

In Situ Burn Testing of Weathered and Emulsified Crude Oils

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Christopher J. Pfützner¹, Steven G. Tuttle¹, Thomas N. Loegel¹, Iwona Leska², Brian T. Fisher¹

¹Navy Technology Center for Safety and Survivability, Naval Research Laboratory

²Nova Research, Inc., Alexandria VA, 22308

Naval Research Laboratory
4555 Overlook Avenue SW
Washington DC 20375, USA
christopher.pfutzner@nrl.navy.mil

ABSTRACT

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This paper investigates the ignitability and effectiveness of burning crude oil spills at sea with respect to the type of oil, weathering time, and seawater emulsion content. In the event of an oil or fuel spill at sea, in situ burning can be a practical method of removing the oil and preventing it from reaching vulnerable coastlines. However, the specific chemistry of the oil and its resulting behavior dictates how well this method works. In order to understand this behavior, Santa Barbara Channel crude oils were tested and burned in combinations of fresh, weathered, and seawater-emulsified at discrete ratios. A cone calorimeter was used to monitor time to ignition, mass loss, heat release rate, and smoke production for laboratory-scale burn tests. Weathering generally increased ignition time, but also changed the miscibility with water; this changed both heat released and burn efficiency. Emulsions with seawater fractions below approximately 20 % were found to improve the heat release rate and burn efficiency compared to oil-only burns; suggesting that some water emulsification can benefit oil burning. The results indicate that a targeted approach to the type of oil and degree of emulsification can expand the window of opportunity for in situ oil burns.

INTRODUCTION

When crude oil spills occur on water, the results can be catastrophic for crew members, marine life, and coastal communities. Methods of cleaning up these spills must balance time, financial, and environmental tradeoffs in order to stop the spread of the spill, recover what may be useful, and do so within the confines of local regulations. Over the past few decades, regulatory bodies and relevant operators have used in situ burning (ISB) of spilled crude oil at sea. This involves herding the spill to achieve a thick layer of crude and then igniting that layer, allowing it to burn off and keeping it from spreading. This method applies in many scenarios, but relies on the ignitability and burn sustainability of the oil. Success depends on time spent weathering and emulsifying, and the use of chemical emulsion breakers to prepare spills for burning. This paper investigates factors that influence laboratory-scale in situ burning, as they relate to the type of crude oil and its properties, with the hope that this knowledge can better prepare responders for future spills.

OBJECTIVE

The goal of this experiment is to study California crude oil in situ burn behavior in the laboratory environment in order to predict burn performance from crude oil physical and chemical properties. A parallel, practical-scale in situ burn experiment was carried out for comparison and validation (Tuttle, Fisher, Pfutzner, Loegel, & Hinnant, 2018).

METHODS

In situ Conditions

This test was done to mimic ocean conditions along the Santa Barbara Channel, California during August, when ocean temperatures, air temperatures, and hours of sunlight would be greatest. This maximizes evaporative, photochemical, and biological weathering to provide a conservative baseline for ignition and flammability behavior. Historical data was gathered from a NOAA buoy and averaged (Table 1), which matched reasonably with industry reports of the field (NOAA, 2016) (Venoco, Inc, 2011). Artificial ocean water was created according to the mix dictated by ASTM D1141-98(2008) standards (ASTM International, 2008).

Table 1: Averages for the month of August as compiled from buoy 46053 in the Santa Barbara Channel (NOAA, 2016).

Wind Speed (m/s)	Wind Direction (°)	Wave Direction (°)	Air Temp. (°C)	Air Pressure (hPa)	Water Temp. (°C)	Current Speed (m/s)
4.4	226	147	18.3	1013	19.7	0.16

Physical Properties

This study was designed to compare burn behavior to oil chemistry and properties in different conditions. Though property databases are available, most are not updated regularly to match changing oilfield conditions (Environment Canada, 2001; Jokuty, Whiticar, Wang, Fieldhouse, & Fingas, 1999). Properties change during the lifetime of the well and can be altered by injection fluids. Therefore, we measured the properties to quantify the changes over the past 20 years. Experiments were done in the lab to determine the specific gravity and viscosity for each oil using hydrometers and capillary viscometers, respectively. The largest discrepancy in specific gravity was a 4% relative change. Viscosity changed at least 20% for all oils; Point Arguello viscosity exhibited a relative change of over 1000%. The properties of the oils used are presented in Table 2.

Table 2: Physical properties of Fresh and Weathered crude oils used, as measured by the authors at 15 °C. Oils listed in order of increasing fresh density.

Crude Oil (abbrev.)	Platforms	API (°)	Viscosity (cP)	API (°) 48 hr	Viscosity (cP) 48 hr
Santa Clara (SC)	Grace	33.4	30	22.3	3,690
Carpinteria (CA)	Hogan, Houchin, Henry	24.0	132	17.0	15,600
Sockeye (SK)	Gail	20.0	924	15.6	92,490
Santa Ynez (SY)	Heritage, Harmony, Hondo	19.4	1,140	14.1	6,267,400
Point Arguello (PA)	Hidalgo, Harvest, Hermosa	16.2	14,500	14.5	161,200

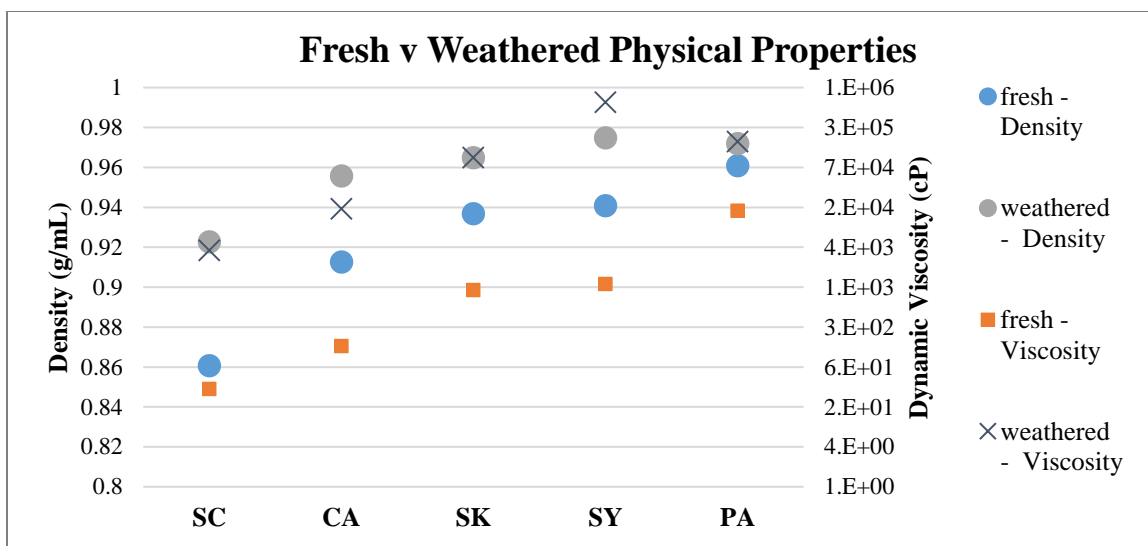


Figure 1: Measured density and viscosity of fresh and after 48-hr laboratory weathering, as measured by authors. Viscosity axis incremented log base ten for wide range of values.

Crude Oil Sample Preparation

Crude oil was tested from five locations in the Santa Barbara Channel, California. Each was tested fresh, weathered, and emulsified. Each oil type was prepared in six different condition combinations (Table 3). “Neat” refers to oil unmixed with water. Fresh, neat oil was a baseline; weathered oil was tested in increasing degrees of emulsification.

Table 3: Testing Conditions for burn tests.

Condition	Simulated Weathering (hrs)	Emulsification (% Seawater)	Nomenclature
1	0	0	N
2	0	40	E40
3	48	0	WN
4	48	20	WE20
5	48	40	WE40
6	48	60	WE60

Weathering

Realistic weathering was impossible to replicate in the laboratory without the influence of wind, waves, temperature, humidity, sunlight, and biology. Instead, evaporative weathering was performed, where mass was lost to the atmosphere; the mass lost corresponded to time at sea. While spills are hopefully remedied quickly, 48 hours is a reasonable timeframe for ISB to be implemented after a spill occurs (National Commission on the BP Deepwater Horizon Oil Spill and Offshore Drilling, 2011) Initially, this mass loss was predicted by NOAA-supplied ADIOS

software to simulate 48 hours weathering (NOAA, 2016). The software's parameters differed from what we measured, so an experimental model was required.

Following the laboratory weathering described in Jokuty et al, a mass loss curve was found for a 48 hour period of weathering (Jokuty, Whiticar, Wang, Fieldhouse, & Fingas, 1999). A 139-mm-diameter petri dish was filled with 20 g crude oil and placed in a temperature-controlled hood. Mass loss was tracked. Average air speed was 0.2 ± 0.05 m/s and temperature was 22 ± 1 °C. The wind speed was significantly different than the NOAA data, but the Jokuty et al correlations used did not take into account the wind speed, which suggested it was negligible for the weathering procedure; this corresponds with data presented by Fingas (Jokuty, Whiticar, Wang, Fieldhouse, & Fingas, 1999) (Fingas M. , 2011). This method did not replicate photochemical and biological effects, which could influence mass loss and emulsibility, although these effects generally play a smaller role in weathering compared to evaporation (Fingas M. , 2011).

Weathering time was dependent on oil type, as shown in the fitted data in Figure 2; each followed a similar trend. MLR was rapid for ten hours and then plateaued. The oils generally follow their density and viscosity: the lighter oils lost more than the heavier, more viscous oils.

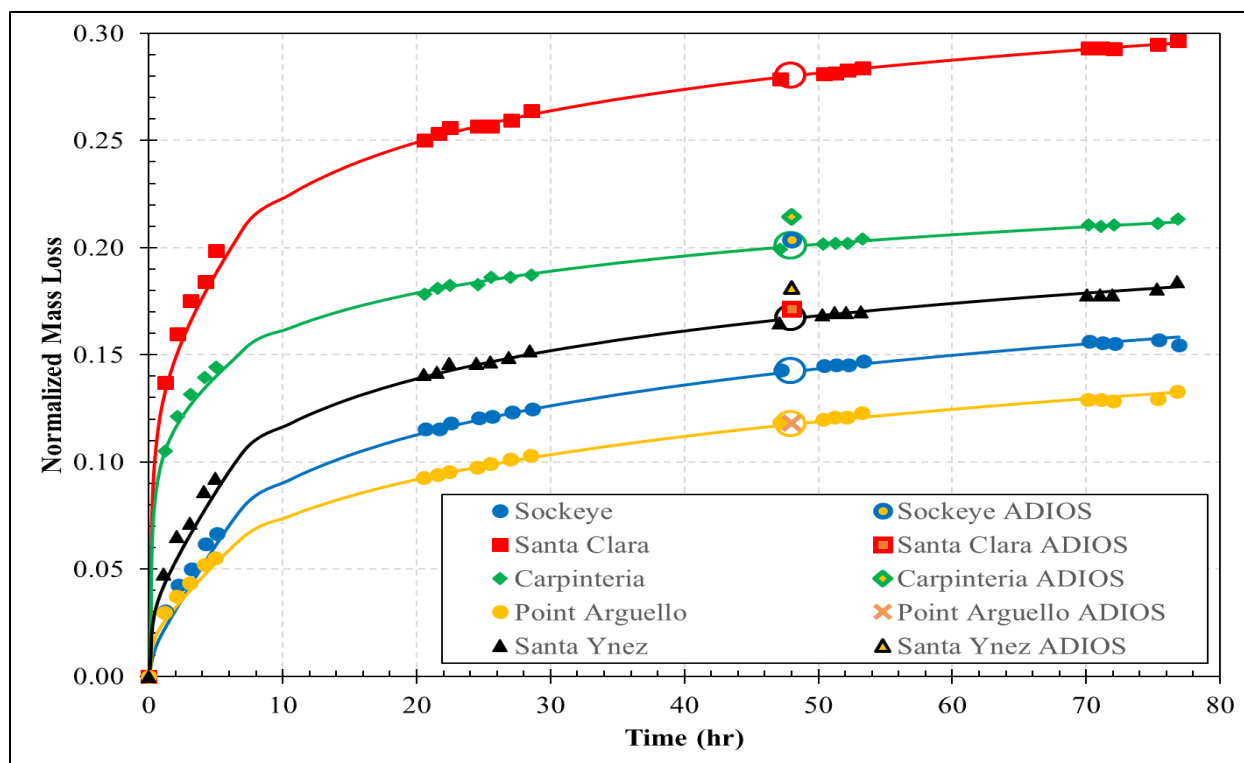


Figure 2: Weathering data with polynomial-logarithmic fits. Equivalent mass loss to 48 hours is denoted by hollow marker. ADIOS predictions match well except for Santa Clara and Sockeye.

These data were taken at a constant temperature, and a logarithmic, polynomial curve was fitted of the form:

$$\delta m = a_3(\ln(t))^3 + a_2(\ln(t))^2 + a_1 \ln(t) + a_0$$

where δm is the normalized mass loss, a_n is the polynomial coefficient, and t is in hours. The corresponding mass loss fractions used in this study are shown in Figure 2. The Santa Clara and Sockeye notably differed from ADIOS. For large batches of oil required for trial replicates and intermediate scale burns, weathering was done with 10 L in a steel pot, slowly heated to 80°C with drum heaters on the outside. The oil was agitated with an 8" rotary mixer at 180 rpm. Temperature and mass were acquired at regular intervals. The weathered oil was stored in sealed pails until testing.

Emulsification

Emulsification at sea is primarily accomplished by wave action. It is generally not desirable to have large quantities of stable oil-water emulsions, because they are difficult to degrade or cleanup (Thingstad & Pengerud, 1983). Products are used in the wellbore and production

pipelines to reduce emulsification and improve extraction. The Santa Clara arrived with Nalco Flow 12021A (NALCO Champion, 2014); Carpinteria arrived with EB596 additive (Tuttle, et al., 2019). These are solvents and inseparable from the bulk oil, so all data collected were done with these additives.

In the laboratory, it was necessary to emulsify approximately 500 mL quantities at once. Simulated seawater and oil were mixed with a high-shear mixer. Some of the oils emulsified easily, as documented in earlier work (Tuttle, Fisher, Pfutzner, Loegel, & Hinnant, 2018). In order to emulsify each oil up to 40% seawater, the surfactant Span® 85 was added at 2% by volume for all emulsified conditions (EMD Millipore Corporation, 2013). This did not stably emulsify 60% seawater for all oils, but more surfactant would be unrealistic in situ. Several oils required over three hours of mixing to emulsify, and Sockeye would not emulsify at 60% seawater, independent of time mixed.

Emulsion stability is not standardized in the industry, and the stability of these emulsion was deemed sufficient if there was no observable separation after two hours. These might be referred to as “tight” or “entrained” by Fingas and Fieldhouse’s terminology, although some had “meso-stable” qualities (Fingas & Fieldhouse, 2009). Samples of emulsions were left several weeks in sealed containers; most broke overnight but some took up to ten days to separate.

Laboratory Scale – Cone Calorimetry

To determine the burning behavior of the oil under standardized conditions, a cone calorimeter and a custom burn pan were used. Ignition time, heat release rate, and mass loss were recorded for each test. Oil samples were placed in a steel pan underneath a heater and igniter. The heater vaporized oil constituents, which were spark ignited; ignition time was recorded and the igniter was removed once the slick’s surface was aflame.

The exhaust was sampled and tested for O₂, CO, and CO₂. The calorimeter’s 1 kg load cell was not adequate for the burn pan’s mass. Instead, the sample was weighed pre- and post-test and average mass loss rate (MLR in g/s) was recorded.

This setup had a uniformly thick “slick” with a heat sink to simulate the ocean water below this slick. A stainless steel, double-lined pan was used, where the oil was not in contact with the water, and chilled water was pumped beneath (Figure 3). This was adapted from the work of van Gelderen et al, with a separated water jacket to ensure the water would not boil while maintaining the necessary heat loss to mimic the ocean (Gelderen, Alva, Mindykowski, & Jomaas, 2017)

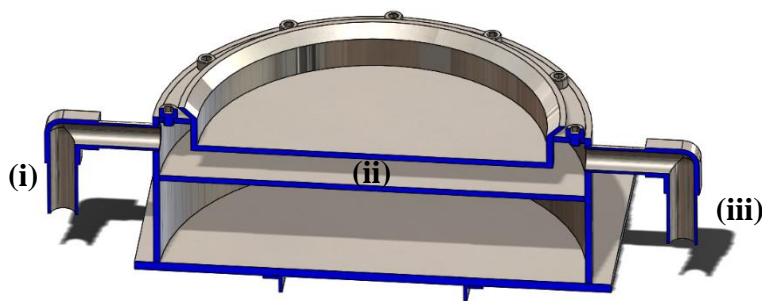


Figure 3: Cross-section of the cone calorimeter burn pan; stainless steel construction with welded seams. Cooling water flows in (i) from the chiller, under the burn sample pan (ii), and returns out (iii) to the chiller. Diameter of pan 109 mm.

Chemical Properties

In order to better understand the combustion behavior of the oils, chemical analysis was performed before testing and after the burns. These tests examined the saturate, aromatic, resin, and asphaltene (SARA) fractions and the mass spectra of the samples. The results are useful for understanding differences in physical properties and burn behavior; the authors refer to a previous publication that goes into detail regarding the chemical analysis (Tuttle, Pftzner, Loegel, & Leska, 2019).

RESULTS

Weathering time and the emulsibility were both dependent on the oil type. The emulsibility was also dependent on the amount weathered. These relations are described above as it relates to the test methods and are expounded on below as they relate to burn behavior.

The most important results were the ignitability (energy needed to ignite) and the residue (burn efficiency). Secondary results included the MLR and burn duration. Additionally, chemical analysis of the pre- and post-burn oil will be briefly discussed.

Chemical Analysis

SARA analysis and mass spectrometry were used to quantify the mass distributions in the oil samples (Table 4). That discussion is presented in Tuttle et al, including mass spectra for the post-burn residue (Tuttle, Pfutzner, Loegel, & Leska, 2019).

Table 4: SARA composition for fresh oil samples

Oil	Saturates	Aromatics	Resins	Asphaltenes
SC	65.8%	22.3%	4.29%	7.68%
CA	52.2%	28.9%	8.60%	10.4%
SK	40.3%	24.6%	23.2%	11.8%
SY	39.7%	33.0%	14.5%	12.7%
PA	32.4%	29.8%	25.8%	12.1%

Ignitability

Ignitability and Oil Type

Ignitability depends on an oil's ability to emit enough flammable vapors to sustain ignition. Even with the slick's surface heated, some trials would not ignite; for others, ignition was almost instantaneous. The energy needed to ignite was proportional to the oil density. Given that lighter fractions evaporate readily, oils with a higher relative saturate and aromatic content (Table 4) ignited quickest.

As shown in Figure 4, there was variability for these California oil types with respect to ignition. From left to right, as fresh-oil density increases, energy required to ignite generally increases. Carpinteria, however, had difficulty igniting when emulsified and disrupts that trend. Similarly for weathered oils, the trends follow excepting Point Arguello, which easily ignited at WN and WE20%, but took over twenty minutes to ignite with 40% or more seawater. Based on available data, no metric accurately predicts relative ignitability across both neat and weathered states.

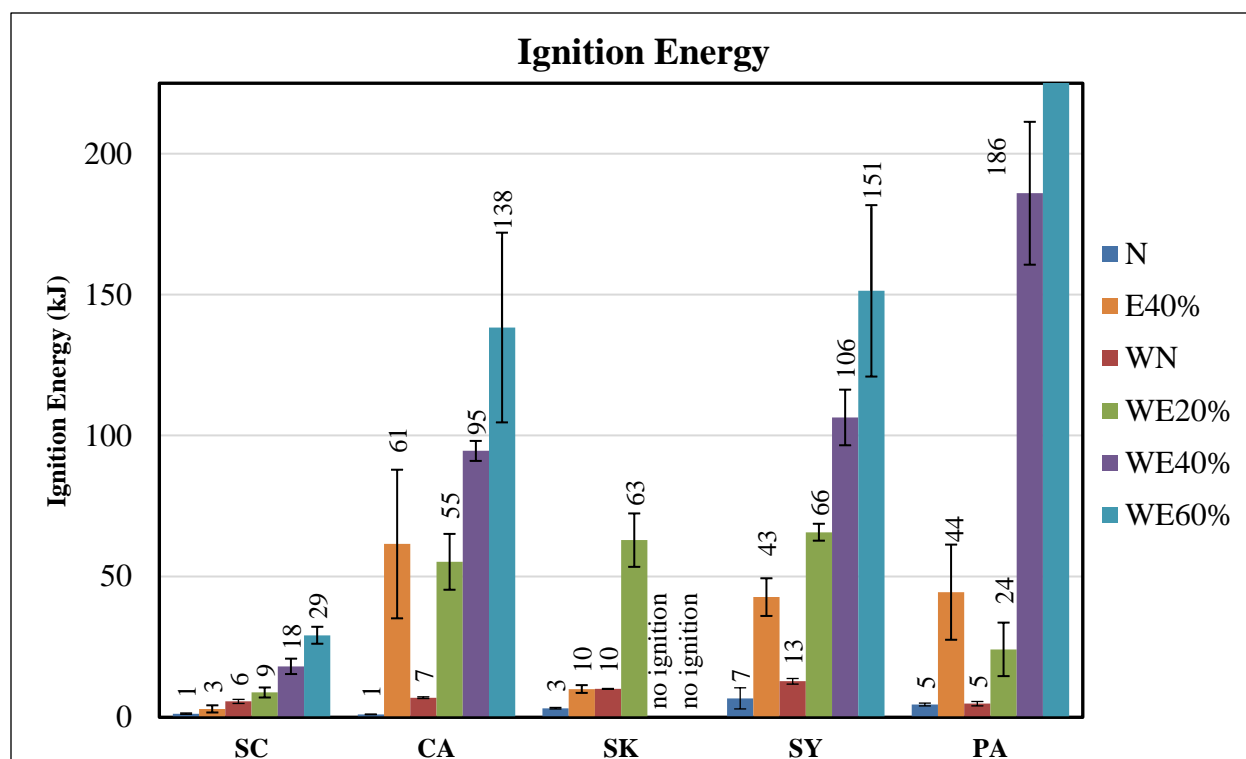


Figure 4: Energy required to ignite. Error bars (\pm) assume normal distribution for all graphs. Sockeye WE40% and WE60% did not ignite. Point Arguello WE60% ignited at 349 kJ (truncated for clarity).

Ignitability and Weathering

Although Carpinteria ignited easily when weathered, and minutes when weathered and emulsified, it ignites quickest when fresh and neat. Sockeye ignited similarly quickly, but was inert once weathered and mixed with more than 20% seawater. This sensitivity illustrates the importance of testing conditioned oil, because a fresh sample may behave differently than expected at sea.

The weathering process brought the oil densities closer to the mean. Neat Santa Clara, for instance, was significantly lighter than the others until it was weathered (Figure 1). This mass loss changed the flammability (Figure 4). Similarly, Point Arguello changed least during weathering and showed little change in ignition between neat fresh and neat weathered. Weathering became a dominant factor once water was added. The asphaltene fractions of all the oils increased, which likely stabilized the emulsions (Ali & Alqam, 2000). They took longer to break and then ignite when weathered.

Emulsion Ignitability

As shown in Figure 5, more seawater required more energy to ignite the slick. The added water has a high heat capacity and retards the evaporation rate of the oil. This is confounded by the emulsion stability: emulsions take energy to separate, increasing the ignition time. However, the ignition energy versus emulsion trend is heavily oil-dependent. Santa Clara was still ignited quickly with water, whereas Sockeye became nonflammable when mixed with 40% or more seawater. Santa Clara emulsions broke down easily, which may be due to its low asphaltene content (Fingas M. , 2011) (Ali & Alqam, 2000). Point Arguello, which ignited easily neat and with 20% water, took over 40 minutes to ignite once mixed with 60% seawater.

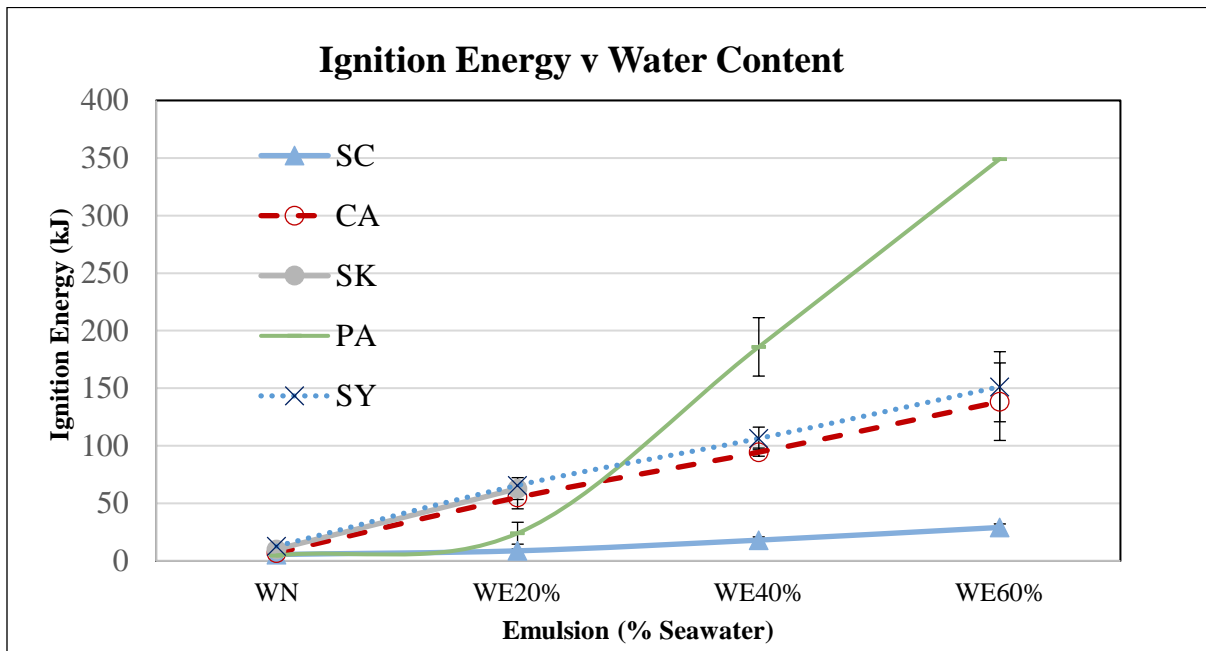


Figure 5: Ignition Energy of Weathered Conditions. Sockeye (SK) was not ignitable beyond 20% seawater. Only one trial with Point Arguello WE60% ignited (349 kJ required).

A less-stable emulsion with a higher water content may require less ignition energy, since the oil can separate from the water without added heat. Santa Clara, Carpinteria, and Santa Ynez all produced linear increases of ignition time versus emulsion percentage (among those three, linear fits had an $R^2 = 0.95$ or better). This should not be extrapolated to higher water contents, as at some point the thermal sink of the water will dominate. That point might be seen with Point Arguello, where it is unlikely to ignite with any more water, or Sockeye, where it experiences an asymptote somewhere between 20 and 40% seawater.

Residue and Efficiency

In situ burning is implemented if it can burn off enough of an oil slick such that the environment can dissolve and dilute the remainder. For these tests, the amount of oil mass consumed by combustion versus the initial unburned mass yielded a burn efficiency. The results are shown in Figure 6.

Burn Efficiency and Oil Type

For most conditions, the oils changed consistently across types. Santa Clara regularly burned cleanest, Carpinteria left the most residue. This did not correspond to density (Table 2.) or SARA content (Table 4) directly. These general trends did not extend to the most seawater. At 60% seawater, the burn efficiency became unpredictable.

Burn Efficiency and Weathering

Weathering produced little effect on the burn efficiency of the neat oils (WN v N in Figure 6), but did across the 40% emulsions (WE40% v E40%). Santa Clara and Point Arguello mixed with 40% seawater saw a significant increase in efficiency with weathered oil; Sockeye was inverted. This likely has to do with the emulsion stability and SARA fractions of the crude. Weathering results in a higher heavy-component fraction (the resins and asphaltenes) which are more polar and aid in emulsification, although there is evidence of a threshold beyond which resin content actually deteriorates emulsion stability (Fingas M. , 2011) (Liu, et al., 2019). A more stable emulsion means that the dispersed water does not absorb heat in a layer beneath the oil, but rather absorbs heat throughout the volume. As emulsions break, the water may boil and increase the burn efficiency, although Sockeye saw the opposite behavior.

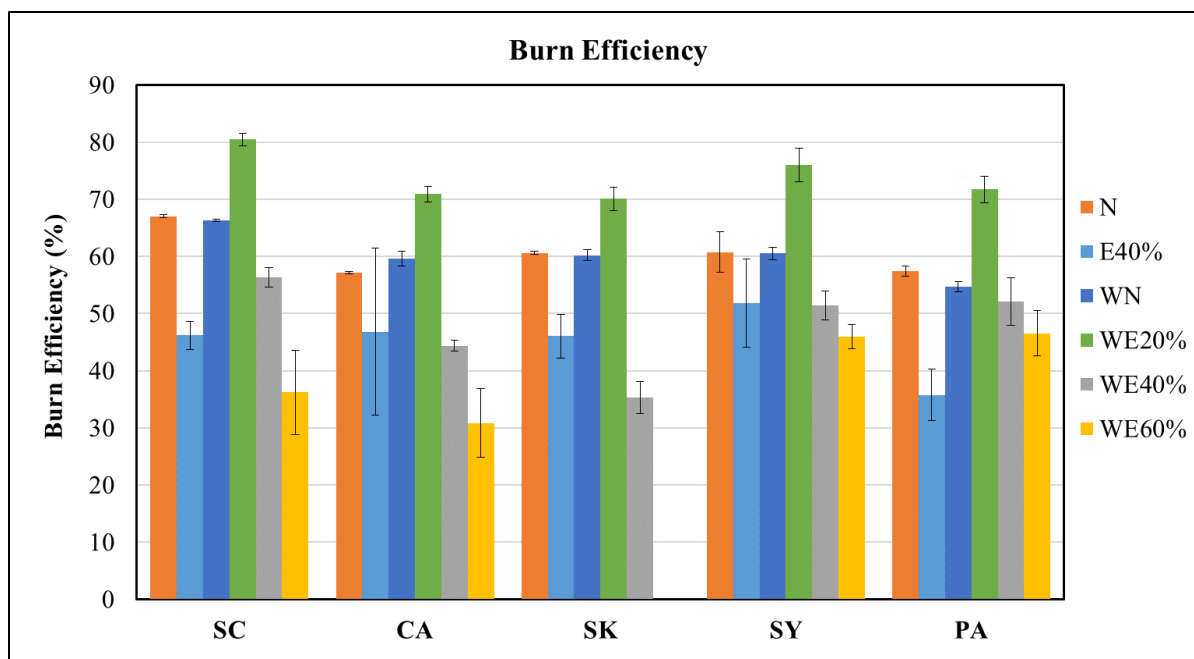


Figure 6: Burn Efficiency (% of initial mass burned) compared across oils and conditions.

Burn Efficiency and Emulsion

The effect of seawater content was noticeable with respect to burn efficiency. The neat trials removed over 50% of the oil, igniting quickly and burning steadily until extinction. The 20% emulsion took longer to ignite (up to 70 kJ), but then rapidly burned. Some loss was water rather than oil, but the residue examined after extinction was found to largely contain water. Un-ignitable oils were still measured for mass loss – the evaporation during attempted ignition was negligible; this indicates that the water’s heat capacity was too much and neither oil nor water reached boiling point. For the case of the 60% seawater emulsions that did burn, approximately half (by volume) of the residue was water. Emulsifying alone (E40% v N) yielded a marked decrease in efficiency, and when combined with weathering (E40% v WE40%) produced no apparent trend.

It was found that if ignition occurred, emulsions degraded significantly by flameout. Any unburned oil was found in a thin film on the bottom of the pan or floating on top of water. This was further validated by the samples collected for chemical analysis: after being decanted, bottled and left to settle, the emulsified oil samples did not break down further.

The amount of splatter was only measured qualitatively by observing the amount of oil collected on the glass cover surrounding the flame. It is only useful to note that emulsions splattered more than neat oils.

Burn Duration

In situ burns are usually done in batches, so a small burn can be timed before proceeding with more batches. If this can be reasonably correlated with burn efficiency, on-site personnel can better decide whether more burns should be completed, how much should be done at a time, and perhaps estimate the level of emulsion. Results are shown in Figure 7. The short times shown by Point Arguello indicate unstable combustion that extinguished quickly.

For neat crudes, both fresh and weathered, a longer burn resulted in a slower burn. Once weathered, that time increased, likely due to the higher concentration of heavy hydrocarbons. Emulsification, which could cool and displace oil vapors, extinguished quicker. However, the same short WE20% tests also resulted in a high burn efficiency, even after water loss was taken into account.

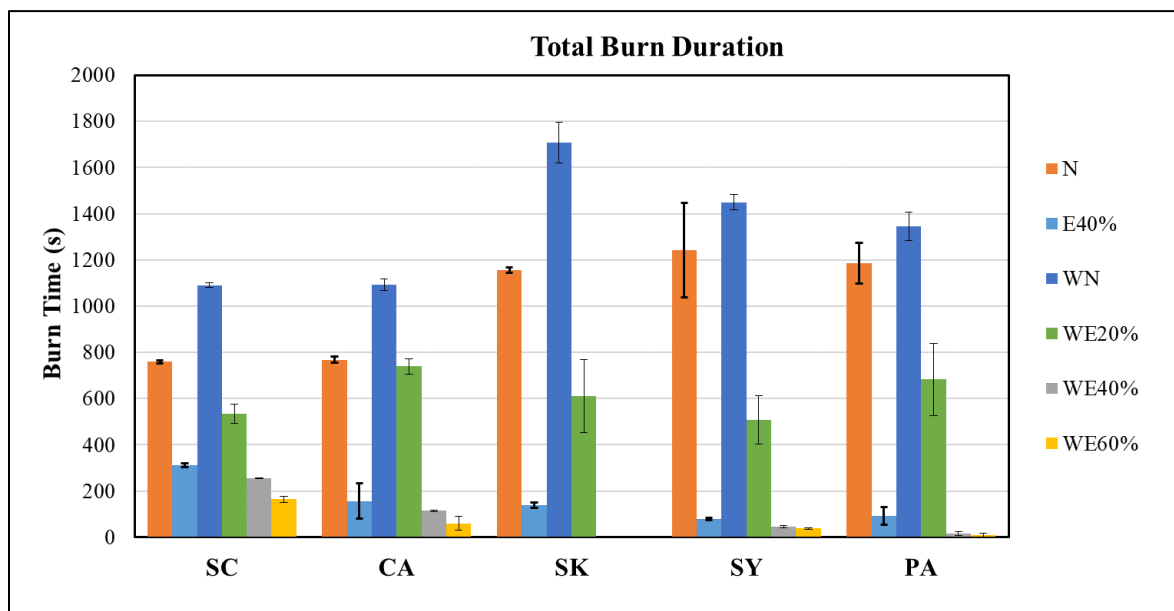


Figure 7: Trial averages of Total Burn Time (s).

CONCLUSIONS

The burn behavior of an oil in an accidental spill scenario is critical to the remediation process. The type of oil, time weathered, and degree it's emulsified can significantly affect the chance of success for in situ burning. Ideally, the oil is easily ignitable, releases enough heat to sustain combustion, and leaves behind minimal residue. Through these laboratory-scale experiments with five California crudes, correlations can be drawn between the oil's properties and its burn behavior. The calorimetry setup can be an appropriate surrogate for large scale tests to determine this behavior.

Properties as Prediction Method

Measuring oil properties in the laboratory and burning samples at small scale can predict burn behavior at sea. Trends appear to one-dimensionally predict burn behaviors for these California crudes. When neat, increased density and saturates generally mean a small increase in ignition energy, a slightly longer burn time, and a worse burn efficiency. Once weathered, the same trends are true but amplified, with the exception of burn efficiency, which changes little with weathering of neat crudes. More importantly, emulsion changed behavior drastically: a fresh 40% emulsion burns quicker but less clean than neat.

The lightest oils, when fresh and high in saturates and aromatics, have a shorter burn time, but that trend inverts once mixed with 40% seawater. Santa Clara is a bellwether for light oils, significantly lighter than anything else tested here, but it also contained an additive that the others did not. As shown in Table 4, this oil contains a large relative portion of saturates and few resins. Likewise, Point Arguello is dense, with a high asphaltene and resin content; this brings it further from the other oils' results. The three middle-weight oils share similar densities but are in most other ways dissimilar. Santa Ynez burns as efficiently as Point Arguello (Figure 6) on average. With more oils from either side of the density and viscosity spectrum, general trends might be found. The geographic proximity of the California oils tested underscores the need to test each field and each well separately.

In situ burning

It is necessary to keep property information up to date. Physical and chemical properties of the oil change with a well's lifecycle, and additives may change the oil's behavior during a spill. An empirical model was created for the purposes of these tests; this model could be further extended to longer times or simplified to accept parameters found in situ, such as density, viscosity, and surface tension.

Energy required to ignite was found to be heavily oil dependent and not directly predictable by the density. Seawater concentrations over 60% were not tested, but volatile oils like Santa Clara might ignite with even more water added. Quantifying the emulsion stability would improve understanding of the ignition's dependence on seawater percentage and the oil's properties.

Notably, there appears to be an optimal emulsion percentage that improves burn efficiency and burn time. With these California oils, this was approximately 20% seawater. As has been reported in previously, water droplets entrained in the oil later superheat and explode, which then atomize and expel the oil droplets into the flame. In a "thin-layer" boilover scenario, the emulsion separates, the oil rises, and the water underneath can boil (Garo, Gillard, & Vantelon, 2000). However, the residue collected after emulsion burn tests still contained water stably suspended in the sample; the emulsions broke down only partially. The boilover witnessed may have been a combination of emulsed water droplets superheating and exploding or partial separating of the emulsion.

Either possibility has ramifications. An oil spill in cold, moving water will likely not experience thin-layer boilover as the water will be constantly cooled. It is possible on warm, still water, but there is little evidence of this occurring in the field. Once emulsified and herded into an adequately thick slick, the water cannot effectively cool the water droplets in the oil layer (Garo, 2009; Gelderen, et al., 2015). With the right thickness and degree of emulsification, ISB results may drastically improve. The possibility of such a burn being quicker is ideal and necessitates further investigation. Traditionally, any time an oil spill spends emulsifying has been considered detrimental, but this information may reduce the need for dispersants as a go-to spill solution and expand the window of opportunity for in situ burning.

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