Fuel 191 (2017) 528–537

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Vaporization order and burning efficiency of crude oils during *in-situ* burning on water

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HIGHLIGHTS

- Crude oil burning on water is linked to a volatility-controlled vaporization model.
- The burning efficiency depends on the vaporization model and heat loss mechanics.
- A new explanation is proposed for the size dependency of the burning efficiency.

ARTICLE INFO

Article history:
Received 25 August 2016
Received in revised form 28 November 2016
Accepted 29 November 2016
Available online 8 December 2016

Keywords:
Crude oil
Vaporization order
Heat transfer
Burning efficiency

ABSTRACT

In order to improve the understanding of the burning efficiency and its observed size dependency of *in-situ* burning of crude oil on water, the vaporization order of the components in crude oils was studied. The vaporization order of such multicomponent fuels was assessed by studying the surface temperature, flame height, burning rate and burn residues of three alkanes (*n*-octane, dodecane and hexadecane), a mixture of these alkanes (1:1:1 volumetric ratio) and two crude oils (light and medium-light crudes). The experimental results were compared to four models for the vaporization order of multicomponent fuels. The alkanes were tested as benchmark fuels with a uniform vaporization order, for which all components evaporate simultaneously. As expected, these pure fuels showed a steady state burning with a near-constant surface temperature, flame height and burning rate. The alkane mixture showed similar steady state results but became dominated by the heaviest component towards the end of the burning. These results indicate that the lightest components had been depleted from the mixture. A near-uniform vaporization order in which the lighter components evaporate preferably best matched these results. The crude oils did not show any steady state behavior, but instead had an increasing surface temperature and decreasing burning rate and flame height, indicating a volatility controlled vaporization order. An increasing concentration gradient from the medium to heavy fraction in the burn residues furthermore showed that the vaporization was diffusion-limited. Analysis of the heat transfer balance for the crude oils indicated that the energy available for evaporation decreased over time due to increasing heat losses, which were caused by the volatility controlled vaporization order. Presumably, larger scale fires can overcome these heat losses, as they typically have higher burning rates, which increase the heat feedback to the fuel surface and therefore can result in the higher burning efficiencies.

1. Introduction

In the Arctic, oil spills pose an upcoming threat to the environment because of the increasing amount of marine transportation and oil exploration [1]. Furthermore, the remoteness and extreme climate of Arctic waters make it difficult for conventional oil spill response methods, such as mechanical recovery, to be deployed effectively [2,3]. However, a promising response method that is suitable under these circumstances is *in-situ* burning (ISB) of the crude oil on the water surface. This technique features simple logistics, can be used in ice-infested waters and can obtain a high burning efficiency (BE) [4,5]. A high BE is the primary target for ISB and is defined as the amount of oil (in wt.%) that is removed from the water surface during the burning. BEs can reach as high as 99% [6] and as low as 32% [7], depending on a variety of conditions (e.g. oil type, slick thickness, pool size, emulsification, the weather and presence of ice). Because low BEs are undesired, it is

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http://dx.doi.org/10.1016/j.fuel.2016.11.109

Nomenclature

BE	burning efficiency (%)	$\dot{Q}_c$	heat release rate of combustion (kW)
DLV	diffusion-limited vaporization	$\dot{Q}_{conv}$	convection from flame to fuel (kW)
EFV	equilibrium flash vaporization	$\dot{Q}_{evap}$	energy used to evaporate fuel (kW)
GC	gas chromatography	$\dot{Q}_{grad}$	energy used to heat fuel layer (kW)
ISB	*in-situ* burning	$\dot{Q}_{loss}$	heat transfer from fuel to water (kW)
PGC	Pyrex glass cylinder	$\dot{Q}_{net}$	total net heat from flame to fuel (kW)
ΔH_c	heat of combustion (kJ/kg)	$\dot{Q}_{rad}$	radiation from flame to fuel (kW)
ΔH_g	heat of gasification (kJ/kg)	$\dot{Q}_{ref}$	radiative reflection from fuel (kW)
ΔH_v	latent heat of vaporization (kJ/kg)	T_b	boiling point (K)
c_p	specific heat coefficient (J/kg K)	T_s	surface temperature (K)
D	diameter (m)	T_∞	ambient temperature (K)
L_F	flame height (m)	χ_c	combustion efficiency (–)
$\dot{m}$	burning rate (g/s)	χ_s	heat feedback fraction (–)
Pe_m	Peclet number for mass diffusion (–)		

important to understand the processes that control the BE to maximize the potential of ISB operations.

For a multicomponent fuel such as a crude oil, the BE is determined by the type and the quantity of compounds that evaporate from the burning fuel, i.e. the vaporization process. Many of the physical parameters that influence the vaporization have been studied and their effects on the ignitability and BE of crude oil are well-known. Examples include the regression rate [8], slick thickness [9], heat losses to the water [10], emulsification [11,12], evaporative losses [11,13] and weather conditions [11]. However, the studied parameters cannot be used to explain the apparent pool size dependency of the BE. Small scale studies (e.g., [7,14,15]) have consistently reported lower BE values than large scale field studies [16–18] under otherwise similar conditions. BEs of the small scale studies varied between 32% and 80%, whereas a minimum of 95% BE was reported for the large scale studies. For ISB to be used successfully as oil spill response method, it is important to ensure that these lower BEs can be avoided during full scale operations.

One aspect of crude oil that has remained relatively unstudied in relation to combustion is its multicomponent nature. The aforementioned studies focused on the quantity and rate of the vaporization process and not the chemical composition that determines the type of compounds that can evaporate. Crude oils consist of thousands of different hydrocarbons, each with their own specific density, viscosity, flash point, boiling point (T_b), etc. [19,20]. The order in which these compounds evaporate during combustion is here referred to as the vaporization order. Although several models have been suggested in literature for the vaporization order of multicomponent fuels [21–23], there is to our knowledge not a single generally acknowledged model for crude oil combustion. Combined with the physical parameters that determine the vaporization quantity and rate, knowing the vaporization order would result in a good understanding of the vaporization process. This will in turn improve the general understanding of the BE and may present an explanation to the apparent oil spill size dependency of the BE.

Herein, the goal is to establish a model that describes the vaporization order of crude oil burning on water. Well-established models from literature were used to make qualitative predictions for four burning parameters: the surface temperature (T_s), flame height (L_F), burning rate ($\dot{m}$) and the residue composition. Experimental data from fresh crude oil and alkane burning experiments were then compared to the model predictions to determine the best fitting model for the vaporization order of crude oil. Using this model, the obtained burning efficiencies were analyzed for the tested scale and for large scale results from the literature.

2. Conceptual model overview

In a recent comprehensive review on ISB, the *Equilibrium Flash Vaporization* (EFV) model was proposed for the vaporization order of burning crude oil [24]. This model was earlier proposed by Petty [21] and describes the vaporization of a multicomponent fuel as being of "essentially constant composition" with a constant vaporization rate. Thus, all components evaporate simultaneously, here defined as a uniform vaporization order, and each individual component contributes to the vaporization rate relative to its concentration in the oil. Characteristics of this model are that the crude oil burns with constant T_s at a constant $\dot{m}$, has a temperature gradient in the oil slick and lighter components are present in the residue [21,24].

An alternative to the EFV model was proposed by Buist et al. [22], based on their studies on crude oil residues. Their results showed that crude oil residues had an increased concentration of heavy hydrocarbon fractions ($T_b > 538$ °C) and complete removal of the light hydrocarbon fractions ($T_b < 204$ °C). This trend was also found in previous studies on crude oil residue compositions [22,25,26]. Buist et al. [22] suggested that the burning proceeded according to an *Imperfect EFV* model in which lighter oil fractions are favored over heavier oil fractions during the burning. Thus, for this model the relative vaporization rate of lighter components is higher than their relative concentrations. Apart from this difference, the model follows the EFV model and as such features a constant vaporization rate and uniform vaporization order.

Also, three models have been developed for the vaporization of multicomponent fuels based on the Peclet number for mass diffusion (Pe_m) (Eq. (1)) [23]. The value of Pe_m of a fuel determines which of these three models is the most appropriate to describe the vaporization [27]. Although these models were not developed specifically for the burning of crude oils, they describe the general vaporization process of multicomponent fuels in great detail.

$$Pe_m = \frac{K}{D_l} = \frac{\text{vaporization rate}}{\text{mass diffusion rate}} \qquad (1)$$

For fuels where Pe_m approaches infinity, usually due to a negligible mass diffusion such as in solids, the composition of the fuel is fixed and no internal changes occur during the combustion. This means that the fuel is burned layer by layer and hence this model is known as the *Onion Skin* model. The vaporization order depends on the internal distribution of the compounds, e.g. uniformly or by density, and will be fuel dependent.

For fuels where Pe_m approaches zero, the fuel can be considered to have a uniform distribution of its components due to its relatively high mass diffusion rate. As a result, the vaporization order