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Observation of Excess Benzene in Post-Fire Crude Oil and Risk Communication Implications

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ABSTRACT

This investigation examines whether benzene in heat-affected crude oil declines as a volatility-only model would predict after tank-fire extinguishment with fluorine-free foam (F3). Among BTEX compounds, benzene has the highest vapor pressure and the lowest molecular weight and boiling point; it should therefore be depleted from the surface layer at least as fast as toluene, ethylbenzene, and the xylenes (TEX), and faster if evaporative loss dominates. Liquid samples were collected from the top 12 in. (30 cm) of a 2.4 m diameter × 2.19 m high test tank before burning and after repeated F3-extinguished burns. Aliquots were aerated in a closed vapor chamber and the headspace was analyzed as whole air. That assay characterizes an enriched source profile; the reported concentrations are not outdoor or breathing-zone exposures. Absolute benzene in the chamber headspace declined (81 ppmv in the single fresh-oil sample versus a post-burn mean of 31 ppmv), but TEX declined far more (for example, toluene from 680 ppmv to a post-burn mean of 26.5 ppmv). Benzene's share of ΣBTEX vapor therefore rose from about 5% before burning to about 43% after burning (about 60% in overnight mixed-oil samples). A volatility-only account does not explain that pattern. A source term is required: conversion of precursors in the hot zone (thermal or steam-related cracking) and/or resupply of benzene from the cooler bulk liquid. Distinguishing those mechanisms is outside the scope of this observational study. The practical implication is that post-fire crude oil in deep tanks should not be assumed to have been stripped of benzene the way thin-film in situ burns are, and risk communication for responders should treat the residual liquid as a continuing benzene source.

1 INTRODUCTION

Despite ongoing risk-mitigation efforts adopted by the petrochemical industry, tank fires and explosions remain a constant threat. Several large-scale oil fire events, including the Buncefield oil storage fire in the UK and the Intercontinental Terminals Company (ITC) petroleum fire in Texas, highlight these risks and the associated risk of hydrocarbon exposure to responders. The 2005 Buncefield oil storage fire in Hertfordshire, UK, was the result of petroleum crude oil overflowing from aboveground storage tanks into the depot, resulting in a large vapor explosion and fire [11]. The Buncefield fire engulfed more than 20 fuel tanks on the site and destroyed a large portion of the depot [11]. In a public health study following Buncefield, 34% of emergency services responders (n=187) reported exposure symptoms including headache and respiratory complaints [22]. However, these symptoms were not associated with specific chemicals nor was any chemical-specific exposure data reported. The public health impact was relatively small—40 members of the public sought medical care—possibly due to the time the explosion occurred (6:00 a.m.) and "the high combustion temperature of this fire which reduced most hazardous chemicals to carbon and water" [22]. In 2019, ITC, in Deer Park, Texas, experienced a large fire from petroleum liquids (pyrolysis gasoline, naphtha, toluene, etc.) that led to the destruction of fifteen 80,000-barrel storage tanks over the course of four days. Once the fire was extinguished, the City of Deer Park issued a second precautionary shelter-in-place order due to reports of benzene and other volatile organic compounds (VOCs) within the city limits [53].

The Occupational Safety and Health Administration (OSHA) Hazard Communication standard (29 CFR 1910.1200(h)(1)) requires that chemical hazards be communicated to employers and employees [42]. The evaporative behavior of benzene and other aromatics is well

described for high-temperature and fire-impacted films, yet most post-fire dissipation studies address thin-film or in situ burns [2, 7, 29, 35, 39]. Those results do not transfer directly to crude oil storage tanks, where most of the liquid column remains far below boiling and only a shallow hot zone is heated from above. This study tests a simple expectation in that geometry: if loss is governed by volatility, benzene should leave the heat-affected layer faster than the other BTEX compounds. The measurements are a source characterization of that layer, intended to inform later occupational-exposure work rather than to estimate responder dose.

1.1 Why Benzene Should Have Been Lost First

Benzene is a primary constituent of aromatic volatile organic compounds (VOCs) in petroleum liquids [45]. Researchers report benzene's composition average values are 0.16% and 0.33% by weight in crude oil [54]. In 1979, benzene was classified as Group 1 human carcinogen [14, 24] and was later reaffirmed as a carcinogen in 2009 [36]. Based on estimates of "0.26 to 1.3 excess cancer cases among 1,000 workers at a benzene exposure" of 1 part per million by volume (ppmv) for 40 years, the World Health Organization maintains there are no recommended values for safe levels of benzene exposure [14, 21, 57]. Despite benzene's ubiquitous presence found in urban and rural ambient air environments [21], industrial hygienists can reduce daily or episodic exposure with better working environments, safe working limits, and hierarchy of controls. In 1971, OSHA established a permissible exposure limit (PEL) of 1 ppmv for a time-weighted average over eight working hours, 40 hours a week, in a working lifetime [43]. In 2024, the American Conference of Governmental Industrial Hygienists (ACGIH) reduced the Threshold-Limit-Value Time-Weighted-Average (TLV-TWA) of benzene to 0.02 ppmv [1]. Therefore, to best protect first responders, understanding the source of

contamination allows control measures to be implemented to reduce exposure below working limits.

Vaporization depletes aromatics and light saturates once liquid temperatures approach their boiling points, as in thin-film fires and within heat-affected layers. Among BTEX, that ranking is unambiguous: benzene boils at 80 °C and has the highest vapor pressure and lowest molecular weight; toluene, ethylbenzene, and the xylenes are progressively less volatile [10, 52]. A volatility-only process should therefore remove benzene from the surface layer in equal or greater proportion than TEX. In situ burns are consistent with that expectation. Petroleum liquid extraction efficiencies of 95% to 98% have been reported [2]. In the Newfoundland Offshore Burn Experiment, 97% (n = 61) of samples were below the 0.1 ppmv benzene detection limit [7]. Marshland in situ burns reduced aromatic hydrocarbons and alkanes in residue by 99% for both diesel and crude oil [35]. Shallow film depth and weathering both favor near-complete stripping of the light aromatics [2, 7, 29, 35, 39].

That near-complete removal is a poor analog for storage-tank fires. Most of a deep inventory never reaches boiling. Storage-tank fires and explosions accounted for 85% (n = 242) of industrial storage-tank accidents in one review [9]. A typical API 650 tank (48 ft high × 150 ft diameter) can hold on the order of 6.3 million barrels [3, 26, 40]. Two features of that geometry can put benzene back into the heat-affected layer as fast as, or faster than, evaporative loss can remove it: (1) a downward-propagating hot zone overlying a large cold reservoir, from which benzene can diffuse or be mixed toward the surface, and (2) thermal or steam-related conversion of precursors (cyclohexane, naphtha, toluene, and related species) in the hot zone or at the flame–liquid interface [33]. Either process would appear in a post-fire sample as “excess”

benzene relative to TEX—not necessarily as an increase above the fresh-oil concentration, but as a smaller fractional loss than volatility ranking predicts.

1.2 Responder Exposure as a Consequence During Tank Fire Incidents

Responders, in particular structural firefighters, are exposed to a variety of airborne contaminants such as polycyclic aromatic hydrocarbons, VOCs, polychlorinated biphenyls (PCBs), dioxins, plasticizers, flame retardants, hydrogen cyanide (HCN), hydrogen chloride (HCl), and combustion-specific particulates [6, 16, 27]. In addition to active fire scenes and industrial accidents, alternative fuel types (i.e., pallets, straw, OSB, and heating oil) are used during live firefighting training events which can allow for exposure to similar contaminants [17]. During a training exercise, median benzene concentrations (7.1–31.7 ppmv) exceeded the OSHA PELs for both eight-hour time-weighted average (1.0 ppmv) and short-term exposure limits (5.0 ppmv). The training exercise median benzene concentrations resembled a similar order of magnitude to the concentrations found during controlled residential fires (37.9–40.3 ppmv) [16, 18, 44]. While structural fires have unique exposure risks, they are similar to industrial fires in that hydrocarbon mixtures are complex and exposure risk may not be limited to a single compound. Industrial firefighting, including training exercises, can involve fuels that result in multi-species exposure risk, and exposure pathways well-researched in structural firefighting remain relevant. However, there is a need to better understand industrial firefighting exposure profiles based on mixture and liquid fuel packages utilized during training events.

Studies assessing the health impact of firefighters' exposure to benzene found evidence of exposure-response relationships for lung cancer and leukemia [12, 20, 50]. Per WHO [57], inhalation is the predominant exposure pathway, with varying severity levels of hematological

effects. A two-fold increase in median exhaled breath concentrations of benzene was observed for attack-and-search firefighters, despite their use of self-contained breathing apparatus (SCBA) [18]. This research supports the findings of dermal absorption as a secondary route of benzene exposure, due to the low attenuation performance of firefighter bunker gear (9.7–11.7%) worn during residential firefighting [38]. While the risk of benzene exposure in structural firefighting is well studied, there remains limited data in industrial firefighting and training events [17].

Although using SCBAs is encouraged, if not a required standard, by most firefighting organizations when actively engaged in industrial fires (including storage tank fires), there is evidence of inconsistency in the use of respiratory protection in many firefighting applications. One study found that "firefighters frequently remove SCBA[s] during overhaul when the firegrounds appear to be clear of visible smoke" [19]. In an epidemiological study of firefighters and their use of SCBAs, researchers found that firefighters used SCBAs for only 50% of the structural fires and 6% of all firefighting engagements [4]. Studies have also found that SCBA use contributed to firefighter fatigue as well as physiological and psychological stress [31, 34, 56].

This work used a target-of-opportunity series of large tank burns. The question is narrow: after F3 extinguishment, does benzene in vapor from the heat-affected layer decline in the proportion that its volatility predicts, or does it remain in excess of the other aromatics?

Whole-air analysis of aerated headspace was used to rank the hydrocarbons that still evolve from that layer. The chamber method was chosen to produce a reproducible source profile of what remains in the liquid, not to simulate the tank berm or a firefighter's breathing zone. If benzene is enriched relative to TEX after burning, first responders handling post-fire crude—and

training grounds that reuse burned fuels—cannot rely on the in situ-burn narrative that the light aromatics have already been consumed.

2 METHODS

Storage-tank fire testing was conducted in March 2022 in Borger, Texas, on a crude-oil inventory that was burned and extinguished with fluorine-free foams (F3). Foam performance was a separate research objective and is not analyzed here. Benzene was prioritized because of responder exposure risk and because it is the BTEX species that a volatility-only model says should disappear first.

2.1 Overview of Experiments

The burn tank (2.4 m diameter × 2.19 m height) contained approximately 9 m^3 (~56 barrels) of a crude oil blend from the Eagle Ford and Permian basins, giving an approximately 2 m fuel column. Published gas composition for similar Eagle Ford liquids is 66.2 mol% methane, 16.3% ethane, 8.52% propane, and 2.71% butane, with a heating value of 1,409 Btu/scf [58]. Blend-specific gravity and a full assay of the tank inventory were not obtained; Eagle Ford shale liquids are generally light oils (literature range about 36°API to >50°API). A thermocouple tree on the tank centerline was used to locate the hot zone, where temperature near the surface approached the boiling range of the lighter oil components.

The burn schedule included five days of testing with multiple burns per day. Each day, a pre-burn crude oil sample was collected before fuel ignition, and post-burn samples were collected immediately following the extinguishment of each burn. To analyze hydrocarbon vapor from the

layer of oil measured to be the most impacted by heat, pre- and post-burn samples were collected from the top 12” of oil located within the hot zone.

From each sample, an aliquot was placed in a vacuum chamber to isolate headspace for air-sample collection. Aeration of crude oil enriches vapors in a confined space above the liquid. Schweitzer and Szebehely noted that cavitation and bubble formation in saturated liquids increase the yield of volatiles beyond equilibrium saturation in a confined vapor space [48]. Aeration was therefore used to drive the volatile components of each aliquot toward a high, repeatable headspace yield. The result is a source profile of what remains in the liquid after fire; it must not be read as an exposure concentration for emergency responders. Following a similar approach [48], vapor was circulated through the chamber and then through the liquid via a frit. Chamber pressure was monitored with a digital manometer (VelociCalc TSI 9545). A photoionization detector (RAE Systems AreaRAE Pro) monitored VOCs through the 30-minute aeration cycle so that every aliquot was treated the same way.

2.2 Experimental Procedure

2.2.1 Liquid Sample Collection

The liquid samples were collected from the top 12” of crude oil from the tank using a single-use Teflon bailer with a dimension of 13.2 cm2 x 30.5 cm. A portion of the resulting 0.4-liter (L) sample volume was then placed into a 266 mL (milliliter) (9 ounce) amber jar, mechanically mixed, and placed into a water bath until the target liquid temperature of 25°C, +/- 5% (~1.25°C) was reached. Then, a liquid aliquot was placed in a vapor chamber for a 30-minute aeration period for further analysis (Fig. 1). This process is further explained in the following section.

Three types of liquid samples were collected: pre-burn, post-burn with mechanical mixing, and post-burn. “Mechanical mixing” here means the homogenizing effect of truck loading and overnight storage of post-burn crude. The pre-burn sample was collected from fresh crude before ignition on Day 1 and is the only sample in the set that had not been burned. A mixed-oil sample was collected at the start of each subsequent day, after burned oil had been transferred to overnight storage and then returned to the tank (Fig. 2). Post-burn samples were collected after foam extinguishment of each sampled burn. After sampling, oil was added (“topped off”) to restore working height. Topping-off was especially important after slopover (overflow of burning crude; Fig. 3). Slopover events were estimated to eject about 2–4 in. (5–10 cm) of crude per event. Topping-off and overnight mixing both add fresh or previously unheated oil to the heat-affected layer and are treated as limitations, not as controlled treatments.

Sampling covered four of five burn days and 16 liquid samples (Table 1): one fresh-oil pre-burn, three morning mixed-oil samples, and 12 post-burn samples (Day 1: 1 post-burn; Day 2: 4; Day 3: 6; Day 4: 1). Day 2–4 mornings each supplied one mixed-oil sample. On Day 4, after the first burn, the tested oil was retired and replaced so the foam-evaluation program could continue; chemical sampling for this dataset stopped there.

2.2.2 Vapor Chamber and Sample Aeration

Air sample preparation and collection were conducted from within an acrylic vacuum chamber with inside dimensions of 16.875” W x 17.5” D x 20” H. [51]. The vapor chamber isolated the sample vapor, protecting it from dilution or contamination due to its containment features. A 50 mL aliquot was drawn from each liquid sample using a graduated syringe, placed into an open cup in the center of the vapor chamber (Fig. 1), and underwent a 30-minute aeration

cycle. During aeration, the industrial hygiene circulation pump was used to draw vapor from inside the chamber into the liquid through a fritted stone and then flushed after each test. To ensure the steady-state condition was reached in a relatively short period, aeration was integrated to effectively agitate the volatiles in the sample.

After the aeration cycle was completed, the chamber pressure differential was observed using the manometer plumbed through a designated port. Chamber pressure was monitored for consistent air sample collection. In addition to pressure, temperature and relative humidity were monitored inside the chamber during aeration to ensure consistency in chamber conditions. The vapor chamber was located inside a climate-controlled space staged at the burn site. Ambient weather conditions (24-hour average) are included in Table 2.

2.2.3 Air Sample Preparation for Lab Analysis

After the 30-minute aeration, a 1 L air sample was drawn into a Tedlar® bag over two minutes with an SKC Pocket Pump TOUCH at 0.5 L/min. Samples were analyzed by EPA TO-14A and/or EPA TO-15 [15]. After collection, the chamber and sample train were purged with nitrogen until a photoionization detector (PID) matched outside-chamber ambient readings. Whole-air samples were submitted to a laboratory accredited by the American Industrial Hygiene Association and the National Environmental Laboratory Accreditation Program. Results are restricted to species above the method limit of quantification. Descriptive and inferential statistics were then applied as described in Section 3.

3 RESULTS

Many hydrocarbon species were detected. Analysis was limited to aromatics and saturates useful for the volatility comparison. Seven aromatics were detected; three (1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and styrene) were dropped because detections were few and low, leaving benzene, ethylbenzene, toluene, and xylenes (BTEX). Twelve saturates were retained as a comparison group. Results are grouped as pre-burn (n = 1), post-burn with mechanical mixing (n = 3), and post-burn (n = 12).

Pre-burn airborne concentrations were observed from vapor exsolved from the liquid sample, grouped by aromatic and saturated hydrocarbons (Fig. 4a). In comparison, airborne concentrations from the final burn test illustrated the fate of hydrocarbon vapor over the course of the burn tests (Fig. 4b). The most prevalent airborne concentrations from the fresh oil pre-burn samples within the aromatics group were toluene and xylene. For the saturated hydrocarbon group, butane, isopentane, and pentane represented the highest airborne concentrations.

Burning and overnight mixing reduced headspace concentrations of both aromatics and saturates (Fig. 5). Mixed-oil concentrations are the morning samples taken before burning resumed. In the fresh-oil sample, benzene was the smallest of the BTEX peaks (Fig. 4a). After the burn series it was the largest aromatic in every morning mixed-oil sample (Fig. 6) and remained high relative to TEX in the post-burn samples from individual burns (Fig. 7). Overnight truck movement mixed fire-impacted oil with a larger bulk volume and partly restored overall volatility, but it did not restore the original BTEX proportions: benzene stayed dominant among the aromatics. That is the opposite of a volatility-only ranking.

Aromatic and saturate concentrations are summarized in Tables 3 and 4 and in Figs. 8 and 9. For mixed-oil samples, mean benzene (35.3 ppmv) exceeded mean toluene (18 ppmv); mean ethylbenzene and xylenes were each about 3 ppmv. Mean butane, isopentane, and pentane were 604, 560, and 639 ppmv. For post-burn samples, mean benzene was 30.7 ppmv—similar to the mixed-oil mean—while toluene and xylenes were more variable (toluene mean 26.5 ppmv, peak 160 ppmv; xylenes mean 10.3 ppmv, peak 100 ppmv). Using the Table 3 means, benzene accounted for about 5% of ΣBTEX vapor in the fresh-oil sample (81 of 1,551 ppmv), about 43% after burning (30.7 of 71 ppmv), and about 60% in the mixed-oil samples (35.3 of 59 ppmv). Absolute benzene fell; its share of the aromatic vapor rose. TEX, which should have been conserved relative to benzene if evaporation were the only process, collapsed.

3.1 Percent Change Analysis

Benzene's mixed-oil and post-burn means are similar, while ethylbenzene, toluene, and xylenes are not. Percent change (Eq. 1) was therefore computed for each post-burn sample against the single fresh-oil headspace value for that analyte. Negative values are losses. The statistic is descriptive: all twelve post-burn percentages share one initial value, so they are not independent replicates of a fresh-oil baseline.

$$\text{Percent change (\%)} = [(X_{fv} - X_{iv}) / X_{iv}] \times 100 \quad (1)$$

where X_{fv} is the post-burn headspace concentration of the component and X_{iv} is the fresh-oil (pre-burn) concentration. Percent change was calculated for each post-burn liquid sample; means and 95% confidence intervals are shown in Figs. 10 and 11. All plotted species declined. Benzene's mean loss lay between about 50% and 75%, in the same band as 10 of the 12

saturates. TEX losses were larger (Fig. 11). Paired t-tests of those percent changes are given in Table 5.

Benzene was reduced less than ethylbenzene, toluene, and total xylenes, and it tracked most of the saturates (Table 5). Each post-burn sample supplied a pair (benzene percent change versus that sample's percent change for the comparison analyte). Benzene's percent change differed significantly from ethylbenzene, toluene, total xylenes, cyclohexane, heptane, and methane. It did not differ significantly from nine of the twelve saturates. For the three other aromatics the differences were large ($P < 0.0001$). In volatility order, benzene should have shown the largest BTEX loss. It showed the smallest.

Mean differences in percent change (benzene minus the other aromatic) were −35.71% for ethylbenzene, −33.96% for toluene, and −36.20% for total xylenes. Those gaps are the quantitative statement of "excess" benzene in this paper: not a rise above the fresh-oil concentration, but a shortfall in loss relative to TEX and relative to benzene's own vapor-pressure ranking.

3.2 Observations of Bulk Liquid Dynamics During Crude Oil Tank Fires

To place the chemical results in the tank's thermal structure, temperature records from a parallel foam-evaluation program at the same tank were reviewed. Those measurements are used only qualitatively here.

The test apparatus was a 2.4-meter-diameter tank with a depth of 2.19 meters. The tank was filled with crude oil, leaving about 8" to 10" of freeboard. A thermocouple tree was installed in the center of the tank with a Type-K thermocouple placed every 2". During the test, the

thermocouples above the liquid level quickly reported open-air flame temperatures, as shown in Fig. 12. The first thermocouple at 10”s deep did not report a temperature change for the first five minutes and then rose to about 220°C. It is recognized that crude oil would not have a single boiling point as it is composed of many volatile constituents. However, many of the constituents analyzed would have experienced volatility at or near 220°C. In this study, this approximation is considered the effective boiling point of the crude oil mixture. This pattern is repeated for each of the thermocouples about every five minutes, showing a temperature propagation front through the bulk liquid of 0.3”/minute. The temperature propagation versus depth develops a hot zone over time (Fig. 13). A convective cell does not form in the bulk of this high-viscosity liquid due to heating from the top, rather than the bottom, and most of the tank’s contents remained at the initial 50°F temperature. Since the bulk of the liquid in this tank fire scenario does not change temperature, it can be inferred that aromatic volatilization does not occur in this zone. For example, Fig. 13 displays that approximately 60” of the 80” column of oil remain unaffected by heat from surface temperature. However, temperature variation in the upper 24” column was noted and may contribute to the persistence of benzene versus the other aromatics. This phenomenon provides research pathways focused on how fresh oil affects volatility of aromatics during tank fire burns in a smaller-scaled, controlled setting. For understanding the benzene anomaly and how it may relate to conventional wisdom, further analysis of the dynamics in the hot zone must be considered.

4 DISCUSSION

The observational result is straightforward. After repeated tank burns and F3 extinguishment, every quantified BTEX species declined in aerated headspace from the top 12 in. of liquid.

Benzene declined least, despite being the species that should have declined most if evaporation and burning were the only sinks. That pattern is what is meant here by excess benzene. Explaining it requires a source term in the heat-affected layer.

4.1 Benzene Production/Regeneration in the Hot Zone

One candidate source is conversion of benzene precursors (naphtha-range material, cyclohexane, toluene, and related species) under heat, with or without steam from foam water [41, 46]. F3 solution is nominally about 97% water. In the upper 12 in. of the column, temperatures of 200 °C and higher were recorded during Test 8 (Fig. 14), well above the boiling point of water and high enough to generate steam in the heat-affected layer. That is not the same process as a refinery steam cracker, but it is a plausible setting for partial thermal or steam-related conversion at the flame–liquid interface and in the hot zone. Industrial practice is explicit that high-temperature conversion can raise benzene above the amount originally present in the feed. U.S. Patent No. 3,625,879 states as an object "to increase the yield of benzene from pyrolysis naphtha over and above the quantity of benzene inherently contained in the pyrolysis naphtha starting material" [23]. The patent is cited only to establish that precursor conversion to benzene is a recognized high-temperature pathway, not to claim that the tank reproduced patented process conditions.

Commercial steam cracking of naphtha typically mixes feed with steam, heats it to about 850 °C for a fraction of a second, and quenches to freeze the olefin and aromatic slate [25, 37]. Modeled Fischer–Tropsch naphtha cracking has produced 4.2–4.8 wt% benzene even when benzene was absent from the feedstock [55]. Benzene yield rises sharply between about 760 °C and 810 °C [30]. During the Borger burns, gas temperatures in the flame and vapor ignition zone

above the liquid were in the 700–800 °C range—on the low side of that industrial window, but not outside it. Optimum benzene formation occurs well above benzene's 80 °C boiling point and can occur on a millisecond time scale. Industry then quenches to keep that yield [60]. In the tank, the cooler liquid at the base of the hot zone is an accidental quench: any benzene formed at the hot surface or in the flame can re-dissolve or remain in the still-liquid layer instead of leaving with the plume. Bulk liquid at 200 °C is far below commercial coil temperatures, so this paper does not treat the hot zone as a steam cracker *per se*. It treats precursor conversion at the hot interface, followed by capture in the cooler liquid, as one possible mechanism that would replenish benzene while TEX continue to be stripped.

4.2 Steam Production in Crude Oil Tank Fires

Slopover—burning crude ejected during extinguishment (Fig. 3)—occurs when water applied to a crude-oil tank fire vaporizes in the heat-affected layer [32]. Water is denser than oil and sinks until the local liquid reaches 100 °C; the resulting steam expands the layer. Expansion ratios from liquid water to steam of about 1,700:1 at 212 °F (100 °C) and 2,300:1 at 500 °F (260 °C) have been cited for heat-affected tank zones [49]. Enough steam ejects burning fuel from the tank [8, 28]. Test 8 slopped over (Fig. 14), consistent with steam formed from water held in the upper 18–20 in. after prior foam application. The same steam that drives slopover is the steam inventory that a conversion hypothesis would use. It does not, by itself, prove conversion.

Conventional briefing language says that constituents with boiling points below the burning-layer temperature are consumed, and that the most volatile residue is gone after the fire is out. These data do not support that sentence for benzene in a deep tank. Headspace benzene remained on the order of 20–50 ppmv after many burns, while TEX collapsed, and benzene's share of

ΣBTEX rose. If that pattern holds in the field, responder risk analysis for post-fire crude—live incidents and training pits that reuse fuel—should treat the residual liquid as a continuing benzene source, not as a stripped residue. A Source–Path–Receiver framing is useful here only in the limited sense that the source term has been underestimated. Chamber concentrations are not path or receiver concentrations and are not comparable to the ACGIH TLV–TWA of 0.02 ppmv (20 ppbv) [1] or to the EPA fenceline action level of 9 μg/m³ (2.82 ppbv). Those limits do illustrate why a mis-specified source matters: action levels sit at or below what many field instruments can resolve, so control has to start at the liquid, not at a late reading downwind.

4.3 Limitations

This study has several limitations. First, the same oil was burned repeatedly; fresh oil was not charged for each evolution. Second, slopover losses were replaced by topping-off, and overnight vacuum-truck movement mixed burned oil with unburned inventory, so fire, dilution, and homogenization are entangled. Third, percent change is taken against a single fresh-oil sample (n = 1), so the twelve post-burn percentages are not independent draws from a pre-burn population. Fourth, the aeration chamber produces an enriched source profile, not a tank-berm or breathing-zone concentration. Fifth, only the top 12 in. were sampled; liquid-phase speciation through the full column was not obtained, and blend-specific API gravity and a full crude assay of the tank inventory were not recorded. Sixth, this campaign was not designed to separate precursor conversion from column diffusion. Both remain viable explanations of the excess-benzene pattern until a purpose-built experiment distinguishes them.

5 CONCLUSION

Aerated headspace from the heat-affected layer of crude oil, sampled after repeated tank burns extinguished with F3, showed a BTEX pattern that a volatility-only model does not predict. Benzene, the most volatile BTEX species, declined the least. TEX declined far more, so benzene's share of ΣBTEX vapor rose from about 5% in fresh oil to about 43% after burning. That is the opposite of the near-complete aromatic stripping reported for shallow in situ burns (95–99% removal) [2, 7, 29, 35, 39]. Deep tanks leave most of the column cold and maintain a hot zone only near the surface. In that geometry a source term—precursor conversion at high temperature, diffusive or convective resupply from the cold inventory, or both—is required to keep benzene in the sampled layer. This paper documents the anomaly. It does not isolate the mechanism.

Risk communication for post-fire crude should not copy the thin-film result. Responders who work next to tank residues or pooled oil after extinguishment, and training sites that recycle burned product, should assume that benzene remains available to the vapor space. Vapor suppression (including foam) still matters after knockdown. Subsequent work should measure liquid-phase profiles and test conversion versus transport under controlled temperature and steam conditions so that the source term can be specified rather than inferred.

6 RECOMMENDATIONS

6.1 Further Research Considerations

Two source-term hypotheses follow directly from the volatility ranking. The first is thermal or steam-related conversion of precursors in the hot zone or at the flame–liquid interface, with

capture of newly formed benzene in the cooler liquid at the base of the hot zone. The second is resupply from the large cold inventory: as the surface layer is stripped, a concentration gradient drives benzene (and other lights) upward faster than TEX. The second hypothesis uses benzene's high diffusivity and vapor pressure as a transport advantage, not as a reason it should have vanished. Both should be tested in apparatus that can hold a controlled hot zone over a cold column, with and without steam, and with liquid-phase sampling versus depth. Follow-on studies by this research group address those tests; they are not part of the present observational dataset.

The present results show benzene remaining in the upper 12 in. after twelve burns of an inventory that was also mixed and topped off. They do not show a net increase above the fresh-oil headspace concentration. Controlled burns that start from a fully specified liquid assay, avoid overnight mixing, and vary steam input are needed before extinguishment water can be assigned a causal role in benzene regeneration. F3 application rates 1.5–3 times those used for AR-AFFF have been recommended for performance parity [5]; more water is then available to the hot zone. Whether that water is only a slopover hazard or also a reactant is an open experimental question.

Due to the phasing out of per- and polyfluoroalkyl substance (PFAS) containing foams (i.e., aqueous film-forming foam (AFFF)), research has focused on foam performance of fluorine-free foam (F3) types. While surface tension and film formation are stable and rapid forming in AFFFs, F3 solutions have shown an inability to form thin films or to outperform AFFF on hydrocarbon liquid surfaces. There is destabilization from oil droplets with F3 foams, making it less effective in suppressing pool fires. AFFF's sealing ability indicates better performance in protection from vapor in low-flashpoint flammable liquids [13, 47, 59]. A closer look at F3 foam

properties and foam application could help provide technological advancements for better extinguishment and vapor suppression.

Firefighters must apply foam near exposed liquids to optimize coverage, which often requires precise foam application during extinguishment. As fire training facilities are likely to recycle and reuse petrochemical products for additional fire training, increased risk analysis and amended risk communication must reflect the impact of foam application and resultant change to the existing chemical profiles on which current risk communication is based. Although firefighters are typically protected with supplied air, the long-term nature of mitigation includes other response personnel who prefer reduced or no respiratory protection, particularly in hot environments or when visual acuity and hand-eye coordination are essential.

Following 12 burns of fresh oil with mechanical mixing, this research introduces the hypothesis that when benzene is present in crude oil contained by storage tanks impacted by fire, it remains volatile post-fire, prolonging the potential for exposure. Should this phenomenon prove to be a recurring consequence of firewater/foam application, responder exposure to benzene should be considered a vulnerability to response strategies. Due to the abundance of tank fires involving hydrocarbons and the potential risk of long duration and proximity engagement by firefighting resources, further analysis and communication of exposure risk must be emphasized as a concern for first responders.

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FIGURES

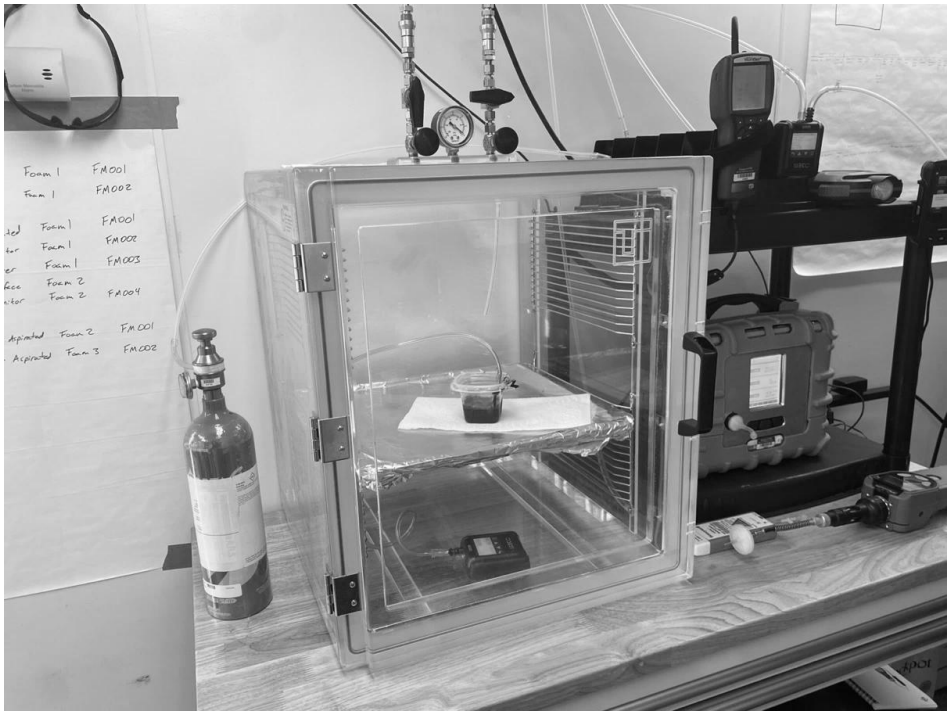


Figure 1. Vapor Chamber during Sample Aeration

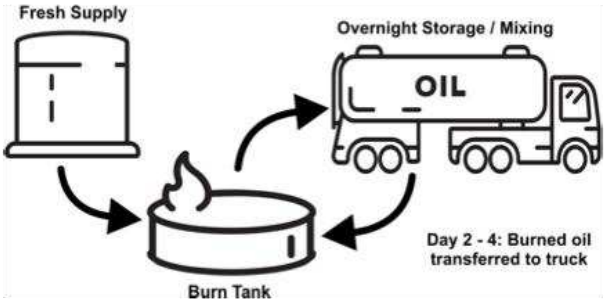
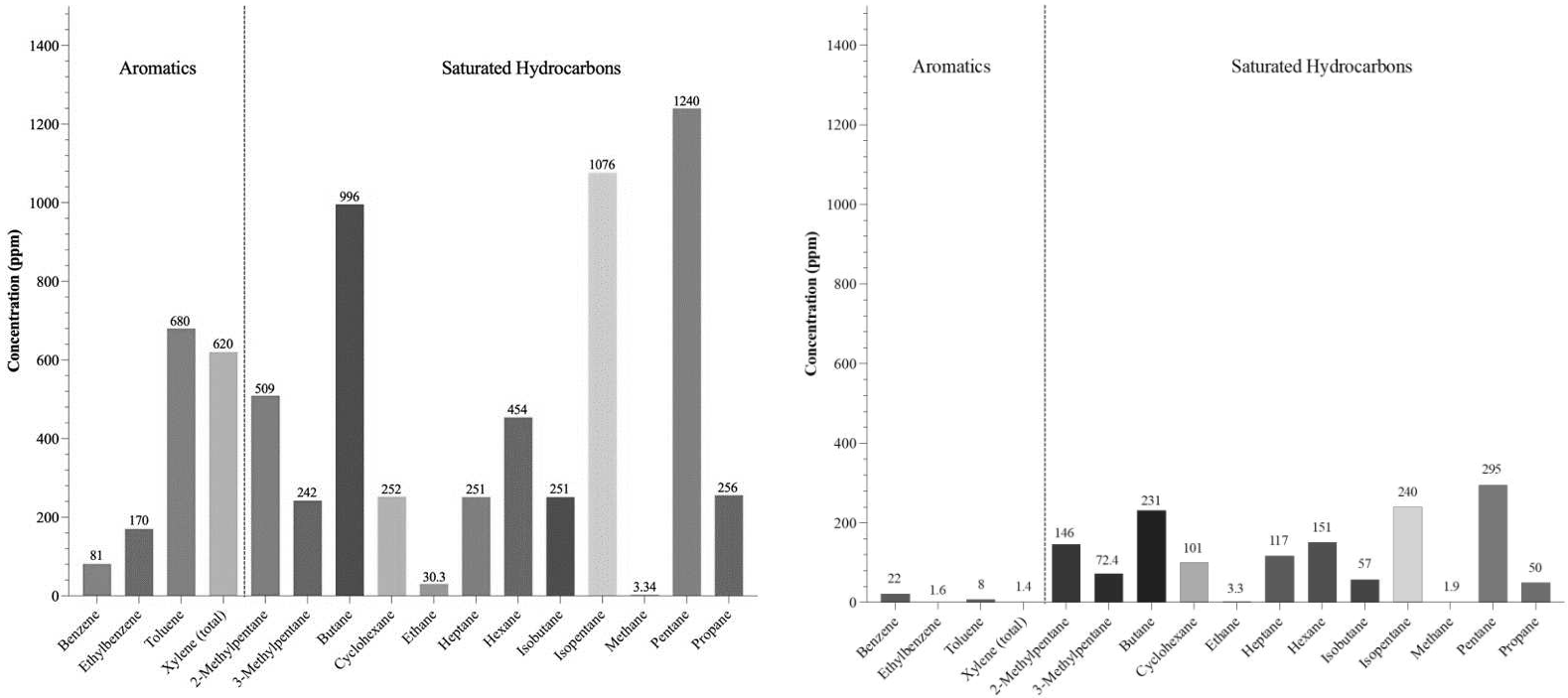


Figure 2. Burn Test Crude Oil Processing Flow

Figure 3. Display of Slopover Event



a) Fresh Oil Pre-Burn b) Final Post-Burn

Figure 4. (a) Fresh Oil Pre-Burn vs. (b) Final Post-Burn Hydrocarbon Detections

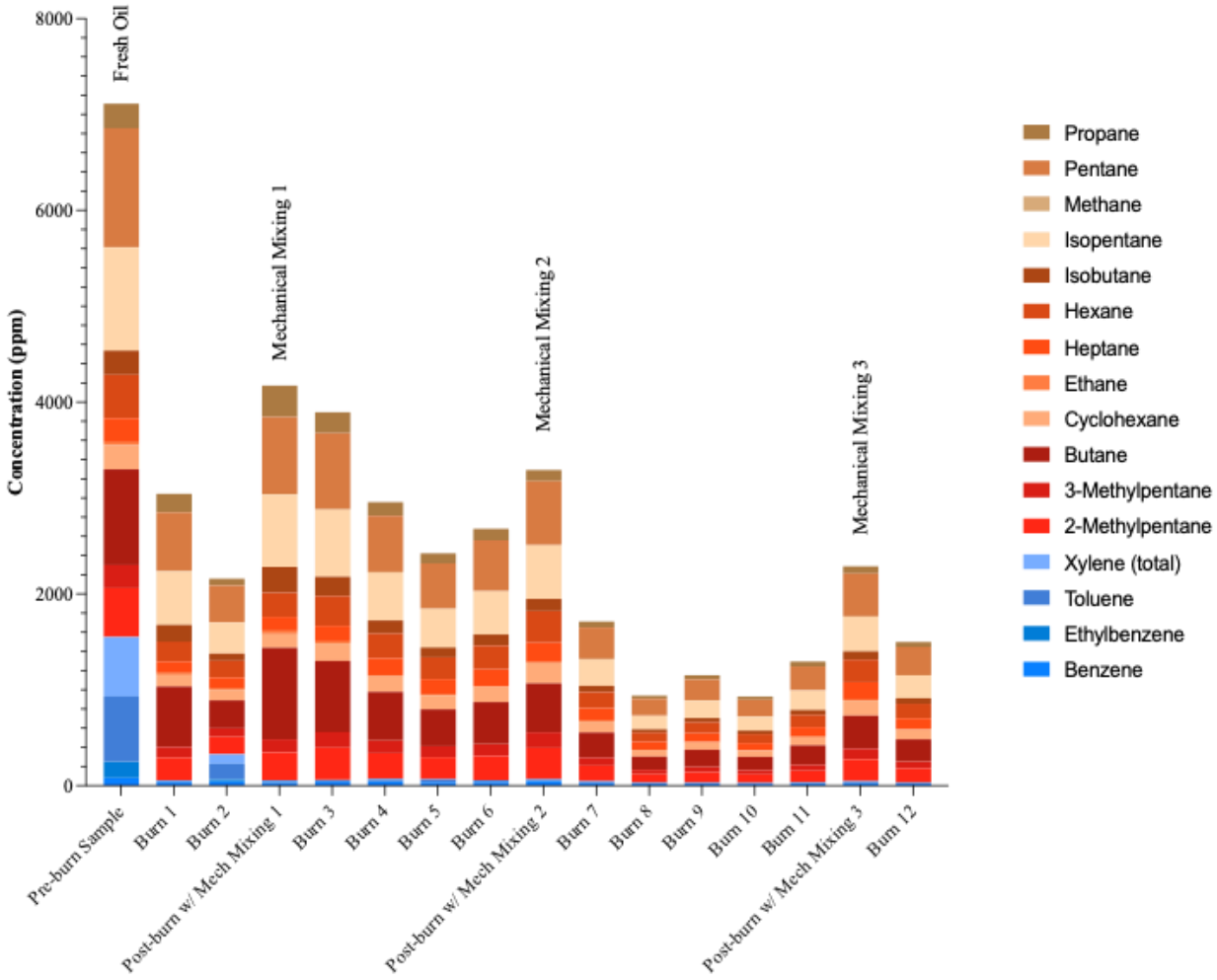


Figure 5. VOC Trends from Event Sequence Graph

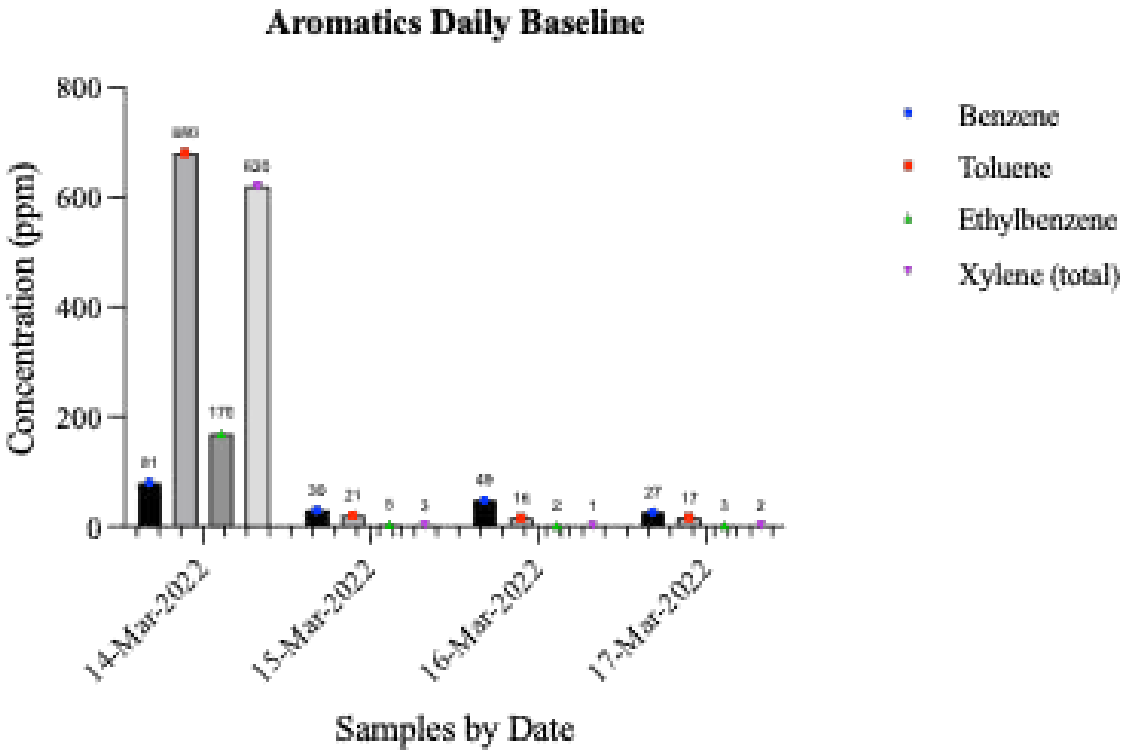


Fig. 6 Daily baseline concentrations

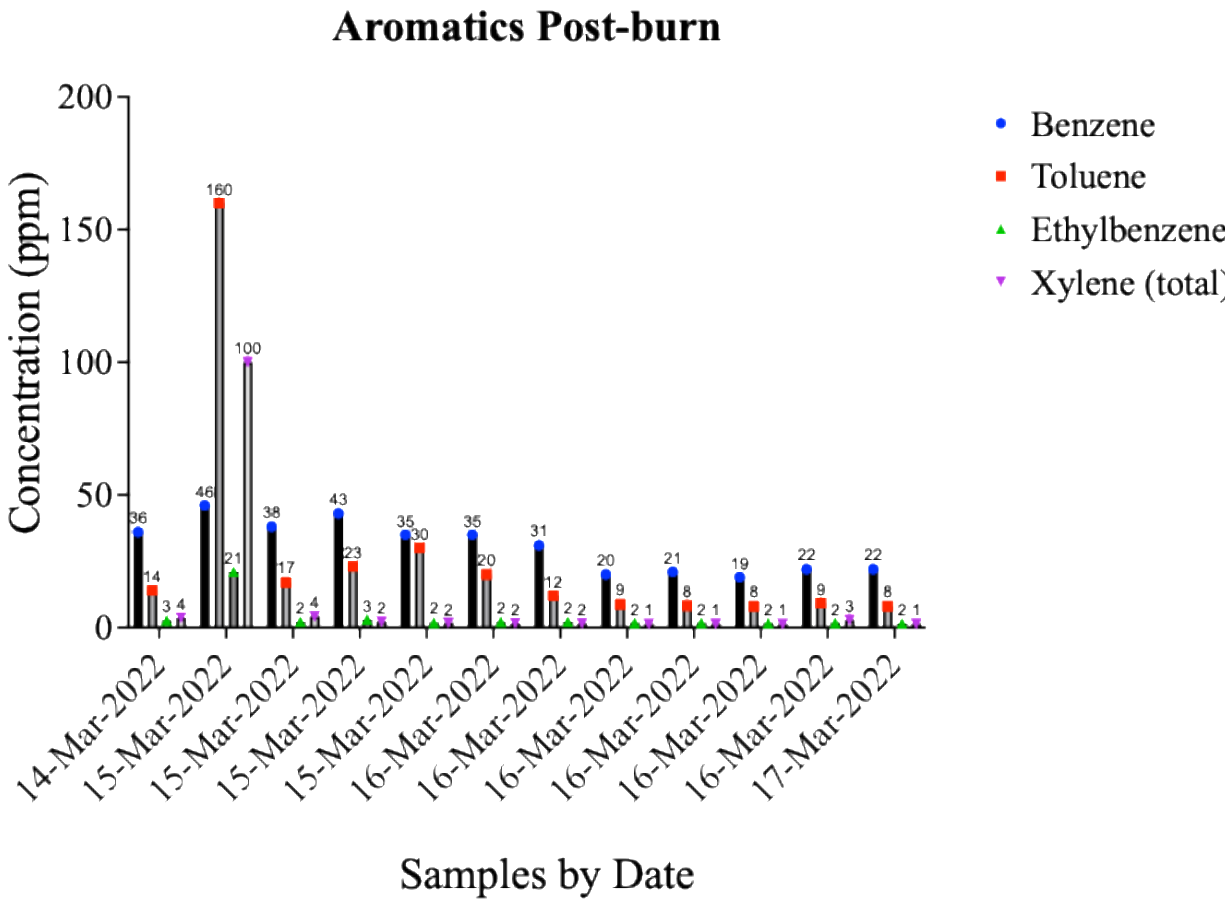


Fig. 7 Daily post-burn concentrations

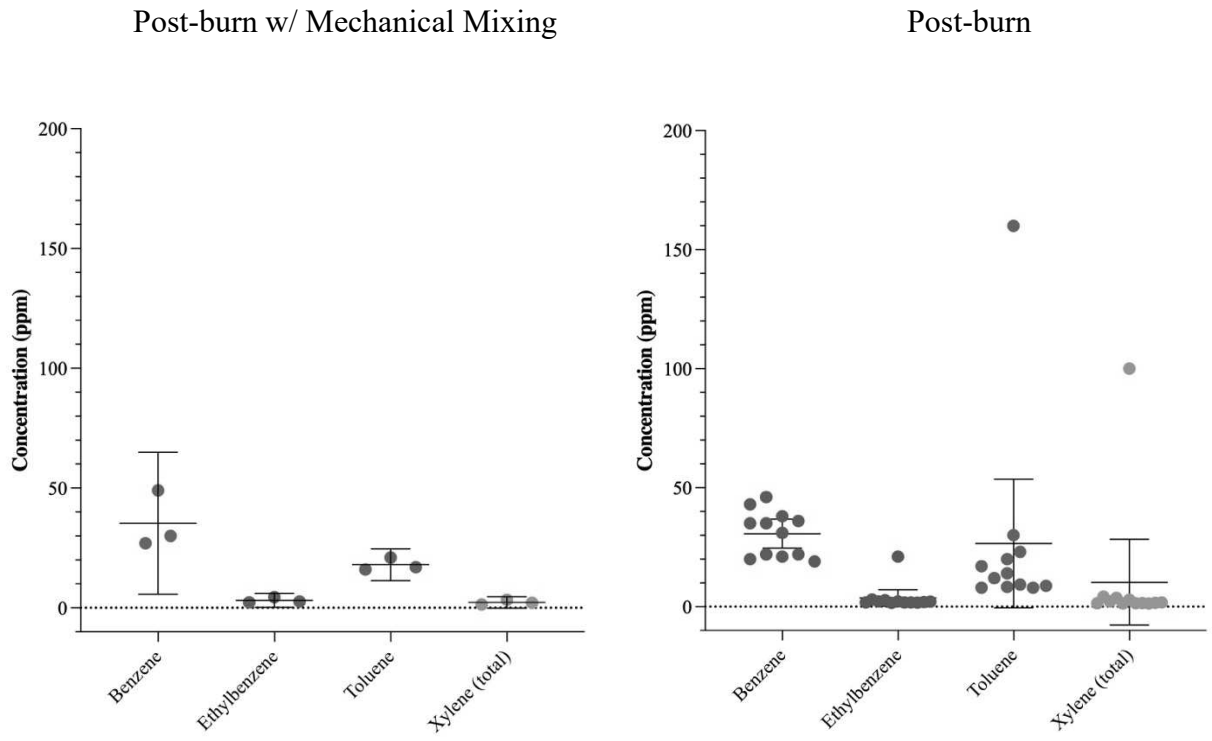


Figure 8. Comparison of Aromatic Means with 95% CI

Dots represent sample result concentrations
Lines represent the mean concentration and the upper and lower confidence intervals (95%)

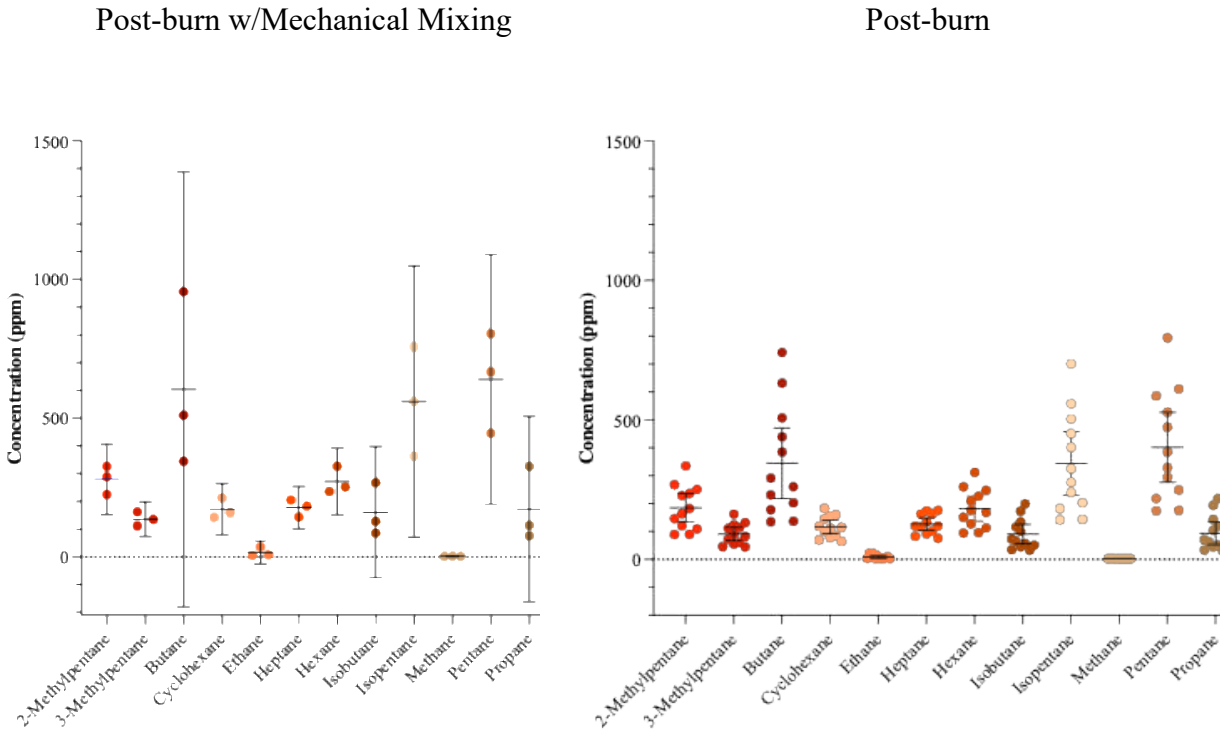


Figure 9. Comparison of Saturated Hydrocarbon Means with 95% CI

Dots represent sample result concentrations
Lines represent the mean concentration and the upper and lower confidence intervals (95%)

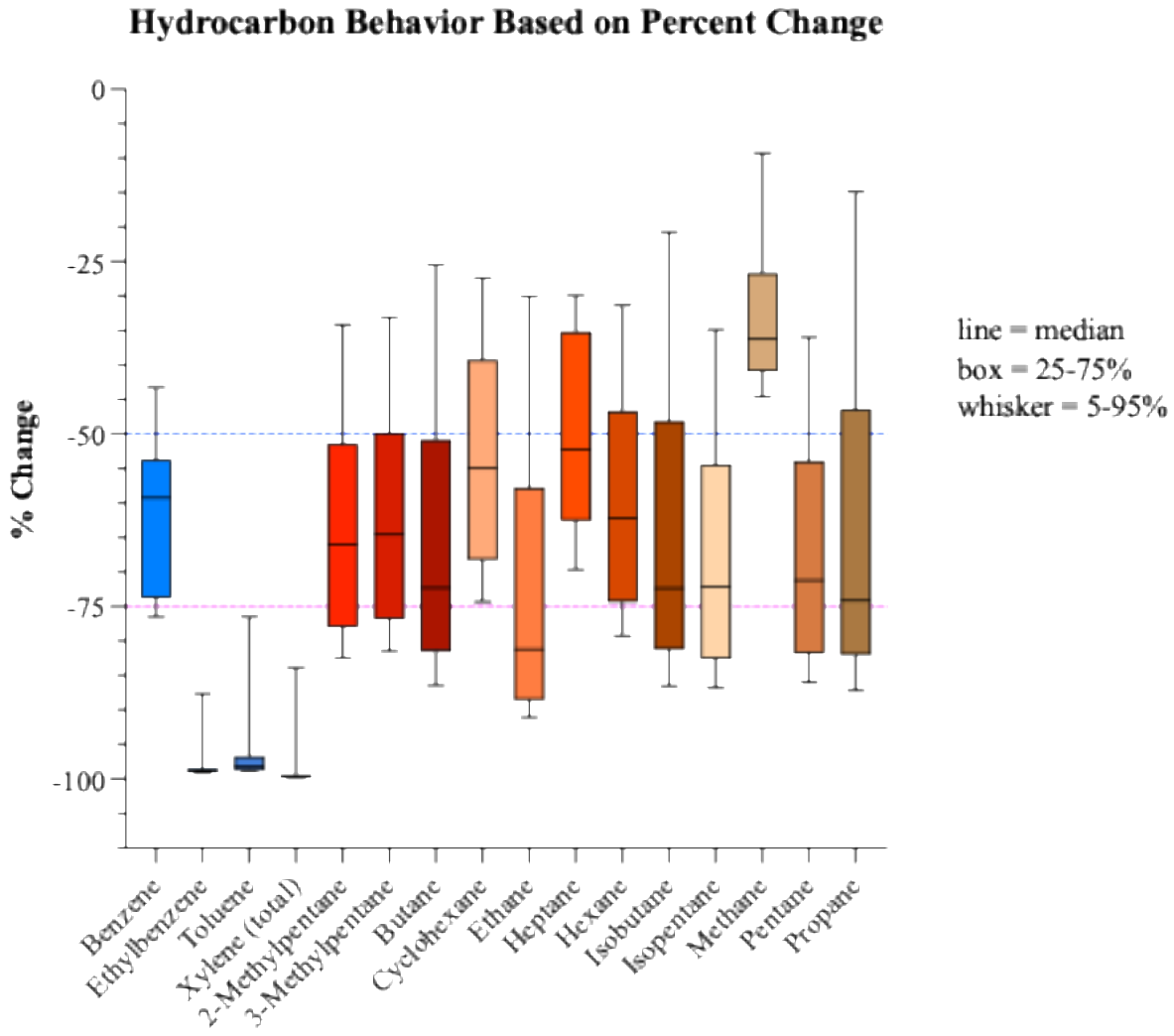


Figure 10. Percent Change Comparisons of Aromatics and Saturated Hydrocarbons' Behavior Post-Burn

All species decline after fire, as expected. Benzene declines least. That ranking is the reverse of vapor pressure and molecular weight among the aromatics, and it is the basis for treating the residual benzene as excess relative to a volatility-only model.

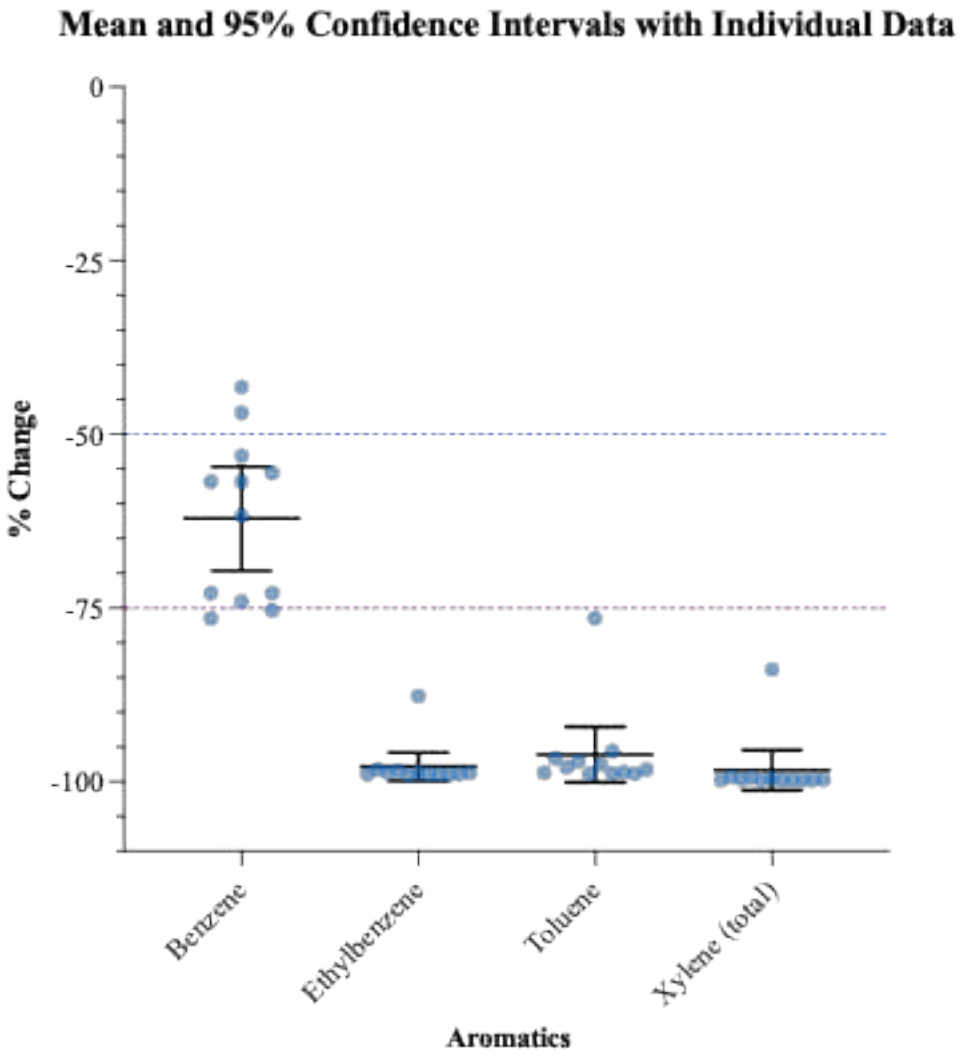


Figure 11. Percent Change Comparison of Means for Aromatics Post-Burn w/ 95% CI

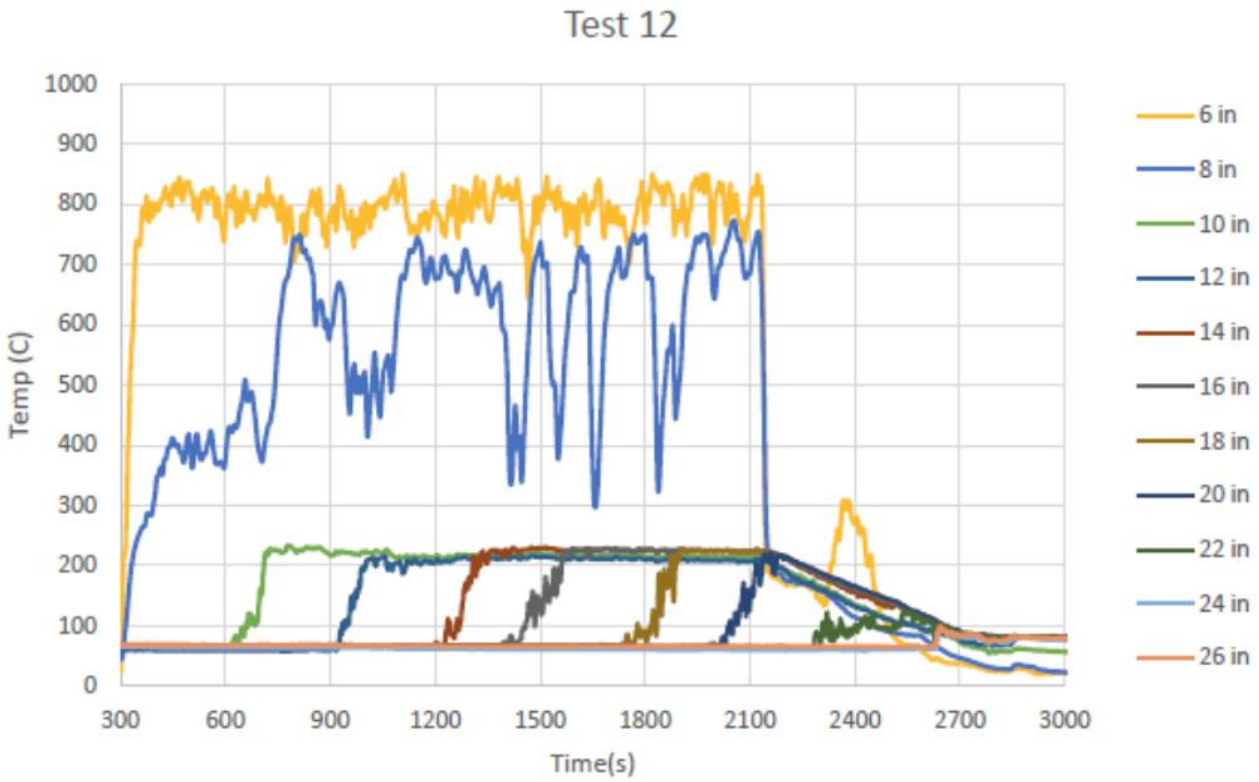


Figure 12. Tank Temperature at Depth vs. Time.

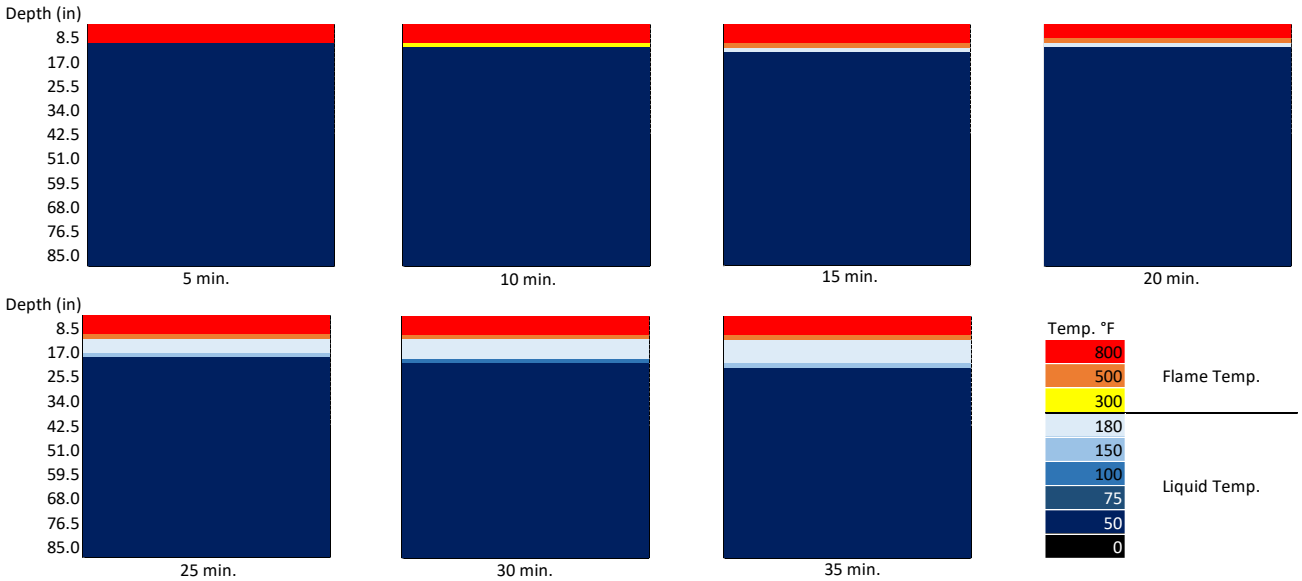


Figure 13. Temperature Penetration into Bulk Liquid during Test 12

Temperature and depth plot with discrete time intervals displaying incremental progression of temperature downward within the bulk liquid (gray band), the gray band represents a temperature stratum in which the effective boiling point resides.

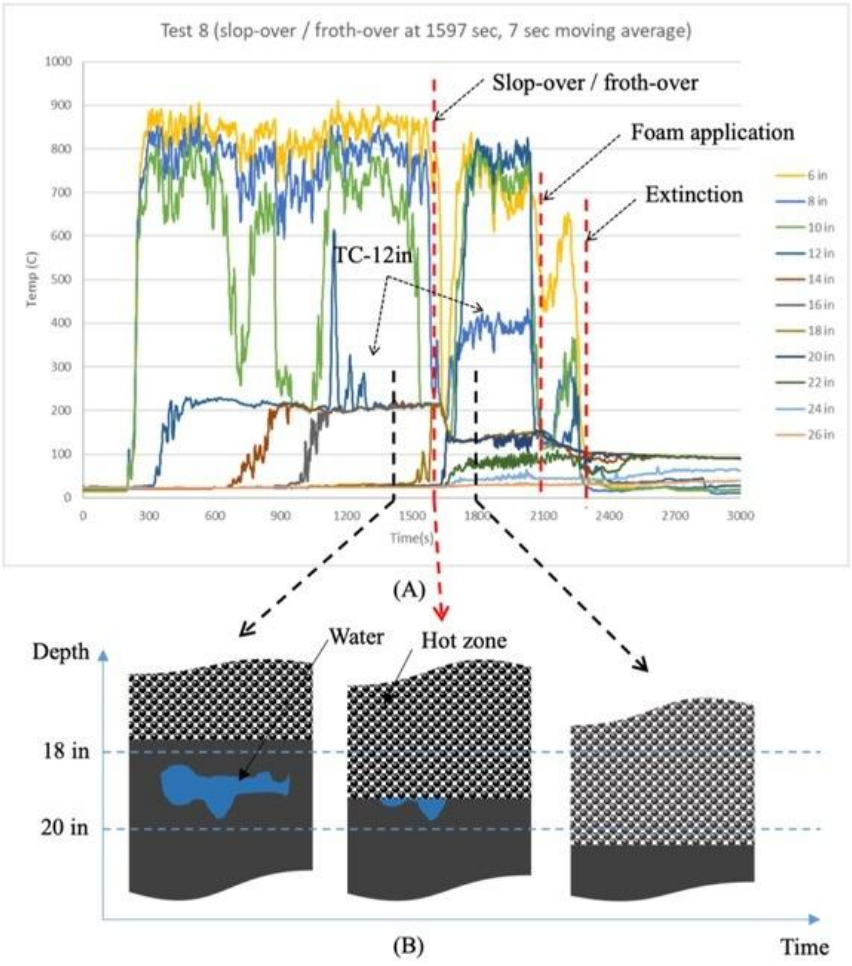


Figure 14. Borger Test 8: Slopover Event

Slopover event occurred at 1597 seconds and estimated water bolus trapped in heat-affected layer of crude oil during hot zone development. Authors used slop-over and froth-over interchangeably when referring to a slopover event. Thermocouples (TC) were utilized to gather temperature data from within the center column of the crude oil tank, TC-12in refers to the TC located 12 inches below the top of tank with 6 inches of freeboard to the oil surface.

TABLES

Table 1. Crude Oil Liquid Sample Collection Summary

Sample Type	n=	Sample Description
Pre-Burn	1	Collected from fresh, unburned oil on Day 1
Post-Burn with Mechanical Mixing	3	Mechanical mixing involved overnight storage, a Vacuum Truck, with a mixture of burn-tested oil from the previous day and the original supply. Sample collected each day before burning.
Post-Burn	12	Collected samples from oil following each extinguishment of each burn test, designated each day in the Sample ID. Day 1 = 1 samples; Day 2 = 4 samples; Day 3 = 6 samples; Day 4 = 1 sample.

Table 2. Ambient Weather Conditions During Burn Days (2022)

Day	Temperature (°F)			Temperature (°C)			Dew Point (°F)			Humidity (%)			Wind Speed (mph)			Pressure (in)		
Mar	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min
14	58	49.2	42	14.4	9.6	5.6	35	22.8	5	54	37.0	17	31	18.6	8	26.5	26.3	26.1
15	70	50.3	30	21.1	10.2	-1.1	28	21.0	13	79	40.2	12	16	10.7	5	26.6	26.5	26.3
16	79	60.4	43	26.1	15.8	6.1	19	15.9	13	31	19.5	9	24	12.8	3	26.3	26.1	26.0
17	58	42.4	33	14.4	5.78	0.5	34	28.0	13	96	63.2	19	33	23.3	7	26.3	26.1	25.9
18	57	41.8	31	13.9	5.4	-0.5	31	25.6	18	92	60.3	22	24	12.0	5	26.4	26.4	26.3

* Source: Wunderground.com (https://www.wunderground.com/dashboard/pws/KTXAMARI308?cm_ven=localwx_pwsdash)

Table 3. Summary Statistics for Post-Burn Samples: Aromatics of Crude Oil Vapor

Analyte	n=	Min. (ppmv)	Max. (ppmv)	Mean (ppmv)	Std. Dev.	95% LCL[a]	95% UCL[b]
Fresh Oil (Pre-Burn)							
Benzene	1			81			
Ethylbenzene	1			170			
Toluene	1			680			
Xylenes (total)	1			620			
Post-Burn Samples w/ Mechanical Mixing*							
Benzene	3	27.0	49.0	35.3	11.9	5.70	65.0
Ethylbenzene	3	2.30	4.50	3.13	1.19	0.170	6.10
Toluene	3	16.0	21.0	18.0	2.65	11.4	24.6
Xylenes (total)	3	1.40	3.30	2.27	0.961	-0.120	4.65
Post-Burn							
Benzene	12	19.0	46.0	30.7	9.54	24.6	36.7
Ethylbenzene	12	1.60	21.0	3.65	5.48	0.168	7.13
Toluene	12	8.00	160	26.5	42.6	-0.539	53.6
Xylenes (total)	12	1.30	100	10.3	28.3	-7.69	28.2

[a] LCL = lower confidence limits; [b] UCL = upper confidence limits

*Mechanical mixing defined in this study is overnight storage and mixture of burn-tested oil and fresh oil.

Table 4. Summary Statistics for Saturated Hydrocarbons of Crude Oil Vapor

Analyte	n=	Min. (ppmv)	Max. (ppmv)	Mean (ppmv)	Std. Dev.	95% LCL[a]	95% UCL[b]
Fresh Oil (Pre-burn)							
2-Methylpentane	1			509			
3-Methylpentane	1			242			
Butane	1			996			
Cyclohexane	1			252			
Ethane	1			30.3			
Heptane	1			251			
Hexane	1			454			
Isobutane	1			251			
Isopentane	1			1076			
Methane	1			3.34			
Pentane	1			1240			
Propane	1			256			
Post-Burn Samples w/ Mechanical Mixing*							
2-Methylpentane	3	225	326	280	51.1	153	407
3-Methylpentane	3	112	162	136	25.0	74.2	199
Butane	3	345	956	604	316	-181	1390
Cyclohexane	3	142	213	171	37.1	79.2	263
Ethane	3	5.44	35.9	16.3	17.0	26.0	58.6
Heptane	3	144	205	177	30.9	101	254
Hexane	3	236	327	272	48.6	151	392
Isobutane	3	86.2	268	161	95.2	-75.8	397
Isopentane	3	363	757	560	197	70.6	1049
Methane	3	1.97	2.66	2.21	0.387	1.25	3.18
Pentane	3	446	805	639	181	189	1089
Propane	3	76.3	326	172	135	-162	506
Post-Burn							
2-Methylpentane	12	89.4	335	185	78.8	135	235
3-Methylpentane	12	44.9	162	91.1	37.7	67.1	115
Butane	12	135	742	345	199	219	471
Cyclohexane	12	64.8	183	116	38.4	91.3	140
Ethane	12	2.70	21.2	8.73	6.68	4.49	13.0
Heptane	12	76.1	176	126	35.4	104	149
Hexane	12	94.0	312	182	70.2	137	226
Isobutane	12	33.7	199	90.4	55.0	55.5	125
Isopentane	12	142	701	344	180	230	458
Methane	12	1.85	3.03	2.23	0.343	2.01	2.45
Pentane	12	174	794	402	198	276	527
Propane	12	32.9	218	93.6	63.1	53.5	134

[a] LCL = lower confidence limits; [b] UCL = upper confidence limits

*Mechanical mixing defined in this study is overnight storage and mixture of burn-tested oil and fresh oil

Table 5 t-test analysis of benzene versus aromatic and saturated hydrocarbons

	Ethyl Benzene	Toluene	Xylene total	2-Methyl pentane	3-Methyl pentane	Butane	Cyclohexane	Ethane	Heptane	Hexane	Isobutane	Isopentane	Methane	Pentane	Propane
Paired t-test (n-12)															
P value	<0.0001	<0.0001	<0.0001	0.5894	0.9326	0.4552	0.0139	0.0932	0.0007	0.4574	0.7015	0.0894	<0.0001	0.0902	0.8170
Significantly different (P < 0.05)?	Yes	Yes	Yes	No	No	No	Yes	No	Yes	No	No	No	Yes	No	No
One- or two-tailed P value?	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed	Two-tailed
t, df	t=11.98, df=11	t=12.58, df=11	t=12.33, df=11	t=0.5559, df=11	t=0.08659, df=11	t=0.7741, df=11	t=2.922, df=11	t=1.838, df=11	t=4.633, df=11	t=0.7702, df=11	t=0.3935, df=11	t=1.863, df=11	t=8.106, df=11	t=1.857, df=11	t=0.2370, df=11
How big is the difference?															
Mean of differences (B - A)	-35.71	-33.96	-36.20	-1.508	-0.2358	-3.214	8.078	-9.041	12.54	2.128	-1.838	-5.891	28.91	-5.475	-1.295
SD of differences	10.32	9.353	10.17	9.398	9.434	14.38	9.575	17.04	9.373	9.569	16.18	10.95	12.35	10.21	18.93
SEM of differences	2.980	2.700	2.936	2.713	2.723	4.152	2.764	4.918	2.706	2.762	4.670	3.162	3.566	2.948	5.464
95% confidence interval	-42.27 to -29.15	-39.90 to -28.02	-42.66 to -29.74	-7.480 to 4.463	-6.230 to 5.758	-12.35 to 5.924	1.994 to 14.16	-19.87 to 1.784	6.580 to 18.49	-3.952 to 8.207	-12.12 to 8.441	-12.85 to 1.069	21.06 to 36.75	-11.96 to 1.013	-13.32 to 10.73
R squared (partial eta squared)	0.9289	0.9350	0.9325	0.02733	0.0006812	0.05166	0.4370	0.2350	0.6611	0.05117	0.01388	0.2398	0.8566	0.2387	0.005081
How effective was the pairing?															
Correlation coefficient (r)	0.5594	0.6128	0.5211	0.7954	0.7963	0.7028	0.7783	0.6446	0.7522	0.7858	0.6915	0.7577	0.3780	0.7684	0.6677
P value (one-tailed)	0.0293	0.0171	0.0412	0.0010	0.0010	0.0054	0.0014	0.0118	0.0024	0.0012	0.0064	0.0022	0.1129	0.0018	0.0088
Was the pairing significantly effective?	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes