoline Reid Vapor Pressure (RVP), the storage tank temperature and the air ingestion volume or vapor to liquid ratio (V/L). The data on total emissions and recovery percentages (far right two columns) are applicable only if the systems are not equipped with vent vapor processing units.

With reference to Table 1, note the range of evaporative emissions for a dispensing facility that pumps 100,000 gallons of gasoline per month: from 0.92 to 10.76 tons per year. Also note that the uncontrolled refueling emissions for this same facility are estimated at 5.04 tons per year. Therefore, depending on the V/L, RVP and storage tank temperature, the evaporative emissions can exceed the uncontrolled refueling emissions by up to a factor of two.

If one considers a centralized vacuum-assist system operating at V/L of 2.0, the evaporative losses can exceed the uncontrolled refueling losses by up to a factor of three. For a central vacuum system, the resulting large losses are combusted and do not result in atmospheric emissions. However, the economic value of the combusted material is lost. Also, the generation of combustion by-products, such as carbon dioxide and oxides of nitrogen, contribute to the formation of undesirable “greenhouse” gases.

Also as seen in Table 1 below, the storage tank evaporative emissions exceed the “uncaptured” refueling emissions for every scenario except the uncontrolled, first case (no Stage II and no ORVR). Even if Stage II and ORVR systems are 95 percent efficient in capturing refueling losses, the evaporative losses from the storage tank significantly reduce the capture efficiency of the refueling emissions.

It is important to note that all of the overall recovery efficiency values are well below the 95 percent minimum required by the Clean Air Act Amendments of 1990 for Stage II systems. Moreover, even if 100 percent of vehicles on the road had ORVR systems, the best overall recovery efficiency one can hope to achieve, without using a vent vapor processor, is only 50 percent ([9.48-4.69]) ÷ 9.48).

One such processor involves the use of a membrane system to separate, concentrate and recover hydrocarbons from air/vapor mixtures. Such a system can significantly reduce evaporative vapor emissions, which, as discussed above, are becoming more significant as the population of ORVR-equipped vehicles increases.

Stage II	ORVR	V/L	RVP (psia)	Storage Tank Temp. (ºF)	Refueling Emissions (Tons/ yr-station)	Evap[2] Emissions (Tons/ yr-station)	Total Emissions (Tons/yr-station)	Recovery (%)
No	No	--	11	65	5.04[1]	4.44	**9.48**	0
No	Yes	--	11	65	0.25[3]	4.44	**4.69**	50
Yes	No	1.2	11	65	0.25[3]	2.38	**2.63**	72
Yes	Yes	1.05	9	65	0.25[3]	0.92	**1.17**	88
Yes	Yes	1.3	9	65	0.25[3]	2.73	**2.98**	68
Yes	Yes	1.05	13	70	0.25[3]	6.26	**6.51**	31
Yes	Yes	1.3	13	70	0.25[3]	10.76	**11.01**	N/A[4]

1 Uncontrolled refueling emissions estimated at 8.4 lb. HC per 1,000 gallons dispensed (EPA , CARB)
2 From ARID’s Evaporative Loss Model
3 Assuming 95 percent capture efficiency of uncontrolled refueling emissions
4 Percentage computation not applicable because evaporative emissions (10.76) exceed base (9.48)

Table 1: Magnitude of Evaporative Vapor Emissions (Monthly Gasoline Volume of 100,000 Gallons)

Membrane vapor processing technology

Working with a leading European research institute, ARID Technologies has designed a vapor recovery system for gasoline storage tanks using a “selectively permeable” membrane. The membrane technology has been proven to be effective over many years in large storage tanks at bulk plants and refineries. ARID has simplified this technology for the retail service station environment.

This system, called PERMEATOR,™ separates hydrocarbon vapors from air; exhausts the cleaned air to the atmosphere; and returns the enriched hydrocarbon vapors to the storage tank head space. By selectively removing air from the storage tank head space, storage tank pressures are reduced and fugitive and vent emissions are virtually eliminated. The system is installed on manifolded tank vent lines. It can be used at uncontrolled stations (no Stage II) as well as Stage II-compliant facilities using balance or vacuum-assist (dispenser based and centralized) vapor recovery systems.

The selectively permeable membrane material is positioned in a compact module that exhibits very low pressure drop and excellent mass transfer characteristics. The entire system is housed in a relatively small enclosure (measuring four feet W x two feet H x two feet D) that can typically be installed without any excavation. Energy consumption is minimized since all streams enter and exit the membrane in vapor phase. Normal operation of the vent lines is not impeded because the system is installed parallel to the vents. No restriction whatsoever is created in the vapor pathway.

Six PERMEATOR™ systems are currently in operation (one in the US and the others overseas) as part of test programs. The units are being monitored to verify ARID’s projected overall estimates of vapor recovery efficiency of 95 percent.

Fig 1: Membrane System
Note: As tank pressure decreases to a pre-set level, the pressure switch automatically deactivates the PERMEATOR™ system. The above sequence is repeated when the storage tank pressure exceeds a pre-set maximum level

Fig 2: How th Membrane Works
PERMEATOR™ System Operation

How the membrane works

The membrane is made of extremely thin, selectively permeable, polymeric films attached to a porous support structure. Membrane films are integrated into modules to provide maximum surface area per unit volume of pressure housing.

Unlike conventional particle filters that separate materials based on physical size differences, the membranes used by ARID separate compounds based on differences in the solubility and diffusivity of specific molecules. Hydrocarbon molecules pass through, or permeate, the thin polymer film more rapidly than other molecules and are returned to the storage tank **(see Figures 1 and 2).** Molecules such as oxygen and nitrogen (air) are much slower permeators, and they are “rejected” by the membrane film and vented to the atmosphere. The difference in permeation rates between hydrocarbon and air molecules allows for separation of gasoline vapors from air.

The system operating cycle is described below and illustrated in Figure 2.

1. Air and hydrocarbon vapors fill the space left in the storage tank when liquid gasoline is transferred to an automobile.

2. The pressure in the storage tank head space increases as liquid gasoline in the storage tank evaporates to increase the hydrocarbon concentration in the head space. The PERMEATOR™ system is actuated by a pressure switch connected to the ullage.

3. The air/hydrocarbon mixture expelled from the storage tank vent line is directed to the membrane module. Here, a vacuum pump creates a differential pressure that causes the hydrocarbon molecules to preferentially permeate, or pass through, the membrane.

4. The hydrocarbon-rich permeate stream is returned to the storage tank while the air-rich retentate stream is vented to the atmosphere. The purity of the exiting air stream that has been depleted of hydrocarbons is determined by feed flow rate, membrane area and the pressure ratio between the feed and permeate streams.

Verification of ARID's evaporative loss model

ARID's model was tested against measured results from a field evaluation that was conducted last spring. The evaluation was done by TUV, Rheinland (Institute for Environmental Protection and Energy Technology) of Cologne, Germany (Ref: Eignungsprufung eines Gasruckfuhrsystems mit Vaconovent, July 1998, Dieter Hassel, Detlef Plettau, Werner Hasselbach and Jens Hunsinger). The actual data for the "Prototype System Field Test Results":

Prototype System Field Test Results:

A. System Measurements Performed by TUV, Rheinland, Cologne, Germany V/L = 1.5 RVP = 10.16 psia (summer grade gasoline) Storage Tank Liquid Temperature = 59 F True Vapor Pressure = 5.18 psia Headspace Equilibrium Concentration = 35 percent

Mass Balances: May 4, 1998: Volume Dispensed = 4,005 L Feed = 3384 L, percent HC = 29.3, g HC = 2699 Retentate = 1515 L, percent HC = 1.24, g HC = 51.3 Permeate = 1869 L, percent HC = 51.4, g HC = 2616

April 27-28, 1998: Volume Dispensed = 3,599 L Feed = 2979 L, percent HC = 28.3, g HC = 2297 Retentate = 1148 L, percent HC = 0.52, g HC = 16.2 Permeate = 1831 L, percent HC = 45.8, g HC = 2281

Measured Vent Emission Values: May 4, 1998: 5.61E-03 lb HC/gallon dispensed April 27-28, 1998: 5.31E-03 lb HC/gallon dispensed

B. Average Value: (5.61E-03 + 5.31E-03)/2 = 5.46E-03 lb HC/gallon dispensed

C. Predicted Value from ARID's mathematical Evaporative Loss Model (ELM): 5.55E-03 lb HC/gallon dispensed

D. Model Accuracy: 5.46/5.55 = 98.4 percent

E. Actual Emissions: (Assuming No Membrane System Installed) 4.91 Tons/yr-station @ 150,000 gallons per month = 1,890 gallons/yr-station

F. Membrane System Recovery Efficiency:

May 4, 1998: 97 percent (2,616/2,699)
April 28, 1998: 99 percent (2,281/2,297)

The two key points from the data are:

1. ARID’s Evaporative Loss Model predicted quantities of vapor generation to within 1.6 percent of the actual figures; and

2. The membrane system exhibited a vapor recovery efficiency of 97 percent and 99 percent. The system has been approved for safe operation by the German PTB, a group analogous to Underwriters Laboratories Inc. Also, the system is certified for recovery efficiency by TUV Rheinland.

Evaporative losses masked by volume expansion

Marketers using manual “sticking” or electronic tank gauges to perform inventory reconciliation are basing their calculations on gross gallons. Gross gallons are measured at the prevailing temperature of the liquid gasoline. As seen in **Table 2,** gasoline density and therefore volume is a function of temperature.

Temperature (F)	Specific Gravity (California RFG)	Volume Correction Factor
30	.727	0.979528
40	.727	0.986291
50	.727	0.993049
60	.727	1.0
70	.727	1.00707
80	.727	1.014271
90	.727	1.021597
100	.727	1.029061
110	.727	1.036667

Table 2: API Volume Correction Factors For Gasoline
Source: Petroleum Measurement Tables for the API, Chapter 11.1 and ASTM D1250, Volume Correction Factors, Standard (Volumes I-IX, and Volumes XIII-XIV).

As gasoline is warmed, the density decreases and the volume occupied by a fixed mass therefore must increase. As seen in Table 2, the volume expansion for this gasoline blend (California RFG) is about 0.7 percent for every 10 degree Fahrenheit rise. Thus, if a petroleum marketer takes delivery of 60 degrees F gasoline and if the average storage tank temperature is 80 degrees F, the marketer will gain about 1.4 percent in salable product inventory.

The worst case evaporative losses from Table 1 are 10.76 tons a year for a station pumping 100,000 gallons per month (1.2 million gallons a year). The loss computes to 0.34 percent. This would still leave a net gain of 1.06 percent for the marketer (1.4 less 0.34). Therefore, the evaporative losses are masked by the volume expansion of the gasoline due to heat gain. To accurately measure the inventory loss due to evaporation, net temperature corrected volumes should be used in the inventory reconciliation calculation. Since most newer electronic tank gauges can incorporate temperature into their algorithms, a proper inventory reconciliation is possible.

Impact on retail operating margins

The evaporation loss translates directly into a reduced gross margin. If a retailer pays for product delivered by tanker-truck, and if the retailer is not able to resell the same volume of product that they paid for, the impact on operating efficiencies is higher than one might expect.

For example, consider a typical station pumping two million gallons per year. Assume the station has a pump selling price of $1.20 per gallon and a cost of $1.00 per gallon (wholesale + delivery + taxes). How much additional gasoline must the station sell to recoup the loss in contribution margin due to evaporation of 0.35 percent of throughput? Consider a station with a pump price of $1.10 per gallon, or a pump price of $1.05 per gallon. (Assume the evaporation rate, annual throughput and the cost per gallon are the same as above). One can show that the following relationship applies to speed up this calculation:

Volume (to make up margin loss) =
([P1/{P1 - P2}] [X] [Y]) where;
P1 = Selling price at the pump, ($/gallon)
P2 = Cost per gallon (wholesale + delivery + taxes), ($/gallon)
X = Annual volume sold (gallons)
Y = Fraction lost to evaporation

For the first case with a pump selling price of $1.20 per gallon, the increased volume required is 41,000 gallons. For the second case, with a selling price of $1.10 per gallon, the increased volume required is 75,000 gallons. As the selling price, throughput and evaporation rate increase and as the margin decreases, the make-up volume figures are magnified considerably.

These increased volumes increase selling, and general and administrative expenses. This, in turn, reduces profitability. Profits are further reduced by taxes paid on wholesale product, which cannot be recouped at the retail level.

Economic viability

The technologies of the past might have been technically feasible to reduce storage tank evaporative losses, but the economic viability was not attractive. Now, with novel membrane technology, both technical and economic benefits are possible. Evaporative losses and inventory shrinkage were always assumed to be “part of doing business” in the petroleum industry. It does not have to be that way anymore. Even before considering the internal or external value of trading emission reduction credits, the savings in salable gasoline inventory with the membrane system yield financial returns up to 40 percent per year.

The challenges of producing cleaner fuels and limiting evaporative emissions present tremendous opportunities for visionary suppliers. The successful petroleum marketers of the new millennium will use their technological leadership to differentiate their product or service offering in the fiercely competitive downstream refueling segment.

Consumers have a choice of where to refuel their automobiles. Ordinary people can take pride in doing their part to minimize atmospheric emissions by filling up at a station using environmentally friendly technology. By using advanced recovery technologies like PERMEATOR™, suppliers can realize their environmental stewardship objectives and generate significant shareholder value at the same time.

Ted Tiberi is founder and president of ARID Technologies, Inc. He has a BS in chemical engineering from Pennsylvania State University and an MBA from Northwestern University's Kellogg Graduate School of Management. He has twenty five years of experience in air pollution control and vapor recovery technology, and he is the author or co-author of several US patents.