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RESEARCH ARTICLE

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Effect of thermal and ultraviolet exposure on volatile organic compounds emitted from basalt-hemp reinforced polypropylene

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Abstract

In recent years, the "new car smell" has been linked to materials off-gassing toxic volatile organic compounds (VOCs) within the chamber of vehicles. Previous studies collected air samples directly from the vehicle chamber and analyzed them using gas chromatography–mass spectrometry (GC–MS). However, there is a lack of data regarding which materials are responsible for each compound and the resulting concentrations. This preliminary research was focused on analysis of VOC emissions emitted from basalt fiber and hemp hurd-reinforced polypropylene (PP) panels, glass fiber reinforced PP panels, and PP panels intended for interior automotive applications such as dashboards and door panels. The panels were subjected to various temperatures and UV radiation that may be experienced within a vehicle. Results showed increasing concentrations as temperature increased, and a reduction in off-gassing in the presence of UV radiation. The major compounds detected were acetaldehyde (<41 μg/m^3), acetone (<29 μg/m^3), and various alkanes (<6786 μg/m^3). Overall, the concentrations detected from all panels were below the suggested standards and limitations.

KEYWORDS

biocomposite, hybrid, natural fibers, volatile organic compound (VOC) analysis

1 | INTRODUCTION

Since the very first Model-T automobile, there has been much excitement around purchasing a new vehicle; having the latest technology in hand to quickly get from point A to point B. Since that era, the amount of time people spend in their car has risen drastically; on average, people spend 45–100 min in their cars every day.[1,2] As car travel increased, so did the number of reports of people suffering from allergies, headaches, dizziness, and respiratory issues after extended periods inside a vehicle.[1–3] Very quickly, the confined vehicle cabin became another space that needed to be considered regarding indoor air quality. Though it may be a debate whether one enjoys the "new car smell" or not, there is no longer a debate on the source of the scent. The materials being used in the interior of vehicles have progressed to include a wide array of fabrics, foam, leather,

adhesives, and polymers within a small, enclosed area, all of which naturally off-gas over time making up the distinct smell.[1,2,4]

For this reason, several researchers have studied the vehicle indoor air quality (VIAQ) to determine potential adverse health effects that may be a result of the off-gassing. It was found that VIAQ can have significantly higher concentrations of chemicals detected than in that of homes and offices.[2,5] In several cases, over 200 different chemicals were found in the air samples directly extracted from vehicles of all ages, makes, and models.[2,3,5] Many of the compounds found are chemicals known as volatile organic compounds (VOCs). Not all VOCs are considered dangerous to humans; however, in circumstances of high exposure, the effects can be deadly. The EPA has listed 97 different VOCs as toxic to humans in the Clean Air Act of 1990,[3] and countries such as Japan, Korea, Russia, and China have set strict standards to regulate these emissions, many of which can be found within vehicle cabins.[1,3,4,6]

Some of the most commonly reported compounds from the vehicles include benzene, toluene, acetaldehyde, *p*-xylene, alcohol groups, and aliphatic hydrocarbons (alkanes).[1–7] Benzene is considered carcinogenic to humans. Exposure to it causes fatigue and headaches, and in the worst cases can lead to genetic disorders and central nervous system (CNS) issues.[8,9] The standards for limitations of benzene varies significantly by country, with Korea limiting general exposure to 30 μg/m^3, China 110 μg/m^3,[6] and the US 100 μg/m^3.[5] It has been found that benzene levels are highest when a vehicle is in idle and decreases when in motion, linking high exposure levels to exhaust; however, benzene has also been detected in vehicles that are not running during testing.[3] Similarly, exposure to toluene has been linked to CNS issues and headaches, as well as nausea, respiratory problems, and reproductive issues.[9] Limited exposure of 1000–1100 μg/m^3 is recommended by China and Korea.[3] Acetaldehyde appears to be one of the most prominent compounds that cause concern in drivers and passengers. This compound is considered extremely carcinogenic and mutagenic, and even in small amounts causes adverse respiratory effects and eye irritation.[3,8,9] It has also been found that people of Asian descent suffer worse side effects from acetaldehyde due to a lack of an acetaldehyde dehydrogenase enzyme, which helps the body better process the chemical when exposure occurs. For this reason, China and Japan have set limitations on exposure to acetaldehyde to 50 μg/m^3 or less.[3]

Various studies that have sampled air from vehicle cabins report VOC levels higher than recommended[4,5] and, in addition, have found that as the temperature within the vehicle increased the level of emissions also increased.[3,6,10] A similar trend was observed when UV radiation was present.[5,6,10] These phenomena are especially a concern in hot, sunny climates where in-cabin temperatures have been recorded upwards of 77°C.[3,11] The environment created under these conditions promotes degradation of many materials present within the car, especially polymers. Lomonaco et al.[8] and Noguchi[10] analyzed VOC emissions of various polymers when exposed to heat and UV radiation and in both cases observed an increase in emissions. However, it was found that over time the emission rates decreased. Additionally, Lomonaco et al.[8] noted higher VOC emissions from branched polypropylene that contained hydrogen on tertiary carbon atoms due to an increase in free radical oxidation inducing more chain scission than linear polymers such as high-density polyethylene (HDPE). It has also been noted that VOC off-gassing is present during the processing stage of polymers and composites and can pose concern in high-production settings. It was found that different coupling agents, anti-statics, UV stabilizers, and coloring pigments are all contributors to VOCs. In order to combat these issues, companies that manufacture maleic anhydride-grafted polymers are working on synthesizing highly pure and stable versions of the material; not only has this resulted in less VOC emissions, but it has also shown better material property enhancements.[12]

The majority of VOC analyses for VIAQ have been done by sampling directly from the vehicle itself and evaluating the effects of age, manufacturer, usage of A/C, ventilation, and even refueling on emission rates. However, the analysis of individual components and materials within the vehicle has rarely been done. Librelon[7] removed small pieces of eight components from the vehicle and tested each separately determining which compounds are emitted. Recently, a year-long study in France was conducted by Badji et al.[13] on VOC emissions off-gassing from weathered PP panels and hemp-reinforced PP biocomposite panels. The panels were placed under windshield glass in a stainless-steel box and exposed to the natural elements. Samples of air were collected and tested using GC–MS periodically throughout the year. Acetic acid and acetone were the main compounds detected from PP panels, but acetaldehyde and several alkanes were also detected with increasing levels of exposure to weathering. The same trend was detected for acetaldehyde from the hemp panels as the PP panels, but furfural compounds were the main emissions detected. Furfural is a compound emitted as a result of biomass degradation and the breakdown of hemicellulose.[13,14] Though concentrations of compounds being emitted were analyzed in this study, the main focus was on the mechanisms responsible for the off-gassing.

There remains a lack of data quantifying the concentration and mass flux of emissions off-gassing from specific materials within cars. Examining VOCs during the design stage would allow car manufacturers to identify significant sources of VOCs prior to being installed, and alternatives could be considered before exposing passengers. This research is focused on VOC analysis through gas chromatography–mass spectrometry (GC–MS) of various fiber-reinforced polypropylene composites for automotive applications such as door panels, instrument panels, and dashboards. The composite panels were exposed to conditions vehicles commonly experience such as high temperatures and UV radiation. The emissions from different fiber types were evaluated and compared to one another to determine the overall safety and environmental impact imposed.

2 | MATERIALS AND METHODS

2.1 | Materials

Polypropylene copolymer (PP) supplied by RheTech (Whitmore Lake, MI) was used as the matrix material paired with AC 950P MAPP, provided by Honeywell (Morristown, NJ), as a coupling agent for the composites produced. The composites in this research were reinforced with 3 mm basalt fiber (BF) from Mafic USA (Shelby, NC) and hemp hurd (HF) supplied by Sunstrand, LLC (Louisville, KY). Additionally, precompounded pellets (GC30P200-01) containing PP and 30 wt % glass fibers (GF) currently used in the automotive industry, were supplied from RheTech and served as a control mixture for this analysis. In total, there were five mixtures or formulations evaluated for VOC emissions which are listed in Table 1.

2.2 | Preparing specimens

Eight, 2 mm thick panels of each formulation were compression molded for the tests using an aluminum (Al) mold following the same process done by Rhodes et al.[15] However, after removing the 30BF 3MAPP panels from the mold, there were many issues with the foil sticking indefinitely to the panels, and several small blisters present across the surface. For this mixture, the open mold was placed in the hot press leaving a small gap between the platens (200°C) for 5 min then carefully removed. The pellets were slightly compressed with a small 2″ × 2″ Al block. The mold was re-inserted into the press and heated again for 3 min, repeating the pressing with the small block. After prepressing the pellets, a layer of wax paper was then laid on top of the pellets and was pressed under the same conditions as the other samples. The blisters were significantly decreased through this method, though they were not completely eradicated. Canola oil was used as a mold release for these panels, but they were wiped down before testing to minimize contamination. It is believed that canola oil had minimal contributions to the resulting VOCs detected, as some panels did not show any detectable VOCs during the analysis even though they were processed through the same conditions.

2.3 | GC–MS calibration

Before testing, the GC–MS response to various VOCs was determined through two calibration methods. For the majority of VOCs, multi-component compressed gas standards (Apel-Reimer Environmental, Florida) were used. This standard contained the following gases: propene, methanol, acetonitrile, acetaldehyde, acetone, isoprene, methacrolein, benzene, toluene, *p*-xylene, 1,2,4-trimethylbenzene, α-pinene, and 1,2,4,5-tetramethylbenzene. This gas standard was dynamically diluted in hydrocarbon-free air (zero grade air) at 50% relative humidity and used to calibrate. The second gas standard (Air Liquide Spectra gases) contained 62 C_2–C_{10} hydrocarbons (alkenes, alkanes, and aromatics) commonly found in ambient air and auto exhaust.

TABLE 1 Composite formulations analyzed for VOC emissions.

Mixture	PP Matrix (wt%)	MAPP (wt%)	Basalt fiber (wt%)	Hemp fiber (wt%)	Glass fiber (wt%)
30 BF	67	3	30	–	–
15BF 15HF	67	3	15	15	–
30 HF	67	3	–	30	–
GF	70	–	–	–	30
97 PP	67	3	–	–	–

2.4 | GC–MS conditions

For each test, a 300 cc sample was extracted from the 150-L chamber and analyzed through gas chromatography-mass spectrometry (GC–MS) utilizing an Agilent GC–MS system (7890B GC and a 5977A mass spectrometer) coupled to Entech 7200 preconcentrator. Each sample was concentrated by the Entech 7200 system in a multistep procedure involving water removal by cold trap dehydration at −40°C, VOC preconcentration onto a Tenax TA trap cooled to −40°C, and cryogenic focusing in an open tube trap. Separation was done on an HP-624 column (length 60 m, diameter 0.320 mm, film thickness 1.80 μm) using a constant flow of helium (He) carrier gas (1 mL/min). For all samples, the GC–MS system starts at 35°C and is held for 1 min is then increased to 50°C at 2°C/min, followed by 210°C at 5°C/min, and lastly 250°C at 10°C/min; the entire process takes 59.5 min to complete. The MS was used electron impact ionization in scan mode with a m/z range of 45–250. The lower detection limit for the system and sample size was 10–50 parts per trillion (ppt).

2.5 | Chamber setup

The molded panels were placed in a 150-L PFA Teflon film chamber where any emissions off-gassing from the samples could be contained for collection. A tube was secured into the front of the chamber with a dry air flow of 15 L/min. Similarly, a sampling tube exited out of the back of the chamber and allowed the same rate of air to discharge also serving as a port for sample collection. A small 12 V fan was placed inside the chamber to help with complete mixing of the air. A 12″ × 12″ Al plate with a 9″ × 12″ 115 V silicone rubber heating pad adhered to one side was fabricated to heat the panels to various temperature ranges (See Table 2). The Al plate was placed inside the air chamber with the heater face down upon a 12″ × 12″ ceramic plate to act as an insulative barrier protecting the bottom of the sealed chamber from damage. A thermocouple was inserted into the side of the Al plate to monitor and control the temperature. UV lights surrounded the air chamber with a UVA/UVB intensity of 28.6 W/m^2 between 300 and 360 nm wavelength. An additional thermocouple wire was inserted into the chamber to monitor the air temperature within. The complete setup can be seen in Figure 1. A blank sample was collected and run at elevated temperatures (77°C) with all components within the chamber to ensure it would not be a source of contamination when testing the panels.

TABLE 2 Time of exposure to temperature under UV radiation.

Temperature	Time (h)
25°C	1
43°C	1
60°C	1
77°C	48

2.6 | Experimental methodology

Two separate experimental plans were created to simulate different conditions experienced within the cabin of a vehicle: a temperature ramp and a temperature ramp + UV radiation. Because this was a preliminary study, only one replicate of each sample was tested under the following conditions. The initial set of testing was completed by subjecting the specimens to various high temperatures starting at room temperature (25°C) and ending at 77°C. Two additional temperatures were tested (43°C and 60°C) splitting the temperature ramp into quarters. The specimens were placed inside the chamber and allowed to reach a steady state air condition (1 h) before starting the test. After an hour, a sample was collected, and the temperature was increased to the next level and again allowed to reach a steady state. To analyze how UV radiation would further impact the emission rates, the same temperature ramp was conducted paired with the UV lights. Continuous, extreme conditions of 77°C with UV radiation were maintained for 48 h, sampling every 24 h to better understand long-term effects. Table 2 displays the exposure time for each temperature. Keep in mind a temperature ramp was completed so the total time of UV exposure was 53.5 h.

2.7 | Analysis of emissions

After obtaining the complete chromatograms, the emission peaks were identified using Agilent MassHunter Qualitative Analysis B.07.00 software through the National Institute of Standards and Technology (NIST) mass spectral database.[16] Once the compounds were identified, quantification was completed using MassHunter Quantification Software[16] by integrating peak areas for the compound's quantification ion (m/z). Table 3 displays the method parameters input for quantification as well as the response factors and molecular weights used for calculating the concentrations of emissions. The identified compounds were evaluated from the retention time found in the chromatograms with a ±0.3 min tolerance.

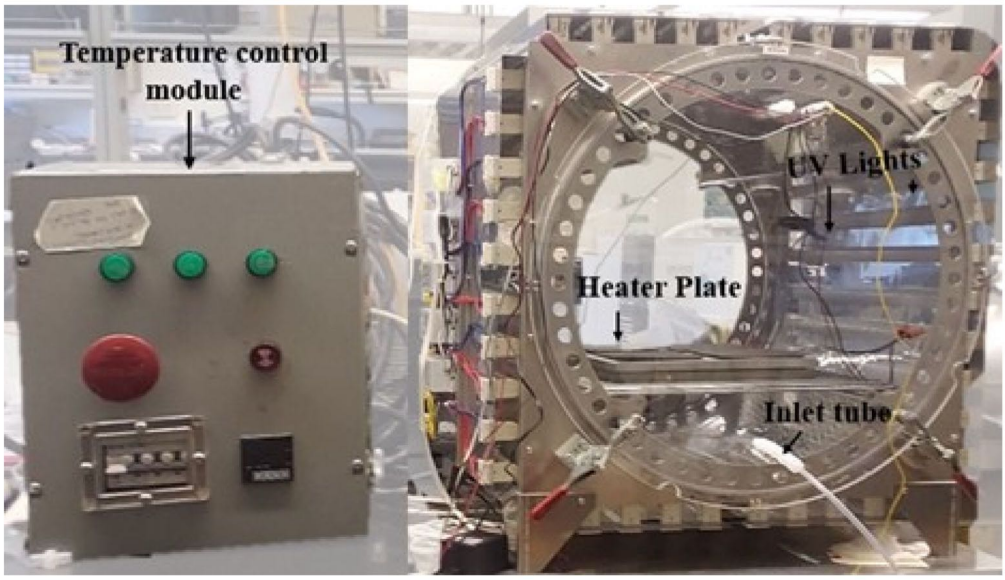

FIGURE 1 Complete chamber setup with heater plate, tubing, and thermocouples.

TABLE 3 Ion parameters input to quantification software for detection, response factors, and molecular weights used for concentration calculation.

Compound	Retention time (min)	*m/z*	RF (counts/ ppbv*cc)	MW (g/mol)
Acetaldehyde	11.28	44	53	44
Ethanol	14.22	45	27	46
Acetone	15.47	43	75	58
Isopropanol	15.87	45	75	60
Acetic acid	16.47	43	75	60
Benzene	22.64	78	76	78
Toluene	27.57	91.1	113	92
p-Xylene	31.92	91	151	106
Alkanes	Various	57	100	128–170

To ensure consistent quantification, each integrated peak was evaluated by inspecting the starting and ending retention time and checking for a Gaussian distribution. The integration outputs of the relative counts of each compound were used to calculate the emission concentrations.

From the integrated peak areas, the VOC mixing ratio (ppbv) in the chamber was calculated using compound-specific response factors. Response factors for each VOC were determined from calibration gases, except for isopropanol and acetic acid, where the response factor for acetone was used as a best estimate. For the various C_9–C_{12} isomers, identified by mass spectral comparison to the NIST Database, a response factor of 100 counts/ppbv*cc was assumed for ease of analysis. The steady-state concentration (C_∞) of compounds emitted were calculated using Equation (1) and the relative counts (n) detected from the Quantification software. The molecular weight (MW) and response factor (RF) for each compound can be seen in Table 3. The air pressure (P) within the chamber was 0.9 atm and the gas constant (R) used is 0.08206 atm L/mol K. The sample size (Q) for each test was 300 cc. The temperature (T) of the air chamber varied depending on the temperature of the heater plate and usage of UV lights and can be found in Table 4. Temperatures listed are in degrees Celsius and should be converted to Kelvin for all calculations.

$$C_\infty\left(\mu g/m^3\right) = \frac{(n/Q)}{RF} * 1 \times 10^9 * \left(\frac{P}{R * T}\right) * MW * 1000\,L/m^3 * 1 \times 10^6 \mu g/g \quad (1)$$

After calculating C_∞, the mass flux of each specimen at the tested conditions can be determined as a function of emissions per surface area using Equation (2). The airflow (L) input to the chamber was 0.015 m^3/min and the surface area (SA) of specimen within the chamber was 333 cm^2. Knowing the mass flux would enable manufacturers to

determine the total VOCs contributing from each part made from a specific material to ensure they remain within safe operating limits before installation.

$$\text{Mass flux}\left(\frac{\mu g}{cm^2 * min}\right) = \frac{C_\infty * I}{SA} \quad (2)$$

3 | RESULTS AND DISCUSSION

3.1 | Temperature ramp

Preliminary testing was completed on each composite first through a temperature ramp without UV radiation and second, through a temperature ramp with UV radiation. An example of chromatograms obtained for 30BF panels at room temperature (25°C) and 43°C can be seen in Figure 2. The peaks of high-emission compounds have been pointed out; however, this does not show benzene since it was not detected until the material was exposed to higher temperatures. From these chromatograms, a large increase in emissions as the plate temperature increased by 18°C can be seen. The temperature of the interior space in the chamber, however, only increased by 6°C, which is common for the surface temperature of the materials within a vehicle to be higher than the interior air temperature.[6]

The concentrations were calculated for each of the major compounds that are commonly found within vehicles. The compilation of each compound found at all temperatures for the composites is summarized in Table 5. If the compound was not detected in the composite at the specific temperature, a dash is shown. For many mixtures and compounds it was found that as the temperature was increased, the emissions also increased. However, this was found to be the opposite of the GF panels for compounds such as the alcohol groups, toluene, and p-xylene. Overall, the 30HF composite panels had the lowest amount of total detected VOCs and, when they were present, it was only at high temperatures. This could be due to the structure of the hemp beginning to break down when exposed to the high temperatures.[13]

TABLE 4 Chamber temperatures recorded under various conditions during testing.

Plate temperature	Chamber temperature—without UV	Chamber temperature—with UV
25°C	25°C	30.5°C
43°C	31°C	35°C
60°C	37°C	40°C
77°C	42°C	45°C

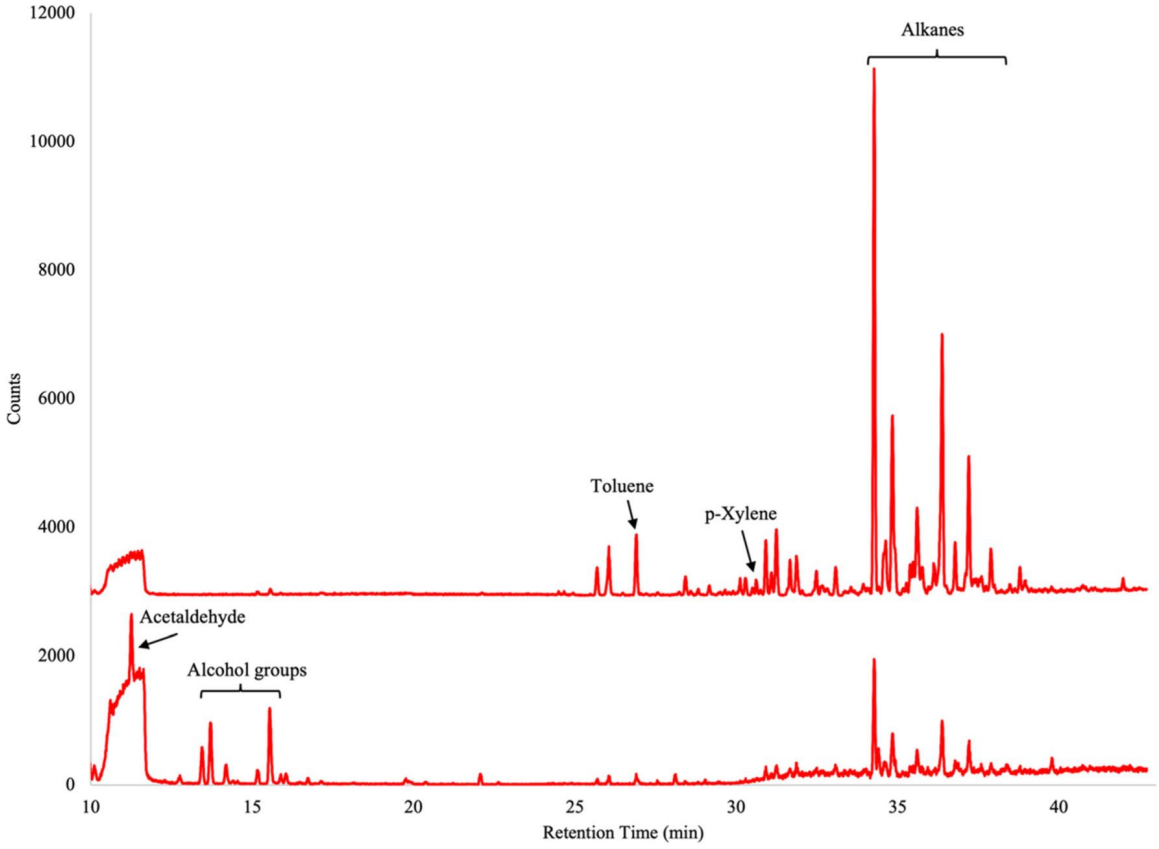

FIGURE 2 Chromatograms of 30BF 3MAPP panels at 43°C (top) and 25°C (bottom) without UV radiation.

TABLE 5 Steady-state concentrations (μg/m^3) of compounds detected in each composite at various temperatures.

Compound	RT (min)	30BF				15BF 15HF				30HF				GF				97PP			
		25°C	43°C	60°C	77°C	25°C	43°C	60°C	77°C	25°C	43°C	60°C	77°C	25°C	43°C	60°C	77°C	25°C	43°C	60°C	77°C
Acetaldehyde	11.3	7.8	–	2.0	10.4	3.3	4.1	9.9	40.4	–	–	–	1.3	2.5	2.3	2.3	3.0	–	–	2.6	5.1
Ethanol	14.2	4.5	–	–	1.8	1.5	2.9	2.3	2.9	–	–	–	–	28.7	8.0	2.2	1.4	0.5	0.7	1.2	1.9
Acetone	15.5	12.6	1.9	4.2	28.8	7.5	7.0	7.9	23.1	–	–	–	1.0	17.4	11.5	5.7	6.9	2.1	4.0	9.4	21.0
Isopropanol	15.9	0.9	0.3	1.0	15.5	0.5	1.0	1.6	24.8	–	–	–	–	12.2	5.1	1.5	2.8	0.9	1.5	4.0	13.8
Acetic acid	16.5	–	–	–	0.8	0.1	0.3	0.7	6.7	–	–	–	0.3	–	–	–	–	–	–	–	–
Benzene	22.6	–	–	–	0.8	0.5	0.7	0.7	1.3	–	–	–	–	0.4	–	–	–	–	–	–	0.7
Toluene	27.6	–	–	–	0.3	–	0.4	0.3	0.4	–	–	–	–	0.6	0.4	0.3	0.2	–	–	–	0.8
p-Xylene	31.9	–	–	–	0.5	0.5	3.8	1.7	0.3	–	–	–	–	0.3	0.2	0.1	0.1	–	0.8	2.5	5.1
C_9 alkane	34.3	9.9	95.9	400.0	4420.3	1.4	7.2	17.1	71.4	–	–	–	–	16.4	16.9	11.8	10.7	137.8	816.6	3587.7	6785.8
C_9 alkane	34.8	4.1	44.8	147.6	1275.1	0.3	2.9	5.0	29.0	–	–	–	0.1	7.5	6.9	4.3	3.7	53.7	336.9	1367.7	3390.6
C_{12} alkane	36.4	7.0	82.5	321.5	2382.3	0.4	2.9	7.5	36.3	–	–	0.1	0.2	8.1	8.4	6.7	6.7	79.5	482.4	1912.5	4535.8
C_{10} alkane	37.2	2.6	25.4	113.7	776.9	–	1.3	2.0	12.0	–	–	–	–	1.6	2.0	1.9	1.9	23.1	136.5	526.8	1255.8

However, unlike Badji et al.[13] and Kim,[14] furfural was not detected in high quantities in the materials for panels containing hemp. Trace amounts of furfural were detected in the hybrid panels at all temperature levels, and was not detected at all in the 30HF panels until 77°C was reached, where then only 1 μg/m^3 was detected.

From this analysis, it was found that all the toxic or carcinogenic VOCs present were below the recommended limits. When observing the benzene concentrations, a higher level of this compound was detected from the hybrid composites at all temperatures, whereas zero to minimal concentrations were detected from the basalt-only, hemp-only, and PP-only panels. Though a 24-h period between each test was used to clear out the chamber, it is predicted that benzene may have absorbed onto the chamber walls or Al heater plate during a trial run where a continuous benzene flow was input to ensure the GC–MS was properly calibrated. The hybrid panels were the first specimen panels tested after the trial run. Additional replicates should be tested before drawing conclusions. The 97PP composite panels without any added fiber reinforcement appeared to experience the most off-gassing of all mixtures. The alkane emissions from this mixture were the highest of all panels at every temperature. The emission of alkanes is present when chain scission occurs, and the polymer breaks down and degrades. Figure 3A–D shows the concentrations emitted of various alkanes at different temperatures. The 30BF composite also has higher concentrations of all four alkanes at 77°C. It is unknown exactly why such high levels of alkanes were detected from the 30BF panels, but it is believed it may be linked to the blistering issue during the molding process of this blend. Overall, the fiber reinforced composites show minimal traces of alkanes, suggesting that the inclusion of fibers may prevent the polymer degradation (probably due to fibers higher thermal stability than that of polypropylene).

The data from Table 5 can be used to find the mass flux of emissions to obtain a total of VOCs from the surface area of an automotive interior part. If the surface area of the desired part is known, a total rate of emissions from that single part can be calculated. A compilation of mass flux data can be found in Tables A1 and A2. The exact dimensions of vehicle components for specific materials were not found throughout literature, so a rough estimation was made in order to display how the mass flux data could be used. For this purpose, we estimated that there is surface area of 5000 cm^2 of PP based materials within a vehicle. The mass flux in μg/min was calculated for some of the toxic compounds at room temperature (25°C) and the maximum temperature (77°C) for each of the panels. The results can be found in

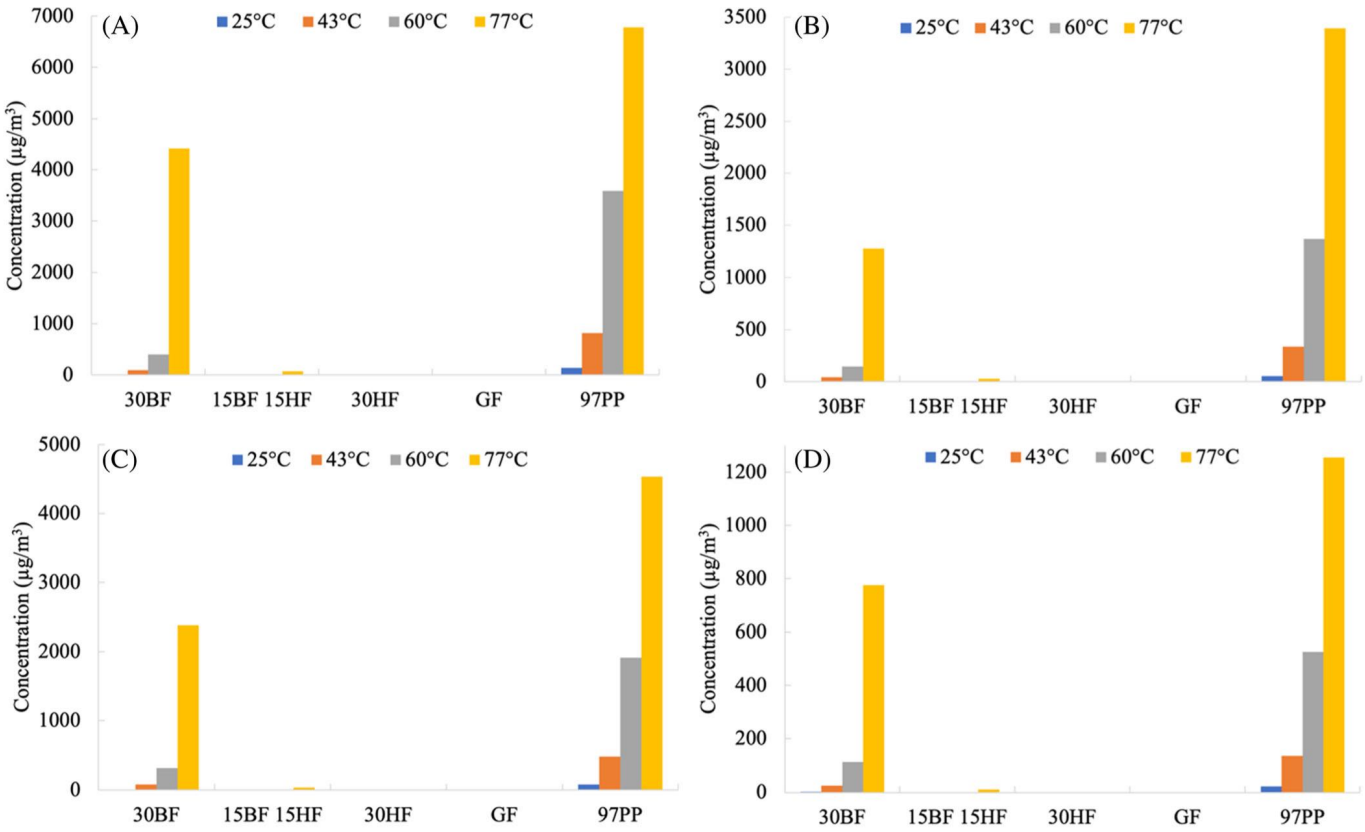

FIGURE 3 (A) C_9 alkane, (B) C_9 alkane, (C) C_{12} alkane, and (D) C_{10} alkane identified in the materials' formulations.

TABLE 6 Mass flux of hazardous compounds emitted from panels at room temperature (25°C) and 77°C.

	Mass flux (mg/min)				
Mixture	**Acetaldehyde**	**Acetone**	**Benzene**	**Toluene**	***p*-Xylene**
30BF, 25°C	7.8	12.6	0.0	0.0	0.0
30BF, 77°C	10.5	28.9	0.8	0.3	0.5
15BF15HF, 25°C	4.9	11.3	0.7	0.0	0.7
15BF15HF, 77°C	40.5	23.1	1.3	0.4	0.3
30HF, 25°C	0.0	0.0	0.0	0.0	0.0
30HF, 77°C	1.3	1.0	0.0	0.0	0.0
GF, 25°C	2.5	17.4	0.4	0.6	0.3
GF, 77°C	3.0	6.9	0.0	0.2	0.1
97PP, 25°C	0.0	2.1	0.0	0.0	0.0
97PP, 77°C	5.1	21.0	0.7	0.8	5.1

Table 6. From this calculation, it is seen that the acetaldehyde levels from the 30BF and 15BF 15HF panels at 77°C are significantly higher than in the other formulations and could potentially cause passengers irritation if exposed for extended lengths of time. Overall, the 30HF panels appear to be the cleanest option in regard to acetaldehyde in the air. At 25°C, none of the compounds would be present and at 77°C, only acetaldehyde and acetone would be present with an exposure of less than 1.5 mg/min. This method of analysis would allow manufacturers to determine the total VOC emission rates for all components within the vehicle before installation. If unsafe levels are identified, the highest emitting materials could be reassessed for alternatives to collectively work toward the safest environment.

TABLE 7 Steady-state concentrations (μg/m^3) calculated after testing composites at various temperatures with UV radiation.

Compound	RT (min)	30BF						15BF 15HF						30HF						GF						97PP					
		25°C	43°C	60°C	77°C	24 h	48 h	25°C	43°C	60°C	77°C	24 h	48 h	25°C	43°C	60°C	77°C	24 h	48 h	25°C	43°C	60°C	77°C	24 h	48 h	25°C	43°C	60°C	77°C	24 h	48 h
Acetaldehyde	11.3	–	0.84	1.18	1.25	0.33	–	–	–	1.74	2.30	–	–	6.19	–	–	–	–	0.68	–	0.18	0.30	0.20	–	–	–	–	2.45	2.47	7.54	9.17
Ethanol	14.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Acetone	15.5	3.03	0.62	1.09	1.97	0.36	0.32	0.63	0.89	1.58	3.14	0.99	0.91	2.17	0.77	1.17	1.96	1.26	1.11	0.13	0.15	0.24	0.51	0.37	0.31	0.81	1.26	2.16	4.01	10.93	15.25
Isopropanol	15.9	–	–	–	–	–	–	–	–	–	0.12	–	–	0.17	–	–	–	–	–	–	–	–	0.05	0.02	0.02	–	–	–	–	0.45	0.61
Acetic acid	16.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.18	–	0.12	–	–	–	–	–	–	–	–	–	–	–	–
Benzene	22.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Toluene	27.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
p-xylene	31.9	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
C_9 alkane	34.3	0.41	–	–	–	–	–	–	0.36	0.82	1.57	–	–	0.59	0.30	0.46	0.65	–	–	0.40	0.66	1.24	1.93	–	–	3.35	17.8	200.7	769.7	513.9	213
C_9 alkane	34.8	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.45	–	–	0.47	4.7	74.2	277.9	177.9	83.6
C_{12} alkane	36.4	–	–	–	–	–	–	–	–	0.47	0.76	–	–	–	–	–	–	–	–	0.24	0.41	0.66	0.93	–	–	1.39	7.3	103.24	414.6	244.7	117
C_{10} alkane	37.2	0.46	–	0.02	0.07	–	–	0.01	0.13	0.17	0.53	0.14	0.17	0.34	0.14	0.26	0.91	1.26	1.87	0.93	0.93	0.50	1.46	0.29	1.36	0.70	3.01	4.12	17.8	62.8	37.1

3.2 | Temperature ramp with UV radiation

The same temperature series was applied to a second set of the composite specimens with the addition of UV radiation. The desired intensity of the UV radiation was found using the National Center for Atmospheric Research (NCAR) TUV calculator[17] and was based on the summation of UV radiation of wavelengths 300–360 nm at high noon, mid-summer in Key West, FL and Yuma, AZ. Key West is the southernmost city in the United States and is very close to the equator so vehicles located here would experience high UV radiation (29.5 W/m^2). Yuma, AZ is considered the sunniest city in the United States again exposing vehicles here to high radiation levels (28.1 W/m^2). Therefore, the chamber lights had a radiation level of 28.6 W/m^2.

The results from this analysis were not as expected. Many of the toxic and carcinogenic compounds (benzene, toluene, and *p*-xylene) were not present at any temperatures from any of the composite panels. The concentrations calculated can be found in Table 7 and mass flux calculations can be found in Tables A1 and A2. With the UV radiation present the only compound that was found in all formulations at every temperature was acetone (Figure 4). The concentration remains relatively low and consistent from each mixture at all temperature levels and time of exposure except from the 97PP panels. This mixture showed increasing acetone emissions as temperature, as well as the time of exposure, increased. Acetaldehyde was also emitted from each formulation, but mainly only at increased temperatures. There have been mixed results of emission responses when materials were exposed to higher temperatures and UV radiation. Badji[14] recorded higher emission rates as the exposure time of specimen panels to being weathered increased; however, Lomonaco et al.[8] showed decreased intensity of emissions as PP specimens were aged with UV radiation. Similar to

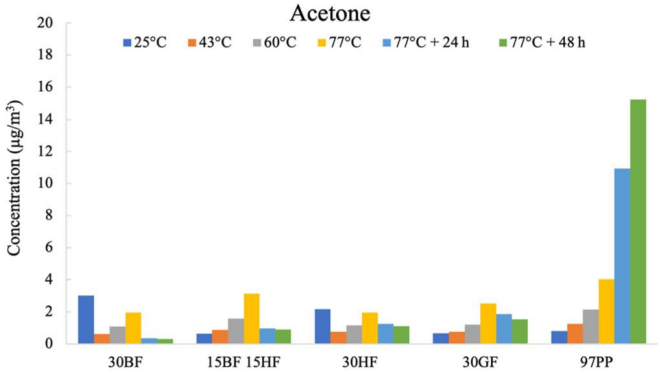

FIGURE 4 Steady-state concentrations of acetone with increasing temperatures and UV radiation.

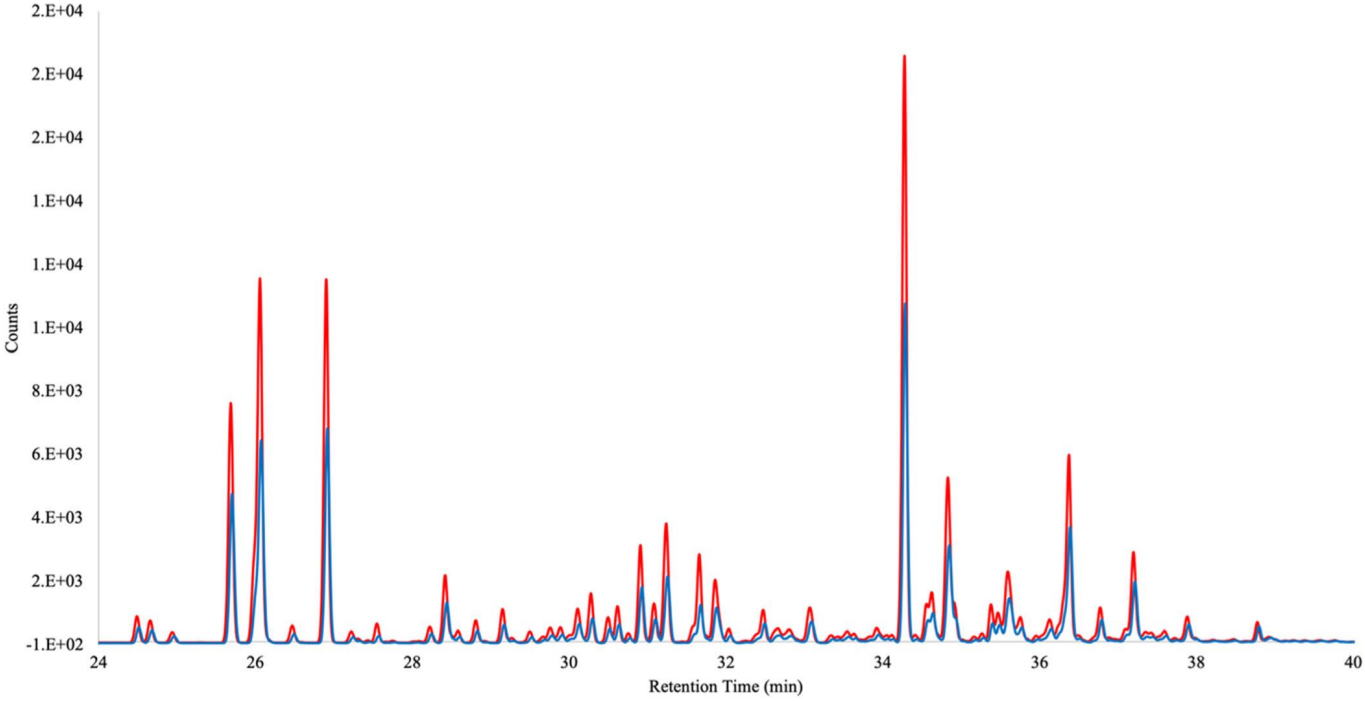

FIGURE 5 Chromatogram from 97PP panels without UV radiation (red) and with UV radiation (blue) at 77°C.

the findings of Lomonaco et al., lower concentrations were observed from the BF/HF/PP, GF, and 97PP panels. Figure 5 displays the chromatogram results from the 97PP panels between retention times of 24–40 min at 77°C, which is where the majority of emissions off-gassing were detected. The red curve displays the results without UV exposure whereas the blue curve displays the results with UV exposure. Though all the same compounds are off-gassing, the intensity of the emissions noticeably decreased. Herein it is believed that the UV radiation may have induced additional bonding between the constituents, causing the VOCs to be locked into the structure rather than diffusing through.

3.3 | Comparison between temperature ramp with and without UV exposure

The effect of temperature appeared to be greater than the effect of UV radiation on the off-gassing of compounds from the PP, BF/HF/PP, and GF/PP panels. The total concentrations detected when no UV exposure was present were higher than the concentrations detected at the same temperatures with UV radiation. Many compounds such as benzene, toluene, *p*-xylene, and alkanes, that were off-gassing from the panels without UV exposure were completely eradicated or only present in trace amounts when subjected to UV radiation. Based on previous literature,[8,13] it was expected to see a decline in concentrations of many compounds with the incorporation of UV lights; however, it was not expected to see the concentrations fall below detection limits, especially the alkanes which are present mostly due to chain scission of the polymer and is commonly induced through UV radiation. The exceptions of these observations were acetaldehyde and acetone, which were present in most if not all composite blends tested; though as expected, the concentrations were lower.

4 | CONCLUSION

A preliminary study of off-gassing from PP, BF/HF/PP, and GF/PP composites indicated that the VOC emissions were more impacted by an increase in temperature and less impacted by the exposure to UV radiation. However, additional replicates should be tested to check for consistency before drawing this conclusion.

When testing the effects of off-gassing due to temperature only it was found that the 30HF panels had the lowest emission rates of all composite formulations. There were no traces of heavy carcinogens such as benzene, toluene, *p*-xylene, or isopropanol, and only minimal emissions of acetaldehyde and acetone at 77°C were observed. As for the other biocomposite panels, an increasing trend was observed for emission rates vs. temperature whereas a decreasing trend was observed from the GF panels. Toxic/carcinogenic VOCs were present in many of the panels, though they did not surpass the standard threshold even at the highest testing temperatures. Observing a larger surface area of the 30BF or 15BF 15HF composites may lead to excessive exposure to acetaldehyde. The risk of exposure

also increases as the time of exposure increases. For instance, people who drive vehicles for their occupation or long trips in a vehicle during hot periods increases risk. Overall, the nonreinforced PP (97PP) showed the highest overall presence of alkanes which is an indication of polymer degradation, suggesting that the fibers may help maintain the polymers integrity.

When exposing the composite panels to elevated temperatures and UV radiation it was observed that only acetone was emitted by all panels at every temperature level. Concentrations remained relatively stable except from the 97PP panels where the concentration increased with increasing temperature and exposure time. Most of the composites showed minimal VOC emissions when exposed to high temperatures and UV radiation. Overall decreased concentrations were observed compared to high-temperature exposure only. The 97PP panels showed the most emissions of all composites. The highest concentration of emissions was from various alkanes, suggesting increased levels of degradation.

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DATA AVAILABILITY STATEMENT

Research data are not shared.

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APPENDIX

TABLE A1 Mass flux (μg/cm^2 min) of compounds at various temperatures without UV radiation.

		30BF				15BF 15HF				30HF				GF				97PP			
Compound	**RT (min)**	**25°C**	**43°C**	**60°C**	**77°C**	**25°C**	**43°C**	**60°C**	**77°C**	**25°C**	**43°C**	**60°C**	**77°C**	**25°C**	**43°C**	**60°C**	**77°C**	**25°C**	**43°C**	**60°C**	**77°C**
Acetaldehyde	11.3	1.6	–	0.4	2.1	1.0	1.2	3.0	8.1	–	–	–	0.3	0.5	0.5	0.5	0.6	–	–	0.5	1.0
Ethanol	14.2	0.9	–	–	0.4	0.5	0.9	0.7	0.6	–	–	–	–	5.7	1.6	0.4	0.3	0.1	0.1	0.2	0.4
Acetone	15.5	2.5	0.4	0.8	5.8	2.3	2.1	2.4	4.6	–	–	–	0.2	3.5	2.3	1.1	1.4	0.4	0.8	1.9	4.2
Isopropanol	15.9	0.2	0.1	0.2	3.1	0.2	0.3	0.5	5.0	–	–	–	–	2.4	1.0	0.3	0.6	0.2	0.3	0.8	2.8
Acetic acid	16.5	–	–	–	0.2	–	0.1	0.2	1.3	–	–	–	0.1	–	–	–	–	–	–	–	–
Benzene	22.6	–	–	–	0.2	0.1	0.2	0.2	0.3	–	–	–	–	0.1	–	–	–	–	–	–	0.1
Toluene	27.6	–	–	–	0.1	–	0.1	0.1	0.1	–	–	–	–	0.1	0.1	0.1	–	–	–	–	0.2
p-Xylene	31.9	–	–	–	0.1	0.1	1.1	0.5	0.1	–	–	–	–	0.1	–	–	–	–	0.2	0.5	1.0
C_9 alkane	34.3	2.0	19.2	80.1	885.4	0.4	2.2	5.1	14.3	–	–	–	–	3.3	3.4	2.4	2.1	27.6	163.6	718.6	1359.2
C_9 alkane	34.8	0.8	9.0	29.6	255.4	0.1	0.9	1.5	5.8	–	–	–	0.1	1.5	1.4	0.9	0.7	10.7	67.5	274.0	679.2
C_{12} alkane	36.4	1.4	16.5	64.4	477.2	0.1	0.9	2.3	7.3	–	–	0.1	0.2	1.6	1.7	1.3	1.3	15.9	96.6	383.1	908.6
C_{10} alkane	37.2	0.5	5.1	22.8	155.6	–	0.4	0.6	2.4	–	–	–	–	0.3	0.4	0.4	0.4	4.6	27.3	105.5	251.5

TABLE A2 Mass flux (μg/cm^2 min) of compounds at various temperatures and UV exposure.

		30BF						15BF 15HF						30HF						GF						97PP					
Compound	**RT (min)**	**25°C**	**43°C**	**60°C**	**77°C**	**24 h**	**48 h**	**25°C**	**43°C**	**60°C**	**77°C**	**24 h**	**48 h**	**25°C**	**43°C**	**60°C**	**77°C**	**24 h**	**48 h**	**25°C**	**43°C**	**60°C**	**77°C**	**24 h**	**48 h**	**25°C**	**43°C**	**60°C**	**77°C**	**24 h**	**48 h**
Acetaldehyde	11.3	–	0.17	0.24	0.25	0.07	–	–	–	0.35	0.46	–	–	1.24	–	–	–	–	0.14	–	0.18	0.30	0.20	–	–	–	–	0.49	0.49	1.51	1.84
Ethanol	14.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Acetone	15.5	0.61	0.12	0.22	0.39	0.07	0.06	0.13	0.18	0.32	0.63	0.20	0.18	0.43	0.15	0.23	0.39	0.25	0.22	0.13	0.15	0.24	0.51	0.37	0.31	0.16	0.25	0.43	0.80	2.19	3.05
Isopropanol	15.9	–	–	–	–	–	–	–	–	–	0.02	–	–	0.03	–	–	–	–	–	–	–	–	0.05	0.02	0.02	–	–	–	–	0.09	0.12
Acetic acid	16.5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.04	–	0.02	–	–	–	–	–	–	–	–	–	–	–	–
Benzene	22.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Toluene	27.6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
p-Xylene	31.9	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
C_9 alkane	34.3	0.08	–	–	–	–	–	–	0.07	0.16	0.31	–	–	0.12	0.06	0.09	0.13	–	–	0.08	0.13	0.25	0.39	–	–	0.67	3.57	40.2	154.2	103.0	42.7
C_9 alkane	34.8	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.09	–	–	0.09	0.94	14.9	55.7	35.6	16.7
C_{12} alkane	36.4	–	–	–	–	–	–	–	–	0.09	0.15	–	–	–	–	–	–	–	–	0.05	0.08	0.13	0.19	–	–	0.28	1.45	20.7	83.0	49.0	23.4
C_{10} alkane	37.2	0.46	–	0.02	0.07	–	–	–	–	–	–	–	–	–	–	–	–	–	0.23	–	–	–	–	–	–	0.09	0.28	5.4	20.4	13.8	6.8