CREATION OF A CLAY FLAMELESS BURNER FOR VAPORIZING AN INSECT REPELLENT CONTAINING PMD AS AN ACTIVE INGREDIENT

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CREATION OF A CLAY FLAMELESS BURNER FOR VAPORIZING AN INSECT REPELLENT CONTAINING PMD AS AN ACTIVE INGREDIENT

By

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Promoter: Dr. G. Dugmore
DECLARATION

In accordance with Rule G4.6.3, I hereby declare that the above-mentioned treatise is my own work and that it has not previously been submitted for assessment to another University or for another qualification.

Faith Mary Akwi

2012
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Abstract

Insecticide treated mosquito bed nets, insecticide aerosol sprays, repellent lotions and creams, repellent candles, vaporizable repellent essential oils, mosquito mats and coils are some of the many malaria personal protection tools that are in use. The latter of these measures are the most accessible and affordable options for the rural population in sub-Saharan Africa. It is therefore important to determine how effective these personal protection measures are by determining their ability to efficiently disperse an active ingredient when the protection measure is in use. In this study, a copper II oxide montmorillonite clay burner (CuO-Montmorillonite clay burner) was created to vaporize repellent formulations containing various concentrations of p-menthane-3,8-diol (PMD) as the active ingredient with the aim of determining the percentage of the active ingredient that is released into the air and the rate of release. The performance of the CuO-Montmorillonite clay burner was also compared to that of the Lampe Berger fragrance burner (LBFB). In addition to this, the percentage of PMD released from 6% wt PMD candles of diameters 40mm, 69mm and 83mm was determined and compared to that released when the CuO-Montmorillonite clay burner and Lampe Berger Fragrance burner where used to vaporize PMD repellent formulations. It was found that the rate of vaporization of the various PMD repellent formulations vaporized using the Lampe Berger fragrance burner is affected by the mass of PMD present in the repellent formulations. The 6% wt PMD repellent candles released the least percentage of PMD as compared to that released when the CuO-Montmorillonite clay burner and the Lampe Berger fragrance burner were used to vaporize the PMD repellent formulations.
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CHAPTER ONE

INTRODUCTION

1.1 GENERAL OVERVIEW

Insects are believed to have existed in this world long before man and are used as a source of food, medicinal [1] purposes and also help in agriculture through pollination. Not only are insects useful to man, they are also destructive and harmful. They spread diseases; destroy crops, harvested foods and property such as wooden items. Mankind, equipped with advanced technology and analytical methods, has continued to research about behavioral characteristics, life cycles and genetic changes of disease spreading insects in order to gain protection from these insects.

Malaria is one of many diseases spread by insects and is a medical epidemic with an estimated 300-500 million new infections and 1-3 million deaths [2] per year of which more than 90% of these occur in the sub-Saharan Africa mostly among the poorest rural areas without access to health facilities. All segments of society are susceptible to malaria infection but the greatest sufferers are children younger than 5 years of age and pregnant women. It is known that about 2% of the persons infected with falciparum malaria usually die because of delayed treatment. Malaria in humans is caused by a protozoan of the genus plasmodium and has four sub-species i.e. falciparum, vivax, malariae and ovale. This protozoan is spread by the mosquito Anopheles gambiae. Of the four sub-species, P.falciparum causes the greatest illness and death in Africa. Fever is the main symptom of malaria and the most severe manifestations are cerebral malaria, anemia in children and pregnant women, kidney and other organ dysfunction problems with severe manifestations of this disease mostly occurring [3] in persons who have not had previous immunity.

Malaria transmission is a problem in both rural and urban areas of sub-Saharan Africa although the most affected population is in rural sub-Saharan Africa. There is said to be a relationship [4] between malaria, climate zones and poverty. It is therefore no surprise that the countries with the highest transmission of malaria are poverty stricken and in climatic zones with favorable temperatures for the life cycle of the malaria parasite within the female Anopheles mosquito.
From the above theoretical model, it can be seen that malaria is mostly absent in a few countries that have unfavorable climate for the female Anopheles mosquito to breed. Anti-malaria drugs, insecticide treated bed nets and indoor residual spraying services are availed to the rural population in the countries where malaria is endemic by Non-Government Organizations and International Aid groups. Due to a number of factors such as poverty, illiteracy on causation and spread of the disease, delayed treatment, under dosage etcetera it is not easy to quickly achieve reduced Malaria infections in these areas. There is therefore a need for a malaria control tool that is easy to apply and use such as spatial repellent application that should be used in conjunction with the existing tools to reduce Malaria infections in rural sub-Saharan Africa. It is also important to determine how efficiently these tools are in dispersing active ingredients of the insect repellents when they are used. The
purpose of this study is to create spatial applications of p-menthane-3,8-diol (PMD) and to determine how efficiently they release PMD when they are used.

In this study, a montmorillonite clay burner doped with copper oxide was prepared to provide a means of dispersing a repellent formulation into the ambient atmosphere. A PMD repellent formulation was used to determine the ability of the CuO-Montmorillonite clay burner to catalytically oxidize and vaporize the repellent formulation and this was compared to that of the Lampe Berger fragrance burner. The effectiveness of an essential oil to repel *Aedes Aegypti* when used in combination with the Lampe Berger was determined by the Testing and Conformity services (Pty) Ltd an affiliate of the South African Bureau of Standards [5] using an olfactometer. From the test results, it was discovered that the Lampe Berger can be used to vaporize repellent formulations since it was able to disperse the repellent oil without completely burning it out. A question therefore arises; how much of the active ingredient in a repellent formulation does the Lampe Berger fragrance burner emit.

In addition to preparing a CuO-Montmorillonite clay burner, 6% by weight PMD repellent candles of diameters 40mm, 69mm and 83mm were also prepared and the percentage of PMD released into the atmosphere when they were lit was determined. The methods of dispersing PMD suggested in this study will be very applicable to persons most affected i.e. the poor living in rural and poor urban areas with no electricity to help in repelling mosquitoes. It should be noted that the methods of spatial application of PMD used here have only been tested and compared in regards to their ability to disperse PMD into the air in an enclosed environment or space and not on their ability to repel mosquitoes.
1.1.1 Objective of the Study

- To compare the performance of three spatial repellent delivery systems; CuO-Montmorillonite clay burner, Lampe Berger fragrance burner and candles in dispersing p-menthane-3,8-diol into surrounding air.

1.1.2 Research Questions

- How does the diameter of the candle affect the amount of PMD released into the atmosphere?

- What is the percentage of PMD released when PMD repellent formulations are vaporized using the copper oxide montmorillonite clay burner and the Lampe Berger fragrance burner?

- What is the percentage of PMD released when 6% wt PMD repellent candles are used?

- What is the rate of vaporization of PMD repellent formulations when vaporized using the CuO-Montmorillonite clay burner and the Lampe Berger fragrance burner?

1.1.3 Hypothesis

- The copper II oxide montmorillonite clay burner and the Lampe Berger fragrance burner release a higher percentage of p-menthane-3,8-diol when used to vaporize repellent formulations containing p-menthane-3,8-diol compared to that released during the use of 6% wt PMD repellent candles of diameters 40mm, 69mm and 83mm.
1.2 A REVIEW OF LITERATURE

1.2.1 Problems affecting implementation of some malaria control tools in rural sub-Saharan Africa

The spread of malaria is essentially centered on three living organisms i.e. humans, an insect and a micro-organism. Humans and the female anopheles mosquitoes act as carriers of the parasite thus the need to protect humans from mosquito bites.

Figure 2: Life Cycle of Malaria


As seen from the cycle above, eliminating the link between man and the infected female anopheles mosquito will help to reduce transmission of malaria in humans. In order to win the fight against malaria and to decrease its effects on society, an integrated approach combining a number of malaria control tools has been used and is still being emphasized. It is stated in the World Health Organization (2008) Malaria report, a combination of tools such as Insecticide treated nets (ITN), Indoor Residual Spraying (IRS), Intermittent Preventive Treatment in pregnancy [6] (IPI) and Artminisinin based Combination Therapy (ACT) reduced deaths in some regions by 50% and countries such as Kenya, Zanzibar and Gambia recorded low cases of death between the years 2006 and 2007. This success was attributed to
the use of long lasting insecticide treated nets and early treatment of uncomplicated cases of malaria.

Due to this success, Bill and Melinda Gates called for a new global strategy for the eradication of malaria. The strategy called for disease control programs other than parasite oriented control programs i.e. renewed emphasis on treatment and protection of man from vectors by use of protection measures against mosquito bites. These protection measures to reduce the parasite load in the community include use of insecticide treated mosquito bed nets, closing doors and windows in the evening, use of mosquito repellents, lotions, creams and mats and also early diagnosis and treatment. This was a good strategy considering the outcome obtained from its implementation sub-Saharan Africa which is an indication that vector control plays a major role in the eradication of malaria.

Biological malaria control tools have also been introduced in the unending fight against malaria transmissions in Africa for example *Bacillus thuringinesis var israelensis* (Bti) used for [7] larval control and the use of Entomopathogenic Fungi [8] which causes death in the adult anopheles mosquito and reduces its feeding activity. This is another example of recently developed methods to combat malaria using the vector control approach. The use of Bti and Entomopathogenic fungi are not yet well established although trials have already been carried out with both showing effective results in reduction of the mosquito larvae in breeding grounds and the *Anopheles gambiae* respectively. Even with such new malaria control tools being introduced, there are still factors affecting the already existing tools that are in use in rural sub-Saharan Africa and these include;

Reduced health budgets in Governments and inadequate funds allocated to the health programs and strategies. In 2005, it was reported that an estimated US$200 million was spent [9] on malaria control by African Governments, donor Governments and UN Agencies.

Resistance of parasites as well as vectors to control medicines is a problem affecting the effectiveness of anti-malaria drugs use and indoor residual spraying. For example plasmodium *falciparum*’s resistance to [10] Chloroquine was noted in the early 1960’s and late 70’s in South America, South East Asia and Africa.

Constant change in vector behavior where outdoor mosquitoes adopt indoor biting habits. A new type of mosquito [11] was found in Burkina Fuso near human settlements. It originally was found in remote locations far away from humans. Researchers say this new mosquito,
which is a sub species of *Anopheles gambiae*, is favored by the malaria parasite. If this outdoor mosquito adopts indoor biting habits, there is likely to be another evolution of mosquitoes and therefore new methods of vector control will have to be used. Extensive research will have to be carried out to determine which insecticide is able to control this mosquito, whether there is parasite strain modification in this mosquito and what drugs will be used to treat it. In cases such as behavior change, research will have to widen to encompass the outdoor mosquitoes as opposed to the focus on indoor mosquitoes.

Under dosage of treatment drugs is a problem that eventually leads to malaria parasite resistance to treatment. It has been reported that a number of patients do not finish their medicine doses and stop taking the drugs as soon as they feel well again or when the symptoms are no longer visible. The parasite, however will not have been completely eliminated from their bodies. The remainder of the medication is usually kept and wrongfully administered when a situation with similar symptoms occurs. A study that was carried out in Senegal to determine the factors that affect patients’ [12] compliance to anti-malaria drugs showed lack of understanding of prescriptions and information provided by the health worker as one of the factors. In the interviews carried out in this study, it was found that for patients to take treatment; they had to be satisfied with the drug provided e.g. taste and side effects of the drug had to be minimal. Health workers therefore have the task of emphasizing the importance of taking full treatment doses and to provide information that is easy for a layman to understand. Repeated under dosage and wrong prescriptions can lead to resistance of the malaria parasite to the medication taken.

Counterfeit drugs are another major problem that frustrates the use of anti malaria drugs against malaria. It is ironic that the best and most efficient anti-malaria drug today is made from a plant that originates from [13] China where most of the counterfeit drugs also originate. Since these drugs are cheaper, they usually find their way to poor countries in sub-Saharan Africa. The use of these counterfeits enables the parasite to adapt to the active ingredient contained in these drugs such that with time, the parasite becomes resistant to medication containing that active ingredient.

Due to poverty in rural areas of sub-Saharan Africa, a malaria patient is most likely to delay seeking proper treatment. This is because the malaria drugs are still quite [14] expensive for most people in these areas so they resort to treating the symptoms of the disease with cheap fever relief drugs. Consequently by the time enough money is collected to afford proper
treatment they are in a bad state of health. Situations such as this could be the cause of high mortality rates due to malaria.

Illiteracy; most people in rural areas lack basic knowledge about the cause of malaria [15,16] which leads to some associating the cause with dirty or stagnant water. A misconception such as this one, in turns leads to misuse of insecticide treated mosquito nets. This is another of many factors influencing the effectiveness of insecticide treated mosquito nets and frustrating the fight against malaria in rural sub-Saharan Africa. In a study done in some parts of the Imo River in Nigeria, from the interviews [17] carried out during data collection, it was found that the people feared to use insecticide treated bed nets because they thought that the chemicals used were harmful to children, adults and pregnant women. In addition to this, the people did not really know the name of the chemicals and the difference between a treated and an untreated bed net. All that they knew was what they had heard over the radio which was that bed nets contained chemicals that kill mosquitoes. Another such study carried out in five West African communities in the Gambia, showed that the people in these communities were more concerned about mosquitoes being a nuisance than a cause of infection. They used herbs as mosquito repellents and malaria was treated by traditional [18] practices including herbal remedies while bed nets were used for privacy, decoration and also in vegetable nursery beds. A similar study, carried out in seven fishing villages in Kenya around Lake Victoria to determine bed net usage showed that the insecticide treated mosquito bed nets that were provided to the people in these villages were used [19] for fishing and drying fish. The people in these villages did not use the insecticide treated nets for their intended use. These studies clearly show that Africans in these rural communities are still a little ignorant about the cause of malaria and how it is spread. In order for ITNs to be used for their intended purpose in these areas, the people must be educated about malaria.

Illegal trade of Insecticide Treated Mosquito nets (ITNs), which are usually distributed for free in endemic areas or sold at subsidized prices in endemic zones by health organizations, are in some cases, resold [20] to those who can afford them thereby causing a shortage in ITNs to be distributed. It has also been noted that because of the remote locations of some populations from the health centers or ITNs distribution points, the people in these areas do not usually receive ITNs. More thorough ITN distribution strategies must therefore be made to achieve total coverage in endemic areas.
Political instability [3] in most African countries particularly in the North of Africa, countries such as Somalia, Eritrea, and Ethiopia can be detrimental to the efforts against malaria because people are forced to live in conditions of poor sanitation which are natural breeding grounds for mosquito larvae therefore promoting the spread of malaria.

The World Health Organization’s 2010 malaria report showed that progress against the disease had been made over the past decade, with deaths estimated to have dropped to 781,000 in 2009 from nearly [21] a million in 2000. As mentioned earlier, an integrated approach is therefore the best method to fight against malaria and the use of insect repellents, mosquito treated insecticide bed nets; indoor residual spraying and early treatment could further reduce the number of deaths caused by malaria in Africa.

1.2.2 Insect Repellent use as a Malaria Control Measure.

Insect repellents are one of the many control measures used to fight malaria and are described as volatile organic substances [22] that are used to protect humans from insect bites. They function by masking the olfactory senses of the insects. Insect repellents are of two categories, synthesized repellents and plant based repellents. Examples of the synthesized repellents include p-menthane-3,8-diol (PMD), N,N-dimethylmeta-toluamide (DEET), picaridin, permethrin and IR3535. On the other hand, plant based insect repellents are obtained from plant parts i.e roots, leaves, barks and even fruits. Plants are known to release volatile compounds as a way of attracting pollinators and repelling herbivorous insects. The volatiles released [23] by plants that have the ability to repel insects include compounds like alkaloids, terpenoids and phenolics. The floral part of the plant emits floral volatiles [24] while the vegetative part emits vegetative volatiles. The vegetative volatiles are of great importance to the natural based insect repellent industry. Examples of plant based repellents include eucalyptol, geraniol, linalool, citronellal, citronellol, nepatalactone, neem, peppermint and so many others with varying registered efficacy.

p-Menthane-3,8-diol also known as PMD, is a bi-product of extraction of essential oil of lemon eucalyptus and has shown the same effectiveness as DEET. It has a mint like scent and is grouped under the toxicity category IV for acute oral toxicity, dermal toxicity and skin irritation. It is also grouped [25] in the toxicity category II for end use product for eye irritation. PMD is solid at room temperature and has a melting point of around 34.5° C.
PMD, unlike most mono-terpenes found in plant essential oils, has a low vapor pressure and provides long hours of protection from a wide range of insect bites.

1.2.3 A Brief History of Insect Repellents

The use of insect repellents [26] dates back as far as before the 2\textsuperscript{nd} World War. During this time, there were four major insect repellents that were in use i.e. indalone, Rutgers 612, citronella and dimethyl phthalate.

Oil of citronella, a plant based insect repellent extracted from dried cultivated grasses was discovered [27] in 1901. It was used for hair dressing and to repel mosquitoes and fleas. It was said to provide a protection time of 4 hours and according to the United States Environment Protection Agency Fact file on oil of citronella, its repellency rate depends on the amount of inert ingredients and citronella oil in the formulation of a repellent product. In 1929, dialkyl phthalates were discovered to have insect repellent properties after it was noted that it’s use as a solvent to dissolve solid repellents reduced their protection time. It was later listed as one of the most common compounds found in insect repellents. Between 1937 and 1940, indalone and Rutgers 612 were discovered.

At the time of the 2\textsuperscript{nd} World War, there was a disease outbreak that caused a large number of military troops to go off duty. It was due to this that a formulation containing 6 parts of dimethyl phthalate, 2 parts of indalone and 2 parts of Rutgers 612 (6-2-2) was made to protect the soldiers against biting arthropods. It however did not provide the protection that was much needed. As a result, there was a search for repellents that could provided the required protection and in 1953 the repellent properties of N, N-dimethyldimethylmeta-toluamide (DEET) were discovered.

In Africa and other parts of the world, before civilization, plant parts such as leaves, branches, bark, roots and stems were used for insect repelling purposes. Some evidence showing the use of plants as insect repellents was unearthed at a rock shelter in [28] Sibudu in the Eastern Province of KwaZulu Natal. It was found that the plant parts of Cryptorya woodii were used by the ancestors of this place to make work surfaces and beds. Cryptorya Woodii has insecticidal and Larvicidal properties. This plant was used by these ancestors to repel insects and to keep bugs away from their sleeping areas. The ancient Egyptians used castor oil which they burned in lamps to keep away mosquitoes and the Romans [29] burned herbs such cumin and bay among others to repel insects.
1.2.4 Insect Repellents Today

Today, the most common synthesized insect repellent used is N, N-dimethylmeta-toluamide, (DEET). It was once believed that it repelled mosquitoes by blocking the olfactory and chemo sensors of the mosquitoes rendering them unable to detect chemical attractants. Upon further research it was however found [25] that DEET is in fact detected by the olfactory sensors and repels mosquitoes regardless of the chemical or physical attractants being present. DEET is known to have a longer lasting effect in repelling insects than its counterparts so much so that it is used as a reference in efficacy tests of other repellents. A study carried out in the [30] United States where four products containing DEET as an active ingredient were compared with one product containing IR3535, three repellent impregnated wrist bands and So-Soft mineral oil based moisturizer. It was noted that the repellent containing IR3535 provided protection for 23 minutes, the repellents containing 23.8% DEET provided protection for 301.5 minutes whereas the wrist bands were concluded to provide no protection at all (with 12 seconds to 18 seconds on average “protection time”).

In another such study, the topical effectiveness of 100% Andiroba oil [31] was compared with 50% DEET as a repellent against *Aedes Sp*. Andiroba oil is a product of the Andiroba rain forest tree commonly known as Bastard Mahogany or Brazilian Mahogany found in the Amazon. In this study, it was found that 100% Andiroba oil was inferior to 50% DEET and showed superiority as compared to its absence. Volunteers that were used for this study did not get bitten until 3600 seconds when they used DEET insect repellent. With the use of 100% and 15% Andiroba Oil, volunteers got bitten at 56 seconds on the first bite and 142.5 seconds on the third bite and 63 seconds on the first bite and 97.5 seconds on the third bite respectively.

There are quite a number of other comparative efficacy studies pertaining to DEET and other insect repellents but in spite of DEET being effective, it is believed to be unsafe for use. DEET also has documented toxic effects, for example seizures and psychosis [32,33] in young children and adults respectively. An example of such occurrences is where a 27 year old male had symptoms of acute onset confusion and combativeness among others after topical [34] use of a DEET based insect repellent that he had applied before and while fishing on a hot humid day. From the medical examination of the male, it was found that there was a DEET concentration of 1.6µg/ml in his serum. The side effects seen in this case were attributed to trans-dermal absorption of the active ingredient of the insect repellent.
It is these reported toxicology cases concerning DEET exposure that have led to renewed interest in natural insect repellents i.e. active ingredients extracted from plants and their ability to repel biting insects although they have been used since ancient times.

1.2.5 Application of Insect Repellents

The application of insect repellents is categorized into spatial insect repellents and topical insect repellents. These have been commercialized into body repellent sprays, lotion, creams, mosquito bed nets, aerosol indoor sprays, electric vaporizers, mosquito repellent coils & mats and candles.

The spatial application of insect repellents, a main interest in this study, is an old practice that is still being used by rural communities in sub-Saharan Africa and all over the world. A survey in uMkhanyakude [35] district, KwaZulu-Natal, South Africa, showed that a total of thirteen plant species were used to repel mosquitoes with about nine of them being documented for the first time, *Lippia javanica* was most commonly used plant species in this study area. Of the plants that were used, 69.2% were trees and the rest were shrubs with leaves as the most used parts as compared to barks, roots and seeds. For repelling mosquitoes, the leaves were dried and then burnt to produce a repellent smoke. This method of application was used for the majority of the plant species apart from three, *M. azedarach*, *C. anista*, *A. ferox*, *L. javanica*, and *C. menyharthii* that were used in their fresh form. In this same study, it was found that in the five villages used in the study, repellent plant species were the most used malaria control method (98.33%) followed by use of insecticide treated bed nets (65%).

Similarly, in an ethno-botanical study carried out in [36] North Eastern Tanzania, it was noted that repellent plant species were mostly used as a mosquito control method because the people in these areas could not afford insecticide treated nets. With plant species such as *Lantana camara, Ocimum suave, Ocimum kilimandscharicum*, *Eucalyptus species* and *Azadirachta indica* commonly used for repelling mosquitoes in this area. The method of application of the repellent plant species according to this study was burning of leaves and hanging of fresh leaves in houses. In Rusinga island [37] and Rambira location in Western Kenya, the inhabitants also used certain repellent plant species such as *Ocimum americanum, Hyptis suaveolens, Lantana camara, T. minuta, O. bacilicum* and *A. indica* with *Ocimum americanum* and *Hyptis suaveolens* as the commonly used plant species. The repellent plant species were also applied by burning and hanging in the house as was found in North Eastern
Tanzania and uMkhanyakude in KwaZulu-Natal. In contrast to the studies in North Eastern Tanzania and uMkhanyakude in KwaZulu-Natal, the people in Rusinga island and Rambira location, were not as prevalent in using repellent plant species. This indicates that the use of a particular kind of malaria control measure could depend on the financial status, belief in the effectiveness and availability of the control measure.

Currently, with the help of scientific research on the efficacy of these repellents, it has also become possible to produce commercial products containing active ingredients or products used to disperse these active ingredients. There are however some products on the repellent market whose efficacy is not known but are claimed to offer protection from biting insects. In this study, the focus is on liquid repellent vaporizers and repellent candles.

Liquid repellent vaporizers are in two categories; electric liquid repellent vaporizers which operate with the help of electricity. The working system comprises of a heating element, a plug, a wick and a bottle with the latest inventions being [38] cordless. They do not need attending to when they are in use and cases of burns are limited. They are easy to use but require a household with electricity.

The second category is non-electric liquid repellent vaporizers, also called flameless burners. They operate by catalytic flameless oxidation of carrier fuels that are usually of low vapor pressure for example alcohols. The flameless burners comprise of a wick, a catalytic burner and a liquid reservoir. They require an open flame to provide the initial heat needed to start the catalytic activity.

The burner is lit for a certain time after which the flame is blown out and the heat that is contained by the burner continues to vaporize fuel that is supplied by a wick as long as there is oxygen available. In an invention by Thomas J. Pisklak (2007), the burner had a Group VIII metal as a catalyst and clay as a binder. It also consisted of Zeolites and had a lower portion [39] which was connected to a wick through which the fuel travels from the reservoir to the upper portion of the burner. In this invention, the catalyst was dispersed onto the clay burner by repeated dipping.

The Lampe Berger fragrance burner is one such device used to catalytically disperse fragrances into the atmosphere in an enclosed environment. The burner is made of Platinum catalyst together with a combination of other metal oxides and is claimed to purify the air in the environment in which it is used. Besides the platinum group metals, transition metal
oxides also find applications in flameless catalytic oxidation processes and are much cheaper than the noble metals. Transition metal oxides have a large number of active sites as compared to the noble metals and are less likely to suffer from catalytic poisoning, masking and fouling. It is because of these advantages that these oxides are now used as an alternative for noble metals. This is the reason cupric oxide was used in creating the burner that was used in this study.

Candles, a cheap alternative to lighting, are also used for aromatherapy and for repelling insects. The major elements of a candle are the wick and wax. The type of wax, the size of the candle and the kind of wick determine the burning rate of the candle. A large candle made of a wax with a high melting point will have a long life. The main role of the wick is to deliver melted wax into the flame by capillary action. The size of the wick also has an effect on the amount of melted wax drawn up into the flame. It has been noted that if the amount of melted wax that is being drawn up by the wick is too much, the candle flame will flare and on the other hand, when the melted wax drawn up is too little the flame is seen to splutter. These candle characteristics coupled with other confounding variables make it quite difficult to quantify the amount of active ingredient that is released when the repellent candles are lighted. The wick is nowadays usually made of twisted, braided cotton but was originally made from bleached twisted cotton yarn. The type of material used to make the wick affects how the candle will burn.
Figure 3: On the left is an illustration of the difference in the how the modern braided/twisted cotton wick burns as compared to the bleached twisted cotton yarn. On the right is a braided wick.

Taken from a technical brief by the Intermediate Technology Development Group Ltd: Candle Making (http://www.uvm.edu/~edstudio/Information/april10/products/candlemaking.pdf)

The types of the waxes used in candle making include bees wax, synthetic wax, paraffin wax and vegetable waxes with additives such as stearic acid, petrolatum, mineral oil, polyethylene and Vybar 260. In this work, synthetic wax was used to make the PMD repellent candles with no additives added and twisted cotton wicks of the same size were used to wick the candles.

Some of the essential oils with insect repellent ability that have been used in candles include citronella, linalool and geraniol. Of these three essential oils used in repellent candles, geraniol candles have been proven to offer [41,42,43] significantly better protection from mosquito and sand fly bites indoors and outdoors. In one of the comparative studies done on evaluating the efficacy of essential oil repellent candles against mosquitoes [44] both indoors and outdoors, it was found that candles containing 5% geraniol and citronella provided indoor repellent rates of 50% and 14% respectively. In this same study, the ability of these essential oils dispersed by diffusers to repel mosquitoes was determined. The diffusers that were placed indoors provided 97% and 93% repellent rates from geraniol and citronella repellent solutions respectively while the citronella, geraniol and linalool diffusers that were placed 6m from the mosquito traps in the outdoors, had a repellent rate of 22%, 75% and 58% respectively. From this study, it was also noted that the spatial use of natural/botanical insect
repellents would provide more protection by being in close proximity to the source of active ingredient. Studies dealing with the efficacy of natural insect repellents have been carried out in order to ascertain their use for protection against biting insects and this sector of research concerning natural insect repellents is still expanding because of the need to use natural products as they are perceived to be safer than the synthetic ones by consumers. It should be noted that natural insect repellents like synthetic repellents can have adverse effects if not properly used according to instructions provided.
CHAPTER TWO

METHODS

The study was carried out in three parts; the first part involved preparing of the CuO-Montmorillonite clay burner and testing/determining the performance of the burner in vaporizing PMD repellent formulations, the second part involved preparing 6% wt PMD repellent candles with diameters 45mm, 69mm and 83mm whereas the third part involved determining the performance of the Lampe Berger fragrance burner (LBFB) in vaporizing PMD repellent formulations.

Table 1: Materials used

<table>
<thead>
<tr>
<th>Materials and Analytical Reagents</th>
<th>Chemical Formula</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ammonium carbonate</td>
<td>(NH₄)₂CO₃</td>
<td>AR</td>
</tr>
<tr>
<td>2. Cupric nitrate</td>
<td>Cu(NO₃)₂·3H₂O</td>
<td>AR</td>
</tr>
<tr>
<td>3. Dichloromethane</td>
<td>CH₂Cl₂</td>
<td>CP</td>
</tr>
<tr>
<td>4. Montmorillonite k10 clay</td>
<td></td>
<td>AR</td>
</tr>
<tr>
<td>5. p-menthane-3,8-diol</td>
<td>C₁₀H₂₀O₂</td>
<td>73% Purity</td>
</tr>
<tr>
<td>6. Propan-2-ol</td>
<td>CH₃CHOHCH₃</td>
<td>GC</td>
</tr>
<tr>
<td>7. Nitrobenzene</td>
<td>C₆H₅NO₂</td>
<td>GC</td>
</tr>
<tr>
<td>9. Sodium Hydroxide Pellets</td>
<td>NaOH</td>
<td>AR</td>
</tr>
<tr>
<td>8. Zirconium Oxide</td>
<td>ZrO₂</td>
<td>AR</td>
</tr>
</tbody>
</table>

AR-analytic reagent. CP-chemically pure. GC- GC grade.
2.1 PART ONE: CuO-Montmorillonite Clay Burner

2.1.1 Preparation of catalyst.

250ml of 0.25M NaOH solution was added drop wise to a 200ml solution containing 10g of Cu(NO₃)₂·3H₂O and stirred at room temperature. The formed precipitate was aged for 260 minutes at room temperature. The precipitate was divided into two equal portions. Each portion of precipitate was filtered and washed thoroughly with 200ml of distilled water. The precipitate was dried at 120⁰C for 10 hours and kept at this temperature for a further 2 hours. The dried precipitate was calcined at 400⁰C for 5 hours. The black cupric oxide so obtained was grinded using a mortar and pestle to form a powder.

2.1.2 Characterization of catalyst.

The surface area of the catalyst powder was determined by BET analysis. The powder was purged overnight using Nitrogen gas. The surface area of the catalyst was found to be 6.192±0.0201m²/g. The aim of this characterization was to establish whether the properties of the CuO catalyst formed would be compatible with the properties of the montmorillonite K10 clay to form a good burner. It was important for the surface area of the clay to be larger than that of the catalyst such that a small quantity of catalyst would be used compared to that of the clay in forming the burner. The particle size was determined by laser diffraction particle master sizer using the wet method and was found to be 1.44µm for diameter [3,2]. Elemental analysis of the catalyst was determined by XRF. The results of these analyses are given in the Appendix.

2.1.3 Formation of CuO-Montmorillonite clay burner.

The burner was prepared by wet powder mixing of montmorillonite clay, copper oxide powder, zirconium dioxide with a small quantity of water to enable plasticity. The composition of the formulation was 11% CuO (0.5g), 22% Montmorillonite K10 clay (1g) and 66% ZrO₂ (3g). Ammonium carbonate (0.33g) was added to the putty which was then pushed into a plastic mold for shaping. The formed shape was dried at 120⁰C for 1 hour after which it was calcined at 800⁰C for 30 minutes and baked at this temperature for another 30 minutes.
Figure 4: The plastic mold used to make the CuO-Montmorillonite clay burner.

Figure 5: CuO-Montmorillonite clay burner fitted onto a glass bottle (repellent reservoir)
2.1.4 Vaporization of PMD repellent formulations using the CuO-Montmorillonite clay burner.

Repellent formulations containing 3g, 9g, 12g, 15g and 18g of PMD dissolved in 500ml of propan-2-ol were used to determine the rate of vaporization of insect repellent formulations by the CuO-Montmorillonite clay burner. The repellent formulations were labeled 3g, 9g, 12g, 15g and 18g. The condensates collected from vaporizing 3g, 9g and 15g PMD repellent formulations were used to determine the percentage of PMD released by the CuO-Montmorillonite clay burner.

The lamp, consisting of a wick, CuO-Montmorillonite clay burner and reservoir was assembled, filled with a repellent formulation and lit to test the performance of the burner. To determine the rate of vaporization of a repellent formulation by the burner, the lamp set up was filled with repellent formulation and placed on a weighing scale. The CuO-Montmorillonite clay burner was lit for five minutes and the flame was blown out. The rate of vaporization was determined by calculating the mass loss of the lamp set up after 60 minutes. The collection of vapor from the lamp and determining the rate of vaporization of the repellent solution from the burner was carried out simultaneously.

To collect the PMD repellent vapor emitted from the CuO-Montmorillonite burner, a glass funnel was held over the lamp set up using a retort stand. A collection flask that was kept dipped in ice was connected to a vacuum pump for suction on one end and a glass funnel using a glass tube and rubber fittings was connected to the top opening of the collection flask. Three portions of 10ml of dichloromethane were used to wash the tubing and funnel channeled to the collection flask containing the condensate. The mixture was then shaken and poured into a separation funnel and left to stand for the layers to form. The layer containing PMD was drained into a 50ml volumetric flask. The vapor collection procedure was repeated five times for each PMD repellent formulation. The burner was extinguished with a cap at the end of each repetition.
2.2 PART TWO: 6% wt PMD Repellent Candles

2.2.1 Preparation of 6% wt PMD repellent candles.

Repellent candles containing approximately 6% wt of PMD were made by adding 24g of PMD concentrate to 387g of melted synthetic wax at a temperature between 80°C-90°C. The mixture was stirred for three minutes and then poured into molds having diameters 40mm, 69mm and 83mm.

To collect candle vapor for analysis, a repellent candle was lit for 275 minutes with a glass funnel held over it using a retort stand. A collection flask that was kept dipped in ice was connected to a vacuum pump on one end and to a glass funnel using a glass tube and rubber fittings at the top opening of the flask. The same setup of apparatus shown in figure 6 was used for this task. Three portions of 10ml of dichloromethane were used to wash the tubing and funnel channeled to the collection flask containing the condensate. The mixture was then shaken and poured into a separation funnel and left to stand for the layers to form. The layer containing PMD was drained into a 50ml volumetric flask. The vapor collection procedure was repeated four times for each diameter, using a new candle for each repetition.
2.3 PART THREE: Lampe Berger Fragrance Burner

2.3.1 Vaporization of PMD repellent formulations using the Lampe Berger fragrance burner.
The PMD repellent formulations used here were prepared using the method in part one. The repellent vapors were collected over a period of 275 minutes. The rate of vaporization of six PMD repellent formulations 3g, 6g, 9g, 12g and 15g using the Lampe Berger fragrance burner was determined by calculating the mass loss in the lamp set up at the end of each vapor collection. The vapor samples for analysis were collected using the same set up described in the collection of repellent vapors from the 6% wt PMD repellent candles and CuO-Montmorillonite burner (see figure 6 for illustration). Extraction of PMD from the collected condensed vapor samples was also carried out using the same procedure used in the CuO-Montmorillonite clay burner and 6% wt PMD repellent candles.

2.4 Analysis of Dichloromethane Extracted PMD Samples from the Condensates.
The dichloromethane extracted PMD samples, obtained from condensates collected from 6% wt PMD repellent candles, vaporization of PMD repellent formulations using the CuO-Montmorillonite clay burner and Lampe Berger fragrance burner were spiked with a predetermined amount of nitrobenzene (internal standard) in 50ml volumetric flasks and made up to volume. The prepared samples were analyzed using Gas Chromatography. Nitrobenzene (0.0018g) was added to the dichloromethane extracted PMD samples from 6% wt PMD repellent candles. Nitrobenzene (0.008g) was added to the extract from the burners (CuO-Montmorillonite clay burner and Lampe Berger fragrance burner). The GC-FID-Agilent (column econocap-5) operating conditions were

- Oven Temperature : 280°C
- Inlet (split/splitless inlet) Temperature : 270°C
- Pressure : 96kPa
- Detector Temperature : 300°C

The carrier gas used was Nitrogen at a flow rate of 0.5ml/min.
The internal response factor (IRF) was determined using the equation below:

\[
IRF = \frac{\text{Amount of Pure PMD} \cdot \text{Area of Nitrobenzene GC peak}}{\text{Amount of Nitrobenzene} \cdot \text{Area of Pure PMD GC peak}}
\]

1)

The calculated IRFs were used to calculate the concentration of PMD in the condensates obtained from vaporizing PMD repellent formulations using the CuO-Montmorillonite burner and the Lampe Berger fragrance burner and also to determine the concentration of PMD in the condensates obtained from lighting the three 6% wt PMD repellent diameter candles. The IRF used to calculate the concentration of PMD in the condensates collected from the 6% wt PMD repellent candles and the burners (CuO-Montmorillonite clay burner and Lampe Berger fragrance burner) was calculated to be 0.9 and 1.01 respectively.
CHAPTER THREE

RESULTS AND DISCUSSIONS

In this chapter, the results obtained from the experiments carried out during the course of this study were statistically analyzed and are presented and discussed here. Proposed regression models, trends in the results and the formulae used to calculate the results are given below.

The rate of vaporization of PMD repellent formulations by the CuO-Montmorillonite clay burner and the Lampe Berger fragrance burner was calculated using the equation below

\[
Rate \ of \ Vaporization = \frac{(M_1 - M_2)}{t}
\]  

Where \( M_1 \) is the mass (g) of the lamp set up with PMD repellent formulation before vapor collection, \( M_2 \) is the mass (g) of the lamp set up with PMD repellent formulation after vapor collection and \( t \) is the duration in minutes within which the PMD repellent formulation vapor was collected.

The calculated percentage of PMD in the condensates obtained from vaporizing the PMD repellent formulations using the CuO-Montmorillonite clay burner and the Lampe Berger fragrance burner was determined by using the mass (g) of obtained condensate and the concentration of PMD (g/ml) in the condensate collected (obtained from equation 1) and is summarized in the equation below;

\[
\% \ PMD \ in \ the \ collected \ condensates = \frac{(C_{PMD} \cdot V_{VF})}{M_C} \cdot 100\%
\]  

Where \( C_{PMD} \) is the concentration of PMD (g/ml) in the condensate collected, \( V_{VF} \) is the volume of the volumetric flask and \( M_C \) is the mass (g) of the condensate collected.

Equation 3 was also used to calculate the percentage of PMD released from the 6% wt PMD repellent candles.
The lower and upper limits at 95% confidence interval of the results obtained were used to determine significant differences in the data. These were calculated according to the equations below:

Lower Limit: \( \bar{X} - t_{a/2} \frac{S}{\sqrt{n}} \)  
Upper Limit: \( \bar{X} + t_{a/2} \frac{S}{\sqrt{n}} \)

Where \( t \)-value was determined by the confidence level and was obtained directly from \( t \)-tables, \( n \) was the sample size, \( X \) the average of the measurements and \( S \) the Standard Deviation.
3.1 PART ONE: CuO-Montmorillonite clay Burner

3.1.1 Rate of vaporization of PMD repellent formulations vaporized using CuO-Montmorillonite clay burner

**Table 2:** Rate of Vaporization (g/min) of PMD repellent formulations vaporized using the CuO-Montmorillonite clay burner

<table>
<thead>
<tr>
<th>Replication</th>
<th>3g</th>
<th>9g</th>
<th>12g</th>
<th>15g</th>
<th>18g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.18</td>
<td>0.20</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.17</td>
<td>0.19</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>3</td>
<td>0.19</td>
<td>0.16</td>
<td>0.21</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>4</td>
<td>0.19</td>
<td>0.16</td>
<td>0.20</td>
<td>0.12</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Where 3g, 9g, 12g, 15g and 18g are PMD repellent formulations that were vaporized. Four replicate vaporization experiments were carried out per PMD repellent formulations.

The average rate of vaporization of the PMD repellent formulations 3g, 9g, 12g, 15g and 18g was found to be 0.19±0.014g/min, 0.17±0.013g/min, 0.2±0.01g/min, 0.12±0.03g/min and 0.17±0.014g/min respectively at 95% confidence interval.

**Figure 7:** Means graph; Average rate of vaporization Vs PMD repellent formulations

From Figure 7 above, overlapping of error bars of the average rate of vaporization of PMD repellent formulations 3g and 12g as well as 9g and 18g shows that there is no significant difference in the average rate of vaporization of these two pairs of repellent formulations. On
the other hand, the error bars of the average rate of vaporization of the 15g PMD repellent formulation do not overlap with any of the error bars of the average rate of vaporization of the other PMD repellent formulations. There could have been a change in the conditions around the burner during the vaporization of the 15g PMD repellent formulation thus the considerably lower rate of vaporization that was observed (0.12±0.03g/min). This is enough evidence that shows that the average rate of vaporization of at least two of the PMD repellent formulations vaporized using the CuO-Montmorillonite clay burner differ significantly.

### 3.1.2 Percentage of PMD in the condensates collected from vaporizing repellent formulations using the CuO-Montmorillonite clay burner.

The percentage of PMD in condensates collected from vaporizing PMD repellent formulations 3g, 9g and 15g using the CuO-Montmorillonite clay burner was determined using equations 1 and 2 given at the beginning of chapter three.

**Table 3:** Percentage PMD in the condensates collected from vaporizing PMD Repellent formulations using the CuO-Montmorillonite clay burner

<table>
<thead>
<tr>
<th>Replication</th>
<th>3g</th>
<th>9g</th>
<th>15g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.360</td>
<td>0.613</td>
<td>0.408</td>
</tr>
<tr>
<td>2</td>
<td>0.143</td>
<td>0.246</td>
<td>0.472</td>
</tr>
<tr>
<td>3</td>
<td>0.158</td>
<td>0.365</td>
<td>0.531</td>
</tr>
<tr>
<td>4</td>
<td>0.212</td>
<td>0.298</td>
<td>0.123</td>
</tr>
</tbody>
</table>

Where 3g, 9g and 15g are PMD repellent formulations that were vaporized. The condensates were obtained from the four replicate vaporization experiments that were carried out per PMD repellent formulation.

The average percentage of PMD in the condensates collected from vaporizing 3g, 9g and 15g PMD repellent formulations using the CuO-Montmorillonite clay burner were calculated to be 0.22±0.19%, 0.41±0.3% and 0.38±0.29% at 95% confidence interval respectively.
**Figure 8:** A means graph showing the average percentage of PMD in the condensates collected from 3g, 9g and 15g PMD repellent formulations vaporized using a CuO-Montmorillonite clay burner.

From the above means plot it can be seen that there is no significant difference in the average percentage of PMD in the condensates collected from vaporizing 3g, 9g and 15g PMD repellent formulations using the CuO-Montmorillonite clay burner. The error bars of the average percentage of PMD in their condensates overlap each other’s centers.

The operation of the CuO-Montmorillonite clay burner depends on the heat it contains and the amount of oxygen supplied. This is reflected on the red glow seen on the burner surface while it operates. It was also observed that disturbance of the air around the burner made it to glow brighter. This factor, disturbance of air around the burner, affects the rate of vaporization of PMD repellent formulations and in turn causes variation in the percentage of PMD in the condensates collected from the replicate vaporization experiments carried out per repellent formulation. This can be seen from the large error bars of the average percentage of PMD in condensates collected from vaporizing 3g, 9g and 15g PMD repellent formulations (see figure 8) hence no significant difference in the percentage of PMD in the condensates that were collected.
3.1.3 The relationship between the percentage of PMD in the condensates obtained from vaporizing PMD repellent formulations (3g, 9g and 15g) and the mass of PMD in the repellent formulations using the CuO-Montmorillonite clay burner.

A scatter plot of the obtained data shows that there seems to be a slight increase in the percentage of PMD in the condensates collected with increase in the mass of PMD in the repellent formulations

Figure 9: A scatter plot showing the percentage of PMD in the collected condensates Vs the mass of PMD in the repellent formulations

![A SCATTER PLOT OF % PMD IN THE COLLECTED CONDENSATES](image)

A linear regression model was proposed: \( Y = \beta_0 + \beta_1X + \varepsilon \) where \( Y \) is the percentage of PMD in the collected condensates, \( X \) represents the mass of PMD in the repellent formulations and \( \varepsilon \), the error. It was hypothesized that there is no linear relationship between the mass of PMD in the repellent formulations and the percentage of PMD in the condensates that were collected from vaporizing the repellent formulations using the CuO-Montmorillonite clay burner. \( H_0: \beta_1 = 0 \)
Table 4: Summary of the Excel regression statistics output

<table>
<thead>
<tr>
<th>Regression Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>R Square</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.203</td>
<td>0.0902</td>
<td>2.26</td>
<td>0.048</td>
<td>0.0025</td>
<td>0.404</td>
</tr>
<tr>
<td>X</td>
<td>0.014</td>
<td>0.0088</td>
<td>1.56</td>
<td>0.149</td>
<td>-0.0058</td>
<td>0.033</td>
</tr>
</tbody>
</table>

From the regression statistics in table 4, the hypothesis $H_0: \beta_1 = 0$ could not be rejected ($P = 0.149$). $\beta_1$ is not significant and thus there is no linear relationship between the percentage of PMD in the condensates collected and the mass of PMD in the repellent formulations. The slight increase in the percentage of PMD in the condensates obtained from vaporizing the 9g and 3g PMD repellent formulations compared to that in condensates obtained from vaporizing the 15g PMD repellent formulation was due to experimental error coupled with the effect of confounding variables.
3.2  PART TWO: 6% wt PMD Repellent Candles

3.2.1. Mass loss in the 40mm, 69mm and 83mm PMD repellent candles

Table 5: Mass loss (g/min) in the three 6% wt PMD repellent candles of diameters 40mm, 69mm and 83mm

<table>
<thead>
<tr>
<th>Replication</th>
<th>40mm</th>
<th>69mm</th>
<th>83mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.059</td>
<td>0.070</td>
<td>0.078</td>
</tr>
<tr>
<td>2</td>
<td>0.066</td>
<td>0.083</td>
<td>0.066</td>
</tr>
<tr>
<td>3</td>
<td>0.047</td>
<td>0.074</td>
<td>0.081</td>
</tr>
<tr>
<td>4</td>
<td>0.057</td>
<td>0.078</td>
<td>0.070</td>
</tr>
</tbody>
</table>

Where 40mm, 69mm and 83mm represent the diameter of the 6% wt PMD repellent candles. Four candles were used to obtain replicate experiments of mass loss (g/min) in each of the three diameter candles.

The average mass loss per minute in the 40mm, 69mm and 83mm PMD repellent diameter candles during usage was found to be 0.06±0.013g/min, 0.08±0.009g/min and 0.07±0.011g/min respectively at 95% confidence interval.

Figure 10: Means graph; Average mass loss Vs PMD repellent candle diameter.

From Figure 10 above, it can be seen that there is a high probability that there is no significant difference in the average mass loss in the 69mm and 83mm diameter PMD repellent candles. The error bars of the average mass loss in the 69mm and 83mm PMD repellent candles overlap each other’s center. On the other hand, there is some evidence to
that shows that the mass loss per minute in the 40mm diameter 6% wt PMD repellent candles differs significantly from the 69mm and 83mm diameter repellent candles. There is no overlapping of the error bars of the average mass loss in the 40mm diameter repellent candles with either of the error bars of the 69mm or 83mm PMD repellent candles.

The mass loss in the three 6% wt PMD repellent diameter candles during use can be affected by a number of factors such as the environment conditions in which the candles are used and the characteristics of the candles (diameter, size of the wick and the material used to make the wick). In this study, the candles were made using a wick of the same size made from the same material. The varying factor here was the diameter of the candles. The mass loss in the repellent candles differs though not by much in this set of experiments. The 40mm diameter candle had the least mass loss per minute (0.06±0.013g/min) compared to that in the 69mm and 83mm 6% wt PMD diameter repellent candles. The mass loss in the 69mm and 83mm diameter repellent candles could have been caused by the larger area that allowed a relatively faster evaporation of melted wax. The slightly lower mass loss per minute in the 40mm diameter PMD repellent candles was because the melted pool of wax mostly ran down the length of the candles and solidified.

3.2.2. The percentage of PMD in the condensates collected from lighting 6% wt PMD repellent candles of diameters 40mm, 69mm and 83mm.

Table 6: Calculated Percentage PMD in the condensates collected from the three PMD Repellent Candle diameters

<table>
<thead>
<tr>
<th>Replication</th>
<th>40mm</th>
<th>69mm</th>
<th>83mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.078</td>
<td>0.023</td>
<td>0.022</td>
</tr>
<tr>
<td>2</td>
<td>0.027</td>
<td>0.051</td>
<td>0.050</td>
</tr>
<tr>
<td>3</td>
<td>0.038</td>
<td>0.050</td>
<td>0.037</td>
</tr>
<tr>
<td>4</td>
<td>0.097</td>
<td>0.042</td>
<td></td>
</tr>
</tbody>
</table>

Where 40mm, 69mm and 83mm represent the diameter of the 6% wt PMD repellent candles. Condensates were obtained from four replicate experiments of mass loss (g/min) in each of the three diameter candles.

From the observed data, it was found that the average percentage of PMD present in the condensates collected from 40mm, 69mm and the 83mm 6% wt PMD repellent diameter candles is 0.06±0.047%, 0.042±0.021% and 0.037±0.035% respectively.
Figure 11 shows that all error bars of the average percentage of PMD present in the condensates collected from 40mm, 69mm and 83mm diameter 6% wt PMD candles overlap each other’s centers.

**Figure 11:** Average percentage of PMD in condensates collected Vs PMD repellent candle diameter in millimeters

Therefore there is no significant difference in the average percentage of PMD released from lighting 6% wt PMD repellent candles of diameters 40mm, 69mm and 83mm.

There is also a high variation in the percentage of PMD among the replicate condensates collected from the 6% wt PMD repellent candles. This variation in the percentage of PMD in the condensates collected from the 6% wt PMD repellent candles is a result of confounding variables such as hotness of the flame of the candle, environmental conditions within which the candles were lit and the flammability of the wax used to make the repellent candles. The 40mm diameter candles were taller than the 69mm and 83mm diameter candles therefore the variation in percentage of PMD that was released could have mostly been caused by air movements around the candles whereas in the 69mm and 83mm diameter candles, there was formation of different volumes of pools of wax in each of the replicate 69mm and 83mm diameter repellent candles that were lighted. This could have caused the variation in the percentage of PMD seen in the replicate experiments.
Figure 12: 83mm diameter 6% wt PMD repellent candles lit for the same period.

Figure 13: 69mm diameter 6% wt PMD repellent candles lit for the same period.
Figure 12 illustrates formation of different sizes of pools in two candles of the same diameter lit for the same period of time. This occurrence could be one of the causes of the variation in the percentage of PMD released per candle. The formation of different pool sizes is due to the hotness of the candle flame and varying conditions in the laboratory like air movement around the candles. The same phenomenon of forming pools was also observed in the 69mm PMD repellent diameter candles (see figure 13). These figures also show the effect of candle diameter on the size of pool formed. The smaller the diameter, the larger the pool formed. The heat from the flame in a small diameter candle reaches the sides of the candle easily than in a larger diameter candle provided the size of the wick in both candles is the same and is placed at the center of each candle.

3.2.3 The relationship between the 6% wt PMD candle diameter and the percentage of PMD in the condensates collected from lighting the candles.

A scatter plot of the percentage of PMD in the condensates collected from the 6% wt PMD repellent candles showed a possible decrease in the percentage of PMD in the condensates with increase in repellent candle diameter. This trend was due to higher variation of the percentage of PMD between condensates collected from the lighting the 40mm diameter repellent candles as seen in figure 14.

Figure 14: Percentage of PMD in the repellent candles' condensates Vs diameter of the repellent candles
3.3 PART THREE: Lampe Berger Fragrance Burner (LBFB)

3.3.1 Rate of vaporization of PMD repellent formulations vaporized using the LBFB

Table 7: Rate of vaporization (g/min) of six PMD repellent formulations (3g, 6g, 9g, 12g, 15g and 18g) vaporized using the LBFB

<table>
<thead>
<tr>
<th>Replication</th>
<th>3g</th>
<th>6g</th>
<th>9g</th>
<th>12g</th>
<th>15g</th>
<th>18g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.215</td>
<td>0.214</td>
<td>0.199</td>
<td>0.192</td>
<td>0.128</td>
<td>0.115</td>
</tr>
<tr>
<td>2</td>
<td>0.197</td>
<td>0.202</td>
<td>0.193</td>
<td>0.181</td>
<td>0.118</td>
<td>0.115</td>
</tr>
<tr>
<td>3</td>
<td>0.206</td>
<td>0.204</td>
<td>0.200</td>
<td>0.183</td>
<td>0.103</td>
<td>0.114</td>
</tr>
<tr>
<td>4</td>
<td>0.216</td>
<td>0.197</td>
<td>0.192</td>
<td>0.169</td>
<td>0.124</td>
<td>0.103</td>
</tr>
<tr>
<td>5</td>
<td>0.212</td>
<td>0.199</td>
<td>0.199</td>
<td>0.165</td>
<td>0.141</td>
<td>0.109</td>
</tr>
</tbody>
</table>

Where 3g, 9g, 12g, 15g and 18g are PMD repellent formulations that were vaporized. Five replicate vaporization experiments were carried out per PMD repellent formulation.

The average rate of vaporization of PMD repellent formulations 3g, 6g, 9g, 12g, 15g and 18g was found to be 0.21±0.0095g/min, 0.2±0.0082g/min, 0.197±0.0045g/min, 0.18±0.012g/min, 0.12±0.017g/min and 0.11±0.0062g/min respectively at 95% confidence interval.

Figure 15: Means graph: Average rate of vaporization of PMD repellent formulations Vs PMD repellent formulations
From Figure 15, it can be seen that there is a possibility of the average rate of vaporization of at least two PMD repellent formulations vaporized using the LBFB, to differ significantly which is indicated from no overlapping of errors bars of the average rate of vaporization of the 15g PMD repellent formulation with either of the repellent formulations containing a mass of PMD less than 15g.

3.3.2 The Relationship between the rate of vaporization of PMD repellent formulations and the mass of PMD in the repellent formulations vaporized using the LBFB.

Figure 16: A scatter plot; Rate of vaporization of repellent formulations Vs mass of PMD in the repellent formulations

From the above scatter plot, there appears to be a decrease in the rate of vaporization of the PMD repellent formulations with increase in the mass of PMD in the repellent formulations.

The following quadratic regression model was proposed; \( Y = \beta_0 + \beta_1X + \beta_2X^2 + \epsilon \) to investigate the relationship between the rate of vaporization of PMD repellent formulations and the mass of PMD in the repellent formulations, where \( Y \) denotes the rate of vaporization of PMD repellent formulation, \( X \) denotes the mass of PMD in the repellent formulation, \( \epsilon \) represents the error while \( \beta_1 \) and \( \beta_0 \) denote the true gradient and intercept. It was hypothesized that the true gradient \( \beta_2 \) was not significant; \( H_0: \beta_2 = 0 \)
From the regression statistics in table 8, H₀: β₂ = 0 was rejected because of a significant p-value (p = 0.0002). 91.1% of the variation in the rate of vaporization of the PMD repellent formulations vaporized using the Lampe Berger fragrance burner is explained by the mass of PMD present in the repellent formulations (R² = 0.911). The estimated rate at which the rate of vaporization of the PMD repellent formulations decreases with increase in the mass of PMD in the formulations (-0.0004), lies between -0.0007 and -0.0002 and this does not include zero.

**Table 8:** Regression statistics showing evidence of a quadratic relationship between the mass of PMD in the repellent formulation and the rate of vaporization of the repellent formulations using the LBFB

<table>
<thead>
<tr>
<th>Regression Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>R Square</td>
</tr>
<tr>
<td>0.911</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>0.2081</td>
<td>0.0100</td>
<td>20.80</td>
<td>3.8E-18</td>
<td>0.188</td>
</tr>
<tr>
<td>X</td>
<td>0.0021</td>
<td>0.0022</td>
<td>0.981</td>
<td>0.34</td>
<td>-0.0023</td>
</tr>
<tr>
<td>X²</td>
<td>-0.0004</td>
<td>0.0001</td>
<td>-4.349</td>
<td>0.0002</td>
<td>-0.0007</td>
</tr>
</tbody>
</table>
From the validation plot below, there is one outlier and there is a pattern in the distribution of data points around the zero line despite the fact that 91% of variation in the data is explained by the model. Therefore it was concluded that the proposed regression model needs to be improvement to fit the observed data better. The regression analysis confirms that the trend seen in figure 16 is existent.

**Figure 17:** Standard residuals Vs predicted rate of vaporization of repellent formulations by the LBFB
3.3.3 The percentage of PMD in the condensates collected from vaporizing PMD repellent formulations using the LBFB

Table 9: Calculated percentage of PMD in the condensates collected from vaporizing six PMD repellent formulations (3g, 6g, 9g, 12g, 15g and 18g) using the LBFB

<table>
<thead>
<tr>
<th>Replication</th>
<th>3g</th>
<th>6g</th>
<th>9g</th>
<th>12g</th>
<th>15g</th>
<th>18g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6949</td>
<td>1.074</td>
<td>3.477</td>
<td>3.459</td>
<td>2.262</td>
<td>0.810</td>
</tr>
<tr>
<td>2</td>
<td>0.6439</td>
<td>0.991</td>
<td>2.693</td>
<td>3.798</td>
<td>2.047</td>
<td>0.772</td>
</tr>
<tr>
<td>3</td>
<td>0.6044</td>
<td>1.114</td>
<td>2.009</td>
<td>4.132</td>
<td>1.452</td>
<td>0.653</td>
</tr>
<tr>
<td>4</td>
<td>0.7058</td>
<td>1.151</td>
<td>2.208</td>
<td>5.323</td>
<td>1.721</td>
<td>0.809</td>
</tr>
<tr>
<td>5</td>
<td>0.6726</td>
<td>1.577</td>
<td>2.297</td>
<td>3.388</td>
<td>2.369</td>
<td>0.780</td>
</tr>
</tbody>
</table>

Where 3g, 9g, 12g, 15g and 18g are PMD repellent formulations that were vaporized. The condensates were obtained from five replicate vaporization experiments that were carried out per PMD repellent formulation.

The average percentage of PMD in the condensates obtained from vaporizing PMD repellent formulations 3g, 6g, 9g, 12g, 15g and 18g using the LBFB was found to be 0.66±0.1%, 1.18±0.2%, 2.54±0.7%, 4.02±0.98% 1.97±0.47% and 0.76±0.08% respectively at 95% confidence interval.

Figure 18: Means graph; Average percentage of PMD in the collected condensates Vs PMD repellent formulations
From Figure 18, the average percentage of PMD released from vaporizing the 9g and 15g formulations do not differ significantly. It can also be seen from this plot that there was a good measure of repeatability in the percentage of PMD in the condensates collected from vaporizing the 3g, 6g and 18g PMD repellent formulations as compared to that in the condensates collected from vaporizing 9g, 12g and 15g PMD repellent formulations.

3.3.4 The relationship between the mass of PMD concentrate in the repellent formulations and the percentage of PMD present in the condensates collected from their vaporization using the LBFB.

A scatter plot of the observed data in figure 19 shows an increase in the percentage of PMD in the condensates collected with an increase in the mass of PMD in the repellent formulations 3g, 6g, 9g and the 12g PMD repellent formulations. The percentage of PMD in the condensates collected from the 12g, 15g and 18g PMD repellent formulations decreases with an increase in the mass of PMD in the repellent formulations.

Figure 19: A scatter plot; percentage of PMD in condensates collected Vs mass of PMD in repellent formulations.

A quadratic regression model \( Y = \beta_0 + \beta_1X + \beta_2X^2 + \varepsilon \) did not fit the data (see figure 19). The observed percentages of PMD in the condensates collected from vaporizing repellent formulations 3g, 6g, 9g, 12g, 15g and 18g were divided into two groups i.e. \( M \leq 12g \) and \( M \geq 12g \) where M represents the mass of PMD in the repellent formulations.
The following regression model: \( Y = \exp(\beta_0 + \beta_1 X) + \varepsilon \) was proposed for the two groups of observed data. \( Y \) and \( X \) represent the percentage of PMD in the collected condensates and mass of PMD in the repellent formulations respectively. \( \beta_0 \) and \( \beta_1 \) represent the intercept and gradient respectively. \( \varepsilon \) represents the error.

From statistical analysis of the percentage of PMD in condensates of repellent formulations containing a mass of PMD less than or equal to 12g (\( M \leq 12 \text{g} \)), it was found that \( \beta_1 \) is significant (\( p < 0.0005 \)). 94.6% of the variation in the percentage of PMD in condensates collected (See table 9) is explained by the model (\( R^2 = 0.946 \)). There was slight fanning out of data points seen in the validation plot of this model (see figure 21). The regression model fit this set of data and can be improved further. This confirms that there is definitely an exponential increase in the percentage of PMD in the condensates collected from PMD repellent formulations containing \( M \leq 12 \text{g} \) of PMD as seen in figure 19.

**Table 9:** A summary of the regression statistics

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-1.023</td>
<td>-10.862</td>
<td>2.47E-09</td>
<td>-1.220</td>
<td>-0.825</td>
</tr>
<tr>
<td>( X )</td>
<td>0.204</td>
<td>17.809</td>
<td>7.07E-13</td>
<td>0.180</td>
<td>0.228</td>
</tr>
</tbody>
</table>

**Figure 20:** Validation plot of the proposed regression model \( Y = \beta_0 + \beta_1 X + \beta_2 X^2 + \varepsilon \)
**Figure 21:** Validation plot of the proposed exponential model fitted to the data obtained from vaporizing PMD repellent formulations containing \( M \leq 12 \text{g} \) of PMD using the LBFB.

Similarly, statistical analysis of the percentage of PMD in repellent formulations with \( M \geq 12 \text{g} \) of PMD, \( \beta_1 \) was found to be significant (\( p < 0.001 \)). 94.8\% of the variation in the percentage of PMD in condensates collected is explained by the model see regression statistics in table 10 below.

**Table 10:**

<table>
<thead>
<tr>
<th>Regression Statistics</th>
</tr>
</thead>
<tbody>
<tr>
<td>R Square</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Standard Error</th>
<th>t Stat</th>
<th>P-value</th>
<th>Lower 95%</th>
<th>Upper 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>4.711</td>
<td>0.270</td>
<td>17.430</td>
<td>0.000</td>
<td>4.127</td>
</tr>
<tr>
<td>X</td>
<td>-0.275</td>
<td>0.018</td>
<td>-15.451</td>
<td>0.000</td>
<td>-0.313</td>
</tr>
</tbody>
</table>

From this statistical analysis, there was sufficient evidence that showed that there is a decreasing exponential relationship between the percentage of PMD in the condensates collected and the mass of PMD in the repellent formulations containing \( M \geq 12 \text{g} \) of PMD vaporized using the Lampe Berger fragrance burner. The validation plot of the model showed no clear pattern in the data points (see figure 22).
**Figure 22:** Validation plot of proposed regression model, $Y = \exp(\beta_0 + \beta_1 X) + \varepsilon$ for $M \geq 12 g$ of PMD

The decrease in the percentage of PMD in the condensates obtained from vaporizing 12g, 15g and 18g PMD repellent formulations can be explained by the increase in the amount of PMD in the repellent formulations. The highest percentage of PMD in the condensates was achieved during vaporization of the 12g repellent formulation as compared to the PMD repellent formulations 3g, 6g, 9g, 15g and 18g.

PMD, being a relatively large molecule and viscous in its crude form would affect the capillary flow of the repellent formulations through the wick to the burner. On the basis of these results, the greater the mass of PMD in the repellent formulations, the harder it becomes for the repellent formulation to be drawn up by this particular wick. The amount of repellent formulation delivered to the burner therefore decreased in turn affecting the percentage of PMD in the condensates collected when the repellent formulations were vaporized. Due to this, the amount of repellent formulation delivered to the burner decreased with the increase in the mass of PMD in the repellent formulations beyond 12g. In addition, when the pores of the burner are saturated with the PMD repellent formulation, the rate at which the repellent formulation is vaporized slows down hence the decrease in the rate of vaporization with the increase of mass of PMD in the repellent formulations.
Figure 23: Scatter plot of Ln (% PMD) Vs mass of PMD in the repellent formulations

Figure 23 above shows the average observed percentage of PMD in the condensates collected with superimposed prediction regression models of the percentage of PMD in the condensates. The prediction regression models for the percentage of PMD released from vaporizing PMD repellent formulations: 3g, 6g, 9g, 12g, 15g and 18g using the Lampe Berger fragrance burner are $y = \exp(0.20x-1.023)$ and $y = \exp(4.71-0.27x)$ for repellent formulations containing $M \leq 12g$ and $M \geq 12g$ of PMD respectively.
3.4 COMPARISON OF THE THREE APPLICATIONS OF PMD AS A SPATIAL REPELLENT

From the laboratory work that was carried out on the PMD repellent candles, the Lampe Berger fragrance burner (LBFB) and the CuO-Montmorillonite clay burner, it was found that the condensates obtained from vapors collected from these three applications all contained PMD. From these experiments, it is clear that the PMD repellent formulation that provides the highest percentage of PMD when vaporized using the Lampe Berger Fragrance burner is the 12g PMD repellent formulation (4.02±0.98%). The rate of vaporization of repellent formulations containing 3g, 6g, 9g, 12g, 15g and 18g of PMD vaporized using the LBFB decreases with increase in the mass of PMD in the repellent formulation beyond 12g of PMD.

The average percentage of PMD in the condensates collected from the 6% wt PMD repellent candles (0.047±0.015%) is considerably lower than the average percentage of PMD in the condensates collected from both the Lampe Berger fragrance burner (0.695±0.47%) and CuO-Montmorillonite clay burner (0.33±0.1%). The average percentage of PMD in the condensates collected from the 40mm (0.06±0.042%), 69mm (0.042±0.021%) and 83mm (0.037±0.035%) diameter 6% wt PMD repellent candles in a period of 275 minutes was low compared to that in the condensates collected from vaporizing 3g PMD repellent formulation using the Lampe Berger fragrance burner (0.66±0.1%) for the same amount of time. It was also noted that the average percentage of PMD in the condensates collected from vaporizing a 3g PMD repellent formulation for a period of one hour, using the CuO-Montmorillonite clay burner (0.22±0.19%) was higher compared to that in the condensates obtained from the 6% wt PMD repellent candles in a period of 275 minutes.
A scatter plot of the calculated average percentage of PMD released per hour by the three applications below shows that 6% wt PMD candles release the least percentage of PMD compared to the burners (LBFB and CuO-Montmorillonite clay burner)

**Figure 24:** Calculated average percentage of PMD released per 60 minutes Vs mass of PMD

Results obtained from the replication experiments show that the Lampe Berger fragrance burner releases more or less the same percentage PMD in the condensates collected from vaporizing a particular PMD repellent formulation. The same observation was also seen in the replication experiments carried out to determine the rate of vaporization of PMD repellent formulations using both the CuO-Montmorillonite clay burner and LBFB. It was also found that the rate of vaporization of PMD repellent formulations vaporized by the Lampe Berger fragrance burner is affected by mass of PMD in the repellent formulations.

Comparing the individual percentages of PMD in the condensates collected from vaporizing PMD repellent formulations using the CuO-Montmorillonite clay burner, it was noted that there was high variation in the percentages of PMD in the replicates condensates collected. This means that there are a number of confounding variables affecting the catalytic activity of the burner in turn affecting the percentage of PMD released from vaporizing the PMD repellent formulations. It was also noted that there was no sufficient evidence to show that percentage of PMD in the condensates collected from vaporizing PMD repellent formulations
using the CuO-Montmorillonite clay burner increases with an increase in the mass of PMD in the repellent formulations \( (p=0.15) \).

**Figure 25:** Means plot of the observed rate of vaporization of the PMD repellent formulations by the Lampe Berger fragrance burner and the CuO-Montmorillonite clay Burner.

The above plot shows that the average rate of vaporization of the 3g, 12g and 15g PMD repellent formulations when vaporized by the LBFB and the CuO-Montmorillonite clay burner does not significantly differ. The error bars of their average rate of vaporization overlap each other’s center.

Statistical comparison of the rate at which the 3g, 9g, 12g, 15g and 18g PMD repellent formulations were vaporized using the CuO-Montmorillonite clay burner and the Lampe Berger fragrance burner using regression analysis showed that both burners used up the same amount of repellent per minute \( (p=0.34) \) in vaporizing each of the PMD repellent formulations i.e. there is no significant difference in the rate of vaporization of PMD repellent formulations (3g, 9g, 12g, 15g and 18g) when either the LBFB or CuO-Montmorillonite clay burner is used. The difference seen in the average rate of vaporization of PMD repellent formulations 9g and 18g vaporized using either the LBFB and the CuO-Montmorillonite in the means plot (see figure 25) could be due to experimental error and different working conditions of the burners.
The lower mass loss per minute for the 6% wt PMD repellent candles may have an influence on the percentage of PMD released. It should be noted that the mass loss observed in the repellent candles used in this study is representative of the laboratory environment within which the measurements were carried out and therefore may vary with the change in environment. On average, the mass loss in the three diameter candles was 0.08±0.0086g/min and was lower than the average rate of vaporization of the any of the PMD repellent formulations vaporized using both the LBFB and the CuO-Montmorillonite clay burner. Therefore the rate at which PMD was released from the repellent candles was slower.
CHAPTER FOUR

CONCLUSIONS

6% wt PMD repellent candles, the Lampe Berger fragrance burner and the CuO-Montmorillonite burner can be used as potential spatial applications of PMD in households. All the three applications are able to release the active ingredient (PMD) when they are used.

The Lampe Berger fragrance burner and CuO-Montmorillonite clay burner are superior to the 6% wt PMD repellent candles as spatial applications of PMD. On average, the 6% wt PMD repellent candles released the least percentage of PMD (0.047±0.015%) compared to that released when the Lampe Berger fragrance burner was used to vaporize 3g, 6g, 9g, 12g, 15g and 18g PMD repellent formulations (0.695±0.47%) for the same amount of time (275 minutes).

The CuO-Montmorillonite clay burner that was prepared in this study was able to vaporize PMD repellent formulations and was also superior to the 6% wt PMD repellent candles. The CuO-Montmorillonite clay burner, on average, released a higher percentage of PMD in the condensates collected from vaporizing 3g, 9g and 15g PMD repellent formulations (0.33±0.1%) as compared to the average percentage of PMD that was found in the condensates collected from lighting the 40mm, 69mm and 83mm diameter 6% wt PMD repellent candles (0.047±0.015%). It should be noted that the condensates obtained from the use of the CuO-Montmorillonite clay burner and the 6% wt PMD repellent candles were collected for a period of 60 minutes and 275 minutes respectively.

The mass of PMD in the repellent formulations has an influence on the percentage of PMD released by the Lampe Berger fragrance burner and the rate of vaporization of the repellent formulations.

The diameter of the 6% wt PMD repellent candles was found not to have an influence on the percentage of PMD released from them when lit. This was indicated from the overlapping of the error bars of the average percentage of PMD in their condensates. (see figure 11)

The 6% wt PMD repellent candles are easier to use as compared to the Lampe Berger fragrance burner and CuO-Montmorillonite burner. This is because they are a compact vaporizing system unlike the burners that have reservoirs, wicks and repellent formulations.
The CuO-Montmorillonite burner, on the other hand, is cheaper to prepare than the Lampe Berger fragrance burner in regards to the cost of catalysts used in both burners.

In this study, the method used to obtain condensates from lighting the 6% wt PMD repellent candles, varying laboratory conditions within which the candles were lit and the varying burning mechanism of the candles, could have caused huge variation in the percentage of PMD released from the replicate repellent candles that were used. There was no significant difference in the average percentage of PMD in the condensates collected from the 40mm, 69mm and 83mm diameter PMD repellent candles. The 40mm diameter PMD candles had the least mass loss (0.06±0.013g/min).

In summary, the CuO-Montmorillonite clay burner that was prepared was able to vaporize PMD repellent formulations without complete decomposition of the active ingredient. The rate of vaporization of the PMD repellent formulation (3g, 9g, 12g, 15g and 18g) by both the LBFB and CuO-Montmorillonite clay burner did not differ significantly. The CuO-montmorillonite clay burner vaporizes the same amount of repellent per minute as the LBFB (p=0.34). The 6% wt PMD repellent candles released the least percentage of PMD although they contained the largest mass of PMD (24g) compared to the mass of PMD in the repellent formulations vaporized using the LBFB and CuO-Montmorillonite clay burner.

In addition, the results obtained from this study provided enough evidence to support the hypothesis that both the CuO-Montmorillonite clay burner and the Lampe Berger fragrance burner release a significantly higher percentage of PMD when used to vaporize PMD repellent formulations compared to percentage of PMD released when 6% wt PMD repellent candles were used therefore the hypothesis was not rejected. In order to obtain a substantial amount of PMD released into the air, liquid repellent vaporizers are recommended for dispersing PMD.

Although it has been established here that PMD is released from the use of 6% wt PMD candles and during the vaporization of various PMD repellent formulations using the CuO-Montmorillonite clay burner, more work needs to be done to improve and further understand the performance of these spatial applications of PMD.

It has been shown that repellent candles are mostly effective in repelling insects when used in close proximity [44] and this also depends on the amount of active ingredient that they contain. Therefore, by establishing a better method of collecting the vapors released when
lighting the candles, collection of the vapors in variable controlled environment/room and
determining how an increase in mass of PMD in the candles affects the percentage PMD
released, important preliminary information that can be used in an efficacy study of the PMD
candles repellent ability against mosquitoes indoors can be obtained.

The high firing temperature-short time conditions used to prepare the CuO-Montmorillonite
clay burner in this study, produced a burner that was fragile. An optimum formulation and
calcination temperature for preparing the CuO-Montmorillonite clay burner, the effect of this
on the porosity of the burner, the effect of the size and type of wick material on the rate of
vaporization of PMD repellent formulations vaporized using the burner and the amount of
heat that the CuO-Montmorillonite clay burner uses to vaporize repellents need to be
established in order to understand the working mechanics of this potential repellent
formulation burner.

In preparation of this study, it was noted that the amount of time that the CuO-
Montmorillonite clay burner stays active during use decreased with time. Its activity was
unstable beyond a period of one hour. This prompted the vapor collections to be carried out
for shorter period of time i.e. 60 minutes. It was also noticed that the cupric oxide on the
surface of the burner is reduced to cuprous oxide. Therefore, it is also important to establish
the cause of this unstability in the catalytic activity of the burner to ensure a long life.
# APPENDIX

**Table 11:** Results from XRF analysis of Montmorillonite K10 clay showing oxides present in the clay sample

<table>
<thead>
<tr>
<th>Compound</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>V₂O₅</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Concentration</td>
<td>1.287</td>
<td>14.252</td>
<td>72.778</td>
<td>0.417</td>
<td>1.483</td>
<td>5.861</td>
<td>0.028</td>
<td>3.814</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>CuO</th>
<th>ZnO</th>
<th>Ga₂O₃</th>
<th>As₂O₃</th>
<th>Rb₂O</th>
<th>SrO</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Concentration</td>
<td>0.006</td>
<td>0.013</td>
<td>0.004</td>
<td>0.004</td>
<td>0.003</td>
<td>0.001</td>
<td>0.007</td>
<td>0.003</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Y₂O₃</th>
<th>ZrO₂</th>
<th>Nb₂O₅</th>
<th>PbO</th>
<th>Re</th>
<th>IrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Concentration</td>
<td>0.001</td>
<td>0.034</td>
<td>0.004</td>
<td>0.001</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Normalization factor 1.549
Minimum He Flow (I/min) 0.63

**Table 12:** Results obtained from XRF analysis of CuO Catalyst showing oxides present in the CuO catalyst sample

<table>
<thead>
<tr>
<th>Compound</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>CuO</th>
<th>V₂O₅</th>
<th>SrO</th>
<th>CdO</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Concentration</td>
<td>0</td>
<td>0</td>
<td>0.372</td>
<td>0.803</td>
<td>0.095</td>
<td>98.714</td>
<td>0.011</td>
<td>0.006</td>
<td>0</td>
</tr>
</tbody>
</table>

Normalization factor 1.645
Minimum He Flow (I/min) 0.65
Figure 26: The LBFB (left) and CuO-Montmorillonite clay burner (right)

There was formation of a yellowish green coating on the surface of the CuO-Montmorillonite clay burner.
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