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Tackling the Behaviour of Vegetable Oil Fire in Case of Maritime Accident: Towards a Crisis Management Decision Support System

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Response to marine accidents can be extremely difficult when Hazard and Noxious Substances (HNS) causing fires with significant consequences. Because of their potential for danger, evidence-based decisions are needed to protect the crew, responders, the coastal population and the environment. However, when an emergency is declared, key information is not always available for all responder needs. A case in point is the lack of knowledge and data to assess the risks that responders or rescue teams might take by intervening, or those that might impact coastal communities by allowing a stricken vessel to dock at a place of refuge.
The work presented in this paper deals with the combustion of two vegetable oils (palm fatty acid distillate and crude palm oil), a mixture of used cooking oils and a mixture of animal fats. The fires were performed in a stainless-steel tank instrumented with thermocouples and a scale was used to measure the mass loss during the combustion of the products. The experimental results of the combustion rate were compared to the literature models and the flame temperature measurements were used to estimate the radiative flux emitted by the flames.

1. Introduction

Maritime transport of hazardous and noxious substances (HNS) has increased over the past 20 years, involving the risk of major pollution accidents with products potentially more dangerous than oil. Chemicals can have long-term effects on the environment, and the risks to public safety can be more severe if chemicals are released (European Maritime Safety Agency, 2007). Approximately 2,000 chemicals are transported by sea and only a few hundred chemicals are transported in bulk, but this represents the main volume of chemical trade (Purnell, 2009). However, the expansion of chemical transport at sea has led to a significant increase in incidents involving chemical tankers. In the event of a maritime accident involving HNS, spill response is difficult due to the lack of knowledge of the behaviour of these products at sea. Indeed, the rapid vaporization or the high flammability of chemicals can have important consequences on the crew, the population in the vicinity as well as the environment and the stakeholders involved in the response to marine pollution. As examples, Figure 1A shows an image of the explosion that occurred in September 2019 in the port of Ulsan, South Korea. This explosion was the result of a styrene monomer leak on the chemical tanker Stolt Greenland that led to a massive explosion with fireball and mushrooming. Figure 1B shows the 2016 PEMEX tanker fire in the Gulf of Mexico. The Mexican-flagged tanker was loaded with 80,000 barrels of diesel and 70,000 barrels of gasoline.
Energy plays a very important role in the daily lives of humans around the world. Indeed, population growth, increasing living standards, and economic development inevitably lead to an increase in energy consumption worldwide, ranging from electricity generation to the transportation sector, forcing nations to seek new sources of energy (Avhad & Marchetti, 2015). The energy needs of these sectors are primarily met by fossil fuels, the use of which would have several negative environmental consequences that make their continued use unsustainable (Perin and Jones, 2019).

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Figure 1: A) Explosion of the chemical tanker Stolt Greenland in the port of Ulsan, South Korea in September 2019. B) Fire of the PEMEX vessel in the Gulf of Mexico in September 2016.

This has led to the search for environmentally friendly and sustainable alternatives, and biofuels have been identified as one such alternative that can help meet global energy demand without the negative consequences associated with fossil fuel use. Biodiesel is presented as having the ability to replace petroleum-based diesel (Pires de Oliveira and Caires, 2019). These biofuels, obtained by transesterification of vegetable oils with a light alcohol, have seen a resurgence of interest since the oil crises of 1973 and 1979. They are considered as a good solution to reduce dependence on fossil resources, both for geostrategic and environmental reasons. The development of this sector has been encouraged by incentive policies in several regions of the world. In Europe, for example, Directive 2003/30/EC on the promotion of biofuels was approved in 2003 by the European Council and Parliament. This directive sets increasing targets for biofuel consumption in transport. These consumptions had to represent at least 2% of the global consumption of gasoline and diesel used in transport in 2005 and 5.75% in 2010. However, since 2019, the European Union's decision to phase out palm oil-based biofuel by 2030 (United Nations Publications, 2020).
From 1947 to 2012, 101 maritime accidents resulting in chemical pollution have been recorded worldwide. The analysis of these accidents shows that chemical tankers and cargo ships are the vessels most often involved in maritime accidents leading to a spill at sea. In addition to this analysis, the study of the type of packaging of chemicals spilled at sea shows that the majority of chemical pollution is due to the rupture of vessels' tanks following a collision, grounding or an explosion onboard. This type of accident, which is the most frequent, is generally the cause of a major spill of chemicals at sea and, consequently, the cause of major pollution. The second most common type of packaging is drums, cylinders or small tanks. These packages are most often transported on board cargo ships and container ships, and the accidents correspond to the loss at sea of these drums due to unfavourable weather and sea conditions. The analysis of maritime accidents has also focused on the chemical nature of the substances involved. The following table lists the most representative chemicals that have been spilled in accidents over the last 50 years (Table 1).

Table 1: Most implicated chemicals in marine spills accident during 50 years old and associated SEBC code (F: Floater, D: Dissolver, S: Sinker, ED: Evaporator that dissolves, DE: Dissolver that evaporates, FE, Floater that evaporates).

Chemical	SEBC code	Chemical	SEBC code
Methyl Tert-Butyl Ether	ED	Acrylonitrile	DE
Butylene	D	Phenol	S
Nitric Acid	D	Hydrochloric Acid	D
Phosphoric Acid	D	Ammonia Anhydrous	DE
Methanol	DE	Sodium Chlorate	D
Ethanol	D	Palm Oil	F
Ammonium Nitrate	D	Naphtha	FE
Sulfuric Acid	D	Xylene	FE

For each chemical listed, the behaviour in the marine environment is determined from the European classification resulting from the SEBC code. This table highlights the significant presence of palm oils in accidental spills at sea (Le Floch et al, 2012). The work presented in this paper is funded by the DG-ECHO from the European project MAFINESTS (Managing risks and impacts from evapourating and gaseous substances to population safety) which studies the risks associated with accidental chemical spills in the marine environment and more particularly on the improvement of the prediction of the consequences of fires of biodiesels or vegetable oils transported by sea.

2. Experimental setup

In spite of the research carried out during the last 30-40 years on the combustion of hydrocarbons, there is still a need for further knowledge regarding the combustion of different types of vegetable oils. The objective of this study was to determine the ignition temperatures, oil temperatures during combustion, flame temperatures and combustion rates. The fire tests were conducted outdoors on a fire department training platform. The fires were conducted in a stainless-steel tank with a maximum volume of 126 L, measuring 80 cm in diameter, 25 cm in height and 4 mm in thickness. This tank is equipped with 5 watertight passages allowing the passage of 20 thermocouples (Figure 2A). The passage of thermocouples through the bottom of the tank allows to minimize the heat transfer by conduction. The thermocouples used are of type K (Chromel/Alumel). Of the 20 thermocouples, 16 are positioned in the hydrocarbon every centimetre between 0 and 15 cm high. The thermocouples were connected to a National Instrument NI-cDAQ 9188 datalogger with two NI9213 cards with 16 measurement channels each. The acquisition frequency of each channel was set at 2Hz for all the tests (1 measurement every 0.5s). In order to measure the combustion rate of each product, the tank was placed on a scale (Kern IFB 300K-2) with a measurement range of 300 kg with a precision of 10 g. In order to avoid a drift of the balance due to the thermal radiation of the flames, this one was protected by a fireproof protection. The sampling of the values was done manually during the tests at an average frequency of 1 point every 5 minutes. All the tests were filmed by an HD camcorder and a Young - 81000 ultrasonic anemometer, with an absolute accuracy of 1%, was positioned near the experimental device in order to evaluate the meteorological conditions during each test (wind speed, direction and ambient temperature). The ignition system consisted of a flashlight connected to a propane cylinder. This flashlight is composed of a bell type burner allowing to obtain a flame at high temperatures (1200°C) necessary to heat and vaporize the hydrocarbon on the surface.
The oils tested during this experimental campaign are biodiesel fillers (Palm Fatty Acid Distillate (Figure 2B), Animal Fats, Crude Palm Oil, Used Cooking Oils).

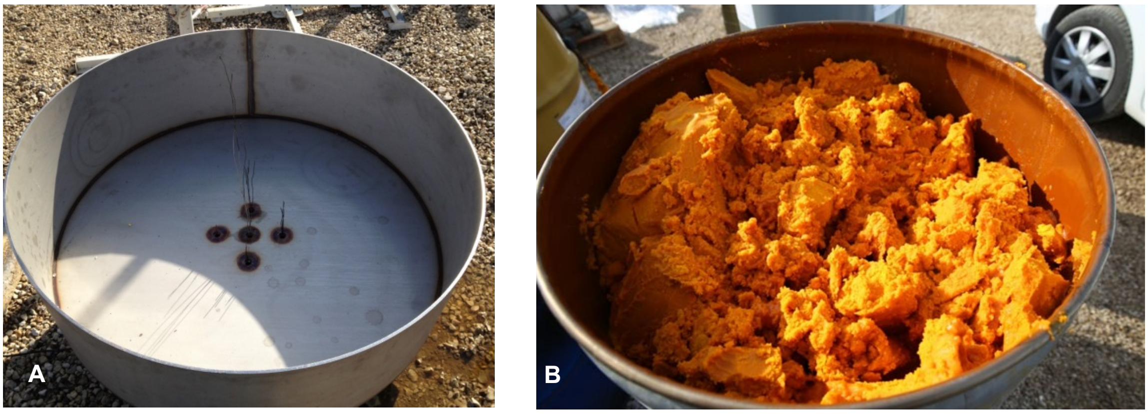

Figure 2: A) Illustration of the fire tank and the position of the thermocouples. B) Illustration of the CPO aspect (Crude Palm Oil) at ambient temperature (16.5°C).

Table 2 summarizes the physical-chemical properties measured in the laboratory for the products used as well as the distillation curves for all the products (Figure 3).

Table 2: Fluid physical properties of oil tested in the present study

Oil name	Density ($kg.m^{-3}$)	Flash point Luchaire (°C)	Dynamic Viscosity at 50°C ($mm^2.s^{-1}$)	Dynamic Viscosity at 100°C ($mm^2.s^{-1}$)
Palm Fatty Acid Distillate (PFAD)	901	204	15.5	4.94
Animals Fats (AF)	915	250	28.6	8.45
Crude Palm Oil (CPO)	915	245	28.2	8.21
Used Cooking Oil (UCO)	924	229	28.4	8.65

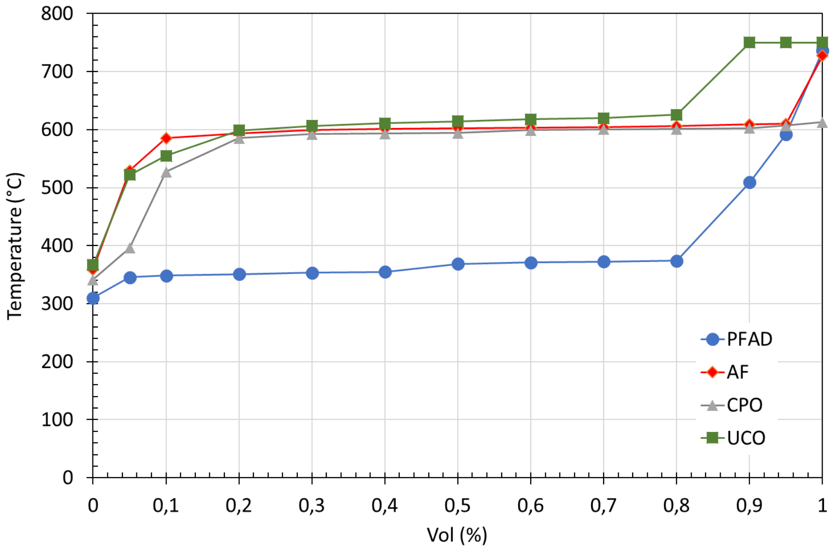

Figure 3: Variation of the distilled fraction in volume as a function of temperature, at atmospheric pressure, for the four tested fluids

3. Results analysis

The analysis of the mass loss data shows that for all the performed tests the mass loss presents a regular and linear slope representative of a homogeneous combustion throughout the test. Table 3 presents the average combustion rates obtained for the four products tested. It can be noted that the combustion rates are substantially identical whatever the product, with combustion rates of about 1kg.min^{-1}. In order to model the combustion of these hydrocarbons during an accident, the experimental data were compared respectively to the model of Babrauskas et al. (1983), Rew, (1997) and Chatris et al. (2001). These models have been developed to model industrial hydrocarbons fires in order to establish the burning rate of pool fires.

Table 3: Summary table of combustion results for experimental fire tests of PFAD, AF, CPO and UCO

Oil name	Combustion rate (kg.min^{-1})	Combustion rate (mm.min^{-1})	Maximum flame temperature (°C)	Calculation of maximum radiative heat flux (kW.m^{-2}.K^{-1})
Palm Fatty Acid Distillate (PFAD)	1.006	2.22	938	129.6
Animals Fats (AF)	0.995	2.16	971	135.5
Crude Palm Oil (CPO)	0.989	2.15	933	119.6
Used Cooking Oil (UCO)	1.038	2.23	945	124.5

Figure 4 shows the comparison of the experimental results with the previous models. It can be noted a very good agreement between the experimental data and the model of Babrauskas et al. with relative deviations lower than 3%. The comparison with the Rew model shows relative deviations with the experimental data lower than 15%, while in the model of Chetris et al. the relative deviations are lower than 50%.
Figure 5 shows the results for all the temperature measurements recorded by the 16 thermocouples positioned every centimetre in the tank. Each curve shows a similar evolution of the temperature in the liquid and the offset between each curve corresponds to the temperature gradient at the surface of the liquid, and at the rate of regression of the combustion front. The temperature increase in the liquid is related to conduction and convection mechanisms, but also to the radiation of the flame at the surface. It can be noted that when the liquid level reaches a thermocouple, this one measures the flame temperature. This flame temperature is illustrated in Figure 5 by the oscillations of the values due to the weather conditions (oscillation of the flame with the wind). The maximum flame temperature values were measured for each product tested and reported in Table 3.
Using Stephan-Boltzmann's law and the maximum flame temperature values, the maximum radiative heat flux emitted by the flames is then estimated (Table 3).

These radiative heat fluxes are important with values higher than 120 kw.m^{-2}.K^{-1}. these values are essential to model the thermal radiation received by a target at a certain distance (populations, safety response services or maritime structures).

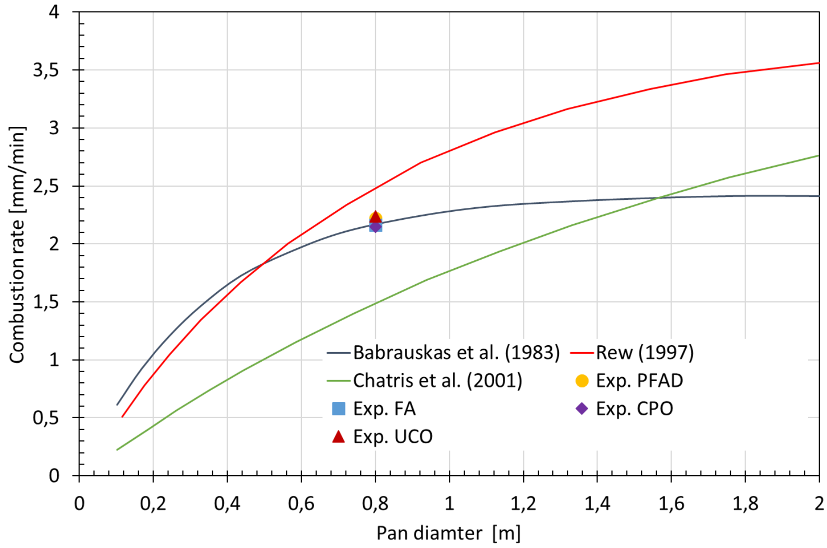

Figure 4: Comparison of experimental results of combustion rate with the model of Babrauskas et al. (1983), Rew, (1997) and Chatris et al. (2001)

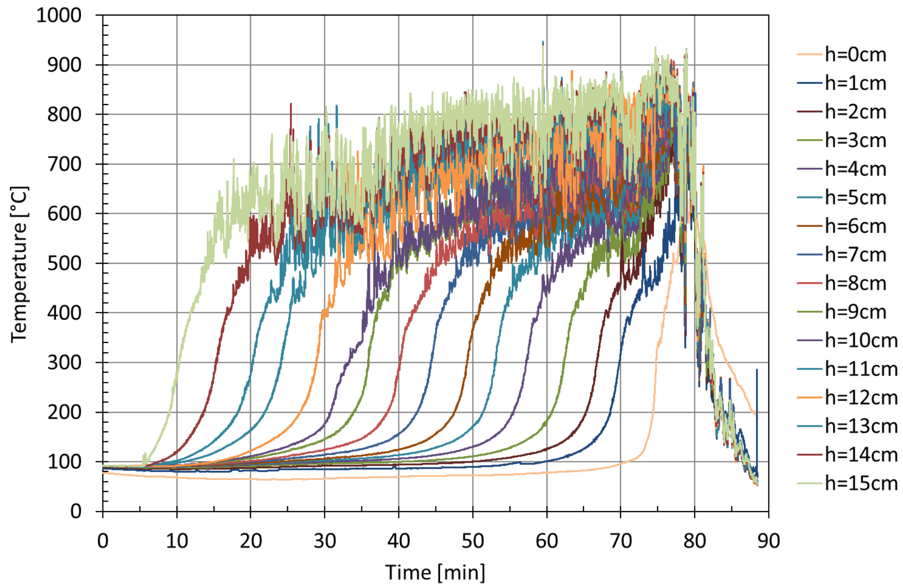

Figure 5:: Variation of liquid and flame temperature with time for PFAD (Palm Fatty Acid Distillate) combustion test

4. Conclusions

The increase in the world demand for energy and the needs to reduce the use of fossil fuels have led to the increasing use of vegetable oils and animal fats to produce biofuels. The increase in demand inevitably leads to an increase in the transport of these products by sea and inexorably entails risks of accidents that can have serious consequences for people, property and the environment.

It is in this context that this work is proposed, and more specifically in the improvement of knowledge on the combustion of vegetable oils and animal fats. This study is part of a European project funded by DG-ECHO, the

MANIFESTS project (Managing risks and impacts from evapourating and gaseous substances to population safety). The experimental results presented in this paper are a first step in the project whose objective is to study the combustion of two vegetable oils (Palm Fatty Acid Distillate and Crude Palm Oil), a mixture of used cooking oils and a mixture of animal fats. The experimental work deals with the measurements of the combustion rate, the liquid temperature and the flame temperature of these four products in a stainless-steel tank of 80 cm diameter and 25 cm height. The comparison of the experimental results with the Babrauskas model showed that whatever the product used, the model could predict the combustion rates with relative deviations lower than 2%. Moreover, the analysis of the flame temperatures showed that the radiative fluxes emitted were very important with values higher than 120 $kW.m^{-2}.K^{-1}$.
The perspectives of this work will consist of testing other vegetable oils and measuring not only the same parameters (combustion rate, flame temperature) but also measuring the flux received at different distances in order to characterize the impact of radiative heat fluxes on people and the environment. The last part of the project will aim to study the flammability of these products on water and to model the radiative heat fluxes received by a target.

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