Chemical Insights
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REPORT

Volatile Organic Compounds (VOCs) Released from Electronic Nicotine Delivery Systems (ENDS)

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1. Introduction

Chemical Insights Research Institute (CIRI) of UL Research Institutes is conducting research with Georgia State University's School of Public Health (GSU) to characterize the airborne aerosols released by electronic nicotine delivery systems (ENDS) as described in our previous technical brief (https://chemicalinsights.org/wp-content/uploads/2019/11/ENDS_Technical-Brief.pdf). The usage of ENDS devices increased over the last decade despite minimal regulation on the products and little data on the emissions characterization or the health impacts when exposed. ENDS devices contain a part called an atomizer to heat and vaporize e-liquid which then generates aerosols and gaseous emissions to be inhaled by the ENDS user (https://chemicalinsights.org/wp-content/uploads/TB-420_ENDS-6.pdf) This report presents CIRI's findings on the volatile organic compounds (VOCs) released from various types of ENDS devices during Phase 1 of this research.

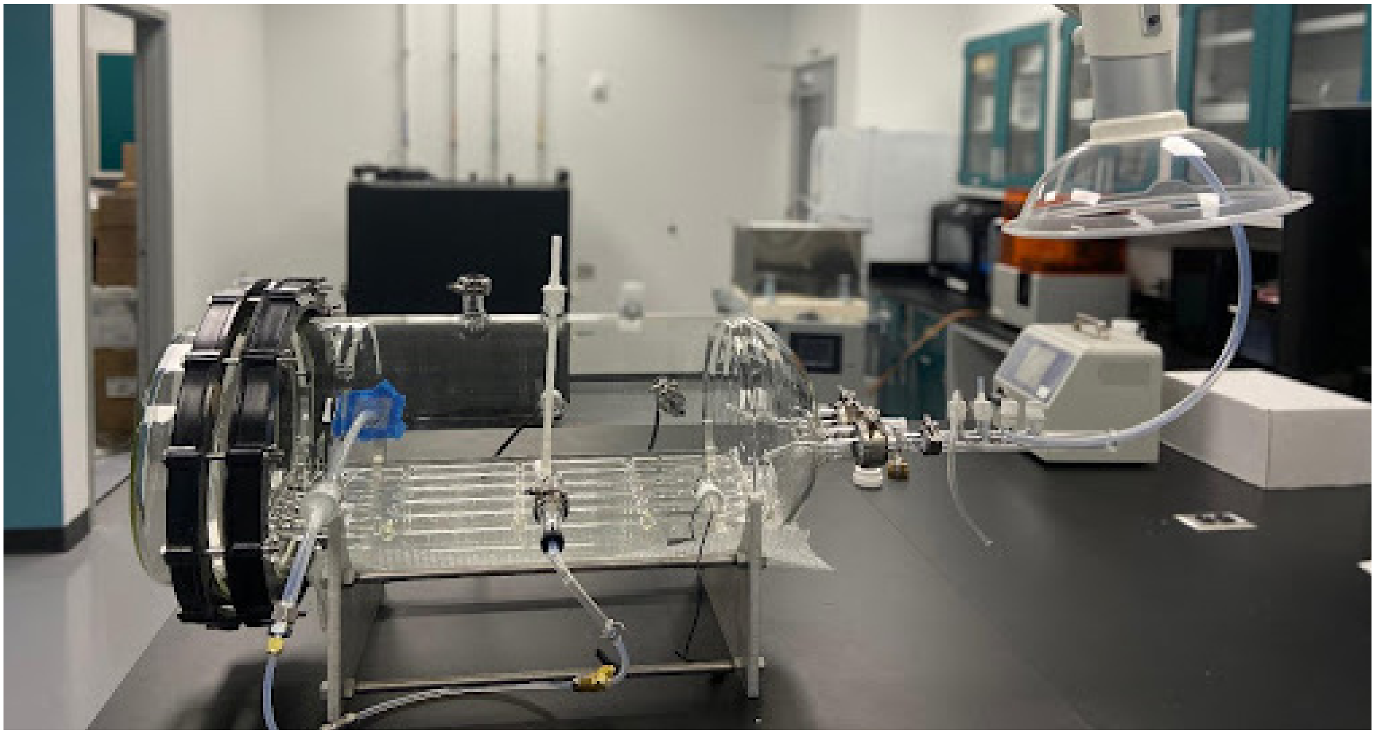
VOCs are organic chemicals with a high vapor pressure that exist in the gas phase at room temperature. In general, they are common indoor and outdoor air pollutants originating from numerous sources. For example, many fragrances are associated with the release of certain VOCs. Exposure to VOCs, depending on the level and duration of exposure, can lead to acute and/or chronic health effects including headache and irritation to eyes, throat, and respiratory systems, as well as developmental toxicity, cancer, and damage to organs and the central nervous system.

2. Methods and Materials

GLASS CHAMBER PRELIMINARY TESTING

Initial characterizations of ENDS samples were conducted using a specialized glass chamber as shown in **Figure 1**. The ENDS devices studied included two pods and two vape pens with plastic containers to house e-liquid; e-liquid flavors studied included a clove flavor and three tobacco flavors. Clean air (with minimal particles and VOCs) was supplied into the glass chamber at 9 air exchanges per hour (ACH). Each puff consisted of a 1.1 liters per minute (LPM) flow rate for 3 seconds following the puff topography of an average adult cigarette smoker as described by Cooperation Center for Scientific Research Relative to Tobacco (CORESTA).

Figure 1: Glass chamber set up. Clean air entering the chamber on the left, vape pen operating in the middle on the glass rack, and air samples collected downstream to the right of the chamber.

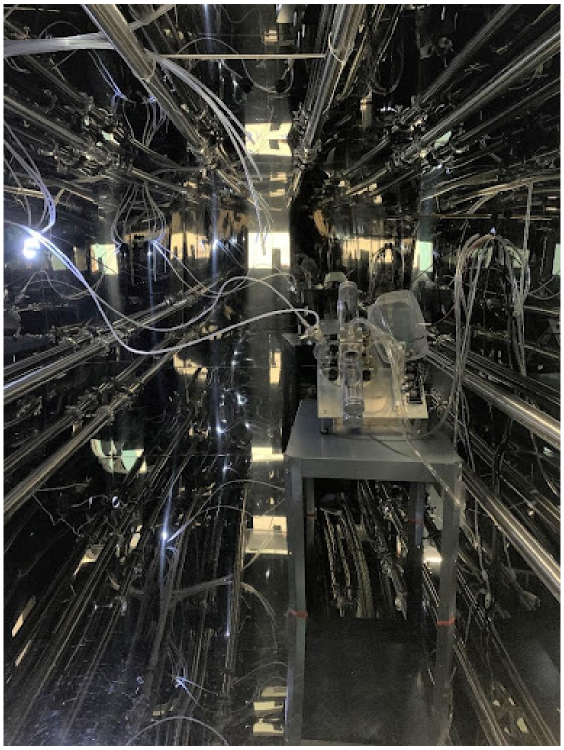


EXPOSURE CHAMBER EXPERIMENTS

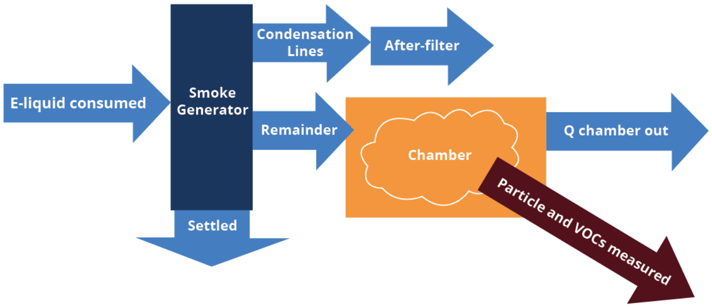
An automated electronic device (ENDS aerosol generation system, EAGS) was designed and built to generate smoke emissions. This aerosol generation system simulates a person smoking ENDS devices with the capability of applying various ENDS device types and adjusting atomizer settings. This system coupled with CIRI's specialized exposure chambers was used to study the VOC emissions during simulated smoking events. Generated smoke emissions entered the exposure chamber to allow for sample collection and analysis. Additional condensation lines were attached to the EAGS outlet for sample collection and toxicity analysis by GSU. **Figure 2** shows the EAGS inside the chamber as well as the schematic of the experimental setup. Most of the smoke generated by the EAGS was pulled into condensation lines using vacuum pumps. The remainder of the smoke generated entered a 6 m^3 exposure chamber supplied with filtered clean air. The temperature inside the chamber remained at 23°C and relative humidity at 40%. The air exchange rate inside the chamber remained at 3 ACH except for the last two experiments when the chamber remained static (the only air flow in/out of the chamber was solely for the instruments to operate).

Figure 2: a) A picture of inside the exposure chamber with the EAGS, and **b)** schematic of the experimental set up with the flow of ENDS emission shown in arrows.

a)



b)



Smoke emissions were generated with specified resistance, voltage, and puff rates listed in **Table 1**. The duration and the volume of each puff was always consistent following CORESTA puff topography. Air going through the EAGS used the same clean air that was delivered to the chamber. Puff rate and dilution flow rate (clean air that carries the smoke into the chamber) through the smoke generator varied per experiment and are listed in **Table 1**.

Table 1: List of experimental parameters for ENDS VOC analysis. Power, coil resistance, and voltage are parameters applied to ENDS, # of ENDS is the total number of pods or tanks operating for the experiment, and ACH is the air exchange rate.

TABLE 1: *LIST OF EXPERIMENTAL PARAMETERS FOR ENDS VOC ANALYSIS.*

Device	E-liquid	Power (W)	Coil Resistance (ohm)	Voltage (V)	# of ENDS	Puff rate (#/min)	Puff #	Dilution flow (LPM)	ACH (1/hr)
POD	tobacco1	6.6	2	3.7	3	6.0	1-150	2.0	3
	tobacco1	6.6	2	3.7	3	6.0	1-50	2.0	3
	tobacco1	6.6	2	3.7	1	0.5	1-62	1.1	3
	tobacco1	6.6	2	3.7	1	2.0	1-50 101-150	2.3	3
	tobacco2	6.6	2	3.7	1	2.0	1-50 101-150	2.1	3
TANK	tobacco3	24	0.6	3.79	1	2.0	1-25	2.1	3
	tobacco3	24	0.6	3.79	1	2.0	2202-2252	2.1	3
	tobacco3	60	0.15	4.6	1	2.0	1-40	2.1	3
	tobacco3	43	0.2	4.5	1	0.3	1-25	2.1	3
	tobacco3	45	0.2	4.5	1	0.3	101-125	2.1	3
	tobacco3	45	0.2	4.5	1	0.3	201-225	2.1	3
	tobacco3	20.9	0.6	4.6	1	0.3	1-25	2.1	3
	tobacco3	20.9	0.6	4.6	1	0.3	101-125	2.1	3
	tobacco3	20.9	0.6	4.6	1	0.3	201-225	2.1	3
	tobacco3	60	0.2	5.5	1	0.3	1-25	3.0	3
	tobacco3	62	0.2	5.5	1	0.3	101-125	3.0	3
	tobacco3	62	0.2	5.6	1	0.3	201-225	3.0	3
TANK (static)	tobacco 3	40.6	0.2	4.5	1	1/ sample	1-4	4.0	0
POD (static)	tobacco 1	6.6	2	3.7	1	Several/ sample	1-20	3.0	0

As shown in **Table 1**, the two e-liquid/device combinations studied for these Phase 1 exposure chamber experiments were 1) Pod device using tobacco flavor with 5% nicotine (tobacco1) and with 3% nicotine (tobacco2) and 2) Tank device using an e-liquid that is tobacco flavored with 0.3% nicotine (tobacco3). **Table 1** shows the device settings, and **Table 2** is a list of information provided on the e-liquid packaging. Pods carried the e-liquid in a plastic container whereas tanks carried the e-liquid in a glass container. Each experiment used a brand-new pod/e-liquid and a new coil except for experiments investigating coil aging effects.

TABLE 2: *INFORMATION AND INGREDIENTS LISTED AS PRINTED ON THEIR ORIGINAL PACKAGING WITH BOILING POINTS IN PARENTHESIS.*

POD/ Tobacco 1 and 2	Tank/Tobacco 3
5% (tobacco1) and 3% (tobacco2) nicotine	0.3% nicotine
70VG/30PG	65VG/35PG
Ingredients: glycerol (290°C), propylene glycol (188°C), nicotine (247°C), benzoic acid (249°C), and flavor	Ingredients: vegetable glycerin (290°C), propylene glycol (188°C), flavors, and nicotine (247°C)

Note: VG = vegetable glycerin and PG = propylene glycol.

During the initial dynamic chamber experiments (with 3 ACH), the condensation lines often clogged over time and the flow through the condensation lines varied throughout the experiment. Consequently, the dilution factor (the fraction of the smoke going into the chamber) could not be calculated accurately. Therefore, only qualitative data was considered when combining data from both the dynamic and static experiments.

To quantify VOC emissions from ENDS, a static chamber setup (ACH = 0) was used with all emissions from EAGS released into the exposure chamber (i.e., no condensation lines). This setup had better control inside the chamber where intermittent emissions from the ENDS has time to equilibrate before sampling. By measuring VOC concentrations inside the chamber at different puff numbers, an emission factor can be calculated using linear regression analysis. This static chamber method was considered as the finalized/optimized ENDS VOC test method for VOC identification, and the data from it was prioritized for the emissions analysis since more consistent data was obtained as compared to the dynamic chamber results.

SAMPLE COLLECTION AND ANALYSIS

For all sample collections, VOCs were collected onto Tenax® tubes at 0.2 LPM for 10 - 60 minutes, to be analyzed by thermal desorption/gas chromatography/mass spectrometry (TD/GC/MS) using a method applicable to organic chemicals with boiling points ranging from 35°C to 250°C. Low-molecular-weight aldehydes were collected onto 2, 4-dinitrophenylhydrazine (DNPH) cartridges pulling at 0.5 LPM for 15 - 60 minutes. The DNPH cartridges were eluted with acetonitrile and then analyzed for low-molecular-weight aldehyde hydrazone derivatives using reverse-phase high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection. The limit of quantification (LOQ) was set at the upper limit of 2 μg/m^3 to cover all chemicals detected. The limits of detection (LOD, reporting limit), though different for each chemical, generally were around 0.2 μg/m^3. However, concentrations below twice the background level were not considered for the analysis. The emission factor of each chemical (in units of μg/puff) was calculated using the mass emitted inside the chamber divided by the number of puffs entering the chamber for the static experiments.

3. Results

GLASS CHAMBER PRELIMINARY TESTING

VOCs emitted from the two pods and two vape pens tested in the glass chamber included aldehydes, alcohols, ethers, ketones, esters, acids, alkanes, and cyclosiloxanes (Table 3). Eleven chemicals were commonly found in all four ENDS setups; the rest seem to be specific to either the brand, flavoring, or the e-liquid itself. Nicotine was only detected in e-liquids stated as containing it. Glycerin, propylene glycol, and benzoic acid (which is included as part of nicotine salts formulation) were detected in all four ENDS setups. Glycerin and propylene glycol were emitted higher than other VOCs detected. Formaldehyde, a Class 1 carcinogen, was also released by the four ENDS devices tested. Caprolactam was released consistently, which may be due to the nylon parts on these devices. Other chemicals of concern including toluene, styrene, xylenes, acetaldehyde, and pentanal were detected.

TABLE 3: *INITIAL VOCS IDENTIFIED FROM THE GLASS CHAMBER EXPERIMENTS WITH FOUR ENDS DEVICES.*

CAS Number	Chemical	Pod Tobacco A	Pod Tobacco B	Vape Pen Clove	Vape Pen Tobacco
2432-11-3	[1,1':3',1''-Terphenyl]-2'-ol		X		
1000309-26-9	1(3H)-Isobenzofuranone	X	X		
1000350-63-6	1(3H)-Isobenzofuranone, 3-[(3,5-dimethylphenyl)amino]-	X	X		
88-99-3	1,2-Benzenedicarboxylic acid	X	X		
57-55-6	1,2-Propanediol (Propylene glycol)	X	X	X	X
1117-86-8	1.2-Octanediol				X
99798-78-4	13-Methyl-12-tetradecen-1-ol acetate				X
71-36-3	1-Butanol (N-Butyl alcohol)		X		
36653-82-4	1-Hexadecanol			X	
104-76-7	1-Hexanol, 2-ethyl	X	X		
13739-48-5	1H-Imidazole, 2-methyl-4-phenyl-	X			
1000245-40-7	1-Methyl-1-(3-tridecyl)oxy-1-silacyclopentane		X		
3658-77-3	2,5-Dimethyl-4-hydroxy-3(2H)-furanone				X
35044-68-9	2-Buten-1-one, 1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-				X

CAS Number	Chemical	Pod Tobacco A	Pod Tobacco B	Vape Pen Clove	Vape Pen Tobacco
116-09-6	2-Propanone, 1-hydroxy	X	X		
24070-70-0	3-Methylcyclopentyl acetate			X	X
1000432-21-6	3-Methylene-7,11-dimethyl-1-dodecene		X		
689-67-8	5,9-Undecadien-2-one, 6,10-dimethyl-	X	X	X	
3796-70-1	5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-				X
75-07-0	Acetaldehyde	X	X		
23616-67-3	Acetamide, N-(2-phenyl-1H-pyrrolo[2,3-b]pyridin-3-yl)-	X			
98-86-2	Acetophenone (Ethanone, 1-phenyl)	X	X	X	
100-52-7	Benzaldehyde		X		
65-85-0	Benzoic acid	X	X	X	X
119-36-8	Benzoic acid, 2-hydroxy-, methyl ester		X		
4889-83-2	Bicyclo[3.1.1]hept-2-ene, 3,6,6-trimethyl-		X		
105-60-2	Caprolactam	X	X	X	X
616-38-6	Carbonic acid, dimethyl ester				X
37139-88-1	Cyclohexanecarboxylic acid, 2-phenylethyl ester		X		
541-02-6	Cyclopentasiloxane, decamethyl	X	X	X	X
541-05-9	Cyclotrisiloxane, hexamethyl	X	X	X	X
112-31-2	Decanal	X	X	X	X
55334-42-4	Dodecane, 1,2-dibromo		X		
296244-70-7	Ethanone, 2,2'-(octahydro-2,3-quinoxalinediylidene)bis[1-phenyl-]		X		

CAS Number	Chemical	Pod Tobacco A	Pod Tobacco B	Vape Pen Clove	Vape Pen Tobacco
1000130-54-0	Ethenamine, N-benzoyl-2-[4-hydroxy-3-methoxyphenyl]-	X			
50-00-0	Formaldehyde	X	X	X	X
1000386-43-1	Glyceric acid (ISP-TFA)		X		
56-81-5	Glycerin	X	X	X	X
102-62-5	Glycerol 1,2-diacetate			X	
55124-79-3	Heptadecane, 9-hexyl-		X		
111-71-7	Heptanal (Heptaldehyde)		X	X	X
18908-66-2	Heptane, 3-(bromomethyl)-				X
629-80-1	Hexadecanal			X	
66-25-1	Hexanal			X	
149-57-5	Hexanoic acid, 2-ethyl				X
995-82-4	Hexasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11-dodecamethyl-				X
629-92-5	Nonadecane		X		
111-84-2	Nonane		X		
112-05-0	Nonanoic acid	X		X	
124-19-6	Nonyl aldehyde (Nonanal)	X	X	X	X
124-13-0	Octanal	X	X		
1000253-26-1	Octanediamide, N,N'-di-benzoyloxy-		X		
124-07-2	Octanoic acid		X		
1000309-25-0	Oxalic acid, hexadecyl hexyl ester				X
629-62-9	Pentadecane	X		X	
1921-70-6	Pentadecane, 2,6,10,14-tetramethyl		X		

CAS Number	Chemical	Pod Tobacco A	Pod Tobacco B	Vape Pen Clove	Vape Pen Tobacco
959261-22-4	Pentafluoropropionic acid, tridecyl ester				X
1000140-77-5	Pentanoic acid, 2,2,4-trimethyl-3-carboxyisopropyl, isobutyl	X		X	
36122-35-7	Phenylmaleic anhydride	X	X		
85-44-9	Phthalic anhydride (1,3-Isobenzofurandione)			X	
123-38-6	Propanal	X	X		
54-11-5	Pyridine, 3-(1-methyl-2-pyrrolidinyl)-, (S)- (Nicotine)	X	X		
1066-42-8	Silanediol, dimethyl-	X	X	X	X
100-42-5	Styrene	X			
110-27-0	Tetradecanoic acid, 1-methylethyl ester (Isopropyl Myristate)			X	
108-88-3	Toluene (Methylbenzene)		X		
1000352-26-0	trans-2-Dodecen-1-ol, heptafluorobutyrate	X			
6846-50-0	TXIB (2,2,4-Trimethyl-1,3-pentanediol diisobutyrate)		X	X	
112-44-7	Undecanal	X	X	X	X
106-42-3	Xylene (para and/or meta)		X		

STATIC EXPOSURE CHAMBER EXPERIMENTS

Chemicals detected above the LOD that were also detected more than twice in each static experiment are listed in Table 4. Twenty-eight VOCs were identified from the pod and 35 from the tank studied, with 16 shared VOCs between the two devices/e-liquid combinations (Pod/tobacco1 and Tank/tobacco3). For both devices, all chemicals listed in the ingredients list (**Table 2**) were identified in the emission samples. Propylene glycol was the most abundant followed by glycerin, nicotine (for the pod as it had more nicotine content), and benzoic acid. ENDS operate in the range of 200-250°C, therefore allowing all ingredients to reach or nearly reach their boiling point (listed in **Table 2**) and thus, be detected in the gas phase emission. Benzoic acid, though not listed on the packaging for Tobacco3, was also detected from the tank. Many chemicals associated with flavoring agents and/or fragrances were detected: benzaldehyde, acetaldehyde, 2-ethyl 1-hexanol, acetophenone, and several esters and alkenes. Triacetin, a triester of glycerol and acetic acid often associated with smoky flavor, were detected in the Tobacco1 pod whereas Tobacco3 tank had fragrance-associated alkenes like D-limonene and alpha-pinene. Siloxanes and alkanes often associated with lubricant/emulsifier substances, along with alcohols and aldehydes were also detected from both devices. More types of alkanes, alcohols, and siloxanes were detected in the tank than in the pod, resulting in a higher number of chemicals detected.

Table 4: List of chemicals identified in the ENDS vapor from a) the pod and b) the tank, marked for those listed in various hazard lists: California proposition 65 (Prop 65), The American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Value® (TLV®), and California Office of Environmental Health Hazard Assessment's chronic reference exposure level (CREL). Chemicals are listed from those of highest concentration to lowest.

TABLE 4 A) *LIST OF CHEMICALS IDENTIFIED IN THE ENDS VAPOR FROM THE POD*

CAS Number	Chemical	Prop 65	ACGIH TLV	CREL
57-55-6	Propylene glycol			
50-00-0	Formaldehyde	X	X	X
56-81-5	Glycerin			
75-07-0	Acetaldehyde	X	X	X
54-11-5	Nicotine	X	X	
65-85-0	Benzoic Acid			
104-76-7	1-Hexanol, 2-ethyl			
107-50-6	Cycloheptasiloxane, tetradecamethyl-			
541-05-9	Cyclotrisiloxane, hexamethyl			
556-68-3	Cyclooctasiloxane, hexadecamethyl-			
124-13-0	Octanal			
541-02-6	Cyclopentasiloxane, decamethyl			
102-76-1	Triacetin			
116-09-6	2-Propanone, 1-hydroxy			
98-86-2	Acetophenone		X	

CAS Number	Chemical	Prop 65	ACGIH TLV	CREL
112-31-2	Decanal			
102-62-5	Glycerol 1,2-diacetate			
111-76-2	Ethanol, 2-butoxy		X	
540-97-6	Cyclohexasiloxane, dodecamethyl			
112-54-9	Dodecanal			
98-56-6	Benzene, 1-chloro-4-(trifluoromethyl)-	X	X	
108-88-3	Toluene	X	X	X
1066-42-8	Silanediol, dimethyl-			
112-44-7	Undecanal			
71-36-3	1-Butanol (N-Butyl alcohol)		X	
1330-20-7	Xylenes (Total)		X	X
544-76-3	Hexadecane (Cetane)			
100-42-5	Styrene	X	X	X

TABLE 4 B) *LIST OF CHEMICALS IDENTIFIED IN THE ENDS VAPOR FROM THE TANK*

CAS Number	Chemical	Prop 65	ACGIH TLV	CREL
57-55-6	Propylene glycol			
56-81-5	Glycerin			
100-52-7	Benzaldehyde			
107-50-6	Cycloheptasiloxane, tetradecamethyl-			
556-67-2	Cyclotetrasiloxane, octamethyl			
36653-82-4	1-Hexadecanol			
50-00-0	Formaldehyde	X	X	X
540-97-6	Cyclohexasiloxane, dodecamethyl			

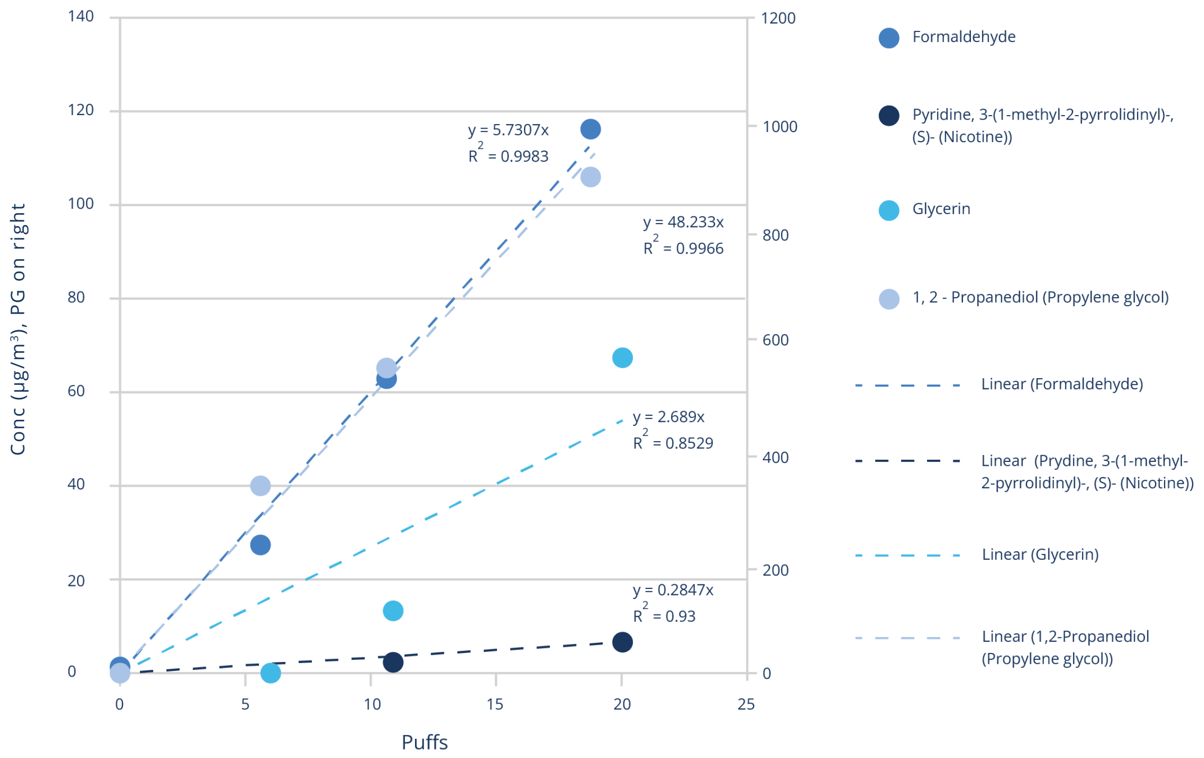
CAS Number	Chemical	Prop 65	ACGIH TLV	CREL
629-62-9	Pentadecane			
541-05-9	Cyclotrisiloxane, hexamethyl			
104-76-7	1-Hexanol, 2-ethyl			
556-68-3	Cyclooctasiloxane, hexadecamethyl-			
124-13-0	Octanal			
78-83-1	1-Propanol, 2-methyl (Isobutyl alcohol)		X	
541-02-6	Cyclopentasiloxane, decamethyl			
2801-84-5	Decane, 2,4-dimethyl			
62016-18-6	Octane, 5-ethyl-2-methyl			
124-19-6	Nonanal			
17301-30-3	Undecane, 3,8-dimethyl			
61141-72-8	Dodecane, 4,6-dimethyl			
26730-12-1	Tridecane, 4-methyl			
544-76-3	Hexadecane (Cetane)			
5989-27-5	D-Limonene			
80-56-8	Pinene, alpha		X	
65-85-0	Benzoic Acid			
629-80-1	Hexadecanal			
629-59-4	Tetradecane			
106-61-6	1,2,3-Propanetriol, 1-acetate			
17301-32-5	Undecane, 4,7-dimethyl			
78-93-3	2-Butanone (MEK)		X	
18829-56-6	2-Nonenal, (E)			
71-36-3	1-Butanol		X	

CAS Number	Chemical	Prop 65	ACGIH TLV	CREL
108-88-3	Toluene	X	X	X
116-09-6	2-Propanone, 1-hydroxy			
98-86-2	Acetophenone		X	

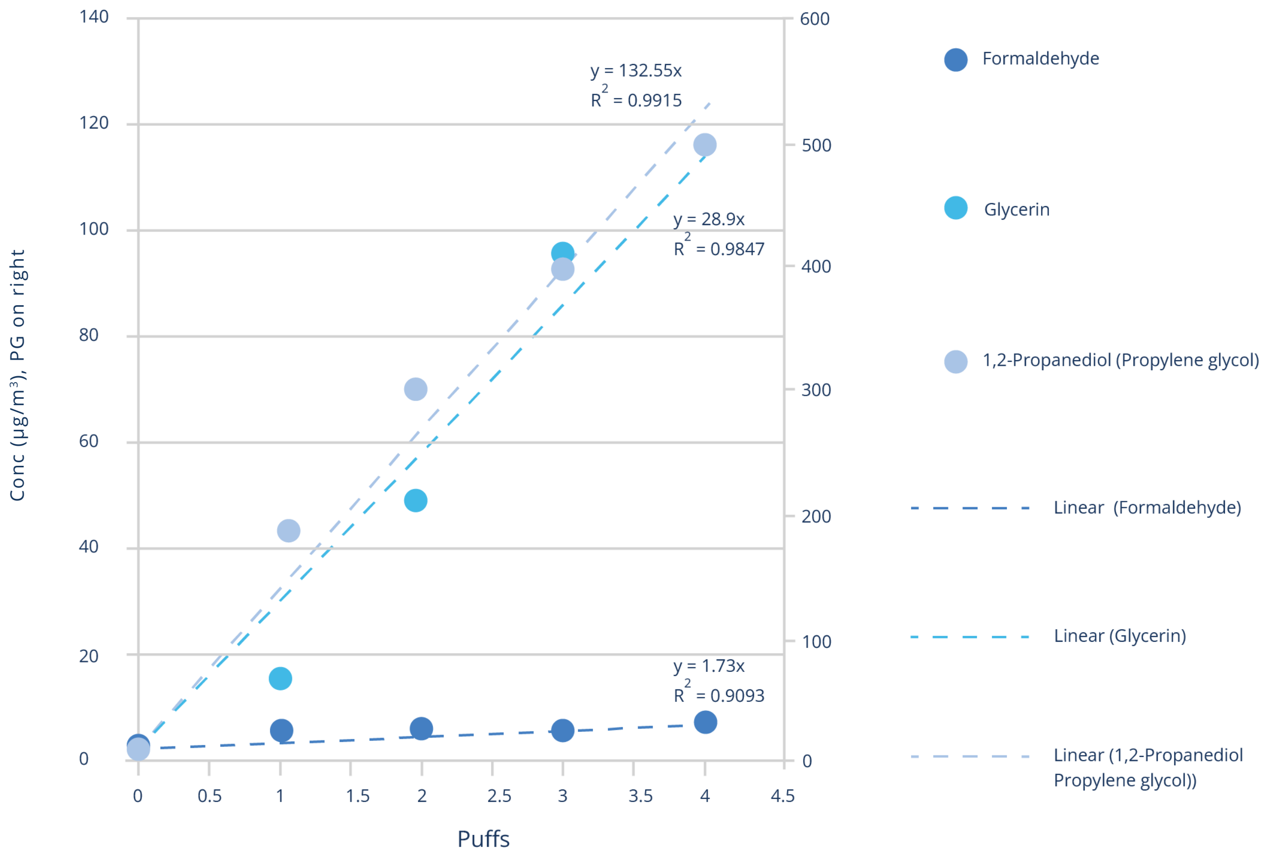
Many of the detected VOCs from the ENDS samples are irritants and carcinogens. In addition to nicotine, other known carcinogens, such as formaldehyde, were emitted from both devices. Also detected from both devices were toluene, which is a reproductive toxin and known to cause developmental effects, and siloxanes, which have been linked to endocrine disruption and reproductive toxicity, and 1-butanol, which causes irritation to eyes, skin, nose, and throat, and can lead to dizziness and central nervous system depression. As listed in the previous paragraph, many ester and alkene odorants were also released from both ENDS devices. The pod also released additional possible carcinogens such as acetaldehyde, 1-chloro-4-benzene, and styrene and irritants such as xylenes. Styrene was only detected in the pod emissions and may have been released due to heating of the surrounding plastic container near the atomizer in this type of device.

Emission factors in units of mass of a chemical per puff were calculated for chemicals detected above LOQ that increased with the number of puffs injected into the chamber. **Figure 3** shows results of emission factor calculations based on the concentrations inside the chamber. Concentrations of propylene glycol, glycerin, formaldehyde, and nicotine for the pod all increased linearly as the chamber was dosed with more puffs of smoke. R^2 values for each of the plotted trend lines were higher than 0.85.

Figure 3: Concentrations of the top 3 emitted chemicals (plus nicotine for pod) inside the static chamber versus the number of puffs generated from the pod (top) and the tank (bottom). Propylene glycol (PG) plotted on the right axis. Linear trends and R^2 values are also presented.



POD

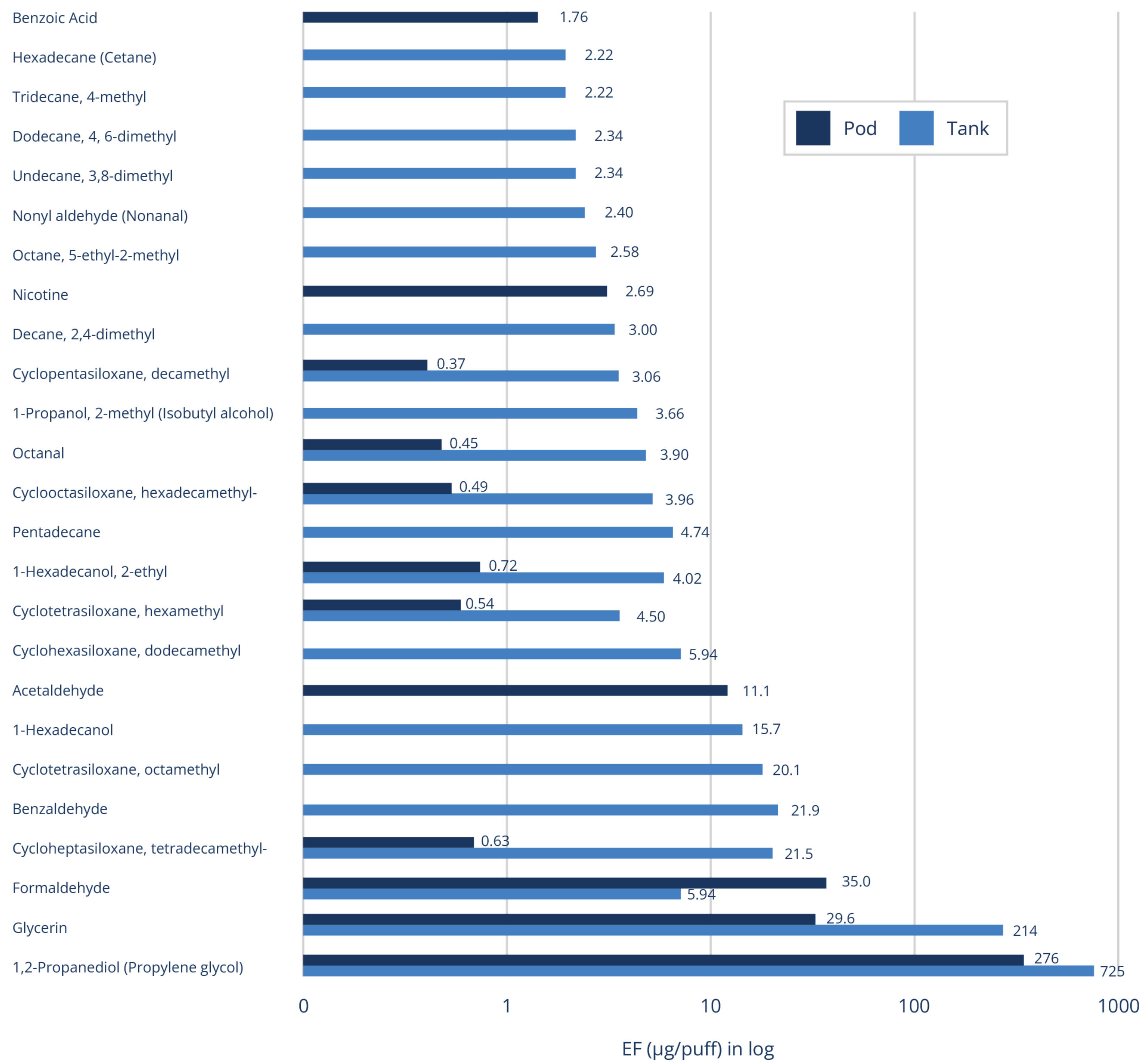


TANK

The emission factors for a total of 25 chemicals are shown in **Figure 4**. These include chemicals from both ENDS devices tested. The propylene glycol emission factor for both devices (725 µg/puff for the tank and 276 µg/puff for the pod) was at least an order of magnitude higher than the rest of the chemicals, followed by glycerin (214 µg/puff for the tank and 29.6 µg/puff for the pod). This is likely due to these chemicals being the two major ingredients in the e-liquids. Even though the e-liquids contain more vegetable glycerin than propylene glycol, propylene glycol has a higher emission factor most likely due to the ENDS atomizer reaching temperatures higher than the boiling point of propylene glycol (188°C) but not for that of glycerin (290°C). While emission factors for propylene glycol and glycerin were higher for the tank than the pod, the emission factor for formaldehyde was higher for the pod (35.0 µg/puff) than that for the tank (5.94 µg/puff). All other emission factors were less than 22 µg/puff.

VOCs released from these ENDS were predominantly from the e-liquid releasing ingredients and their byproducts as well as potentially from the plastic parts of the device when heated. However, based on these results, ENDS has the potential to cause exposure to chemicals that are not shown in the ingredients list yet have emission factors higher than nicotine. There were 15 such chemicals detected in this study, among which many are aldehydes, siloxanes, and alcohols with adverse health effects as mentioned previously.

Figure 4: Emission factors calculated from the static chamber experiments for the pod (navy) and the tank (blue). Note the figure is plotted against a log scale x-axis.



Despite both being labeled as tobacco flavored products, the VOCs emitted, and their emission factors, varied between the two devices. The tank typically had higher emission factors than the pod except for formaldehyde and those chemicals only detected from the pod experiments. This may be due to higher power applied to the tank (41 W) than the pod (7 W). Nicotine was not detected consistently in the tank as the nicotine concentration was much lower in the e-liquid used (0.3%, a tenth that of the pod). Additionally, during tank experiments, the chamber was dosed with fewer puffs. Similarly, benzoic acid was above the detection limit but lower than LOQ for the tank, therefore the emission factor is not presented in **Figure 4**.

DYNAMIC CHAMBER EXPERIMENTS

The detection frequency of VOCs detected in the static and dynamic chamber experiments are presented in **Tables 5** (for pods) and **6** (for tanks). Out of the dynamic experiments for the pods, four data sets had sample concentrations above the background. Propylene glycol, formaldehyde, acetaldehyde, hexamethylcyclotrisiloxane, and dimethylsilanediol were consistently detected in the pod experiments (**Table 5**). Although detected lower than LOQ at times, dimethylsilanediol (an emollient) was always detected in the pods with tobacco1 and tobacco2. While styrene was detected in the static chamber experiment, caprolactam was detected for the dynamic chamber experiments. This could be due to the pod e-liquid containers potentially being manufactured with different materials (i.e. ABS versus nylon plastics). Other chemicals that were detected in dynamic experiments (at least twice) but not in static are nonanal, hexanal, and benzene.

Table 5: List of chemicals identified in the ENDS vapor with detection frequency (in % of experiments) for all experiments using pods with tobacco1 and tobacco2 (n=5). Chemicals detected just in static chamber in navy, dynamic only in teal, and both in blue.

TABLE 5: *LIST OF CHEMICALS IDENTIFIED IN THE ENDS VAPOR WITH DETECTION FREQUENCY*

POD

Propylene glycol	100%	Acetophenone	60%	Benzaldehyde	20%
Formaldehyde	100%	Decanal	80%	Nonanal	80%
Glycerin	80%	Glycerol 1,2-diacetate	20%	Hexanal	60%
Acetaldehyde	100%	Ethanol, 2-butoxy	20%	Phenol	20%
Nicotine	80%	Cyclohexasiloxane, dodecamethyl	60%	Caprolactam	40%
Benzoic Acid	60%	Dodecanal	20%	2-Butanone (MEK)	20%
1-Hexanol, 2-ethyl	60%	Benzene, 1-chloro-4-(trifluoromethyl)-	20%	D-Limonene	20%
Cycloheptasiloxane, tetradecamethyl-	20%	Toluene	60%	Pinene, alpha (2,6,6-Trimethyl-bicyclo[3.1.1] hept-2-ene)	20%
Cyclotrisiloxane, hexamethyl	100%	Silanediol, dimethyl-	100%	Benzene	40%
Cyclooctasiloxane, hexadecamethyl-	20%	Undecanal	60%		
Octanal	80%	1-Butanol	60%		
Cyclopentasiloxane, decamethyl	60%	Xylenes (Total)	60%		
Triacetin	20%	Hexadecane	20%		
2-Propanone, 1-hydroxy	40%	Styrene	20%		

Static
Dynamic
Both

The detection frequency of VOCs detected from the tanks is presented in **Table 6**. Out of the dynamic experiments, nine data sets had concentrations above background. However, four of these detected just propylene glycol and glycerin. Propylene glycol and glycerin were detected above 80% frequency, and formaldehyde and nonanal were detected frequently as well (>50%). Acetaldehyde was not detected in the static experiments likely due to lower dosing resulting in lower concentrations inside the chamber, but was detected in the dynamic chamber experiments, resulting in a 50% detection frequency. Nicotine was detected in one experiment when the puffing rate was higher. Other chemicals that were detected in dynamic experiments (at least twice) but not in static were heptanal, dimethylsilanediol, decanal, ethyl propionate (fragrance), and 4-hydroxy-4-methyl 2-pentanone (solvent).

Table 6: List of chemicals identified in the ENDS vapor with detection frequency (in %) for all experiments using tanks with tobacco3 (n=10). Chemicals detected just in static chamber in navy, dynamic only in teal, and both in blue**.**

TABLE 6: *LIST OF CHEMICALS IDENTIFIED IN THE ENDS VAPOR WITH DETECTION FREQUENCY*

TANK					
Propylene glycol	100%	Cyclopentasiloxane, decamethyl	10%	Undecane, 4,7-dimethyl	20%
Glycerin	80%	Decane, 2,4-dimethyl	10%	2-Butanone (MEK)	10%
Benzaldehyde	10%	Octane, 5-ethyl-2-methyl	10%	2-Nonenal, (E)	10%
Cycloheptasiloxane, tetradecamethyl-	10%	Nonanal	50%	1-Butanol (N-Butyl alcohol)	30%
Cyclotetrasiloxane, octamethyl	10%	Undecane, 3,8-dimethyl	10%	Toluene	10%
1-Hexadecanol	10%	Dodecane, 4,6-dimethyl	10%	2-Propanone, 1-hydroxy	10%
Formaldehyde	60%	Tridecane, 4-methyl	10%	Acetophenone	10%
Cyclohexasiloxane, dodecamethyl	10%	Hexadecane	10%	Acetaldehyde	50%
Pentadecane	10%	D-Limonene	10%	Heptanal	20%
Cyclotrisiloxane, hexamethyl	30%	Pinene, alpha (2,6,6-Trimethyl-bicyclo[3.1.1]hept-2-ene)	10%	Propanoic acid, ethyl ester	20%
1-Hexanol, 2-ethyl	10%	Benzoic Acid	10%	Silanediol, dimethyl-	20%
Cyclooctasiloxane, hexadecamethyl-	10%	Hexadecanal	10%	Nicotine	10%

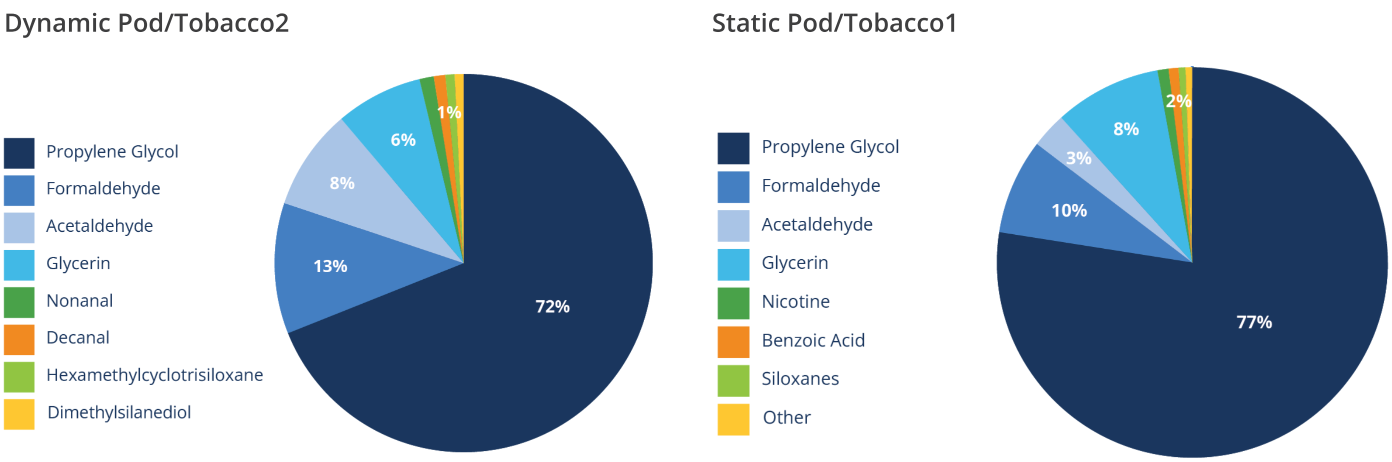
TANK

Octanal	20%	Tetradecane	10%	Decanal	30%
1-Propanol, 2-methyl (Isobutyl alcohol)	10%	1,2,3-Propanetriol, 1-acetate	10%	Benzene	10%
				2-Pentanone, 4-hydroxy-4-methyl	20%

Static **Dynamic** **Both**

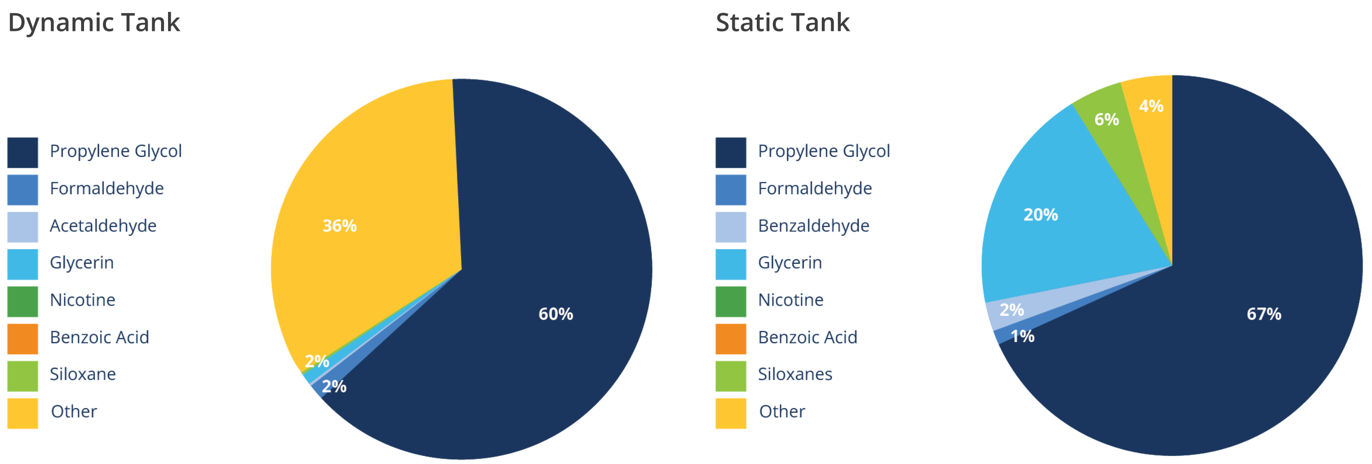
Emission fraction (by mass) of VOCs emitted from dynamic and static experiments are shown in **Figure 5** for pods and Figure 6 for tanks. The pods devices emitted comparable fractions of propylene glycol, formaldehyde, acetaldehyde, and glycerin, the top four emitted VOCs. Propylene glycol remains the predominant VOC released (72% and 77% for pod devices) followed by formaldehyde (10% and 13%). Glycerin and acetaldehyde each make up less than 10% of the total VOCs released, and nicotine, benzoic acid, siloxanes, and others make up a smaller percentage of the total VOCs released.

Figure 5: Emission profiles from a dynamic (left) and a static (right) experiment with the pods.



As for the emission profile from the tanks (**Figure 6**), propylene glycol is still the predominant VOC released (60% and 67%) but at a lower fraction than the pods. Formaldehyde and acetaldehyde were released at a slightly (a few percent) lower fraction than the pods. What differs the most between the dynamic and static data is the amount of glycerin detected. The static experiments showed more fraction of glycerin to be released from the tanks as expected with the higher wattage applied to the atomizer. However, the dynamic data did not capture this effect. Both data sets show that the tanks released a larger variety of chemicals. Many aldehydes and alcohols were combined under the “other” category in **Figure 6**.

Figure 6: Emission profiles from a dynamic experiment (left) and a static experiment (right) with the tanks both with tobacco3.



4. Conclusion

Phase 1 emissions testing with the use of an exposure chamber has been shown to be useful in identifying and quantifying VOC exposures during ENDS use. An optimized and validated procedure was established for identifying VOCs released during the use of two device types, a pod and a tank.

Overall research data showed that ENDS smoke can consist of more chemicals than what might be listed in the ingredients list. Some of these additional chemicals are linked to potential adverse health effects. In this study, over 70 different VOCs were found to be associated with ENDS use, and those VOCs commonly detected in all three experimental setups (glass, dynamic, and static chambers) were propylene glycol, glycerin, benzoic acid, formaldehyde, dimethylsilanediol, and siloxanes. Specific chemicals of concern linked to health risks included formaldehyde, acetaldehyde, acetophenone, 2-butoxyethanol, isobutyl alcohol, 1-chloro-4-(trifluoromethyl)-benzene, toluene, styrene, and caprolactam. The results showed that major components of VOCs released from ENDS are linearly correlated with the number of puffs or the mass of e-liquid consumed.

The levels of emitted VOCs varied based on e-liquid formula and/or device type and settings. Further investigation of additional e-liquids and ENDS operating parameters (voltage and resistance) is recommended to fully understand the range of VOC emissions from ENDS. Further research is also needed to assess exposure levels, impact, and human health risks. As exposure to available VOCs increases with increased ENDS use, human health risks are likely to increase beyond popcorn lung effect and lung damage, including the potential for cancer and other respiratory, allergic, or central nervous system effects.

The measured VOC emission factors from an operating ENDS device may be applied to predict the mass of VOCs retained in the ENDS user's respiratory tract. A few publications on the retention percentage of VOCs being inhaled versus exhaled found that VOCs that are water soluble are mostly (>90%) retained in a human respiratory tract.[1–3] Using this estimate for the current study, VOCs likely to be retained include propylene glycol, formaldehyde, glycerin, acetaldehyde, nicotine, and 2-butoxy ethanol. In addition to inhaled VOCs, exhaled VOC emissions from ENDS users could be a source of secondhand exposure, presenting a risk to children and those susceptible to the adverse health effects of VOC exposure and poor air quality.

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2211 Newmarket Parkway, Suite 106, Marietta, Georgia 30067
Website: chemicalinsights.org | **E-mail:** chemicalinsights@ul.org