Development of Predictive Tool on Boilover Onset Time Using Energy Balance Approach

By

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(15049)

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

Universiti Teknologi PETRONAS

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Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A Project Dissertation Submitted To The

Chemical Engineering Programme

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Approved by:

____

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or person.

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DANESKUMAR MANOGARAN

ABSTRACT

The Boilover phenomenon can be characterized as the sudden ejection of certain hydrocarbon caused by prolonged burning during a storage tank fire. The boilover happens due to the vaporization of water that resides at the base of a storage tank which leads to the sudden release of hot fuel from the tank, massive fireballs and fire enlargement and also extensive ground fire. Boilover phenomena have getting various considerations all through the commercial ventures. As mishaps happen, individuals had been broadly researching all the more on this event. In view of past scientist, boil over peril mishap ordinarily happen for crude oil or fuel oil. Boilover is an exceptionally hazardous inadvertent phenomenon, which can prompt heavy wounds particularly to crisis responders. The boilover can happen a few hours after the fuel in a storage tank burst into flames. The boilover event is an unpredictable parameter when dealing with the emergency responding operations. In this proposal project paper, the author proposed a study on the prediction of the boilover onset time using energy balance approach. The method that was used for this experiment is basically about a simple combustion using a small scale fire to study the characteristics of the boilover of fuel and develop an energy balance equation to predict the boilover onset time. Throughout this paper, the author explained on the problem statement of the study, objective and the scope of study. Next, literature review from past research paper related to boilover was summarized followed by some elaborations on the methodology of the experiment. Next, author would enclose the results and propose the recommendations for the study and finally conclude the study’s findings with references.

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CHAPTER 1:

INTRODUCTION

1.1 Background of Study

Based on the past studies boilover is mainly defined as the sudden ejection or increase in flame size which happens at an unpredictable condition during a prolonged storage tank fire. Boilover will only happen when there is an oil-water mixture and the temperature of the mixture component reaches the water's boiling point. Basically, Boilover is the vaporization of water that settles at the base of a tank. Boilover is very hazardous as it can happen after a certain amount of unpredictable time from the time the tank caught fire. This is a very hazardous condition especially for the emergency response team. (Buang, 2014)

As stated earlier, the key reason for this condition to happen is due to the difference in density between two liquid. As water is poured onto the oil, it will quickly sinks to the bottom of the container, due to the water density is much higher than the oil. Burning oil on the surface will heat up the solution until the heat reaches the bottom of the container. The water on the bottom rapidly vaporizes into steams - provided the temperature reach water boiling point, causing it to expand and expels the oil above upward. This will result in the expulsion of the oil onto large and unrestrained area outside the container.

There were many cases where boilover accident happens in the industry. Some cases resulting in death, some are not. Nevertheless, throughout the year, the society had been investigating more on this phenomenon for the sake of public safety.

Figure 1 - Boilover phenomena

1.2 Problem Statement

Milford Haven boilover was one of the worse boilover in history, although there were no life harmed the cost of loss is estimated to be around 10 Million euro value in 1987 which could easily worth around 40 M now. They were many fire-fighting techniques applied such as draining the tank's fuel, shot with water cannons, but the flame lasted 60 hours before producing the classical boilover that resulted in fireball height 150m with radius 90 m.

Figure 2 - Boilover Incident in Milford Haven

Consequences of Milford Haven Boilover Incident

Six firemen sustained mild injuries during the first boilover. One of them was hospitalised. The tank TO11 was destroyed, the adjacent tanks were seriously damaged and 17,800 tonnes of fuel were consumed. The cost of this accident was assessed at about 10 M £ (value in 1983, i.e. about 26 M € in 2007). The thick column of black smoke that rose several hundred metres above the refinery resulted in "soot rains" in the villages and the surroundings.

Based on the accident, it is important especially for the emergency responder to understand the mechanism of boilover. In addition, the significant parameters that need to be known to the emergency responders are the boilover onset time so that emergency response activities can be planned accordingly to avoid the severe consequences. Hence, it is aimed for this study to produce a way to predict the boilover onset time.

In Malaysia, on 4th November 2013, ten firefighters were badly injured in a firefighting operation of an abandoned tire factory in Kota Bharu, Kelantan. The exact type of fuel in the cylinder was unknown, but the investigator believe it was used engine oil that had been left for the horizontal fuel storage tank suddenly burst into flame at a tire manufacturing company. Special firefighter's team that has knowledge on methods to control a boilover fire accident only located in a huge plant own by big enterprises. However, in small medium enterprises, fire accident will be control by the local fire department. The problem that can be seen here was that most of the local fire department has lack of knowledge on boilover phenomena and ways to control them. As accident like this were rarely happen, most safety department in companies and the fire department themselves are lack of awareness on this type of storage tank accident. Boilover phenomena incident can cause fatal accidents. It is important for the fire department to gain knowledge and at least know how to control this type of fire hazard. A predictive tool can help the fire-fighting team to fight the fire effective as they can predict the time they have until the explosion occurs.

1.3 Objectives

As of today, many studies had been conducted on the effects of boilover in various types of oil under various conditions. However, none had developed a prediction tool of boilover onset time using simple energy balance calculations. Therefore, the main objective for this project is to study on the heat transfer mechanism and thermodynamics properties and come up with the energy balance equation for predicting the time for boilover onset.

This project study must be capable of estimating:

i. The potential of crude oil and petrol-diesel mixture to boilover
ii. The time to boilover for crude oil and petrol-diesel mixture
iii. The amount of fuel remaining in the tank prior to boilover and hence the quantity of fuel that would be ejected during boilover
iv. The reliability and deviation of predicted result from experimental results

The main criterion of the study is to produce reliable and simple predictive tool to guide the emergency response personnel on handling the boilover phenomenon. At the end of the study, all objectives should be achieved.

1.4 Scope of Study

The study will involve in studying the characteristic of the crude oil and petrol-diesel mixture and from the characteristics the author will develop a tool which can be used to predict the time for boilover onset. The parametric study will focus on:

i. Type of fuel – Crude oil & Petrol-diesel mixture
ii. Depth of fuel against the time to boilover
iii. Volume of fuel against the time to boilover
iv. External factors against the time to boilover

CHAPTER 2:
LITERATURE REVIEW

The main purpose of this chapter is to provide a timed review of the notable work done up to date on the characteristics and prediction of boilover. The information and intellectual work available can be used as a reference for further experiments and comparison of results. This chapter is organized in a chronological order, where the progress is stated in timeframe of oldest to the latest significant information available.

The first attempt towards understanding the boilover phenomenon was a series of large-scale pool fire experiments carried out in 1920s (Hall, 1925). Using varying tank sizes and numerous types of oils, it was discovered that a layering effect formed in those tests in which boilover occurred. Temperature changes beneath the surface of the oil were deduced by Hall based on experiments. There were three different layers consisting of very hot, isothermal hot and colder layer. Very hot layer consist of components with heaviest boiling point, whereas, isothermal layer consist of uniform composition and temperature.
According to a research study – *Heat Transfer Mechanisms and Boilover in burning oil-water systems (1995)* by Broeckmann and Schecker, there were three categories of fuel ejection from burning oil tanks. A boilover occurred when the bottom of the hot zone layer reached the water at the bottom of the tank which was then vaporised. One of the most important findings of Hall's study was the identification of three physical conditions which must exist in order for a boilover to occur. These conditions are: (1) presence of water, (2) occurrence of a hot zone, and (3) viscous liquid fuels (Hall, 1925).

Based on the theoretical interpretation of Hall's (1925) experiments, it was established that the formation of the hot zone is possible for compound fuels consisting of components having a wide range of boiling points. Burgoyne & Katan (1947) extended the work of Hall and similarly reported that boilover occurred when the hot zone reached a water layer at the bottom of the tank. Burgoyne and Katan also put forward a theory that the hot zone is formed due to bulk circulation of the fluid. As the fuel burns, some energy is used to vaporise light ends of hot-cold interface which supply fire, and some heat is hold to run the mass circulation of the hot zone. As the hot zone grows, the vaporized light ends mix with stirring effect of the mass circulation within the hot zone. Hence it was suggested that the temperature and composition of the hot zone are determined by the heat transfer coefficients at the bottom of the hot zone and at the surface of the fuel and the thermal properties of the fuel rather than by mass transfer effects as proposed by Hall (1925).

In 1961, experiments undertaken by Russian researchers on boilover at the laboratory scale revealed that the water under the burning fuel became superheated without boiling and the subsequent explosive phase change lead to boilover (Blinov & Khudyakov, 1961). When water is heated to its boiling point, nucleation points are required for boiling to occur and form vapour bubbles. If suitable nucleation points are not available then the water becomes superheated. In the case of a tank fire, the wall usually provides adequate nucleation sites.

In 1988, boilover tests were conducted by the National Research Institute of Fire and Disaster (NRIFD), Japan, using a range of open top cylindrical tanks to burn diesel, gasoline and mixture of diesel and gasoline (Hasegawa, 1989). Detailed observations of temperature changes below the surface, density of the fuel and thermal radiation were measured and analysed. In the tests, the vaporisation of light components of a fuel mixture at the base of the hot zone was observed. The vapour bubbles of the light components formed at the interface enhanced the mixing and stirring of fuels within the hot zone. Through this observation, it was shown that the hot zone was uniform in composition and temperature both horizontally and vertically, supporting the bulk circulation mechanism proposed by Burgoyne & Katan (1947).

When the bottom of the hot zone reaches the water sub-layer and, providing the temperature of the hot zone is sufficiently above 100^{O}C, the water is superheated and hence vaporizes explosively, pushing large quantities of hot oil out of the tank (Hasegawa, 1989). In addition a boilover event can endanger the lives of fire fighters and/or emergency responders attending the incident. Figure 2 shows the potential temperature profiles within the fluid during a storage tank fire containing a fuel that: (a) generates a hot zone and (b) does not cause a hot zone to be formed. (Hasegawa,1989)

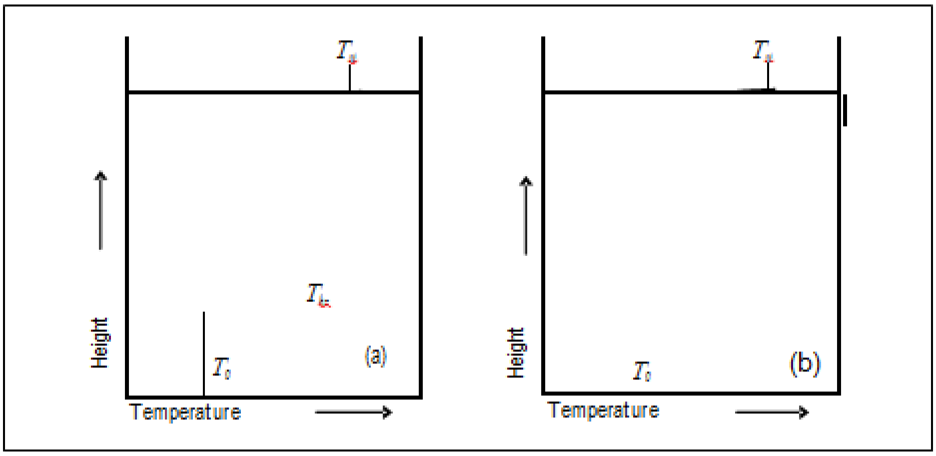

Figure 2 **Fuel temperature that (a) generates and (b) does not generate a hot zone.**

A study by Koseki *et al*. (1991a) showed the importance of the initial thickness of the fuel towards onset of boilover and its intensity. Regression rate of the fuel surface, the speed at which the base of the hot zone progressed towards the bottom of the tank, external radiation and the time to boilover were measured for Arabian light fuel burning in tanks with diameters ranging from 0.3 to 2.0 m. The speed with which the hot zone progressed towards the bottom of the tank was obtained through the relationship between the initial fuel layer thickness and the time to boilover. After analysing the results, the authors cautioned that the formation of the hot zone could be the key mechanism for the occurrence of boilover. The time to boilover and its intensity were found to be directly proportional to the initial thickness of the fuel layer. It was also found that a hot zone of at least 5 to 10 mm thickness was necessary for the appearance of boilover. Koseki (1994) published further work on boilovers in which he delved further into the theory of hot zone formation with respect to heat transfer mechanisms which involves the observations of 1. Uniformity of the hot zone is due to strong convection currents induced by fuel. 2. Sharp discontinuity in temperature profile as proposed by Hall(1925) is because heat only being transferred by conduction. 3. Boilover will only occur when the hot zone propagation speed is higher than regression rate of fuel surface.

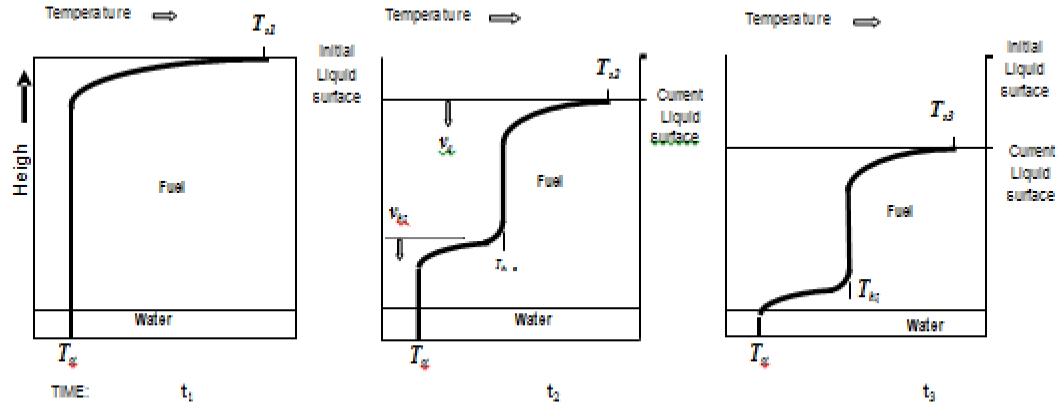

Figure 3: Schematic illustration of boilover. Three Stages in the formation and propagation of a hot zone during a fire (Time: $t1 < t2 < t3$ / Surface temperature: $Ts1 < Ts2 < Ts3$)

In the year (1995), a study specifically focused on the heat transfer mechanisms occurring in a storage tank fire was carried out for a wide range of fuels. The work was undertaken to determine which heat transfer mechanisms occurring in the liquid fuel leads to boilover (Broeckmann & Schecker, 1995). Experiments were conducted using cylindrical open steel tanks with diameters of 0.19 - 1.91 m. The temperatures in the fuels were measured using NiCr/Ni thermocouples with a diameter of 1.5 - 3.2 mm. The effects of water evaporation were recorded using a video camera, the temperature of the flames were observed through a thermal imager and the regression rate of the fuel surface was measured according to the time when the fuel surface was observed to reach the thermocouples.

Based on the analysis of the results, the authors stated that fuels could be classified into two broad categories:

i. Non-hot-zone forming fuels: These are fuels such as solvents or compounds comprising of components with similar boiling points that do not give rise to the formation of a wave of heat (hot zone) and therefore cannot cause boilover.

ii. Hot zone forming fuels: These fuels can produce a hot zone and, hence, can cause boilover when the hot zone reaches the water layer. This is the case of fuels made up of components with a wide range of boiling points.

One of the recent development in boilover is studied in the study of *Pipeline Rules of Thumb HandBook (2009)* by McAllister which stated that, at the point when a boilover happen it can prompt blazing item spreading over a region of a few tank widths far from the tank. Albeit no complete work has been completed to approve figures, there is a "dependable guideline" that a boilover drop out can expand 5-10 times distances across in every bearing from a tank. Genuine separation will rely on upon the amount of fuel included, the measure of vaporized fluid and wind heading. The consequences of a boilover can be disastrous and clearly will uncover anybody in the region to an abnormal state of danger. Consequently on the off chance that it is understood that extinguishment is not going to be accomplished and the fuel has the potential for boilover, it is crucial that all staff retreat to a safe separation. Tragically, despite the fact that there are a few assumptions with respect to indications of a fast approaching boilover, there is right now no authoritative technique for deciding when a boilover will happen. It must be perceived that the fall of hot item through the fuel is not so much uniform over the entire surface of the tank. Thusly, measuring fall of the hot zone at the tank shell by warm imaging cams or hotness delicate paint can't be depended upon. A by and large acknowledged "general guideline" is that the hot zone will travel downwards at a velocity of pretty nearly 1-2 meter consistently. This must be utilized as an unpleasant gauge as real speed will rely on upon fuel sort and constituents. Likewise, it is conceivable that the hot zone does not need to achieve the bottom of a tank to make a boilover - pockets of water or fuel constituents that will bubble can be stratified inside the tank at distinctive levels, particularly in unrefined oils. So as to minimize fuel stock in the boilover it is proposed to pump out the water that is started at the earliest opportunity. It is viewed as that this is possible actually when the firefighting operation is going on the grounds that the turbulence and item development brought on is so little there is no option have any noteworthy impact on froth viability.

Existing models on Boilover onset time prediction.

$$\dot{Q}_f\ t_{bo} = z_{vap}\ \rho_L\left(T_{b,av} - T_{st}\right) + z_{vap}\ \rho_L\ \Delta h_{lh} + z_{bo}\ \rho_L C_p\ (T_{hz} - T_{st})$$

Equation 3

Where,

$\dot{Q}_f$	is the rate at which heat from the flame enters the fuel through unit area of the surface, W m-2
ρ_L	is the density of fuel at ambient temperature, kg m-3
t_{bo}	is the time from ignition until the occurrence of boilover, s
z_{vap}	is the thickness of the fuel consumed by the fire (more volatile components) prior to boilover, m
z_{bo}	is the thickness of the remaining fuel (less volatile components) prior to boilover, m
Δh_{lh}	is the latent heat of vaporization of the liquid fuel,
C_p	J kg-1 is the specific heat of the liquid fuel at *Tst*, J kg-1 K-1
$T_{b,av}$	is the average boiling point of the liquid fuel, K
T_{st}	is the storage temperature of the liquid fuel, K
T_{hz}	is the temperature of the hot zone wave prior to boilover occurrence, K

This model is developed by Michaëlis, Dumas and Gautier in 2005. Where this equation is then rearranged to find, $t_{bo,}$ which is the time taken for boilover occurrence.

Another model that has been developed to find the boilover onset time is by Casal (2008). The maximum value of time to boilover, can be predicted from a heat balance of the fire i.e. the fuel surface is heated by the flame until all thefuel has reached the hot zone temperature, (Casal, 2008):

$$t_{bo} = \frac{\rho_L \; z_f \, C_p \; (T_{hz} - T_{st})}{\dot{Q}_f - \dot{m}\left(\Delta h_{lh} + C_p \left(T_{b,av} - T_{st}\right)\right)}$$

Equation 4

The most recent studies consist of the study conducted by Laboureur, Aprin, Osmont, Buchlin and Rambaud (2013) contributed further to the understanding and the modeling of boilover apparition and consequences. Small scale experiments have been performed with glass and metal reservoirs filled with a diesel-oil mixture.

In this research, two types of experiments have been conducted. First, field tests have been carried out with reservoirs of large dimensions, but experienced a strong dependence on environmental conditions such as wind. Next, laboratory experiments have been performed to guarantee a calm and uniform environment. The effect of the fuel and water thickness, of the lip height were investigated.

From this research study, it can be conclude that the mass boilover intensity depends on both the fuel thickness and the reservoir diameter. It is also indicates that, when the burnt mass ratio increases, more fuel is likely to be expelled from the reservoir and lead to a strong flame increase and / or to several boilover.

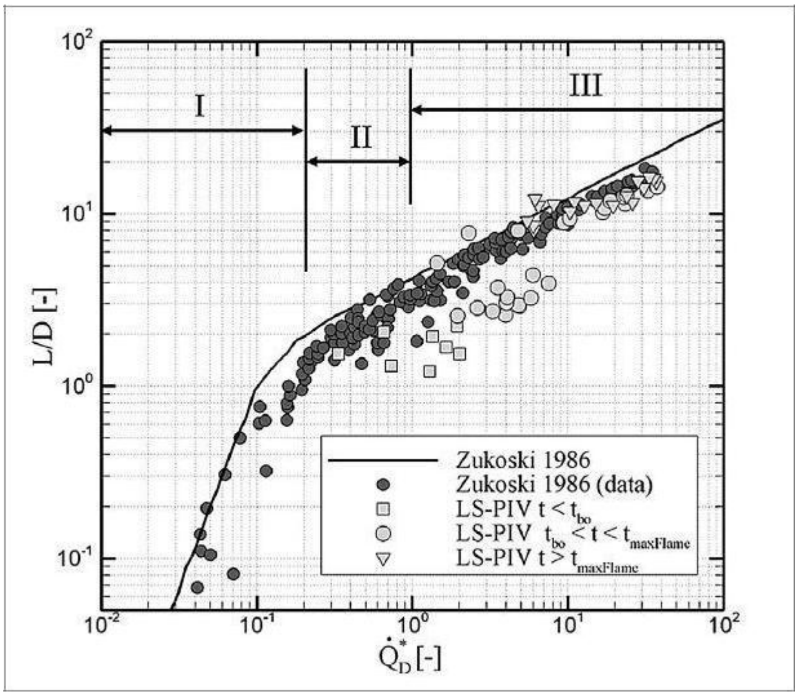

FIGURE 5 Flame height correlated with a non-dimensiol heat release rate.
(Laboureur, Aprin, Osmont, Buchlin, & Rambaud, 2013)

CHAPTER 3:
METHODOLOGY

3.1 Project Flow Chart

Below is the project flow chart for this study project that must be followed in order to achieve the objective of this study:

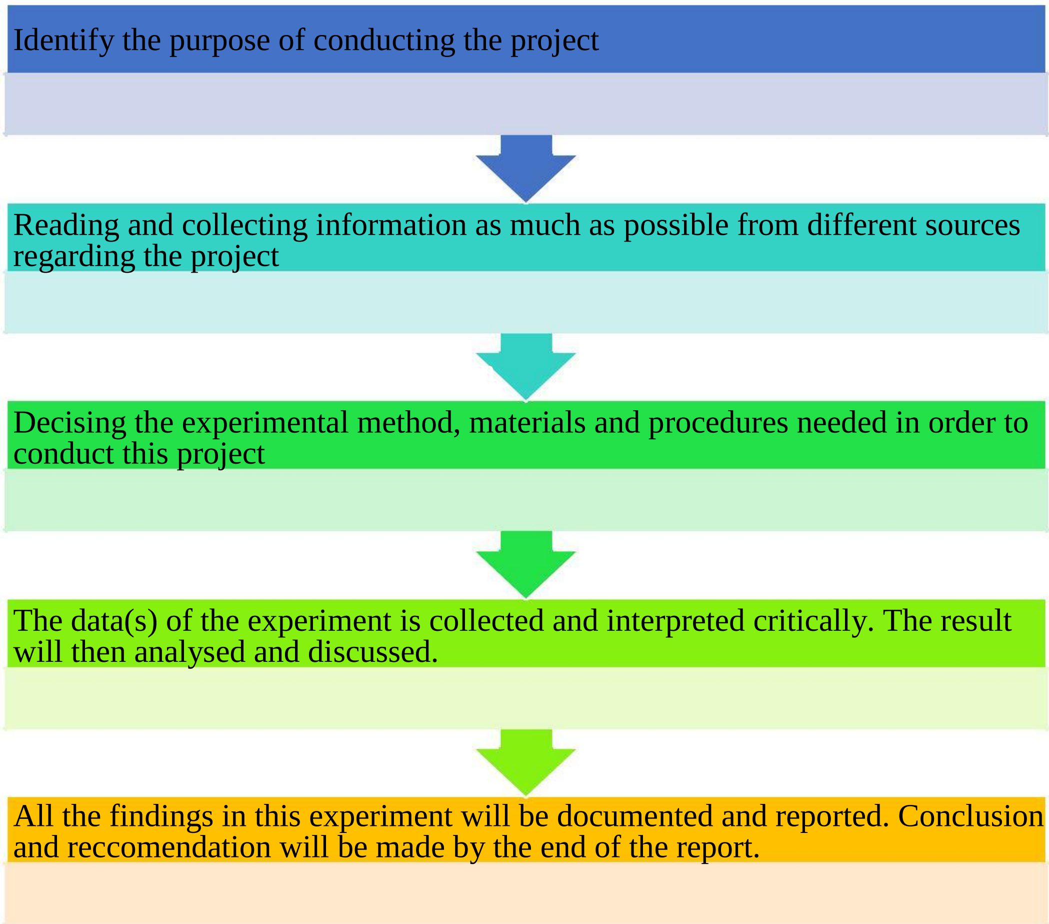

Figure 3: *Project Flow Chart*

3.2 Gantt chart and Key Milestone

Table 1: Final Year Project I Gantt chart and Key Milestone

FYP I

No	**Details**	**Weeks**													
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	**Selection of the project title**														
2	**Preliminary research work and proposal preparation**														
3	**Submission of Extended Proposal**														
4	**Proposal Defence Presentation**														
5	**Project work continues - to improve on all necessary elements**														
6	**Submission of interim draft report**														
7	**Submission of interim report**														

Key:

Process	Key milestone

FYP II

Table 2: Final Year Project II Gantt chart and Key Milestone

No	**Details**	**Weeks**													
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	**Materials and equipments preparations**														
2	**Experiment conducted-progress Report preparation**														
3	**Submission of Progress Report**														
4	**Experiment continues-Data recording and analysis**														
5	**Pre-SEDEX**														
6	**Submission of Draft Final Report**														
7	**Submission of Dissertation (soft bound) and Technical paper**														
8	**Viva**														
9	**Submission of Project Dissertation (hard bound)**														

Key:

Process	Key milestone

3.3 Experiment Methodology

3.3.1 Materials and Equipment

1. Fuels

Fuels consist of crude oil, diesel, and petrol.

2. Water

Water was used as a material for inducing boilover. It can be obtain almost anywhere around the campus. In this experiment, volume of water was fixed at 269ml for each run.

3. Oil tank

In this experiment, a cylindrical tank, Tank A with the diameter of 18.5cm and depth of 8.3cm is be used as to represent the real fuel storage tanks.

Tank A

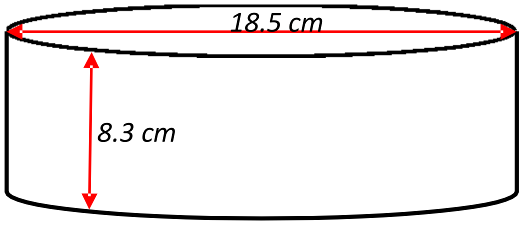

Figure 3 *Measurement for Tank A*

4. Fire Source

A lighter is be used to light up the fuel with water.

5. Digital camera

This equipment purpose is to record the fire behavior during the ongoing experiment, and the indication of the fire spreading after the boilover.

3.3.2 Experiment Procedure

Below are the standard procedures for this experiment. However, the procedure is changed slightly based on the parameters; volume of fuel, thickness of fuel and water in the tank, size and geometry of the tank.

1. To measure the volume of fuel used and water.
2. To mix both solutions in the tank – water will sink as the density is higher.
3. To record the initial depth / thickness of fuel and water in the tank.
4. To ignite the surface of the fuel.
5. To record the onset time when the boilover happen.
6. To record the fire behavior using a camera.
7. Procedures repeated using different volume of fuel and different type of fuel.

3.3.3 Series of Experiments

For this current project, each tank will have five runs of experiment, with different volume of fuel. Different volume will give different depth or thickness of oil inside the tank. For each run, the depth of oil and the onset time to boilover will be recorded. Below is the table for recording purpose.

Table 3

Crude Oil

Exp No.	Ini. Depth of Water (cm)	Ini. Depth of Fuel (cm)	Vol. of Fuel (ml)	Boilover Onset Time (s)	Vol. of fuel leftover (ml)
1	1	2	538		
2	1	2.5	672		
3	1	3	807		
4	1	3.5	942		
5	1	4	1076		

Table 4

Petrol-Diesel Mixture

Exp No.	Ini. Depth of Water (cm)	Ini. Depth of Fuel (cm)	Vol. of Fuel (ml)	Vol. of Petrol (ml)	Vol. of Diesel (ml)	Boilover Onset Time (s)	Vol. of fuel leftover (ml)
1	1	2	538	376	162		
2	1	2.5	672	471	201		
3	1	3	807	565	242		
4	1	3.5	942	659	265		
5	1	4	1076	753	323		

3.3.4 Prediction of Boilover Onset Time based on Thermodynamic Law

The time to boilover is related to the time taken for the lower boundary of hot zone to reach the fuel-water interface and boil the water. The heat apply by flame to the oil surface will vaporize the light end and also increase the temperature of the bulk liquid in the tank. Such concept can mathematically represent by below formula:

$$\boldsymbol{Q}=\dot{\boldsymbol{m}}\boldsymbol{C}_{\boldsymbol{p},}(\boldsymbol{T}_{\boldsymbol{bo}}-\boldsymbol{T}_{\boldsymbol{st}})+\dot{\boldsymbol{m}}\boldsymbol{h}_{\boldsymbol{v}} \qquad \text{(Equation 3-1)}$$

Q = Heat Flux (J/s)

$\dot{m}$ = mass burning rate in (kg/s)

Cp,st = Specific heat capacity of fuel at storage temperature (J/kg.K)

T_{bo} = Boilover temperature (K)

T_{st} = Storage temperature (K)

Hv = heat vaporization in (J/kg)

Using the time element of Q = J/s, we can predict the onset time of the boilover occurrence.

Since, $\dot{m} = \frac{p.A.h}{t}$, (Equation 3-2)

Then, $Q = \frac{\rho l.A.hl}{t} Cp(Tbo - Tst) + \frac{\rho v.A.hv}{t} Hv$ (Equation 3-3)

$\frac{Q}{A} = \frac{\rho l.A.hl}{t} Cp(Tbo - Tst) + \frac{\rho v..hv}{t} Hv$ (Equation 3-4)

Where, $\frac{Q}{A}$ = heat flux from the flame (W/m^2)

ρ_v = density of the vaporized fraction (at boiling point) (kg/m^3)

ρ_l = density of liquid (at storage temperature) (kg/m^3)

h_v = height of the vaporized fraction (m)

h_l = height of remaining liquid (m)

t = time to boilover (s)

The height of the remaining liquid is determined by,

$$hl=h_0-hv \qquad \text{(Equation 3-5)}$$

Where, $h0$ = initial height of oil

The height of vaporized fraction correlates to the burning of the lighter ends, hence,

$$h_v = \dot{m_v}.t \qquad \text{(Equation 3-6)}$$

Therefore, $h_l = h_0 - \dot{m_v}.t$ (Equation 3-7)

Rearranged the heat balance to give the correlation to determine the time to boilover as shown:

$$\frac{Q}{A}t = \rho_v.\dot{m}_v.t.H_v + \rho_l.(h_0 - \dot{m}_v.t).C_{p,st}(T_{bo} - T_{st}) \qquad \text{(Equation 3-8)}$$

$$\frac{Q}{A}t - \rho_v.\dot{m}_v.t.H_v + \rho_l.(h_0 - \dot{m}_v.t).C_{p,st}(T_{bo} - T_{st}) = \rho_l.h_0.C_{p,st}(T_{bo} - T_{st})$$

$$t = \frac{\rho_l.h_0.C_{p,st}(T_{bo} - T_{st})}{\frac{Q}{A} - \dot{m}_v.[\rho_v.H_v - \rho_l.C_{p,st}(T_{bo} - T_{st})]}$$

(Equation 3-9)

3.3.5 Estimates of Specific Heat, Latent Heat of Vaporisation, Heat Flux Radiated (from flame to fuel) and Heat of Combustion

For the calculations of the boilover time for crude oil and petrol-diesel mixture, empirical models are used to calculate the parameters directly related to the calculations based on methods shown in literature review.

3.3.5.1 Specific Heat Capacity

Specific heat is defined as the quantity of heat required to raise a unit mass of material through one degree of temperature. Estimation methods are an obvious choice to provide heat capacities for compounds when there is a complete lack of data. In this work, the specific heat is estimated through a correlation proposed by Speight (2001). Based on many experimental measurements made on various hydrocarbon materials, the specific heat data (kJ kg^{-1} $^oC^{-1}$) for liquid hydrocarbon at temperature T (in ^oC) were generalized by the following equation:

$$Cp = (1.685 + 0.039\ T)/SG^{0.5} \qquad \text{(Equation 3-10)}$$

Equation 3-10 is used in the estimation of fuel's specific heat due to its simplicity and empirical basis.

3.3.5.2 Heat of Vaporization

The latent heat of evaporation for a hydrocarbon liquid can also be calculated by the following equation proposed by Speight (2001), once the boiling temperature, and specific gravity of the liquid are known:

$$Hv = (251.47 - 377.136 \times 10 - 3 * Tbp)/SG \qquad \text{(Equation 3-11)}$$

3.3.5.3 Heat Flux

For a generic correlation where the experimental flame temperature data is not available, the heat flux radiated from the flame to the fuel surface is often expressed as (Hamins *et al*., 1991, 1995; Zalosh, 2002; Engelhard, 2005):

$$\dot{q} = \chi_R \, m''_V \, \Delta h_c$$

where

m''_V is the mass burning flux or mass burning rate per unit area, kg m^{-2} s^{-1}

Δh_c is the heat of combustion of the fuel, J kg^{-1}

(Equation 3-12)

3.3.5.4 Mass Burning Rate

In the case that the relevant empirical factors are not available, the mass burning flux could be estimated by (Gottuk and White, 2002; Engelhard, 2005; Fay, 2006):

$$\dot{m}_v = \frac{1.0 \times 10 - 3. \mathrm{Hc}}{\rho v. [\mathrm{Hv} + \mathrm{Cp}, \mathrm{Tbp}(\mathrm{Tbp} - \mathrm{Tst})}$$

(Equation 3-13)

with the numerical constant of 1x10-3 kg^2 m^{-5} s^{-1}. The temperatures are expressed in Kelvin.

3.3.5.5 Heat of Combustion

If the enthalpies of formations of the combustion reaction products and reactants are not known, the following correlations can be used to estimate the heat of combustion, *hc* (Chulkov, 1968; Bugai *et al.*, 1998):

$$\Delta h_c = 50462.7 - 8546.1\ SG$$
$$\Delta h_c = 46423.2 + 3169.4\ SG - 8792.3\ SG^2$$

(Equation 3-14)

where Δhc is the heat of combustion (kJ kg^{-1}) and *SG* is the fuel's specific gravity.

CHAPTER 4:

RESULTS & DISCUSSIONS

Experiment was conducted during Final Year Project II course. The allocated time are fourteen weeks, up from conducting the experiment until the submission of final report for the outcome result. Based on the literature review and past research, this experiments current results and outcome as per below.

4.1 Boilover Potential for Petrol-Diesel Mixture and Crude Oil

The experiment was conducted in two difference sets. The first one would be using 70% Petrol and 30% Diesel while the second one is using 100% crude oil. The combination of petrol and diesel is selected because these are the most common and largely used fuel. As most of the literatures are based on more diesel, which is in the heavier end of crude oil we opt for the opposite by using more petrol which is in the lighter end of crude oil. After conducting the experiment, it is observed and proven that boilover can occur in both Petrol-Diesel mixture and Crude Oil. Due to both fuels are having multiple components, it offer a wide range of boiling point during the combustion period. Below figures are the observations of fire behavior and boilover for the experiment conducted in Tank A.

Observation for Crude Oil Mixture

FIGURE 5 Steady State

FIGURE 6 Initial boilover

FIGURE 7 Second boilover

FIGURE 8 Third boilover

FIGURE 9 Post boilover

FIGURE 10 After boilover

Observation for Petrol-Diesel Mixture

FIGURE 11 Steady State

FIGURE 12 Initial boilover

FIGURE 13 First major boilover

FIGURE 14 Second major boilover

FIGURE 15 Post boilover

FIGURE 16 After boilover

Figure 5 – Figure 10 shows the boilover phenomena of crude oil mixture and Figure 11- 16 is the boilover phenomena for petrol-diesel. In Figure 5 and Figure 11, it can be observed that the flame burning rate started to become steady and stable for both the fuels. However, boilover potential cannot be seen in this period of burning. Based on previous study, the potential 'indicators' for boilover include boiling, fuel and steam ejection and audible indication. In many literatures, it has been mentioned that the start of the boilover event is normally accompanied by a noise characteristic (a crackling sound) which relates to the explosion of vapour bubbles that carry the fuel into the flame.

Shortly before the boilover happens, as shown in Figure 6 and Figure 12, a loud crackling sound can be heard as far as 100m from the tank. The crackling sound can be heard for around 15-20 seconds before the boilover happened. It can be observed that during the initial boilover, the flame enlargement and fuel injection for the petrol-diesel mixture has occurred. In a study, Buang (2014) stated that boilover is also seen through fuel ejection due to the violent boiling of water and frothing over the tank contents which resulted in an increase in the flame height two or three times larger than during steady burning period.

In Figure 7 and Figure 8 for crude oil and figure 13 and 14 for petrol diesel mixture, major boilover had occurred. Both major boilover showed the same characteristic; flame enlargement and fuel ejection. However, it can be observed that flame enlargement for these two major boilover is larger than the flame enlargement during initial boilover. Moreover, the flames during the initial and major boilover were observed to be approximately 2 to 5 times the diameter of the tanks and hot burning fuel was thrown out from the tank which landed several meters away.

In Figure 9 and Figure 15, post boilover occurred for used both fuel. During this period, the flame on the surface of the fuel started to extinguish. However, fuel injection still occurred throughout this period but with minimum amount of injection. In Figure 10 and Figure 16, after the boilover have occurred, flame started to extinguish and no flame enlargement or fuel ejection can be observed. It can be assumed that when the water at the bottom of the tank being ejected during the boilover, it tends to suppress the fire on the surface of the fuel. In summary, to identify the potential of boilover, physical observation such as the presence of higher sound levels and flame enlargement can be observed.

4.2 Boilover Onset Time of Fuels

4.2.1 Data Table

4.2.1.1 Crude Oil

Table 5

Exp No.	Ini. Depth of Water (cm)	Ini. Depth of Fuel (cm)	Vol. of Fuel (ml)	Boilover Onset Time (s)	Vol. of fuel leftover (ml)
1	1	2	538	701	300
2	1	2.5	672	1080	300
3	1	3	807	1300	320
4	1	3.5	942	1342	350
5	1	4	1076	1380	360
6*	1	3.5	942	1362	348
7*	1	4	1076	1398	354

* Repeated Experiment

4.2.1.2 Petrol-Diesel Mixture

70% Petrol & 30% Diesel

Table 6

Exp No.	Ini. Depth of Water (cm)	Ini. Depth of Fuel (cm)	Vol. of Fuel (ml)	Vol. of Petrol (ml)	Vol. of Diesel (ml)	Boilover Onset Time (s)	Vol. of fuel leftover (ml)
1	1	2	538	376	162	650	284
2	1	2.5	672	471	201	751	204
3	1	3	807	565	242	990	305
4	1	3.5	942	659	265	1114	375
5	1	4	1076	753	323	1155	400
6*	1	3.5	942	659	265	1108	370
7*	1	4	1076	753	323	1185	379

* Repeated experiments

4.2.2 Effect of Depth of Fuel on Boilover Onset Time

Based on the data table, graph of boilover onset time vs depth of the fuel has been plotted for both tank A and tank B. The graphs are shown below.

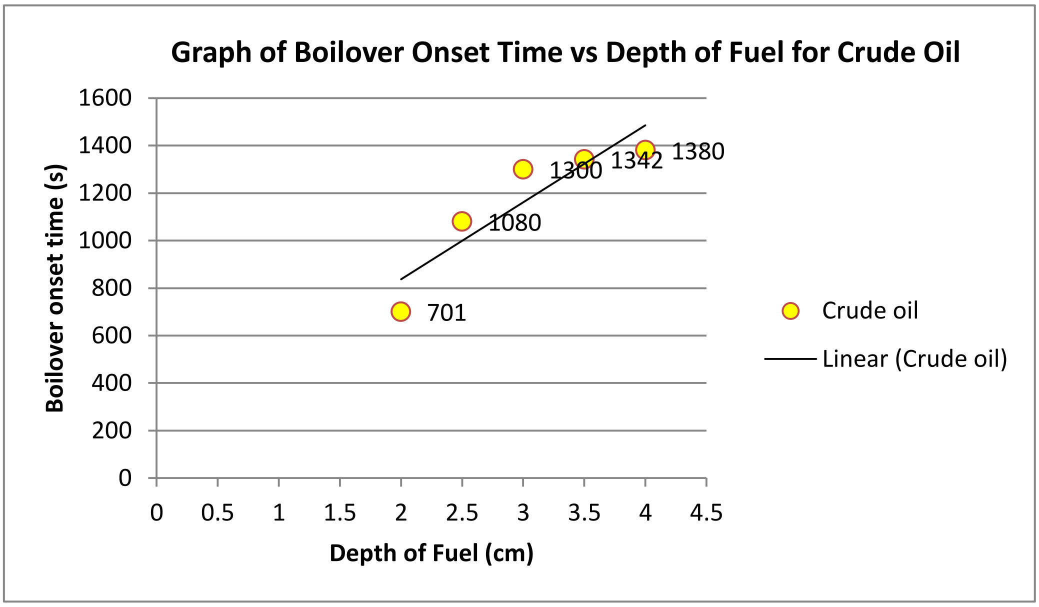

Figure 17- Boilover Onset Time vs Depth of Fuel for Crude Oil

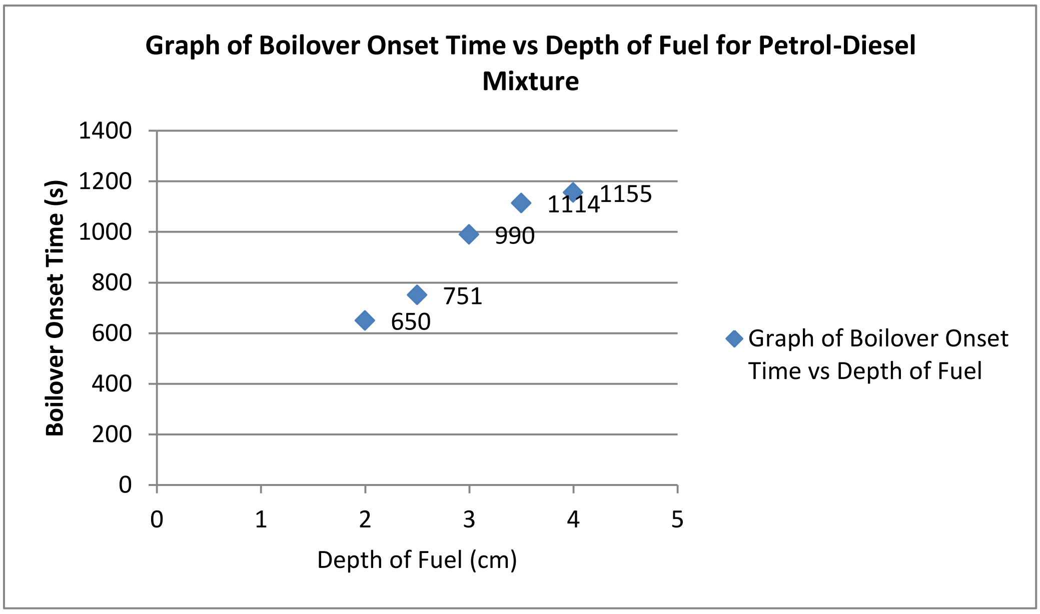

Figure 18- Boilover Onset Time vs Depth of Fuel for Petrol-Diesel

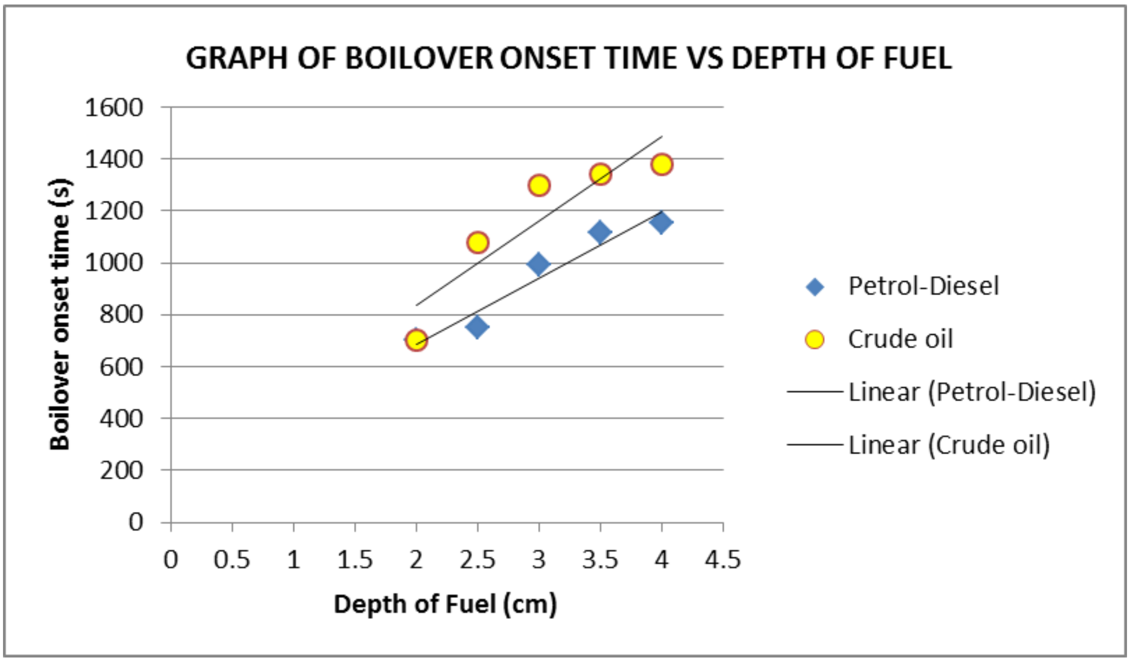

Figure 19 – Boilover onset time vs depth of fuel

From the graph we can interpret that, as a whole, for both type of fuel the boilover onset time increases when the depth of fuel increases. In other words, more fuel requires more time for boilover to occur. It can also be seen that crude oil requires more time to boilover compared to petrol-diesel mixture. This condition might be mainly due to crude oil's density higher than petrol-diesel. As we know, the heavier hydrocarbon has higher boiling point compared to lighter hydrocarbon.

For both fuel also we can see a slight decrease in rate of time to boilover in both fuel from 0.035m and 0.04m compared to when lesser volumes of fuel are used. Also it is to be noted that these data might not be fully accurate as it was obtained from uncontrolled environment where the result depends on the external conditions such as wind, humidity of the air and other atmospheric conditions.

4.3 Prediction of Boilover Onset Time based on Thermodynamic Law

In order to verify the feasibility, predicted results of the model are compared to the results of the experimental study. Below calculation show the predicted boilover onset time based on thermodynamic equation.

<u>Fuel Properties 1</u>

Type	: Crude oil
Boiling temperature	: 573.15K
Storage temperature	: 298.15K
Density at storage temperature	: 847 kg/m^3
Specific gravity	: 0.85

<u>Fuel Properties 2</u>

Type	: Petrol-Diesel Mixture
Boiling temperature	
Petrol	: 95°C / 368 K
Diesel	: 238 °C / 511 K
Combine	: 138 °C / 411 K
Storage temperature	: 298 K
Density at storage temperature	
Petrol	: 737 kg/m^3
Diesel	: 885 kg/m^3
Combine	: 781 kg/m^3
Specific gravity	
Petrol	: 0.737
Diesel	: 0.885
Combine	: 0.781

4.3.1 Calculated parameters

4.3.1.1 Vaporized oil density at boiling point,

Crude oil

$$\rho_v = 847 - [7.10 \times 10^{-4}(615.15 - 298.15)] + [2.37 \times 10^{-7}(403.15 - 298.15)^2]$$

$$\rho_v = 846.75\ kg/\ m^3$$

Petrol- Diesel Mixture

$$\rho_v = 781 - [7.10 \times 10^{-4}(411.15 - 298.15)] + [2.37 \times 10^{-7}(411.15 - 298.15)^2]$$

$$\rho_v = 780.9\ kg/\ m^3$$

4.3.1.2 Specific heat oil at storage temperature,

Crude oil

$$C_{p,st} = \frac{1.685 + 0.039 * (25)}{0.85\text{^}0.5}$$

$$C_{p,st} = 2885\ \frac{J}{kg.K}$$

Petrol-Diesel Mixture

$$C_{p,st} = \frac{1.685 + 0.039 * (25)}{0.78\text{^}0.5}$$

$$C_{p,st} = 2789\ \frac{J}{kg.K}$$

4.3.1.3 Specific heat of oil at boiling point,

Crude oil

$$C_{p,bp} = \frac{1.685 + 0.039(300)}{0.85\text{^}0.5}$$

$$C_{p,bp} = 14518\ \frac{J}{kg.K}$$

Petrol-Diesel Mixture

$$C_{p,bp} = \frac{1.685 + 0.039(138)}{0.78\text{^}0.5}$$

$$C_{p,bp} = 8001.8\ \frac{J}{kg.K}$$

4.3.1.4 Heat of vaporization,

Crude oil

$$H_v = \frac{251.47 - 377.136\ \times\ 10^{-3}\,(411)}{0.78}$$

$$H_v = 41{,}613\ \frac{J}{kg}$$

Petrol-Diesel Mixture

$$H_v = \frac{251.47 - 377.136\ \times\ 10^{-3}\,(411)}{0.78}$$

$$H_v = 123{,}675\ \frac{J}{kg}$$

4.3.1.5 Heat of Combustion

Crude Oil

$$H_c = 46513 - 8800\ (0.85)^2\ +\ 3132\ (0.85)$$

$$H_c = 3.75\ \times 10^7\,\frac{J}{kg}$$

Petrol-Diesel Mixture

$$H_c = 46513 - 8800\ (0.78)^2 \ + \ 3132\ (0.78)$$

$$H_c = 3.87 \ \times 10^7 \frac{J}{kg}$$

4.3.1.6 Burning rate (surface regression rate)

Crude Oil

$$\dot{m}_v = \frac{1.0 \ \times \ 10^{-3}\ (3.75 \ \times \ 10^7)}{846.75\ [\ 41613 + 14518\ (403.15 - 298.15)]}$$

$$\dot{m}_v = 2.83 \ \times \ 10^{-5}\ \frac{m}{s}$$

Petrol-Diesel Mixture

$$\dot{m}_v = \frac{1.0 \ \times \ 10^{-3}\ (3.87 \ \times \ 10^7)}{780.9\ [\ 123{,}675 + 8001.8(411.15 - 298.15)]}$$

$$\dot{m}_v = 4.82 \ \times \ 10^{-5}\ \frac{m}{s}$$

4.3.1.7 Mass burning Rate,

Crude Oil

$$r_{comb} = 2.83 \ \times \ 10^{-5}\ (847)$$

$$r_{comb} = 0.024 \frac{kg}{m^2.s}$$

Petrol-Diesel Mixture

$$r_{comb} = 4.82 \ \times \ 10^{-5}\ (781)$$

$$r_{comb} = 0.038 \frac{kg}{m^2.s}$$

Heat flux from flame radiated to burning fuel surface (assuming x_r to be in order of 0.1%, hence $x_r = 0.001$

Crude Oil

$$\frac{\dot{Q}}{A} = (0.001).\ (0.024).(\ 3.75\ \times 10^7)$$

$$\frac{\dot{Q}}{A} = 898\frac{W}{m^2}$$

Petrol-Diesel Mixture

$$\frac{\dot{Q}}{A} = (0.001).\ (0.038).(\ 3.87\ \times 10^7)$$

$$\frac{\dot{Q}}{A} = 1470.6\frac{W}{m^2}$$

4.3.2 Predicted Time Results

In order to solve for the time to boilover, the proposed experimental setup requires the input of boilover temperature. Currently, the determination or calculation of boilover temperature is extremely complex due to the huge number of parameters it depends on. Hence, an experimental measure value is used in the calculation, T_{bo}=130℃ = 403.15K.

Hence, the final equation to predict the onset time,

Crude Oil

$$t = \frac{847\ \times h_0 \times 2885 * (403.15 - 298.15)}{(898) - (2.83\ \times\ 10^{-5}\,) \times [\ 846.75\ \times 41613 -\ 847 \times 2885\ (403.15 - 298.15)]}$$

$$t = \frac{25.66\ \times\ 10^7}{7161.9}h_0$$

$$t = 35{,}825\ h_0$$

Petrol-Diesel mixture

$$t = \frac{781\ \times h_0 \times 2789 * (411.15 - 298.15)}{(1470.6) - (4.82\ \times\ 10^{-5}) \times [\,780.9\ \times 123{,}675 -\ 781 \times 2789\ (411.15 - 298.15)]}$$

$$t = \frac{24.61\ \times\ 10^7}{8679.4} h_0$$

$$t = 28355\ h_0$$

The predicted time to boilover for crude oil and petrol-diesel mixture is shown in the table below.

TABLE 7 Predicted time to boilover for Crude oil

Fuel initial height, h_0 **(m)**	**Predicted time to boilover (s)**
0.020	716.5
0.025	895.6
0.030	1074.8
0.035	1253.9
0.040	1433.0

4.3.3 Comparison Between Predicted Data and Experimental Data for Onset Time

TABLE 8 Result comparison table for Crude oil

Fuel initial height, h_0 **(m)**	**Experimental time to boilover (s)**	**Predicted time to boilover (s)**	**Percentage Difference %**
0.020	701	716.5	2.16
0.025	1080	895.6	17.07
0.030	1300	1074.8	17.38
0.035	1342	1253.9	6.57
0.040	1380	1433.0	3.84

TABLE 9 Predicted time to boilover for Petrol-Diesel Mixture

Fuel initial height, h_0 **(m)**	**Predicted time to boilover (s)**
0.020	567
0.025	709
0.030	851
0.035	992
0.040	1134

TABLE 10 Result comparison table for Petrol-Diesel Mixture

Fuel initial height, h_0 (m)	Experimental time to boilover (s)	Predicted time to boilover (s)	Percentage Difference %
0.020	650	567	14.60
0.025	751	709	5.92
0.030	990	851	16.33
0.035	1114	992	12.30
0.040	1155	1134	1.85

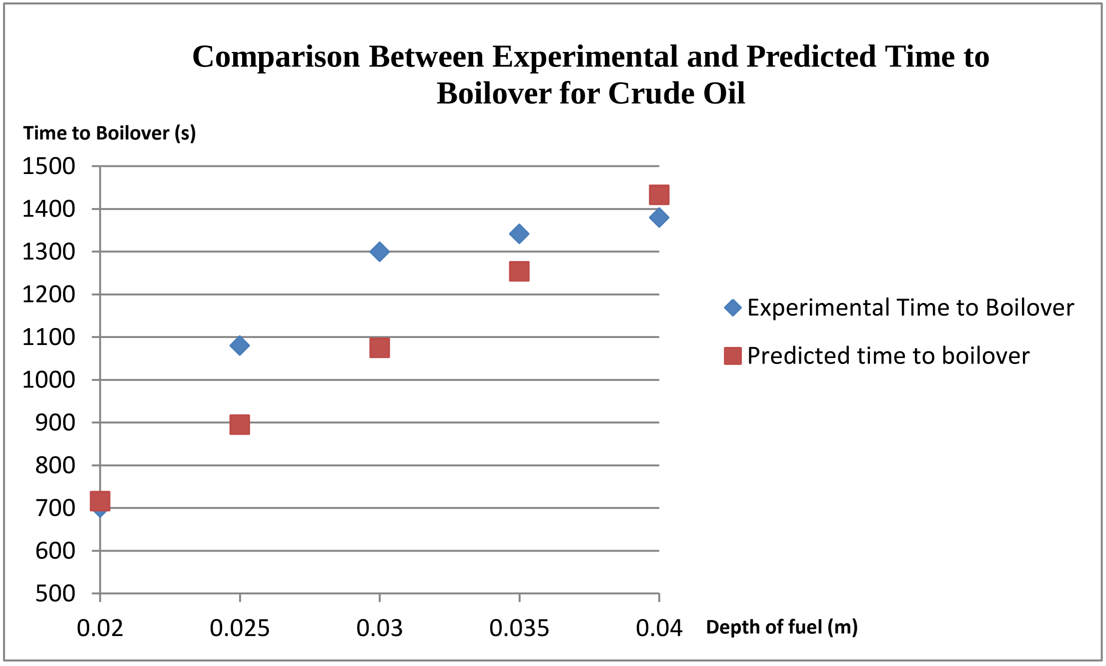

Figure 20 Graph of Result Comparison for Crude Oil

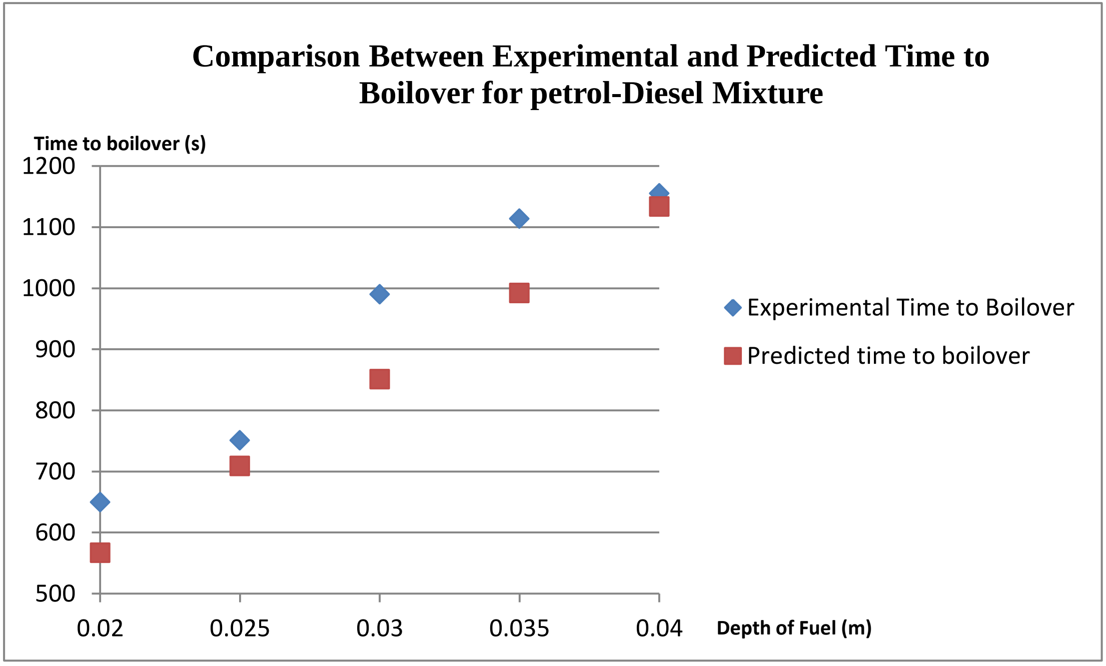

Figure 21 Graph of Result Comparison for Petrol-diesel Mixture

4.4 Discussion

The results predicted by using the predictive tool are overall always faster than the experimental results. This may be due to uncontrolled factors present during the experiment such as wind, air humidity and atmospheric pressure and temperature which cannot be kept constant.

4.4.1 Characteristics of Predictive Tool

The results show that the predictive tool is capable of providing good estimates on the onset time of the boilover phenomenon of crude oil and petrol-diesel mixture. The predicted results are not absolutely accurate but it is reliable as it only has a deviation less than 20% from the experimental results. It is also to be noted that most of the results are significantly accurate with less than 10% deviation.

4.4.2 Limitations of Predictive Tool

The predictive tool does not include meteorological parameters to calculate the time to boilover. The modeled combustion parameters e.g. mass burning rate of fuel, fuel surface regression rate and mass burning flux of fuel does not consider the wind speed, but on the fuel specification only. This limit of the model could be overcome by the use of a wind speed integrating correlation to calculate the rate of combustion or burning.

Besides this, the time results from the predictive tool does not consider the occurrence of slop over or froth over before the boilover occurrence and any emergency strategies to minimize fuel in tank e.g. tank being emptied during fire-fighting activities. The predictive tool can only predict single boilover occurrence.

Furthermore, the time results from the predictive tool highlight the great dependence on the heat flux feedback to the surface and into the fuel. The heat flux is determined by fraction of heat radiated that contributes to the hot zone formation. A better method to determine or to estimate the fraction of heat radiated that contributes to the hot zone formation will ensure valid and reliable prediction.

4..4.3 Application of Predictive Tool

Since the predictive tool developed from this project manages to provide a predictive result within accepted deviations, this predictive tool can be a significant input to the development of safer and more effective fire-fighting techniques for boilovers of storage tanks. This can be done by assessing the boilover prediction time using the predictive tool obtained and take emergency actions according to the predicted time.

CHAPTER 5: CONCLUSION & RECCOMENDATIONS

The conclusions of this project are:

1. All of the tests involving crude oil and petrol-diesel mixture resulted in boilover.
2. Hence, for boilover to occur it is necessary to have a fuel with wide boiling range and for the boiling points of the heavier components to be significantly greater than the boiling point of water.
3. The onset time of boilover showed a linear increase as the initial depth of the fuel increased.
4. The predictive tool developed is capable of providing good estimates of boilover onset time with acceptable deviations.

Due to the lack of equipment, the temperature profile does not being measured in this experimental study. Nevertheless, in the future, it is recommended to use a thermocouple to measure the temperature profile in the fuel tank, as this data is very useful for more thorough analysis to produce better results.

Apart from that, for future studies it is recommended to identify the accurate properties of used fuels by doing fuel characterizing tests or other laboratories tests rather than finding by calculations or literature review to get more accurate and precise results. Furthermore, it is recommended to extend the experiment further to 6,7,8,9,10 cm of fuel depth to see the trending.

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