Instituto Tecnológico y de Estudios Superiores de Monterrey

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School of Engineering and Sciences

DESARROLLANDO UNA SUPERFICIE QUE PROPICIA LA CONDENSACION PARA COSECHAR AGUA DEL MEDIO AMBIENTE AL TRATAR UNA TEJA DE ARCILLA CON NANOPARTICULAS DE SiO_2-OTS

DEVELOPING A SURFACE WITH DEW ENHANCING PROPERTIES TO HARVEST WATER FROM THE ENVIRONMENT BY TREATING A CLAY SUBSTRATE WITH SiO_2-OTS NANOPARTICLES

By

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Dedication

To my family: my caring mother, my supporting father and my dear sister. You have always had my back and have reminded me that hard work pays off. Thank you for believing in me and for all the effort done so that I can be where I am today. I am eternally grateful for having you. Thanks for all your unconditional confidence, support, patience, and encouragement. You were my main motivation for pushing through this work.

This work and this triumph is as much mine as it is yours.

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DEVELOPING A SURFACE WITH DEW ENHANCING PROPERTIES TO HARVEST WATER FROM THE ENVIRONMENT BY TREATING A CLAY SUBSTRATE WITH SiO_2-OTS NANOPARTICLES

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Abstract

The demand for drinkable water by the world population is increasing each year due to the aggressive exploitation of natural resources and bodies of water. Mexico is a country rich in natural resources, but its population's demand for drinking water has led to a rapid deterioration of these. Additionally, with the population spread throughout the national territory many communities have found themselves isolated and with few commodities- water is scarce. Thus, it is imperative to develop an alternative that allows the acquisition of water for the population and various communities who require this element vital for life. There is currently a race of diverse solutions for this world-wide problem. While some studies choose high cost mechanical means, others are seeking low cost solutions by the creation of new materials with nanotechnology and biomimecry. However, neither has created a proper surface or method by which such humidity can be harvested and used by the population. Thus, this proposal, developed at the Instituto Tecnologico y de Estudios Superiores de Monterrey, offers a solution focused on the replication of the Stenocara Beetle through the creation of a hybrid surface on a clay substrate with SiO_2-OTS particles that harvests the environment's humidity in an alternative that can be introduced into the construction industry.

Chapter 1:

Introduction

1. Motivation

The world is facing a critical problem of water scarcity. Studies have forecasted that by 2025 two thirds of the world will be facing a complete drought and lack of water- this resource won't be available [1]. Even nations rich in natural resources such as Mexico are facing this reality. Mexico has 27% of its population living in the central-northern region of its territory, producing the 79% of the country's PIB and having only 32% of the nation's natural resources for acquiring water. On the other hand, the southern region of the country holds 68% of the region's natural resources that can provide this vital element with only 23% of the population living there and generating only 21% of the country's PIB. However, the country counts with 90.2% of its territory with sewage and piping infrastructure. But, urban and developed areas, where most of the population has settled, count with 96.4% of this infrastructure. Rural areas only have 69.4% of this infrastructure [2]. The forecast of the future is duller when 70% of the country's hydric resources are currently over-exploited. Thus, a solution for this dilemma has become a national priority. Proposals are varied but the vision has been focused down to the protection and regulation of these non-renewable resources. This creates a social tension as the population and the world's population has been accustomed to depending on and consuming these bodies of water, ignoring the consequences these entail. One new proposal, however, focuses on meteorological data and claims that the environment itself has a latent supply of water that is constantly being recorded and measured as a percentage, Relative Humidity and Humidity [3-6]. If this latent supply could be harvested and incorporated into the hydric resources available for the population, the exploitation of bodies of water would be decreased and the development of societies would receive an unprecedented boost. Water would be available anywhere for its provider and means of acquisition would be the wind itself.

Water shortage has been a major problem faced by the modern civilization in both arid and humid environments [7, 8]. A viable alternative to collect water has been the condensation and "harvesting" of fog and dew. Inspired by nature's organisms such as the Lotus Flower and Stenocara Beetle, which exhibit unique properties of hydrophobic and hydrophilic surfaces, research regarding the replication or imitation of such surfaces has been at a rise [9-28]. However, there is a constant debate over the most efficient method by which such an alternative can be viable. That is because humid air needs to be cooled down to the dew point for water vapor to condense into liquid water (from a physics standpoint)[13]. Thus, the optimal wettability and geometry of the condensation substrate to maximize water collection efficiency is the research topic various groups have targeted [9-12]. In the field of heat transfer, condensation on cold surfaces has been widely studied for applications in HVAC (heating, ventilation and air-conditioning) systems [4,14,29]. However, for the creation of a surface, the science regarding condensation and the enhancing of dewing by means of surfaces is still a new area. It has become a general fact that the condensation of liquid droplets on solid surfaces is governed mainly by two parameters: the chemical composition and the geometrical microstructure [15-17]. Studies and investigations on these two main parameters identified have led to the confirmation that hydrophilic–hydrophobic surface patterns exhibit superior water collection performance to surfaces with uniform wettability, either hydrophilic or hydrophobic [18-20]. However, the definition of a chemical composition or combination with an overwhelming performance for such structures is still undefined [21,22]. Thus, many studies are reverting to the origin of this technology.

The stenocara beetle is the main source of inspiration for the creation of a surface that can manifest dewenhancing abilities through the combination of patterned hydrophobic and hydrophilic surfaces [9-12]. When its wings come into contact with humid air, water vapor condenses on the hydrophilic spots. Once the water droplet diameter exceeds the size of the hydrophilic zone and droplets encroach into the superhydrophobic zone, they coalesce and roll off the surface [23-25]. This is due to a random array of smooth hydrophilic bumps present on the Stenocara beetle's back

(0.5 mm in size, and arranged 0.5-1.5mmapart) [12]. These hydrophilic regions are surrounded by waxy areas comprising physical features (approximately 10 μm in size), arranged in a hexagonal array that exhibit the superhydrophobic physical property. Water collection onto the nonwaxy hydrophilic regions occurs by the beetle tilting its back wings into the fog and dew present in the wind direction. Any humidity incident upon the waxy hydrophobic regions is blown along the surface until it reaches a nonwaxy hydrophilic region. The droplets grow until they cover the entire hydrophilic bump, and then, under their own weight, they detach and roll downward into the beetle's mouth. Despite being a "unique" adaptation mechanism, this naturally occurring microcondensation surface has been previously mimicked in the laboratories [12,23-25]. The synthetic replication of such a surface would entail a great technological accomplishment as its potential in industrial applications covers a broad range of opportunities and purposes.

2. The Problem

As science and technology provide us with new knowledge, we have been able to reevaluate and reexamine our lives, our world and our reality in different perspectives. New generation materials, product of sciences such as nanotechnology and biomimecry, have provided us with new means and processes by which we can solve problems [27-29]. Despite the world has taken on the challenge of solving water scarcity in different ways, the vision is the same. Rural or isolated communities, far from the influence of the urban areas, are the ones that suffer the most from water scarcity [7,8]. Usually focused on economic activities of mining or agriculture, these communities are deprived of technological advances and progress [2]. Relocating all these individuals is an unrealistic solution if not impossible. Meanwhile, the urban jungles that are industrialized and boast high advances in technology and infrastructure are hubs of consumerism. The demand for resources is insatiable and unrealistic to meet with current technology, especially the most vital one- water. Thus, solutions must be ample and adaptable to be able to be competitive and efficient to permeate into the world market [1-4].

Water condensation or "harvesting" is not a new concept; studies on such an idea dates back over 50 years as Chile researchers developed the first concepts and proposals. Today, various countries and investigation groups are concentrating their efforts in making the harvesting of water from this untapped medium a reality [30-35]. In Tojquia (Guatemala) the largest (in expanse) fog harvesting project functions with 60 fog humidity capturing meshes that condense the water. Likewise, near Lima (Peru) the organization Alimon has installed similar fog harvesting meshes to provide water for human consumption and agriculture [28,33]. In Namibia, smaller dew and fog harvesting meshes of smaller dimensions have been installed, each with a capacity for 15 lt/night [26,33]. In the town of Chungungo, northern Chile, there's a network of fog and dew harvesters located on the mountain region, connected by pipes and traversing seven kilometers to bring water to 120 homes [26,28,33]. In Spain a massive project of dew and fog harvesters are being installed along the Mediterranean coast [28,33,35]. All of these proposals are the starting points from which the research groups interested in this problem have begun to seek and create more efficient methods. Chile is perhaps the country that has invested the most amount of time in this technology branch, it has been decades of ideas and solutions that have ranged from the current dew and fog harvesters to even desalinization of ocean water [32]. There are even ambitious plans of superstructures that could condensate the humidity in the air by rapidly transporting it closer to the ground and, thus, condensing the water [31]. Other ideas have shifted to mechanical and energy dependent alternatives that condense the air by means of a machine and, thus, producing potable water [4,36]. The later had even become an entrepreneurial endeavor by the name *FreshWater* that plans to bring fresh, clean, cheap and ecological water to the people of Chile [32]. In essence, the technology developed is a mechanical device that sucks the surrounding air and condenses the water as an air conditioner would [32]. It has recorded a production efficiency of

9 to 30 liters of water without sodium, fluoride, heavy metals nor chemicals at an economical cost of 20 to 25 pesos (Chile currency) [32].

The race for this technology has begun and there is a strong growing interest to harness the potential water present in the humidity of the air. Water is a vital element for life, allowing societies and civilizations to grow, to cultivate food and to expand. The availability of water is very dependent on its transportation, a heavy investment on piping infrastructure- a hindrance. Even so, without a technology to be able to transport water, civilizations would still be limited to living and expanding along natural bodies of water. Such is our nature. Thus, it is a natural and survival necessity to expand our options and horizons.

3. The Unsolved Problem

Massive structures tend to be the first ideas developed- more volume and more consumed space mean greater production potential [31,34-39]. However, big structures tend to be very invasive and have a detrimental impact on the surrounding ecology; more efficient options are preferred. However, an effective way to measure the efficiency of these technologies that "harvest" water from the environment does not exist. As such, the common units with which these technologies are evaluated regarding efficiency are their production of cubic centimeters (cm3) or milliliters (mL) over a period of time. This allows for a proper assessment of each technology's competitiveness and a clear relation between its development and its practical application. However, as everything is always viewed under the lenses of cost-benefit, we tend to ignore the stress and damage we have on the surrounding ecosystems. Thus, not every solution has an immediate application as its technological and ecological cost is too steep [30,36].

The direct condensation of humidity in the air into water is the main technological focus in the search to solve the water scarcity issue. Thus, the use of electrical energy to power mechanical air condensers (similar to air conditioner machines) is the most direct solution as these can produce water in a quick and effective way [36,37]. These ideas have reached Mexico and research on these technologies, adapted to the region, have been developed. In Mexico City, a prototype for a humidity condensation machine for residential and personal was studied and tested [3,4]. Such a concept and interest is natural, especially in a location such as Mexico City since it is located over an ancient lake (high humidity). However, this technology has many more regions (national and regional) it can be applied to, especially in coastal areas such as Veracruz [3]. This prototype, however, suffered of many inconsistencies due to its orientation towards residential and particular use, despite it being quite efficient. Similar projects of a greater scale have been developed in other places. Marc Parent got his patent (US8820107)[12] approved back in 2014 for such a variation of massive scale [36]. Though the idea and concept dates back to 1956, it has evolved to incorporate todays' technology and knowledge and to grant governments and societies the much desired possibility of actual "water harvesting farms" by using wind turbines [27,37]. However, this variability and diversity are the reason why a clear focus is required and that technology must be accessible, economical and efficient. When it comes down to the application of technologies economical costs, regulations, government taxes and expenses all affect the final cost. Thus, the reality of life imposes strict and harsh limitations on technologies that wish to find a real-world application. Many tend to become overly simplified just to find a place in the market.

While mechanical solutions have become increasingly popular, low cost alternatives have a greater competitiveness and are more commonly used. *WarkaWater* is the leading group in this area as they've had a very successful series of social projects in Africa. Using an innovative and tailor made structure of bamboo stocks, ropes and special textiles they employ biomimecry and rise from the ground to expose as much area as they can of their special textile so it can harvest dew, rain and fog water. Their simple yet realistic and quick to setup structures, which can be modified to the amount of water necessary to harvest for the communities of indigenous African people, have won them immense prestige [31]. From this project researchers around the world are going back to the basic principles of science and seeking simple and new ways to address the problem. Ethiopia has invested in research and development over the last years precisely to address the water scarcity problem that they live. Located, along with other African nations, in the great and arid plains of the savannah and some even in the great Saharah Desert, they desperately need technologies that can allow them to reshape this inhospitable and sterile territory into new veins of life and culture where they can develop and prosper as a nation [38,39]. It is, in essence, the will to survive that pushes them to research. Africa, a continent known for suffering from malnutrition, starvation and dehydration, is struggling to change its reality [38,39]. A low cost technology that can give them a hydric resource would save their future [31].

"Harvesters" come in many ways, shapes, sizes and even "harvesting" capabilities. Biomimecry is a new field that imitates and tries to replicate things in nature [15,16]. We humans have always taken inspiration from nature, it is perfect in its creation and we wish to replicate its solutions. Thus, for the problem of water scarcity, people have found inspiration in the Stenocara Beetle and the Lotus Flower- organisms that have specialized covers with hydrophobic and hydrophilic properties [10-12]. Other studies have decided to focus in the creation and use of MOFs. The duality of these surfaces that can capture and transport water in nature are unique, yet we seek to achieve such behavior. MOFs, specially, are peculiar engineering products for their name "Metal-Organic Framework" grants them properties of both metallic structures and elements, along with those of organic tissues or origin [6,29]. As some metals manifest ionic charges that can attract other molecules and create chemical reactions, these have begun to be used to attract and capture water molecules (which also has an ionic charge). Thus, MOFs have begun to have an increasing presence in studies related to the harvesting of water from the air. The leading group of investigators in this new technology and material group is MIT, with an increasing number of papers that focus on the application of these materials [5].

4. Purpose of Investigation

Traditional scientists that seek to study and comprehend our natural world have always sought to be as close to nature as possible. The Lotus Flower has been the inspiration for hydrophobic and superhydrophobic surface properties over the last years [9-17]. Likewise, the Stenocara Beetle has become the inspiration for hydrophilic and hybrid surfaces. The creation of surfaces and materials (meshes, textiles, etc) with selective capabilities are highly desired in many fields (especially medicine). However, a complete understanding on how the Stenocara Beetle's carapace manages to be so efficient in harvesting humidity is still an undergoing investigation [9,11,12]. As more papers shed light on its geometry and composition the more outstanding its survival in the desert becomes. It has the unique ability to burry itself and lifts its carapace at an angle where the wind both crashes and on it and runs over it. With the low temperature of the desert and the cold wind, water condensates on hydrophilic patches and (once the water drop is too big) it slides by its dominant hydrophobic carapace to its mouth [23-25,40]. This has been the way this little beetle has survived for years. Thus, the race and ambition to replicate this carapace into a man-made product is a goal many investigation groups are struggling for. However, few (if any) have considered on the possible applications of such a surface.

Various methods have recently been proposed to create superhydrophobic surfaces, including electrochemical deposition, plasma fluorination, sol–gel, UV irradiation, etc. It is well known that, the wetting property of a solid surface is governed by both its chemical composition and geometric microstructure [41-55]. In the case of a hybrid surface, the chemical components that allow the development of hydrophilic and hydrophobic behaviors must be both compatible as well as resistant to mutual and individual deterioration. Studies have varied greatly with the components employed to replicate these behaviors individually and in hybrid alternatives, seeking to replicate the structure of the stenocara's carapace. Some studies have used electrospinning to create meshes from gel like components using TEOS, PEO, FDTS, TMA, PMA, among others [22]. Other studies have employed fluorine components paired with PAH and PAA components with SAMs layering to manifest hydrophobic properties and selectively "seeding" hydrophilic properties. With the aid of PODS and SiO2, two components who exhibit high water affinity, these studies using such polymers mentioned have been able to create patterned and stable surfaces [20]. Garrod et al. [12] even created a basic test by creating a wax coating over a glass surface, leaving patches where the glass was exposed (a hydrophilic patch). The use of plasmachemical fabrication processes using plasma-flourinated polymers and Oxides (O2) such as Titanium (TiO2) are less common but have been employed as well [10,11]. This variety of options, where neither has given an overwhelming efficiency over the rest, offers an opportunity where an efficient surface of patterned hydrophilic pixels on a hydrophobic surface is yet to be standardized. Thus, there is an absolute liberty on the method by which the properties of a hybrid hydrophobic and hydrophilic surface may be achieved.

There is a growing and clear tendency, however, of those molecules that have been better to work with. Silicon Dioxides have found a constant use in the creation of hydrophobic surfaces [56,57]. Such a consistent molecule that has been easy to work with can be considered a control or constant. Newer studies have been choosing new molecules that may offer a more economical and/or easier method of creating these surfaces. Thus, Halloysite nanotubes are a new addition to the creation of nanostructured surfaces. In particular, tubular halloysite clay nanotubes have gathered particular interests in material science due to their versatile features of large surface area, high porosity, and tunable surface chemistry, which enables this nanomaterial to be utilized as an attractive support for M-NPs [55, 58]. Furthermore, the clay nanotubes possess the advantages of high stability, resistibility against organic solvents, and ease of disposal or reusability as well [59], which is an advantage over SiO2 molecules which suffer a degree of degradation as they interact with water molecules [60-66]. However, their implementation has been limited as anchors for other molecules, mainly metallic oxides such as AgO [67, 68]. However, being a carbon-based molecule, a growing interest towards their individual use has been prominent. To achieve such a desired behavior and surface architecture with these molecules there is a theoretical opportunity by the means of electrospray particle deposition. Achieving halloysite molecules to become an independent and viable surface that allows for hybrid properties to manifest would allow for these technologies to become more accessible.

Nowadays, clay roofing tiles are widely used as exterior building components [69]. The economy and development of cities has created an extensive market where the development towards more high rise buildings is more frequent [70]. However, with this growth comes a consequence which has relegated the implementation of common roofing tiles and covers to those on housings and lower height structures. Roof tiles for houses and other buildings of such characteristics include double lap plain tiles in which relatively small rectangular plain tiles are fixed side by side in horizontal rows with two thicknesses of tile all over the roof and three thicknesses at the frequent laps [71]. This has led to a growing interest to create new roofing materials and covers. Studies such as Arkom and Umpaisak (2016) [72] proposition of roofing tiles made from agricultural residues are paving a new road for "ecological" materials in the construction industry. Thus, a new area of opportunity has risen as the market for such novel and new materials has been opened. Every structure we inhabit has a roof system of some sort, even if it's a simple concrete slab. This means that there is an ever expanding potential area that can be adapted to various needs. This means that we can move water harvesting systems closer to "home", to the very structures we inhabit and use daily.

There are many manuals and norms already made to regulate these systems. Using roofs as collecting surfaces is an initiative that has dated since the 1980s [73-77]. While not all countries regulate these structure, the USA has offered an extensive set of rules and criteria [78]. The Texas Manual on Rainwater Harvesting is one of such guides where systems, methods and uses for rainwater harvesting, storage and usage are explained and government approved. The purpose of these manual are not only to promote the incorporation of this systems into households or buildings but also to offer a transparent and clear explanation on what actions and uses for these waters are allowed by the government. Even if people can provide water for themselves and be self sustainable, the government seeks to regulate such a vital resource. However, these guidelines serve more uses as they are established and approved methods that come from an experimental and academic base. Following these criteria can help to optimize harvesting systems on these common and empty structures we can simply exploit. However, it must be noted that these systems must be changed as we will not only harvest rainwater (as usually used for) [78], but to further increase the efficiency of these structures to actually consistently harvest water from our environment.

At the Instituto Tecnologico y de Estudios Superiores de Monterrey, ITESM (Tec de Monterrey), studies that are seeking to participate in this technological race have begun. However, with a more social and application science focus, the studies being developed seek to create alternatives that can find a practical and effective use in society. With a philosophy and commitment to create technology and knowledge that can serve and help humanity, problems are tackled with a clear objective. Seeing how the regional situation of water scarcity if alarming, efforts are being narrowed down to a solution that can aid the countries of Latin America. However, any solution that is proposed must be able to adapt to the times and locations where it can be applied. Thus, this study seeks, ambitiously, to bring a practical solution that can aid any nation, taking as a starting point the critical realities being lived by many Latin America nations.

5. Investigation Question

Can a surface be treated by the modification of its surface properties to manifest dewenhancing properties that can harvest water from the environment without the use or assistance of energy or mechanical sources?

6. Hypothesis

The surfaces, clay roofing tiles, with hybrid properties of superhydrophobicity and superhydrophilicity could be created by the deposition of functionalized and unfunctionalized Silicon Dioxide ($SiO2$) particles with a hexagonal surface geometry and topology similar to the Stenocara Beetle, and achieve dew-enhancing properties to harvest water from the relative humidity in the environment, and this behavior can be supported by computer simulations.

7. Objectives

7.1. Main Objective

To develop a hybrid surface that manifests dew enhancing properties, much like the stenocara beetle, on a clay-based substrate with a surface geometry and topology to harvest water from the humidity in the environment, with the assistance of fluid simulations.

7.2. Specific Objectives

- Develop a deposition method by which silicon oxide particles (SiO_2) can adhere properly to a clay-based substrate.

- Design a surface geometry that can properly separate and identify the hydrophobic and hydrophilic areas.
- Develop a method by which a hybrid surface can be created following the surface geometry previously designed.
- Simulate and analyze the influence and force wind has over the surface of roofing tile pieces and how this can affect the ability or potential of the pieces and their treated surfaces to harvest water
- Simulate, analyze and compare the surface designs used in previous and other studies with the surface geometry designed for this proyect.
- Develop and propose an experimental scenario and environment by which the amount of water harvested by condensation by the treated surface.
- Characterize the materials used and the treated surface developed for certain properties such as: contact angle, surface architecture, angle of coalescence, etc.
- Carry out experiments on the surface treated and designed to compare results between the simulation and reality.
- Characterize and analyze the water harvested from the physical experiments to identify the quality of the water condensed by the surface and if the surface's chemical composition has any influence over the chemical and physical properties of the water.

8. Methods and Materials

8.1. Particles

SiO_2 (silicone dioxide) are naturally hydrophilic particles that are commonly used for the treating of surfaces and that have been thoroughly studied [56,57]. OTS The SiO_2 particles were used in two formats, one being functionalized and the other in its natural state. The unfunctionalized SiO_2 particles were joined through a chemical process with OTS particles [41]. This creates hydrophobic particles of SiO2-OTS that can be dispersed in a selected medium to be deposited later [41]. The particles will follow a process of chemical adsorption with which they will "fuse" to the surface. Repeating this process a couple of times in a controlled area will allow for a heriarchitecture to form with which hydrophobic or hydrophilic properties can be manifested along with the nature and treatment of the molecules. For SiO2-OTS particles, the creation of a hydrophobic surface is a documented fact [17,79], and gave us confidence in its selection. Untreated SiO2 particles were selected for their affinity to the SIO2-OTS particles over which they would be deposited [17]. This way it was ensured that adhesion of the hydrophilic particles to create a topological architecture and geometry as desired.

For the present study, a micropipette was used in a process of "drop coating". The SiO2-OTS particles were dispersed in Toluene and the untreated particles were dispersed in Isopropyl Alcohol. The same medium was not used as sharing the same medium could damage the surface treatment done with the first particle deposited and adhered to the surface. The hydrophobic surface was created first in which the untreated surface was covered by the toluene and later placed in a furnace at 80°C to ensure the evaporation of the toluene and fusion of the particles. This was done a second time after which the hydrophilic particles were deposited selectively over the hydrophobic surface with the assistance of a mask. The deposition was done inside a furnace that offered an environment at a constant temperature of 60°C. This was done two (2) times as well, after which the mask was removed and the hybrid surface was left to cure at ambient temperature for 24 hours.

8.2. Clay-Based Tile

The material to be used was a common roofing cover used in housing. To specify, the current study used ceramic clay-based roofing tiles acquired from a local LOWE'S and produced by LADRILLERA MECANIZADA®. This material was chosen as it is the most commonly used in the housing industry both in Latin American and USA market. Additionally, it was identified that the stenocara beetle's shell (which is trying to be imitated) consists of an organic and carbon-based structure similar to ceramic clay or even "light cement" [23-25,40]. As such, its implementation and use was according to those specified by the construction industry and their respective patents such as US4890432, US5268028, US5974756, US6178703 and similar [80-83]. However, pieces were cut to manageable dimensions for the experiments.

8.3. PTA 3D Printed Tiles

In order to obtain data from the influence of wind over roofing tile designs and structures, PTA 3D printed pieces with (especificar máquina y rollo) were used. The material and machine were used do to the speed and quality with which pieces can be created. These were solely used in the wind tunnel and smoke tunnel test to recollect data on the behavior of wind over roofing tiles. The material was not utilized nor considered as a deposition substrate as the particles used would be in a toluene medium and the PLA plastic has a warning that it can deteriorate when exposed to such chemicals. Thus, it is not viable.

A total of 8 pieces were printed with 6 being of dimensions 7cm x 7cm and their heights according to proportion and 2 pieces being assembly designs of 15cm x 15cm and heights of 7cm. The small pieces consisted of flat (concrete tile) designs and ceramic clay roofing tiles designs and were used in both the wind tunnel and smoke tunnel. The two pieces of greater dimensions were used exclusively in the wind tunnel and slanted at 15° as they would be on a real roof. These pieces, which had an assembly array of a concrete tile roof and a ceramic clay roof were used to obtain data on the interaction of wind over their surfaces at a larger scale. The larger scale allowed for the wind to propagate and travel a larger distance while being influenced by their designs.

8.4. Experiments

8.4.1. Particle Deposition

The experimental aspect for data recollection on the sample surfaces is simple as it will focus on the characterization of these and their efficiency at microcondensation and water recollection. A proper order must be established prior as the samples are exclusive and must avoid being subject to deterioration or damage for the tests. Thus, characterization tests took priority over the practical tests that focus on functionality and application of technology.

Characterization tests consisted of the Confocal Microscope, contact angle and rolling (coalescence) angle in order to collect as much physical data as possible on the behavior of the surface. FTIR tests were also done to analyze if there was a proper adherence between the SiO_2 particles, the SiO_2-OTS and the clay tile used. Confocal images allowed for a proper visualization of differences on the surface that are created by the different curing methods used. Additionally, it allows for a clear differentiation between the architecture created between Silicon Dioxide (SiO_2) particles and the original surface architecture of the clay tile.

For the measurement of the contact angle and rolling angle a specialized machine was used. (detalles de la maquina). The samples was placed on a flat surface where the camera can capture the water droplets and their shape. With the aid of a scale the flat surface samples were placed on the platform and kept without an angle so that lectures can be as accurate as possible and water droplets don't roll despite hydrophobicity. For each angle, after the contact angle is properly measured, the observation camera will be moved so that the angle at which the surface is being tilted can be appreciated. With the aid of a small lift, one side of the surface will be elevated slowly to manifest and angle and, thus, capture the angle at which the drop of water will slide off the surface. With the rolling angle identified for each surface, these will be fixed in placed at that angle as water molecules are softly sprayed over the surfaces and the camera is zoomed to capture a larger spectrum where both hydrophillic and hydrophobic segments can be appreciated. This is to enable a clear image on how the hybrid property of the surfaces function. Additionally, it will become evident the speed at which water molecules coalesce in each surface.

The confocal microscope employed was the (detalles de máquina). This equipment was used to create a 3D mapping of the surface of the treated tiles. This would allow for a comparison between the original tile and the treated tiles. The pieces were all analyzed as each went through a different degree of treatment and detailed information is necessary on how these levels of treatment affect the surface architecture. Contrary to the SEM, the confocal microscope allows for a proper mapping of the surface and it offers detailed information regarding the height differences between the original piece and the treated pieces as well as the differences between each treated piece. Additionally, it allowed for a clear visualization of the quality of the surface created by the treatment and its surface roughness. This was important as physical properties of the surface were affected by these microscopic details.

The application tests for microcondensation and recollection were done simultaneously with the aid of a condensation chamber. Water vapor was passed before the turbine, by a glass which held boiling water in a separate chamber, so that it can be dispersed inside the chamber. The chamber consisted of a base where the tile was placed and it had a clear canal to move water condensed towards a beaker used specifically to measure the condensed water. Additionally, the chamber had a slanted ceiling and an isolated bottom with a second beaker in order to measure the water that condensed naturally and would "become waste". The Surface was placed at 24° which is the Stenocara beetle's positioning angle [23-25]. The piece was exposed to a humid environment and tested for a period of 24 hours. After each 24 hour test, the sample would be left to dry and was not aided by any other material or mean (dryer, towel, sponge, etc.) as these may damage or deteriorate the sample's surface. The drying process was of 1 day between tests.
(Figure of condensation Chamber)

8.4.2. Sample Preparation

The current study created two surfaces which are identical and would allow for more tests to be made regardless of the drying process. As such, these surfaces are identified as samples "A" and "B". These samples underwent a brief series of characterization tests focused on their behavior and efficiency towards microcondensation and their proper characterization in order to verify that the properties desired were properly manifested. Each sample was properly prepared for each test.

Prior to the practical or functional tests, the pieces must be kept dry for at least 24 hours at room temperature. Their placement in the chamber was done with care to avoid damages to the pieces and/or surface through the side door and using gloves. Rigorous control and care was kept at all times during these tests as mentioned in the previous section to ensure that the data captured is as accurate and consistent as possible. Additionally, the pieces must be photographed after each test and being subject to both wind and water molecules. After the final test, the pieces were left to dry at room temperature for at least 48 hours before characterized again and examined for any changes or damages suffered from their exposure to wind and water. Any deterioration observed from photographs must be documented.

The chamber was kept in a controlled room temperature and clean at all times with all of its doors open. The proper order used for the experiments was that the piece was placed first and properly aligned so that condensed water would flow toward the proper beaker. The glass with boiling water was heated to 100°C prior and placed on an isolating surface in the separate chamber below the turbine, allowing for the s++team to flow upward and enter the condensation chamber. These conditions were then left for 24 hours.

8.4.3. Wind Tunnel and Smoke Tunnel Tests

Through the use of both a Wind Tunnel Machine and a Smoke Tunnel Machine, pieces were tested in 2 formats: single piece and installation assemblies. This was done with the purpose of testing the behavior wind would have over the pieces as prepared as they would be in a real situation, as well as acquiring their individual characterization as a unit and material. A similar test of this nature was developed by David Smith and Forrest Masters in the University of Florida [84,85]. However, for these experiments, there was a heavier focus in their mechanical behavior and all pieces were exposed to high and low speed winds according to their dimensions to acquire all data required to assess their aerodynamic behavior, properties and how the wind interacts with their surfaces.

Each material was placed in groups of 5 pieces and assemblies (10 testing samples total) that were first subjected to the Wind Tunnel Test Machine and tested for the different groups of wind ranges: 8, 14 and 18 m/s. These are wind speeds that are common in the region of northern Mexico. For each wind speed the material was analyzed for its aerodynamic behavior (lift force measurement) and mechanical capabilities. The tests are similar to those done in studies that require and focus on roofing system safety and are even standardized by international criteria [84,85].

Upon completion of the prior experiment, the untested pieces are evaluated for damages and discarded for multiple selections of 5 pieces and assemblies that will be subjected to mechanical tests for characterization. This characterization is through the means of destructive testing. For assemblies, the pieces were mounted on a roofing base and they were arranged in a way so the forces affect as much of the assembly as possible. Additionally the roofing base was tested as an individual piece to deduct its contribution from the values recorded from the assemblies.

9. Background

The history of tiles as a roof covering is as old as the development of societies. Their usage dates back more than 5,000 years, across multiple civilizations in different regions and as diverse as the amount of civilizations that have covered the planet [86]. However, the root of such tiles is a blurry one as evidence suggests their use by the Chinese and Greeks up to 5,000 years ago. Later, the Romans adopted a variation of Greek flat roofing tile patterns in areas with suitable clay throughout the Roman Empire [86]. This Empire which expanded across various nations and lasted for centuries embedded this technology into many more regions and civilizations. Prior to this, many roofing materials included stone, slate and structures composed of straw, reed, and timber [86]. This ancient technology evolved with time and it made its way to “the new world”. To be precise, use of roofing tiles in the U.S. began during the colonial period and it has been a stable business and an integral part of living and housing since [86].

Nowadays, clay roofing tiles are widely used as exterior building components [87]. The economy and development of cities has created an extensive market where the development towards more high-rise buildings is more frequent [88]. However, with this growth comes a consequence which has relegated the implementation of common roofing tiles and covers to those on housings and lower height structures.

Roof tiles for houses and other buildings of such characteristics include double lap plain tiles in which relatively small rectangular plain tiles are fixed side by side in horizontal rows with two thicknesses of tile all over the roof and three thicknesses at the frequent laps [83]. Thus, the durability, intended as the ability to withstand adverse climatic conditions, of all type of covers to be employed is one of the most important requirements to be considered in the structural design of modern buildings [87]. This has become a particular necessity as a growing interest to create new roofing materials and covers is growing in popularity. Studies such as Arkom and Umpaisak (2016) [89] proposition of roofing tiles made from agricultural residues are paving a new road for "ecological" materials in the construction industry. As such has been the dilemma with residue-based materials that are growing in popularity, the durability and mechanical properties of these materials is of vital importance.

Though the ASTM is the common regulation employed, many regions have their own codes and regulations that determine construction safety and quality [88]. As such, Mexico has its own Manual of Construction, a compilation of norms, rules, regulations, calculation guidelines and stipulations that has been recognized internationally for its thoroughness and for its meticulous quality control and building safety requirements and stipulations [90]. A region with seismic activity and with a city that suffers a peculiar and unique soil phenomenon (Mexico City), this manual is a very complete work that has been selected for this work as its guideline. Additionally, CFE norms and NTC04 are being employed as the nature of this study considers the influence and effects of wind forces, stress and loads on structures and covers.

By definition of this manual, the wind is considered as the movement of air that is created, in great measure, by the thermal currents that form in the 15 kilometers over the Earth's surface. However, the Earth's surface isn't a consistent feature and this distance varies greatly on "where" the surface "ends" [90]. As such, the CFE norms have identified and considered 3 zones in mainland areas and 4 for coastal areas. These areas consider and identify the speed, turbulence and resistance the path of these winds do to terrain and structures. In coastal regions the 4th zone is defined as areas directly offshore and immediately on the coast as winds will find no opposition in their path as they sweep over the low resistance and turbulence of the ocean water [90]. This can be appreciated in Figure 1 and 2.

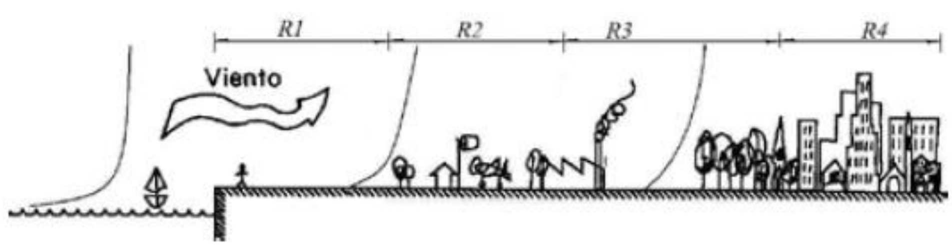


Fig. 1. Difference of the wind speed based on the height and roughness of the terrain (NTC04) [90].

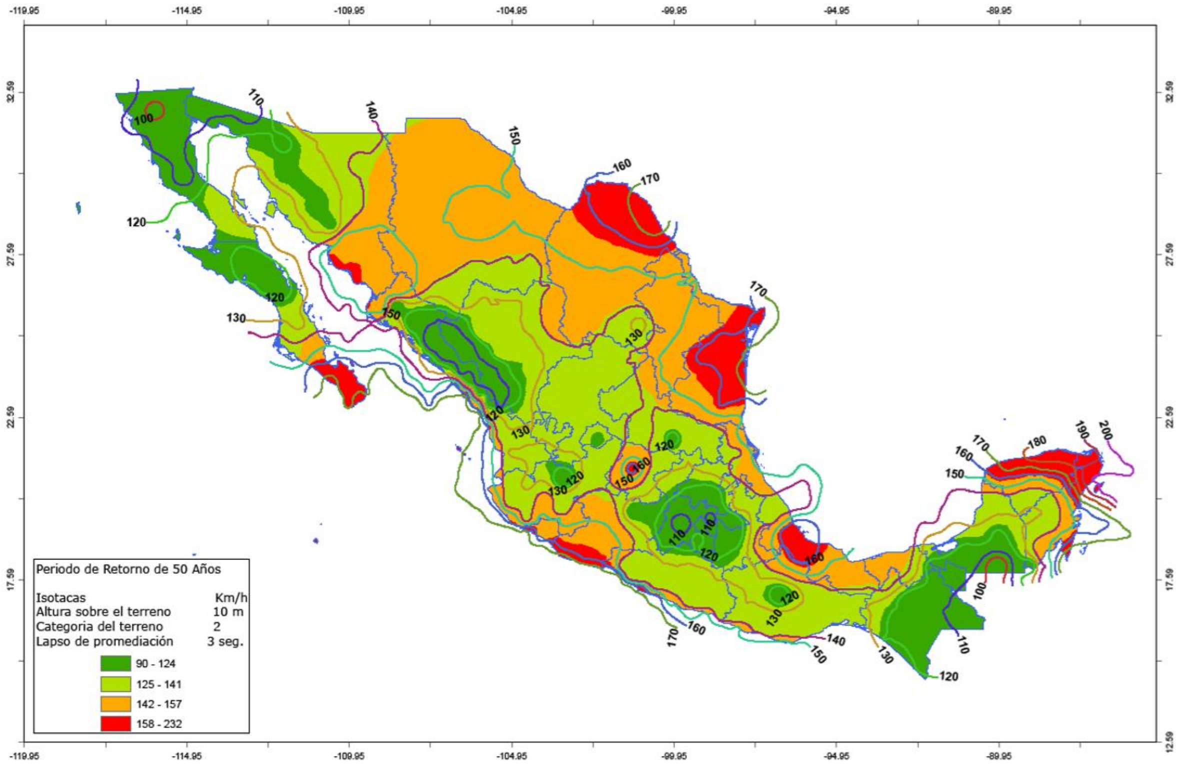


Fig. 2. Map of Wind Speeds of Mexico Territory with a Return Period of 50 years [90,91].

Regarding solid elements found in the path of wind, the fluid is considered to envelope and deviate from its path to pass by the structure. However, in doing so, the structure will receive and suffer different forces, loads and stresses as the wind acts on its different surfaces [90]. This can be appreciated in Figure 3.

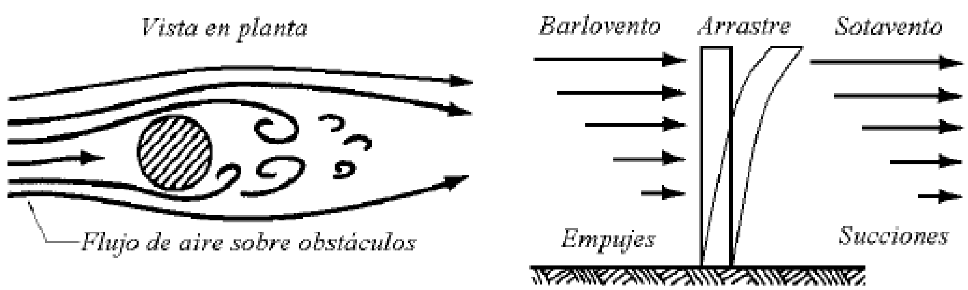


Fig. 3. Flow of air over fixed obstacles (Scruton and Flint, 1964) [90].

As such, every element that is subject to the pass of wind is subject to experience positive and negative pressures that are both of pushing forces and suction forces. These forces must always be considered in the least favorable and most critical circumstance and have been identified to behave under the following Equation 1 [90].

$$p_z = 0.47 C_p {V_D}^2 \qquad \text{(Eq.1)}.$$

The definition of these variables is defined, furthermore, by premade tables (Figures 4 – 5) that investigation groups have already developed for this manual [90,91]. The tables that are considered for calculations and analysis of the behavior and desired behavior of roofing tiles will be those already focused on materials that will serve as covers for structures.

Zona	Efecto	Coeficiente de presión, C_p
1	succión	$-1.1 < -1.2 + A/100 < -0.75$
	empuje	$0.8 < 1.1 - A/130$
2	succión	$-2 < -2.2 + A/150 < -1.3$
	empuje	$0.8 < 1.2 - A/130$
3	succión	$-2 + A/13 < -0.85$
4	succión	$-2.5 + A/20 < -1.75$
5	succión	$-4 + A/8 < -2$

Fig. 4. Pressure Coefficients for cladding in buildings of 20m or more in height [90].

Zona	Efecto	Coeficiente de presión, C_p
1	succión	$-2 + A/50 < -1.1$
	empuje	$1.5 - A/100$
2	succión	$-1.4 + A/50 < -1.2$
3	succión	$-3.0 + A/10 < -2.0$
4	succión	$-1.4 + A/50 < -1.2$
	empuje	$1.3 - A/50 > 1.1$
5	succión	$-1.7 + A/35 < -1.4$
	empuje	$1.3 - A/50 > 1.1$

Fig. 5. Pressure Coefficients for cladding in buildings of a height below 20m [90].

While these equations and considerations are not inherent or essential in this study, they are criteria with which decisions were made to determine the proposal of this thesis. Understanding the influence and effect of wind over structures and surfaces is of great importance for many fields. Even if it does not seem apparent, this thesis is oriented towards the application of surface treatment nanotechnologies in order to create a new type of material or surface that can be industrialized. However, the scope of the present work is to lay down the foundation and technological concepts and proof that such a surface is possible. Additionally, this work is assisted by simulations. The digital environment requires a clear understanding and definition of variables, boundary conditions and parameters in order to generate accurate results. These previous considerations and the CFE norms and NTC04 guidelines [90,91] were helpful in that. Even if the equations were not used.

Chapter 2:

Base Knowledge

In this paper, dew-enhancing properties are a vital and essential attribute sought on the surface created. However, prior to even working on creating the surface, an understanding on what this property is and how it works is a priority. Additionally, in order to properly simulate and experiment to see if this property manifests then the components and physical phenomenon that make it possible must be understood. In essence, understanding the mathematical models and equations are crucial to create a proper method to test this thesis's hypothesis.

1. Condensation

Dewenhancing properties can be understood and interpreted as an extension of condensation. Condensation is a crucial process of the water cycle, the process by which water in a gaseous state returns to a liquid state. However, condensation does not always lead to precipitation, nor is it a phenomenon exclusive to the atmosphere and clouds. Understanding the water cycle and the phases of water is complex. Works, such as Abascal and Vega's [92], are clear examples of the complexities of these different "forms of water".

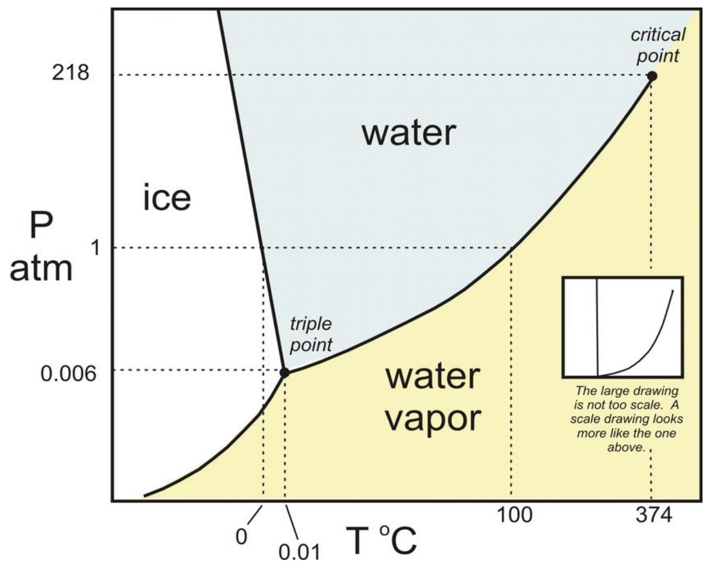


Fig. 6. Water Phases Diagram.

While an accurate mathematical model is worked on [93-98], there is a general consensus on how and when water exists or manifests in its different phases. This generally accepted explanation is Figure 6. Water and its phases do not exist only according to the temperature but also based on the pressure. While other variables and considerations can be made to determine the phases of water [93,94], water can exist in one phase or simultaneously in two or three phases. It is due to this volatile nature of water why mathematical equations to explain the changed between phases is not so simple. This work only focused on the interchange of phase between water vapor (gas) and water (liquid), the most prominent phase behavior [93]. However, this phase change covers the largest spectrum and the one most present in nature. The water cycle is based on it, and so the capabilities of other surfaces and films regarding water condensation [93,94].

Materials have the ability to condensate water- aiding in the change from a gaseous state into its liquid state [93-97]. It is this ability and this process that happens from the contact between a moist atmosphere and surfaces of materials that must be explained and understood physically and mathematically. Thus, mathematical models or equations to explain this physical phenomenon and other that relate and depend on it are crucial. Condensation cannot be explained in a single equation [93].

2. Physics and Mathematics

Physics and mathematics are intricately related when explaining our natural world. Condensation is just one part of our big world that helps keep things running. However, the math behind it is a subject that is constantly being questioned. However, one must start from somewhere in order to be able to analyze and work with condensation. Working with the mathematical equations allows for simulations and experiments to occur, for one to be able to segment and understand what elements and variables can be worked on. Thus, condensation is a group of equations that must be understood properly for this paper and its objectives. To do so, the work of Kasper Risgaard [93] was used as it compiled a diverse and very complete array of equations used for condensation, as well as other more detailed works and equations.

According to Kasper Risgaard's work [93], condensation can be explained by different approaches of diverse governing equations. Of these, the most prominent equations can be divided into certain groups: energy, surface properties, and adsorption. Additionally, these equations can be used together in different arrays for certain simulation models [95-97]. Understanding how each equation seeks to explain condensation is necessary to determine if a simulation model can be used [94-97], if a new model is to be proposed or how to set up a simulation with assistance of a program.

2.1. Thermodynamics

From a thermodynamics point of view, the phase transition of condensation is expected to occur when the chemical potential of the vapor phase exceeds the chemical potential of the liquid phase [93]. This is the basis of a general and simplified set of equations that deal with energy and enthalpy. Working with water, these equations take my conditions into consideration. When relative humidity exceeds 100%, temperature is lowered below the dew point temperature, or when vapor pressure is increased above the saturation vapor pressure are all aspects that can be explained through energy equations. This may seem as a relatively simple approach but it is the core for heat and mass transfer models (100-103). These models are used for the prediction of condensation and cover a large group of data (100-103). However, there is much more to just the initial considerations to explain condensation.

Condensation is a continuous effect [93]. This means that condensation is an ongoing effect (according to the energy and thermodynamic point of view) regardless of there being a dry, moist or wet surface- even if a water film is present. In essence the energy equations consider that water exists in both phases simultaneously when condensation occurs (as observable in Fig. 6). The transition from gas to liquid phase requires the formation of an interface between the two phases [93]. Thus, the equations are complemented by other energy equations that take this condition into account. When droplets are formed, as is the case in dew formation, two terms add to the change of Gibbs energy, according to the classical nucleation theory (CNT), and thereby determine whether the droplet formation takes place. One term is the negative contribution from the volumetric Gibbs energy, Gv, which favors the transition. The other term is an unfavorable positive contribution originated from the surface Gibbs energy, which is also called interfacial free energy or surface tension. These complementary equations are:

$$\Delta G = -V\Delta G_V + S_\gamma = -\frac{4\pi R^3}{3}\Delta G_V + 4\pi R^2\gamma_\infty \qquad \text{(Eq.2.1).}$$

Where the maximum is at $\frac{\partial \Delta G}{\partial R} = 0$ of which the following equation is derived:

$$\Delta G_{cr} = \frac{16\pi {\gamma_\infty}^3}{3(\Delta G_V)^2} \qquad \text{(Eq. 2.2).}$$

Where:

Variable	Description
γ	Surface energy or Surface tension
V	Liquid volume
S	Liquid Surface area
R	Drop Radius
γ_∞	Surface tensión of a planar surface

Table 1. Definition of variables.

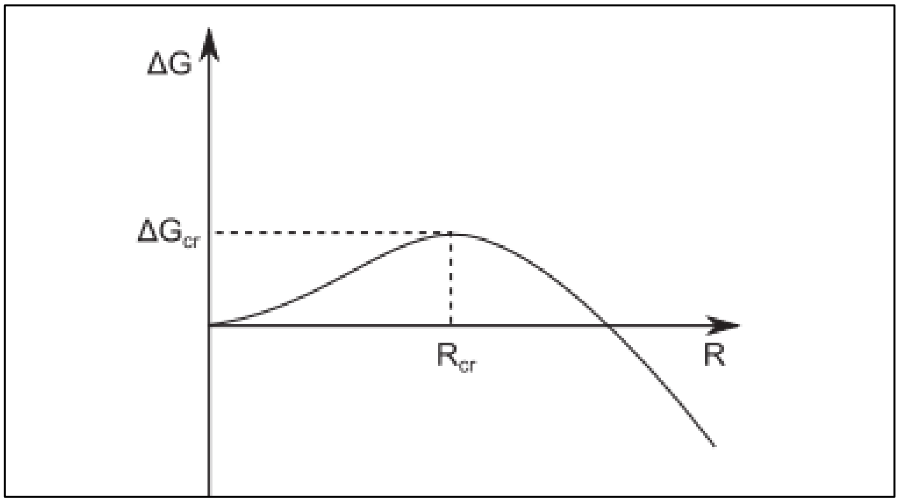


Fig. 7. Diagram of Droplet Growth and Gibbs Energy [93].

Of these equations the variables are as presented in Table 1, where (Rcr) is an equation that can be graphed [93]. The equation and graph (Fig 7) can be interpreted as the influence of droplet growth on condensation. Through the means of the energy equations, the influence of existing droplets of water and their size on the rate of condensation and particle growth can be explained [93]. However, the energy equations can't explain this influence completely. A different set of energy equations related to pressure can be used to complement these equations as well. This equation (Eq. 3) considers the influence of a droplet's curvature against a flat surface and how it affects the vapor pressure of the medium- a variable directly influencing the phases of water as seen in Fig. 1 [93].

$$p_c = p_\infty e^{2\gamma V_m / rRT} \qquad \text{(Eq. 3)}.$$

It must be noted that this equation and the interaction of the different surfaces (curved droplet vs a flat surface) is dimensionless, thus it can be used for any scale. However, the effect of nucleation is explained through a different complementary energy equation. However, the equation regarding nucleation cannot ignore the properties of a surface and it is (itself) a surface characteristic.

The surface equations used for condensation are a very debated mathematical area as different works take different approaches [93]. Surface equations are hybrid equations that use surface and material properties, geometry, topology, energy equations, microfluidics and many other different fields [93]. These equations are considered in this work due to the objectives and hypothesis stated. A surface with dew-enhancing properties relates directly to the interaction of a surface with a multiphase moist medium where condensation is occurring (a premise considered from the start). Among these equations, one of the most important ones is an energy equation that explains nucleation (a concept considered previously). The Arrhenius equation for behavior:

$$J = J_0 \exp\left(-\frac{\Delta G_{cr}}{k_g T}\right) \text{(Eq. 4)}.$$

Where:

Variable	Description
J_0	Kinetic constant
k_g	Boltzman constant

Table 2. Definition of variables.

2.2. Surface-Substrate-Material Equations

However, it is here where an area of opportunity arises as stated in Varanasi et al work and mentioned in Karter's. The Eq. 4 can take into consideration lower energy barriers and even the nature of the surface as a hydrophillic or hydrophobic surface. Works as Na and Webb [104] have created figures as Fig. 8 [93] to even show how surface topology and nature affects nucleation even with hybrid surfaces (alternating hydrophobic and hydrophilic). However, to consider such a nature properly, the contact angle must be considered, which deviates from the energy equations and moves towards a more physical and material property realm where dimensionless values are subjective. However, Karter [93] justifies this by stating that it is a necessary consideration as a

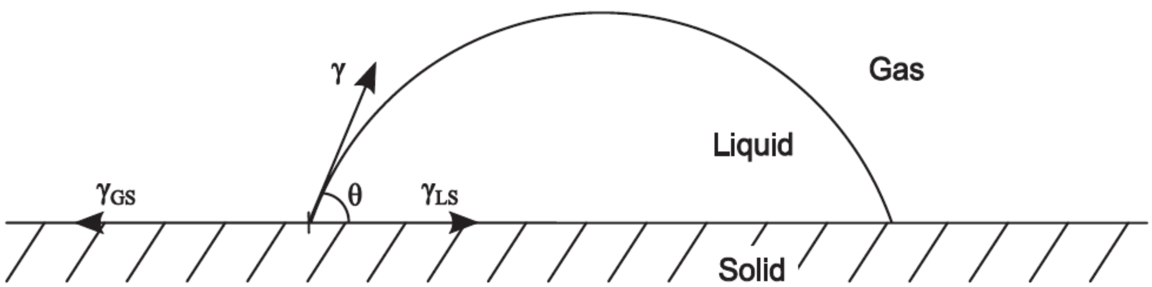


Fig. 8. Schematics of gas–solid, liquid–solid, and gas–liquid surface tensions at the contact line of a drop on a solid substrate. The contact angle of the drop is θ [93].

surface is a separate interphase that is interacting with a multiphase system, thus creating more and new interphase pairings. Furthermore, Karter's work uses Young's equation:

$$\cos\theta = \frac{\gamma_{GS} - \gamma_{LS}}{\gamma} \qquad \text{(Eq. 5.1)}.$$

Where:

Variable	Description
γ_{GS}	Gas-Solid surface tension
γ_{LS}	Liquid-Solid surface tension
γ	Gas-Liquid surface tension

Table 3. Definition of variables.

To incorporate the contact angle of a surface that is heterogeneous (hydrophobic and hydrophilic) the equation must be modified to consider the separate behavior of both type of surfaces:

$$\cos\theta_{het} = f_1 \cos\theta_1 + f_2 \cos\theta_2 \text{ (Eq. 5.2).}$$

Where:

Variable	Description
f	fractional areas of surface type (1 or 2)
θ	Local contact angle of surface type (1 or 2)

Table 4. Definition of variables.

And these equations, deriving from Young's, are still partial energy equations. Additionally, nucleation has its counterpart surface equation according to the CNT. However, the physical explanation of this equation is different as it considers the contact angle of the liquid, contrary to the previous equation which considers the contact angle of the interphase. Thus, a contact angle of 0° is viewed as the creation of a liquid film over the surface and 180° is viewed as a dry surface or (if possible) that the liquid forms a complete sphere- a possible consideration towards rolling droplets. Where the geometric factor of the contact angle is calculated differently than Eq. 5.2.

$$f(\theta) = \frac{1}{(2 - 3\cos\theta + \cos^3\theta)/4} \text{ (Eq. 5.3).}$$

2.3. Droplet growth on a Surface

Nucleation is only the first phase for droplet growth. There are two more stages that determine droplet growth: diffusion of vapor and coalescence [93]. These are governing equations that are attached to surface properties, while taking into account particle behavior. However, diffusion can be considered as single molecules in the gas phase and diffusion of clusters and adsorbed molecules along the surface [93]. A couple of considerations are currently made to properly explain these behaviors [93] since droplet size and growth are changing and variable parameters. Which is what gives rise to all of the previous equations. It is considered, through experiments and observation, that a droplet is formed or is considered to be forming when it is perceivable. In other words, droplets exist once they are created on the surface. As such, the equations focus on the fluid of mechanics and CNT to explain how droplets grow.

However, as Kasper remarks [93], the current equations that define the complete aspect of nucleation on a surface has yet to consider surface topology and roughness as nucleation sites. The fact that these factors are not considered is a consideration that greatly affects the behavior and condensation of a surface. While in general surfaces are homogenous with only one topological characteristic and behavior, this work focuses on a hybrid surface with a patterned (thus heterogenous) surface. Additionally, everything is worked on at a macroscopic level. Currently, the models are adjusted based on the concept of "perceivable droplets of water".

Droplet growth still has a defined set of equations for computer modelling. Despite its apparent shortcomings, computer software and mathematical models have been able to consistently, and with a low error, track and analyze how droplet growth is influenced and affected by surfaces and other means. For these separate type of models, computer mathematic models are used. The most common ones are usually Rose's thermodynamic considerations [105] and Sikarwar et al. Model [106] where:

$$r_{min} = \frac{1\gamma T_w}{h_{LV}\rho_L(T_V - T_w)} \text{(Eq. 6.1)}.$$

Where:

Variable	Description
r_{min}	Radius of nucleation sites
T_w	Wall Temperature
T_V	Vapor Temperature
h_{LV}	Latent heat of condensation
ρ_L	Liquid density

Table 5. Definition of variables.

Thus:

$$\frac{dr}{dt} = \frac{4\Delta T_t}{\rho_L h_{LV}} \cdot \frac{1 - \left({r_{min}}/{r}\right)}{\left({2}/{h_i}\right) + \left({r}/{k_l}\right)} \cdot \frac{1 - \cos\theta}{2 - 3\cos\theta + \cos^3\theta} \text{(Eq. 6.2)}.$$

Where:

Variable	Description
T_t	Total temperature drop
h_i	Interfacial heat transfer coefficient
k_l	Thermal conductivity of the liquid
θ	Angle of the Surface from the horizontal

Table 6. Definition of variables.

2.4. Nanoscopic effects and Analysis

There are different analysis and proposals that part from CNT and try to further explain the behavior and the event of condensation and condensate droplets by mathematical means [93]. Some works have also simulated these models in order to properly explain these and visually present their results and conclusions [94–98]. Variations go from individual surface nanoscopic models like Kasper [93], to Yeoman´s use of Lattice Boltzman [94,95]. However, all of these are simply focusing on improving one key aspect that is necessary for condensation droplets to form on a surface. Adsorption.

Adsorption parts from drop growth and moves towards the addition of fluid mechanics or behaviors to droplets on surfaces. However, adsorption is still currently viewed at a macroscopic level. As such, the governing equations and considerations are forces: Van dee Waals, hydrogen Bonding, Electrostatic and Steric. Thus, the main equation considered is defined as:

$$\gamma_{GS} = {\gamma_{GS}}^0(1 - \varphi) + {\gamma^\alpha}_{GS}\varphi \text{(Eq. 7)}.$$

Where:

Variable	Description
${\gamma_{GS}}^{0}$	Surface tension of the bare solid surface
$\gamma^{\alpha}{}_{GS}$	Surface tension when entirely covered by adsorbed water (thin film)
φ	Fraction of solid surface covered by adsorbed water (thin film)

Table 7. Definition of variables.

However, Kasper mentions in his work [93] that other works [107-109] have shown that nanometer-sized droplets and topological differences, as well as the consideration of non-ideal conditions (below 100% relative humidity) can greatly affect condensation due to the adsorption of water molecules on a surface.

2.5. Monte Carlo and Molecular Analysis

While nanometric scales are a dimensional issue, a different proposal and set of equations were made. These set of methods to solve for equations are known as Monte Carlo methods (MC) and they work with molecular interaction and energetic potentials. Using Newton's equations for movement, these methods track multiple individual molecules. In essence, it is an assortment of thermodynamic and chemical equations that consider the nature of molecules (pure element, molecules, dipole molecules, etc.). Hence, equations such as Leonard-Jones potential, Van der Waals, Pauli repulsion and Coulomb potential are mixed (among others) [93].

$$V_{LJ} = -\left(\frac{A}{r}\right)^{6} + \left(\frac{B}{r}\right)^{12} \quad \text{(Eq. 8.1).}$$

$$V_{Coulomb} = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r} \quad \text{(Eq. 8.2).}$$

These equations and models are favored as they are less demanding on computer resources and can even be used to modify CNT equations. Thus, it is one of the most common computer modelling methods used [93]. However, these equations do not offer visual representations of behavior and only offer a set of values that can be later paired with other equations (CNT method or others) to explain the behavior of a liquid.

3. Humidity, Dewpoint and Condensation

Relative Humidity is a physical behavior at all temperatures and pressures defined as the ratio of water vapor pressure to the saturation pressure of water vapor [110,111]. It is, essentially, an estimate of how close an ambient or medium is to the point of saturation and, thus, for the gaseous state of water to begin to change into a liquid state. Relative Humidity, however, is mathematically expressed as an equation dependent on pressure and temperature [110,111]. As such, it cannot be considered as an energy equation. To understand this, the ruling equations and its variables and constants are:

$$RH = \frac{P_w}{P_{ws}} \cdot 100\% \qquad \text{(Eq. 9.1).}$$

$$\upsilon = 1 - \frac{T}{T_C} \quad \text{(Eq. 9.2).}$$

$$\ln\left(\frac{P_{ws}}{P_C}\right) = \frac{T_C}{T}(C_1\upsilon + C_2\upsilon^{1.5} + C_3\upsilon^3 + C_4\upsilon^{3.5} + C_5\upsilon^4 + C_6\upsilon^{7.5} \text{(Eq. 9.3)}.$$

Where:

Variable	Description
T	Temperature of environment in Kelvins (K)
T_C	Critical Temperature, 647.096 K (constant)
P_{ws}	Saturation Vapor Pressure in HectaPascals (hPa)
P_C	Critical Pressure, 220640 hPa (constant)
C_1	Constant Coefficient, -7.85951783
C_2	Constant Coefficient, 1.84408259
C_3	Constant Coefficient, -11.7866497
C_4	Constant Coefficient, 22.6807411
C_5	Constant Coefficient, -15.9618719
C_6	Constant Coefficient, 1.80122502

Table 8. Definition of variables.

However, temperature, pressure and condensation are not isolated variables or conditions of each other [110,111]. As previously shown in Fig. 1, condensation covers a vast range where the energy interphase varies according to the pressure and temperature to which the medium is subject to. Thus, a change in pressure or drop in temperature is not the only mean by which condensation can occur, but also by the difference of temperature between the medium with humidity and any other element or surface.

The dewpoint is a temperature value that can be calculated from the relative humidity [110]. It is understood as the temperature at which condensation will form [110]. This open and broad definition is due to the idea that condensation does not solely occur in the environment, nor is it exclusive to the medium [93,110], but it can also occur over surfaces or materials. When a surface in contact with the medium presents a temperature that is equal or lower than the dewpoint, water is attracted and trapped (condensed) on it. The label “dewpoint" is due to the name given to this condensed water that forms on a surface or material- dew.

The dew point calculation comes from equations 9.1-9.3, where Pw must first be obtained from the previous equation 9.1. The dew point temperature can then be calculated by:

$$Td = \frac{T_n}{\left[\frac{m}{\log_{10}\left(\frac{P_w}{A}\right)} - 1\right]} \text{(Eq. 10)}.$$

Where m, Tn and A are constants obtained from this table [110]:

Temperature Range	Variables		
	A	m	Tn
-20°C to +50°C	6.116441	7.591386	240.7263
+50°C to +100°C	6.004918	7.337936	229.3975

Table 9. Definition of variables according to the work temperature [110].

However, these equations do not take into consideration the full extent of the phenomenon that is occurring [93]. It is a simplified set of equations that allow us to understand what we define as humidity. As temperature falls, the relative humidity rises (at that specific interphase of solid-gas). This forces the relative humidity to reach 100% (its saturation point) and for water to change into its liquid state (drop growth formation, nucleation and solid-liquid interphase). As such, the higher the relative humidity is of a system, the closer the dewpoint will be to the ambient temperature. However, one must understand that temperature plays a key role as well. High temperatures reduce or dissipate the relative humidity (concept of dry air) as water has a boiling point that affects its behavior even if already in a gaseous state [93].

The following examples of dewpoints, temperatures and HR values were taken and considered for this paper. These were taken both from common values of the region of Monterrey, Nuevo Leon and on the conditions that experiments could be worked with.

Ambient Temperature (°C)	Humidity (% RH)	Dew Point Temp. () °C below ambient
30	20	4 (-26)
30	30	10 (-20)
30	40	14 (-16)
30	50	18 (-12)
30	60	21 (-9)
30	70	23 (-7)
30	80	26 (-4)
30	90	28 (-2)

Table 10. Dewpoint calculation for simulations and experiments developed.

4. Simulation Mathematical Models

Kasper mentions a couple of mathematical and physical models and the equations that take priority in these in order to explain condensation [93]. This can be viewed as different approaches, as condensation and any physical phenomenon can be explained in different ways. However, not all of these approaches can be considered as valid or useful.

Drop Growth models are perhaps the most desired models and mathematical equations as they can most accurately incorporate how water droplets can form on a surface. However, these models are still very crude and idealistic as many premises and considerations are made. Drop growth models are still established as macroscopic models with dimensional parameters and variables that require these defined values in space. Additionally, drop growth models are still lacking fluid mechanics considerations, thus they are idealistic on particle behavior [93]. Drop growth models behave closer to probability maps and predictions of possible nucleation and particle growth contrary to the actual behavior of a surface subject to condensation.

Nucleation models differ from drop growth models as they eliminate completely the element of particle growth. Disregarding this behavior is risky but offer a wide range of different data as nucleation can be taken to a micro and dimensionless level using energy equations and partial equations as previously mentioned [93]. As such, nucleation models may not consider particle growth and fluid mechanics but they can properly map and detail the quantity of condensation on a surface [93]. However, they differ and cannot be considered as simple probabilistic maps or behaviors as the concentration of particles determine actual nucleation hot spots or zones. Additionally, nucleation models work by addition, and where particles adhered or form on the surface these become new points for future nucleation. This leads to nucleation being able to be 3D models as well. Although the computational demand would be high and time frames would have to be restricted.

Heat and Mass Transfer models are perhaps the most robust models and equation packages out there. They are the basis for many Simulation platforms and calculation platforms such as COMSOL, ANSYS, and others [112-115]. Based on energy equations, energy interchange and multiphase interactions, they offer a variety of data and options on how to customize, set up and run simulations regarding more than just condensation [112-115]. Regarding condensation, however, heat and mass transfer models are a bit simplistic. The preconditions for the equations are always that the environment must meet certain saturation conditions and temperature conditions. While the equations can adapt to non-ideal conditions, they are always bound to the assumptions made initially for the equations. However, these equations properly model the behavior of particles as they move between different and multiple phases in the time dimension and are very adaptable. These are the equation packages most people know and use today in simulation platforms.

Simulation of Solid-Liquid Interface (SLI) are a set of equation packages that offer a robust addition to Heat and Mass Transfer models [93]. While different, SLI simulations work with energy and surface equations. Equations are mostly energy equations, but they tend to have simplified elements and sections (depending on the simulation platform) [112-115]. They are accurate in being able to join fluid mechanics, particle behavior and many other aspects that involve interaction with a solid surface [93]. However, while COMSOL and ANSYS and other platforms incorporate these equation packages into their systems, these are all different [112-115]. Do to the computational demand of the equations and how they can all relate to other parameters and variables in an experimental set up, these equations tend to have modified aspects or different considerations for some variables in order to make them more manageable and the equations adaptable [112-115]. It is a tradeoff that is still necessary as not all equation work at microscopic or dimensionless parameters.

Chapter 3:

State of the Art

Simulations and mathematical models are the first step in order to create technology. However, technology without application is not all that useful. Technology and its theoretical background (mathematical models, simulations, theories, etc.) need to address and solve a problem that is present and real. This is sometimes difficult to understand when one simply looks and formulas and explanations of our physical world through mathematical and physical theoretical explanations. However, these same formulas and explanations are the foundation over which a solution can be found or made for a problem. Such is the case for condensation.

The world is facing a critical problem of water scarcity. Studies have forecasted that by 2025 two thirds of the world will be facing a complete drought and lack of water- this resource won't be available [1]. Even nations rich in natural resources such as Mexico are facing this reality. Mexico has 27% of its population living in the central-northern region of its territory, producing the 79% of the country's PIB and having only 32% of the nation's natural resources for acquiring water. On the other hand, the southern region of the country holds 68% of the region's natural resources that can provide this vital element with only 23% of the population living there and generating only 21% of the country's PIB. However, the country counts with 90.2% of its territory with sewage and piping infrastructure. But, urban and developed areas, where most of the population has settled, count with 96.4% of this infrastructure. Rural areas only have 69.4% of this infrastructure [2]. The forecast of the future is duller when 70% of the country's hydric resources are currently over-exploited. Thus, a solution for this dilemma has become a national priority. Proposals are varied but the vision has been focused down to the protection and regulation of these non-renewable resources. This creates a social tension as the population and the world's population has been accustomed to depending on and consuming these bodies of water, ignoring the consequences these entail. One new proposal, however, focuses on meteorological data and claims that the environment itself has a latent supply of water that is constantly being recorded and measured as a percentage, Relative Humidity and Humidity. If this latent supply could be harvested and incorporated into the hydric resources available for the population, the exploitation of bodies of water would be decreased and the development of societies would receive an unprecedented boost. Water would be available anywhere for its provider and means of acquisition would be the wind itself.

New generation materials, product of sciences such as nanotechnology and biomimecry, have provided us with new means and processes by which we can solve problems [27-29]. The world has taken on the challenge of solving water scarcity in different ways [30-37]. Rural or isolated communities, far from the influence of the urban areas, are the ones that suffer the most from water scarcity [7,8]. Usually focused on economic activities of mining or agriculture, these communities are deprived of technological advances and progress [2]. Relocating all these individuals is an unrealistic solution if not impossible. Meanwhile, the urban jungles that are industrialized and boast high advances in technology and infrastructure are hubs of consumerism. The demand for resources is insatiable and unrealistic to meet with current technology, especially the most vital one- water. Thus, solutions must be ample and adaptable to be able to be competitive and efficient to permeate into the world market [1-4].

1. Water Harvesting

Water condensation or "harvesting" is not a new concept; studies on such an idea dates back over 50 years as Chile researchers developed the first concepts and proposals. Today, various countries and investigation groups are concentrating their efforts in making the harvesting of water from this untapped medium a reality [30-35]. In Tojquia (Guatemala) the largest (in expanse) fog harvesting project functions with 60 fog humidity capturing meshes that "condense" the water. Likewise, near Lima (Peru) the organization Alimon has installed similar fog harvesting meshes to provide water for human consumption and agriculture [28,33]. In Namibia, smaller dew and fog harvesting meshes of smaller dimensions have been installed, each with a capacity for 15 lt/night (15 liters per night)[26,33]. In the town of Chungungo, northern Chile, there's a network of fog and dew harvesters located on the mountain region, connected by pipes and traversing seven kilometers to bring water to 120 homes [26,28,33]. In Spain a massive project of dew and fog harvesters are being installed along the Mediterranean coast [28,33,35]. All these proposals are the starting points from which the research groups interested in this problem have begun to seek and create more efficient methods. There are even ambitious projects of superstructures that could condensate the humidity in the air by rapidly transporting it closer to the ground. Other ideas have shifted to mechanical and energy dependent alternatives that condense the air by means of a machine and, thus, producing potable water [4,36]. The later had even become an entrepreneurial endeavor by the name *FreshWater* that uses a technology developed as a mechanical device that sucks the surrounding air and condenses the water by an internal system similar to air conditioners [36,37]. It has recorded a production efficiency of 9 to 30 liters of water without sodium, fluoride, heavy metals nor chemicals at an economical cost of 20 to 25 pesos (Chile currency) [32].

Dew catchments or humidity harvesting, however, is a relative new technology. The foundation of this technology dates back centuries as the first idea of "water harvesting" comes from rainwater [26,34]. It is an idea and series of concepts that have begun to gain interest recently do to the scarcity of water and the new construction industry interest in sustainability. Water harvesting has recently been standardized and studied, with manuals and regulations that determine how, when and where one can recollect and store this type of water [78]. However, water harvesting has always been considered different to fog harvesting and humidity is a possibility until recently. In general, harvesting water by "unconventional" means has been divided by the technologies themselves and how and what each focus on procuring.

2. Mechanical Systems

The direct condensation of humidity in the air into water is the main technological focus in the search to solve the water scarcity issue. Although recent, there is a growing interest in being able to acquire mass volumes of water. Harvesting, however, a large quantity of water from such a large medium (the atmosphere) has become difficult. This has lead for investigation groups to seek alternatives that can constantly "work" on providing this water. This "work" has been understood as the electrical energy to power mechanical air condensers (similar to air conditioner machines). These machines are the most direct solution to the problem as these can produce water in a quick and effective way [4,27,36]. Concepts on such machines are varied, as seen in figures 9-10, but the knowledge and technology behind them is the same. Research on these technologies is quickly expanding and being adapted to the regions where they are being applied. In Mexico City, a prototype for a humidity condensation machine for residential and personal use was studied and tested [4]. Such a concept and interest is natural, especially in a location such as Mexico City since it is located over an ancient lake (high humidity). However, this technology has many more regions (national and regional) it can be applied to, especially in coastal areas such as Veracruz

[3]. This prototype, however, suffered of many inconsistencies due to its orientation towards residential and particular use, despite it being effective.

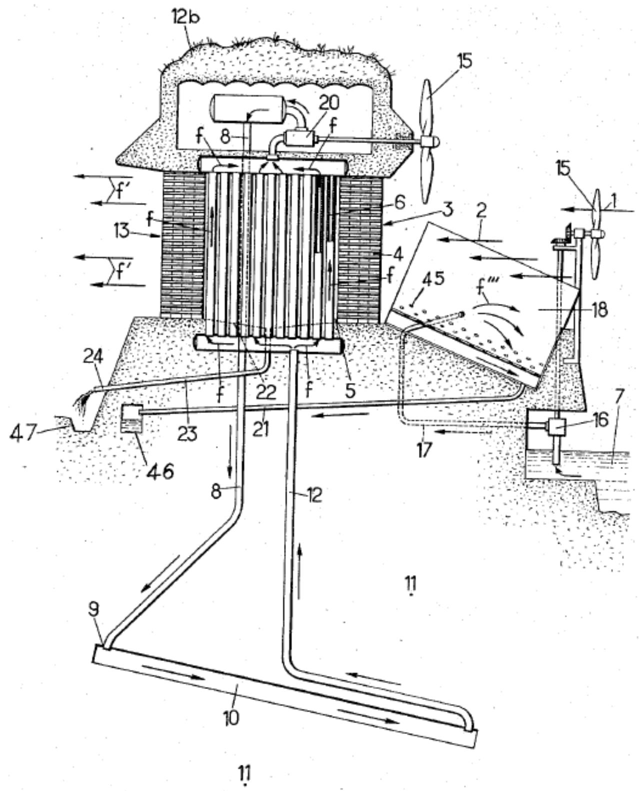


Fig. 9. Initial proposals for “self-sustaining” water harvesting structures [27].

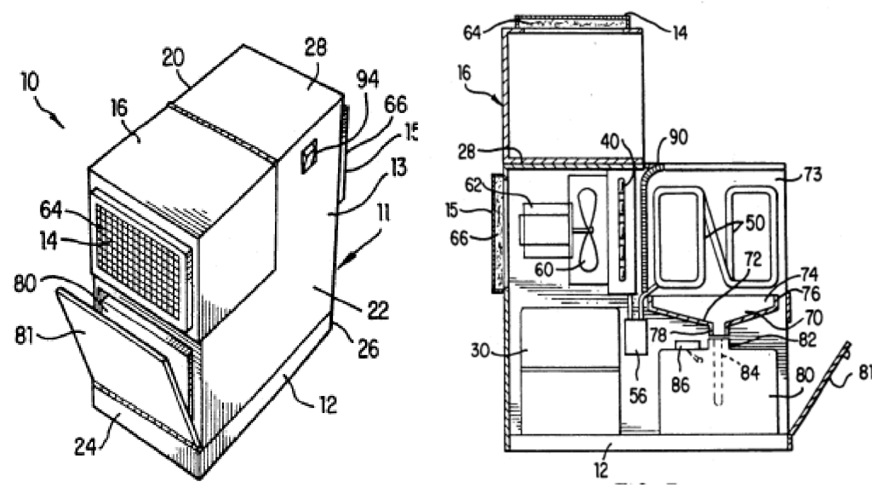


Fig. 10. Schematics for a electrically powered and motorized water harvesting unit [37].

Similar projects of a greater scale have been developed in other places. Marc Parent got his patent (US8820107) [36] approved back in 2014 for such a variation of massive scale. Though the idea and concept dates back to 1956 (figure 9), it has evolved to incorporate todays' technology and knowledge and to grant governments and societies the possibility of actual “water harvesting farms” by using wind turbines, as seen in figure 11 [27,36]. However, this variability and diversity are the reason why a clear focus is required and that technology must be accessible, economical and efficient [30]. Utilizing the technology of air conditioners, wind turbines have their rotors and generator stocks expanded to house an air conditioning system that will intake the wind that is blowing into the turbines and condense water. The energy of the air conditioning system is provided by the wind turbine itself and the excess energy generator can be harvested as well [27,36]. It sounds as an ideal solution that can sustain itself, but the amount of resources required to produce a single machine of these new "wind turbines" is very costly. When it comes down to the application of technologies economical costs, regulations, government taxes and expenses all affect the final cost. Thus, the reality of life imposes strict and harsh limitations on technologies that wish to find a real-world application. Many tend to become overly simplified just to find a place in the market.

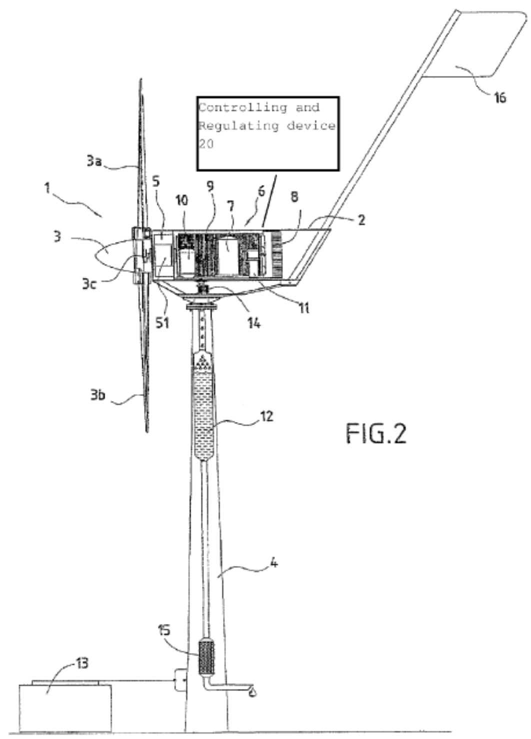


Fig. 11. Schematics for "self-sustaining" water harvesting super structures with Eolic turbines[36].

Marketable technology has its own limitations when it comes to problems as broad and severe as water scarcity. With the looming fear of such an essential element of life going amiss, other groups have tried to create systems that can serve masses or localities. *FreshWater* uses a technology related to air conditioners except that it requires a constant intake of energy (electrical) [32]. Their devices can be seen in figure 12, offering a clear idea on the market and use these devices are designed for. Freshwater systems require the machine to be in a location with a relative humidity (RH) over the 50% threshold. This is because the machine will constantly intake air by a rotor and move it through its internal systems that are very similar to air conditioners [32]. It has recorded a production efficiency of 9 to 30 liters of water per day without sodium, fluoride, heavy metals nor [32]. Despite being stated as an economical technology, the production and operation requirements for these "portable" systems are great difference and deterrent. With a negative aspect being cost efficiency, these technologies require further investigation and investment in order to make them accessible.

Fig. 12. *Freshwater* devices as of 2019 [32].

The direct condensation of humidity in the air into water is the main technological focus in the search to solve the water scarcity issue. Thus, the most direct solution is the use of electrical energy to power mechanical air condensers (similar to air conditioner machines) is the most effective way [30]. However, electrically powered machines require production of their mechanisms and their energetical costs and consumption. When it comes down to the application of technologies economical costs, regulations, government taxes and expenses all affect the final cost. Thus, the reality of life imposes strict and harsh limitations on technologies that wish to find a real-world application. Many tend to become overly simplified just to find a place in the market.

3. Physical Structures

Massive structures tend to be the first ideas developed- more volume and more consumed space mean greater production potential [31,34-39]. However, big structures tend to be very invasive and have a detrimental impact on the surrounding ecology; more efficient options are preferred. However, an effective way to measure the efficiency of these technologies that “harvest” water from the environment does not exist. As such, the common units with which these technologies are evaluated regarding efficiency are their production of cubic centimeters (cm3) or milliliters (mL) over a period of time. This allows for a proper assessment of each technology’s competitiveness and a clear relation between its development and its practical application. However, as everything is always viewed under the lenses of cost-benefit, we tend to ignore the stress and damage we have on the surrounding ecosystems. Thus, not every solution has an immediate application as its technological and ecological cost is too steep [30,36].

While mechanical solutions have become increasingly popular, low cost alternatives have a greater competitiveness and are more commonly used. *WarkaWater* is the leading group in this area as they’ve had a very successful series of social projects in Africa [31]. Using an innovative and tailor made structure of bamboo stocks, ropes and special textiles they employ biomimecry and rise from the ground to expose as much area as they can of their special textile so it can harvest dew, rain and fog water. The design and dimensions, however are not small as seen in figure 13. However, their simple yet realistic and quick to setup structures, which can be modified to the amount of water necessary to harvest for the communities of indigenous African people, have won them immense prestige [31]. From this project researchers around the world are going back to the basic principles of science and seeking simple and new ways to address the problem. Ethiopia has invested in research and development over the last years precisely to address the water scarcity problem that they live. Located in the great and arid plains of the savannah and some even in the great Sahara Desert, African nations desperately need technologies that can allow them to reshape this inhospitable and sterile territory into new veins of life and culture where they can develop and prosper as a nation [38,39]. It is, in essence, the will to survive that pushes them to research. Africa, a continent known for suffering from malnutrition, starvation and dehydration, is struggling to change its reality.

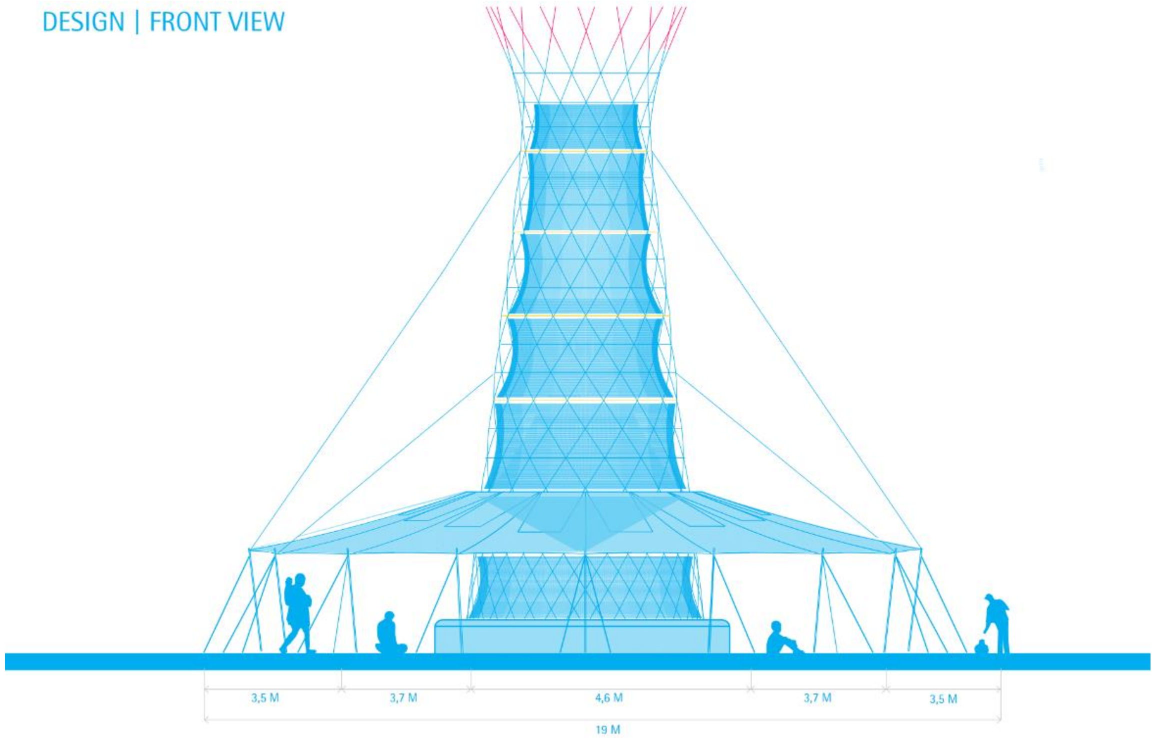


Fig. 13. Warkawater structure design and dimensions [31].

African nations such as Ethiopia have begun to raise investigations in water harvesting in desertic landscapes [38,39]. Many of their researches are divergent from the technological concept of "water harvesting" in the sense that they are taking into towards "terraforming". Terraformation is a stretch and inflation of the concept "water harvesting" to the magnitude at which water can be "recollected" and the means they can be recollected by. In a desertic landscape, oasis or locations with bodies of water that can sustain life have been of great importance both to people and ecology [38,39]. Many oasis have dried out and disappeared and this has only made the problem of water scarcity even worse. Irrigation or plant research both in an open environment and in a greenhouse have been the main interest in these regions as their focus shifted from "water for consumption" to "water for survival". For an African nation, this means food production [38,39]. By creating desertic landscapes into workable and green planting fields, they can improve their life quality. Additionally, their research has extended to the impact of how the introduction of certain plants and their arrangement can promote the creation of bodies of water- or for water to begin to recollect and soak the earth [38,39]. These results are different types of "water harvesting" structures as they are natural or artificial (greenhouses) creations that begin to concentrate and recollect water in a specific point which people may then consume and use.

On other regions that are completely the opposite to desertic, humidity is a constant reality, but water scarcity may be a reality. Latin American countries are recognized for their tropical climate and environment. This makes them very humid regions and nations with a variety of flora and fauna. It is here where "water harvesting" has taken a new form which tries to exploit this vast humidity in their natural environment [26,33,34]. Besides the tropical environment, many Latin American countries have many mountain chains. With a high humidity and locations of high altitude, there are many places where clouds and fog are in constant contact with the earth. These natural circumstances and events of the environment had no practical use in many countries, so they were an ignored resource. With many of their citizens living in rural areas and most of the economical resources being concentrated in other locations, the exploitation of this resource was left to the people for a long time [2-4]. Over time, research began to take notice and interest in these regions with a constantly high humidity as people who lived there had enough water to live, drink and use despite not having water pipe lines. Mexico, Guatemala, Chile, Ecuador and other countries have since begun to take an interest in this technology and the latent potential of this resource [26,33,34]. The technology is rudimentary, but effective. It dates back to a couple centuries ago. Vertical meshes. Fog was a concept that civilizations understood for many years as it was both beneficial and detrimental to human activities [26,28,33-35]. More recently, it has been understood that water can be effectively trapped by simply placing surfaces or meshes (permeable) in the path of clouds and fog. These simple approaches and concepts have lead to many researchers in creating each time more complex structures. Works such as Carrera-Villacres et al [26,34], have focused on the development of such structures and how to maximize the surface area of the meshes that can "harvest" water and use the least amount of area for their installation and operation. However, there are many more works that have dived into this subject, much as Pascual et al. explain in their work [28]. From their work we can analyze the Figures 14-16 to understand how people have survived by trapping water from fog and the efficiency of these first concepts.

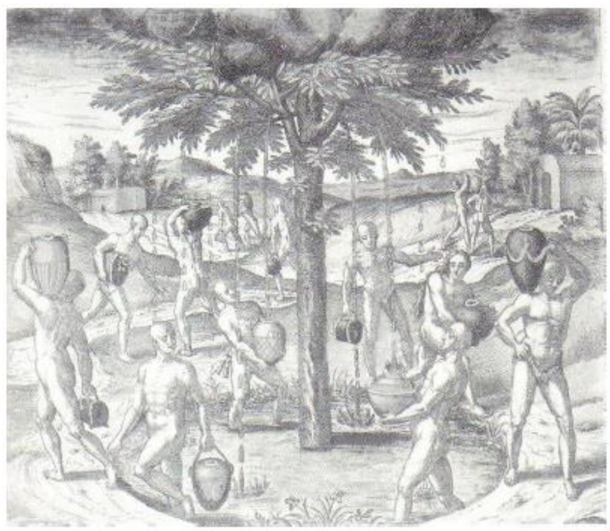


Fig. 14. Garoe tree on the Iron Isle of the Canarian Islands [28].

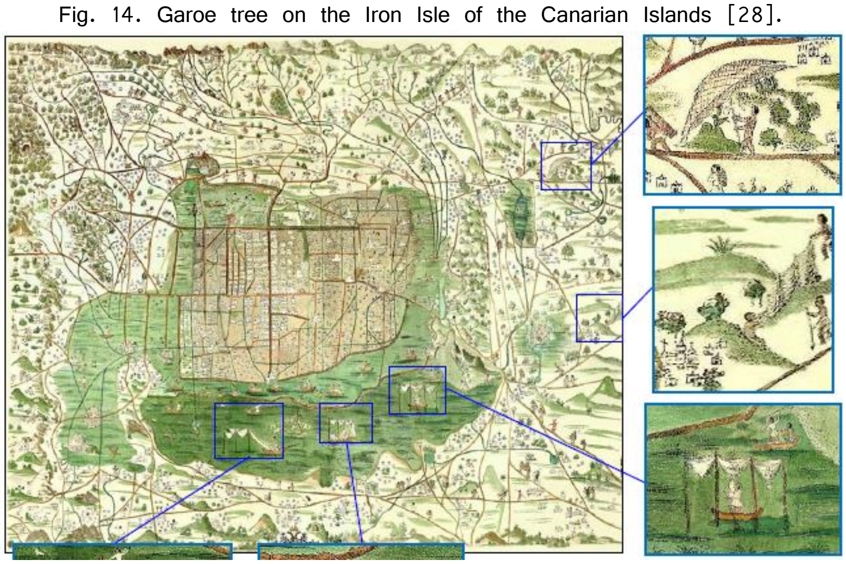


Fig. 15. Evidence of ancient fog harvesters by Mexico-Tenochtitlan cultures [28].

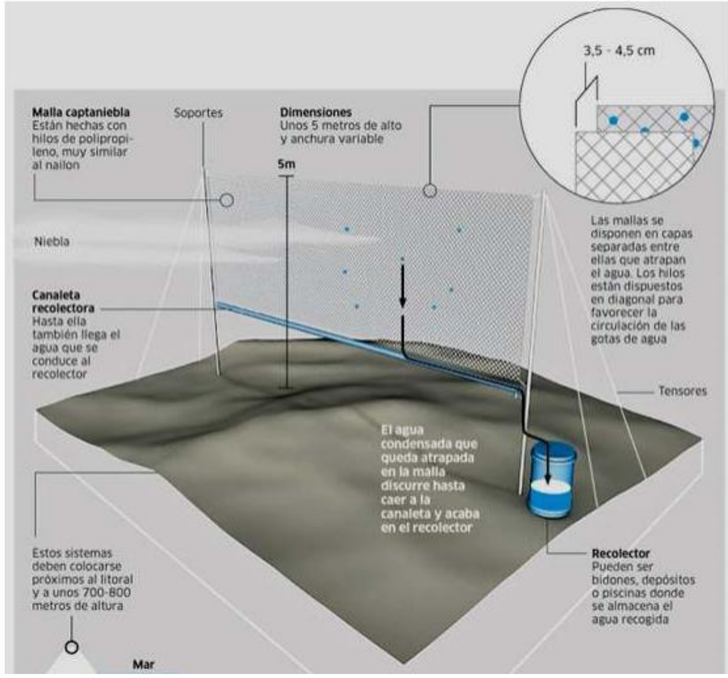


Fig. 16. Common structure for fog harvesters [28].

Type of System	Materials	Efficiency	Year of Creation	Observations
Macrodiamante Macrodiamond (First artifact developed for the catchment and harvesting of water from fog in Chile and the world by Carlos Espinosa. Patented by the UNESCO)	Tubes covered with Raschel meshes	3.9 L/m2/day	1958	It has a high efficiency and a high resistance to the force coming from wind at high wind speeds found at great heights. It has a high cost per square-meter, per amount of water captured.
Cilíndrico Cilindric (Developed by Pilar Cereceda, Horacio Larraín, Joaquin Sánchez and Nazareno Carvajal along with a group of students from the Universidad Católica, Geography Department.)	Vertical Polyethylene strings with a metal drum	4.75 L/day	1980	It has a high efficiency. It is rarely affected by high wind speeds do to its low height of 2 meters.
Bidimensional (It was implemented at El Tofo, Chile) It can work with panels of varying sizes: 48m2, 96m2 and 120m2	A pair of pillar separated at 12m between which a Raschel mesh of 4m in height is mounted with tensors and a horizontal channel is mounted to assist with water drainage and transportation.	About 3 L/m2/day	1980-1984	Easy installation, low cost system that can selfsustain itself and can be built with a wide range of construction materials. It requires very specific geographical conditions, suffers and can be easily damaged by high wind speeds and adversive climatical conditions can deteriorate its lifespan or damage the structure entirely.

Fig. 17. Types of fog collection structures commonly used [28].

Even if ancient technology has offered us a clear path on the technology and designs that are proven to be efficient in collecting water, humanity and this technology requires research to create new structures and improve this technology in order to improve it, evolve it and make it viable. As seen in figure 17, research and studies have allowed for these once primitive structures to evolve with a scientific support. This scientific support has allowed for a better understanding on what design and what factors can help make these systems more effective. Figure 18 instead allows us to understand and observe which regions have offered the best recollection data and quantities.

País	Localización	Captación promedio de agua de niebla ($l/m^2/día$)
Chile	Cerro Moreno	8,26
Chile	El Tofo	2,98
Chile	Parque Nacional del Bosque de Fray Jorge	3
Chile	Santuario de Padre Hurtado	5,4
Chile	Falda Verde	1,43
Chile	Iquique (Alto Patache)	7,81
Perú	Cerro Orara	4,6 – 5,8
Ecuador	Comunidad Pachamama Grande	4
Guatemala	Lago Atitlan	6,51
Colombia	Desierto de Guajira	1,4
República Dominicana	-	3,58
México	Chiapas	0,5
Sudáfrica	Ciudad del Cabo	14,4 (incluye lluvia)
Sudáfrica	Lepelfontein	5,3 – 5,9 (88% agua de niebla)
Sudáfrica	Soutpansberg	2 (25% agua de niebla)
Namibia	Swartbank, Klipneus, Soutrivier	0,5 -2
Islas de Cabo Verde	-	11,5
Eritrea	-	8
República de Yemen	Hajja	9,5
Nepal	-	1 (estación seca) 40 (Monzón)
Omán	-	30 (Monzón)
Croacia	-	< 27,8
España	Islas Canarias (El Gaitero)	1,8
España	Islas Canarias (Erjos)	0,2
España	Islas Canarias (Cumbres de Anaga)	4,5
España	Islas Canarias (El pulpito)	0,2
España	Islas Canarias (Parque Rural de Teno)	4,1 – 5,5
España	Alicante (El Montgó)	5,6

Fig. 18. Locations of fog harvesters and their efficiencies [33].

Despite the various array of methods by which we, humanity, have found to acquire water. Our methods are still rudimentary. However, recent efforts and the rise of new technologies are quickly changing that. Nanotechnology and others new scientific fields have begun to explain and propose solutions to problems. For the problem of water scarcity, nanotechnology and other fields are proposing very different solutions. Inspiration from nature and adapting materials to our needs.

4. Nanotechnology vs Biomimicry

"Harvesters" come in many ways, shapes, sizes and even "harvesting" capabilities. Biomimecry is a new field that imitates and tries to replicate things in nature [15,16]. We humans have always taken inspiration from nature, it is perfect in its creation and we wish to replicate its solutions. Thus, for the problem of water scarcity, people have found inspiration in the Stenocara Beetle and the Lotus Flower- organisms that have specialized covers with hydrophobic and hydrophilic properties [10-12]. Other studies have decided to focus in the creation and use of MOFs [6,29]. The duality of the surfaces that can capture and transport water in nature are unique, but efforts are made to replicate these with other materials. However, the science and method by which these surfaces manifest a behavior that has come to be defined as dew enhancement, is still unclear. MOFs, on the other hand, are peculiar engineering products for their name "Metal-Organic Framework" grants them properties of both metallic structures and elements, along with those of organic tissues or origins [6,29]. As some metals manifest ionic charges that can attract other molecules and create chemical reactions, these have begun to be used to attract and capture water molecules (which also have an ionic charge). Thus, MOFs have begun to have an increasing presence in studies related to the harvesting of water from the air. The leading group of investigators in this new technology and material group is MIT, with an increasing number of papers that focus on the application of these materials [5,6].

Traditional scientists that seek to study and comprehend our natural world have always sought to be as close to nature as possible. The Lotus Flower has been the inspiration for superhydrophobic and superhydrophobic surface properties over the last years [9-17]. Likewise, the Stenocara Beetle has become the inspiration for hybrid surfaces- a surface that has simultaneous superhydrophillic and super hydrophobic behaviors. The creation of surfaces and materials (meshes, textiles, etc) with selective capabilities are highly desired in many fields (especially medicine) [10-22,65,116]. However, a complete understanding on how the Stenocara Beetle's carapace manages to be so efficient in harvesting humidity is still an undergoing investigation. Works have analyzed the various species of Stenocara beetles for their peculiar shell composition [24]. Additionally, test regarding its water catchment and drainage abilities have also been measured [23-25,117]. Figures 19-21 show some of the results from these tests. The stenocara beetle's shell holds many mysterious on how its efficiency allows it to survive. Understanding the behavior and properties of this beetle have been extensive in that regard in order to properly assess and understand what makes his survival possible. His positioning (at a 24° angle), a mixed shell that has a wax-like coating on what serve as drainage canals, hexagonal scattered arrays of hydrophilic crests that are made of a composition similar to cement mix, and the consistent elliptical and aerodynamic shape of its shell are all pieces of the puzzle that is this small creature [23-25,117]. As more papers shed light on its geometry and composition the more outstanding its survival in the desert becomes. With the low temperature of the desert night and the wind, water condensates on its hydrophilic patches and (once the water drop is too big) it slides by its dominant hydrophobic carapace to its mouth [23-25]. Replicating this carapace into a man-made product is a goal many investigation groups are struggling for [9-12,40]. However, few (if any) have considered on the possible applications of such a surface.

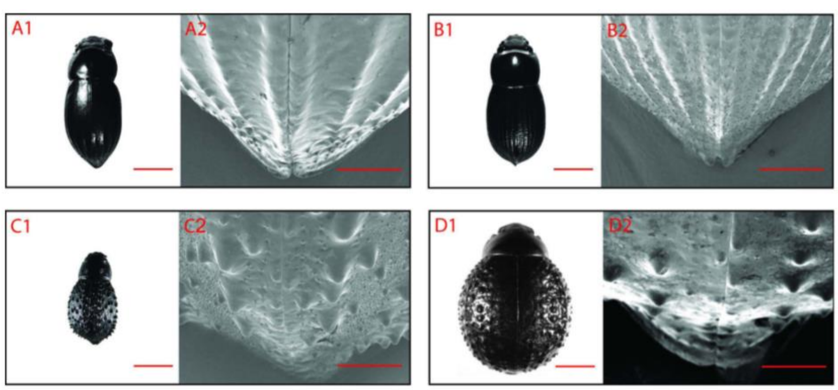


Fig. 19. A)Onymacris unguicularis, B)Onymacris laeviceps, C)Stenocara gracilipes, and D)Physasterna cribripes. A1-D1) Extended Depth Focus images of examples of the experimental animals obtained with a dissection microscope. Scale bar = 5 mm. A2-D2) Scanning Electron Microscope images of the apex of the elytra. Scale bar = 1 mm [24].

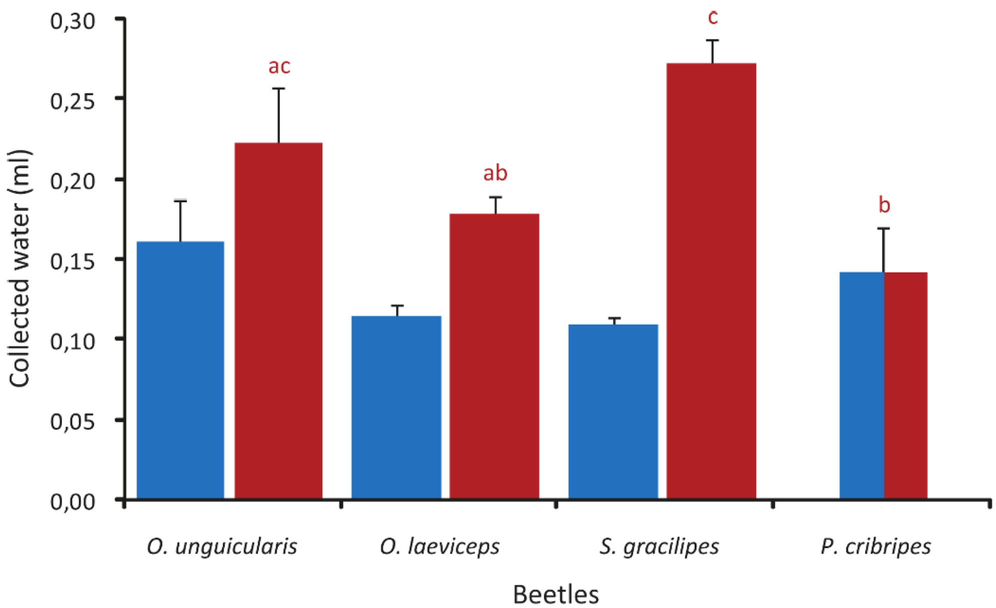


Fig. 20. Fog harvesting efficiency tests conducted over dead beetle carapaces [24].

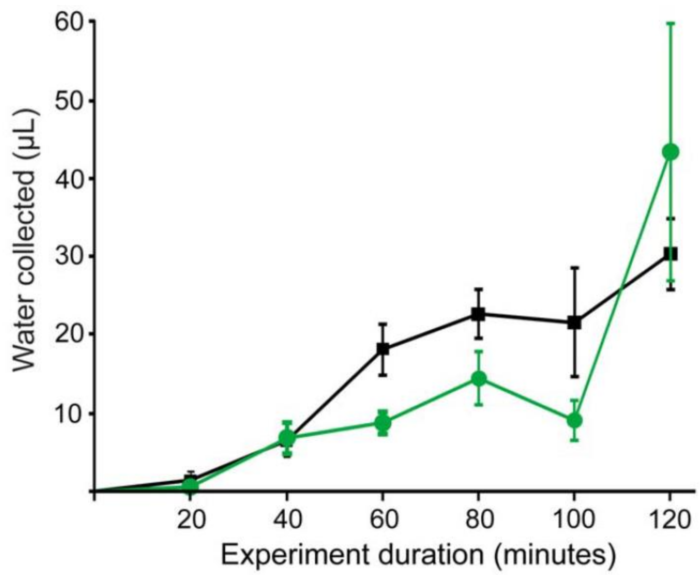


Fig. 21. Comparison on fog harvesting efficiency tests conducted over dead beetle carapaces and grass patches [117].

Metal Organics Frameworks (MOFs) are the other proposal nanotechnology places as a contender for passive technologies to harvest water. MOFs are a new material generated completely through nanotechnology. Thus, MOFs have gained a consistent method of production over time with defined and controlled variables [5,6,29]. MOFs are a technology that exploits the physical phenomenon of how porous materials can trap water [5,6,29,118]. They are a porous material made of organic components decorating metallic structures that can exhibit different properties. For water harvesting, MOFs affect the desorption and adsorption of water using only solar energy [5,6,118]. Additionally, many studies regarding MOFs has confirmed that their abilities to adsorb water cover a broad range of conditions [5,6,29,118]. However, a MOF based system to properly harvest water is a fairly new area where certain investigation groups have begun to gain interest and even to make prototypes [5,118]. Most of these function under a similar schematic: MOFs are placed as a shield facing the sun inside a container that houses a drainage system (by gravity) and a condenser (surface that is hydrophilic). During the day, the MOF adsorbs water from the air and traps it progressively in the container where it stays in a vapor phase. At night, the temperature differential is such that the condenser inside, assisted by the MOF that retains the water molecules, begins to condense water that is later transported or stored for its use [5]. This is explained and can be visually appreciated in figure 22. MOFs have been very efficient in these setups, harvesting up to 2.8L of water from 1kg of MOF at RH conditions of 20% in prototypes much like Figure 23 [5,118]. This exceeds current passive water harvesting systems that require fog, clouds or RH conditions over the 50% threshold [3,33]. However, MOFs are still struggling in their application do to the possibilities and requirements to industrialize their production as well as the dimensions required for a harvesting system. The limitations currently imposed on MOFs are the reality and costs of production, despite being efficient at condensing and harvesting water as seen in figure 24. To date, MOFs are leading in becoming the most realistic alternative as an unconventional method to harvest water [5,6,29,118].

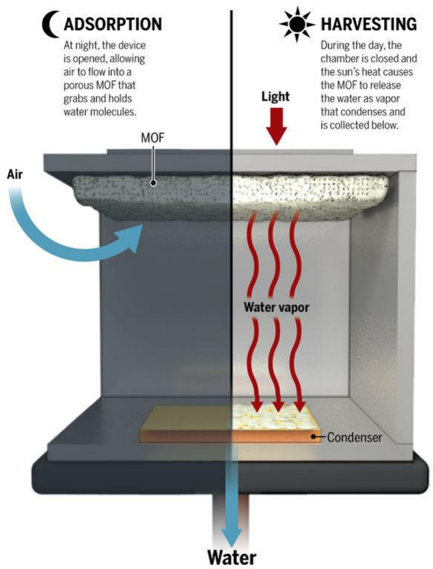


Fig. 22. Visual explanation on the process by which MOF heat condenser prototype functions [5].

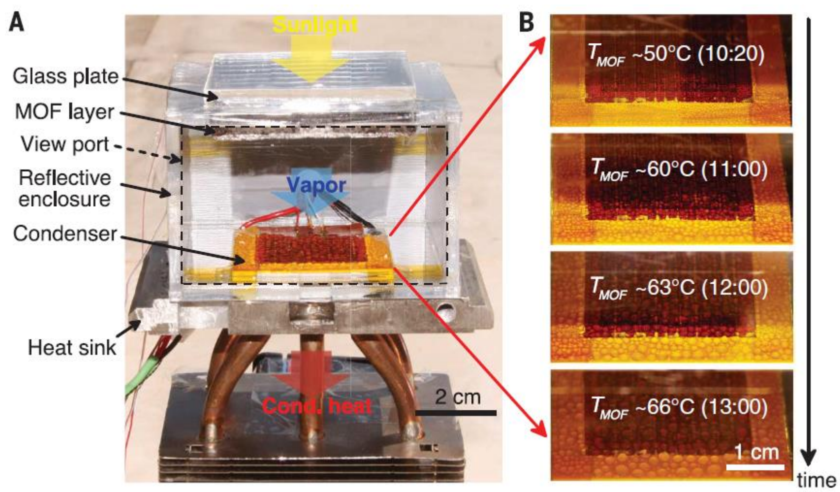


Fig. 23. (A)Image of the water harvesting prototype with its elements. (B) Time based images on the internal conditions of the system and the formation/growth of water droplets [5].

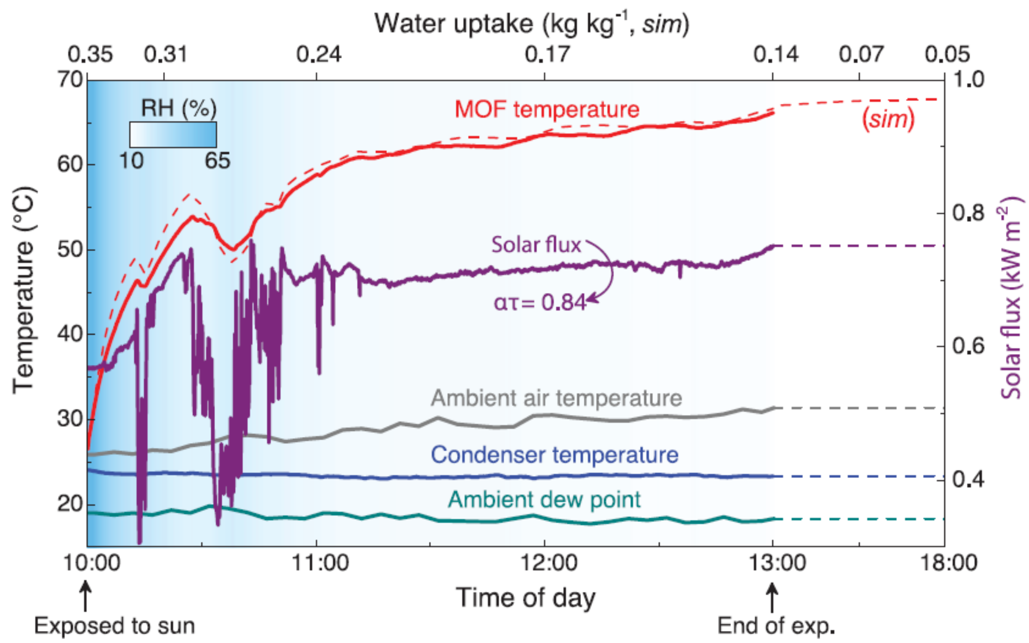


Fig. 24. Graph detailing the change in temperature of each element considered in the prototype as time passed and conditions changed [5].

Nanotechnology is a broad field, and in that sense, biomimicry has begun tread into a different path. If biomimicry has lead to dead ends, then nanotechnology has the ability to adapt and change concepts and knowledge to create different technologies with different orientations. The recycling of ideas is part of a creative process and scientific process. Water harvesting has begun to be answered in new ways that also involve passive technologies. Surface treatments or surface modifications has become a dominant and strong field, where materials (substrates) can have their topology or heriarchitecture modified by other particles in order to gain different properties from the bulk material [9-22]. Solutions such as a self-filling water bottle, or the creation of hybrid surface or materials to clean unhealthy water sources have begun to rise [9-22,41-57]. It is here, at the crossroads of the synthetic and the natural world where new proposals can rise to answer problems.

Chapter 4:

Surface Creation

Surface manipulation or alteration has been an area where nanotechnology has excelled at and contributed to immensely. With many processes and methods capable of creating and modifying the surfaces of materials (substrates) by etching, deposition and others methods, surfaces can have completely different properties [9-22,41-69]. Amongst these changes in properties, hydrophobicity and hydrophilicity have been studied extensively [9-22,41-69]. With industries such as medicine that require selectively phallic materials and other industries such as the construction industry that favor self-cleaning phobic materials, nanotechnology has been supported and used consistently [9-22,41-57].

Despite hydrophobic and hydrophilic technologies finding niche markets where they are constantly developed and researched, hybrid surfaces are different [9-16,79]. The combination of hydrophobic, superhydrophobic, hydrophilic and superhydrophilic properties (among others) simultaneously on a single surface is a relatively new concept and research area [9-22,56,57]. The main challenge is that these properties must manifest exclusively in certain locations of a surface and coexist (not inhibit the effects of the other) [9-16,79]. Additionally, depending on the desired end behavior, the design and proportions of each effect have to be optimized. Thus, research has covered ample examples, iterations and combinations of these different behaviors [9-16,79]. This type of research has also extended towards water harvesting as nanotechnology has opted to create surfaces with dew enhancing properties [9-16,79]. A synthetic counterpart to the imitation of the stenocara beetle.

Synthetic counterparts or proposals differ from biomimicry as biomimicry seeks to imitate or replicate naturally existing materials, properties, etc. Synthetic approaches seek to use the properties manifested by processed or modified materials to imitate the natural world. Though they seem similar, they are fundamentally different as one seeks to further explain and thus use nature, while the other simply seeks to replicate it by other means and/or materials. This is common as we use chemicals and other materials to create and shape our environment to meet our needs. However, replicating complex systems such as condensation require more effort and research as to what way can it be reproduced artificially.

For the sake of a hybrid surface that is inspired on the stenocara beetle, the three most crucial aspects are: the method of creating the hybrid surface, how the hybrid surface functions and with what will the hybrid surface be made. In other words, how the hybrid surface will work, how will it be made and what it will be made with [9-16,79].

1. Selection of Substrate

The selection of a substrate is crucial towards the creation of a surface for it is the virgin material or the starting point over which the surface will be created. As such, the material chosen must manifest the proper characteristics that may ensure proper adhesion and growth of a thin film as a surface treatment. Substrates that can be defined as "organic" or "earth based" are (commonly) substrates with Carbon groups and metal groups. The most distinguishable material with such properties are clays [69,86,87]. Clay is a material that has been present in human history for a long time and has been consistent in its uses and mechanical and chemical properties [86]. As technology has evolved, clay has been used in different processes and some particles of this group have begun to be used in surface treatment as well [69,86,87]. The particles known as halloysite (which is a type of clay) has demonstrated to be able to be used to treat surfaces. Paired with Octadecyltrichlorosilane (OTS), Halloysite nanotubes that are naturally hydrophilic can become hydrophobic as well. However, hardened or furnace blasted clay has not seen much progress [21,60,67].

Furnace blast clay is a common material in the construction industry as it serves as a roofing cover that is both economical and resistant [69,86,87]. Despite being a rudimentary material, it has a very standardized production process and it follows international quality and material mechanics norms such as ASTM [69,87]. Additionally, it is a material known for having great heat insulation properties. In Mexico, which is where this investigation was made, this material is easy to acquire and the company Ladrillera Mecanizada® that operates in Monterrey, Nuevo Leon (where the experiments where made) provided with the material [119]. These pieces use local clay which has a composition with Alumina Silicates, metals and hydroxides, along with other components. Additionally, the material used comes in two formats: laminated and raw. The laminated material has a treated surface which makes it ideal for exterior use since it reduces the water absorption capabilities of the material. However, for this work, the raw material was used. Despite it having a predefined geometry as seen in figure 25, the material was cut into smaller pieces.

Fig. 25. Substrate material used. A standard clay tile by Ladrillera Mecanizada [119].

2. Selection of Particles

There is a vast array of particles that are viable for creating a hydrophobic or superhydrophobic surface. Particles that can manifest hydrophilic properties are even more common and even found naturally. However, particles that can manifest both properties or that can be treated to manifest one or the other in a facile and low cost way are not common [9-22,41-69]. Additionally, for a work such as the one developed, the particles required must be compatible with the substrate. Particles that have low energy or weak adherence strength with a substrate will not be efficient in the creation of a thin film surface, or of creating a stable thin surface. Thus, the selection of particles is the most important and first step when it comes to treating or creating a surface with properties such as superhydrophobicity and superhydrophilicity [9-22,41-69].

There are different particles that may be treated to manifest either hydrophilic or hydrophobic particles [9-22,41-69]. For the present study, a particle with a facile method of treatment, as well as having adherence strength and compatibility with our substrate are essential criteria and properties. While many particles have been used over different substrates, one of the particles most commonly used and that have been studied extensively are Silicon Dioxide nanoparticles (SiO_2) [9-22,41,63-66]. These particles have been found to manifest a naturally superhydrophilic behavior and there are various methods and nanoparticles with which their behavior can be changed to be superhydrophobic [9-22,41,63-66]. Among these, one of the most facile, quick, and consistent methods is decorating or functionalizing the particles with Octadecyltrichlorosilane (OTS) [9-22]. OTS is another well studied and commonly used chemical to treat surfaces in order to give them superhydrophobic properties [9-22]. With this pairing of particles, the creation of a hybrid surface is more realistic. SiO_2 particles are known to have a broad range of affinity with materials, as observed in studies such A. B. Gurav et al [17]. This is due to the functional groups they manifest, as observed in figure 26. Additionally, the functionalization or decorating of SiO_2 particles with OTS creates a particles with a structure that looks like a furry ball, as seen in figure 27.

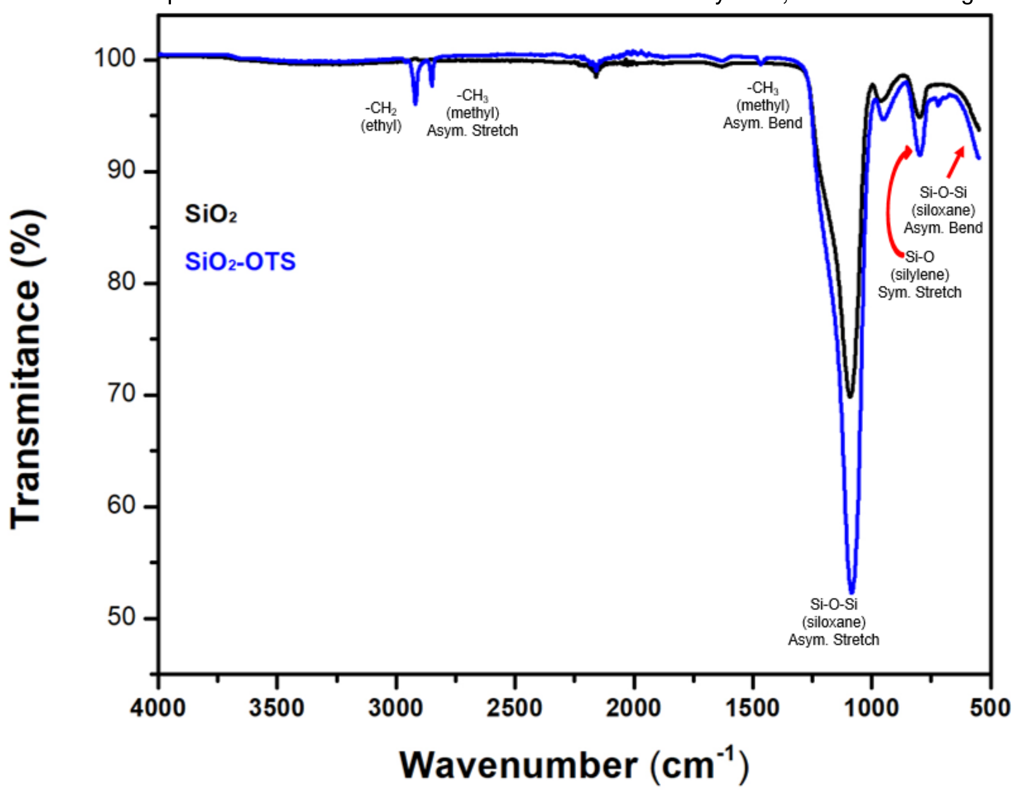


Fig. 26. FTIR analysis of SiO_2 Nanoparticles vs functionalized SiO_2-OTS particles.

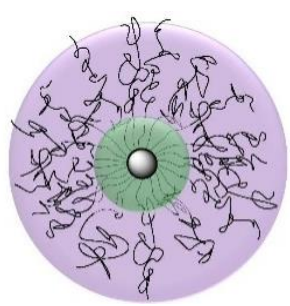


Fig. 27. Visual representation of SiO_2 particles functionalized with OTS strains to create SiO_2-OTS particles.

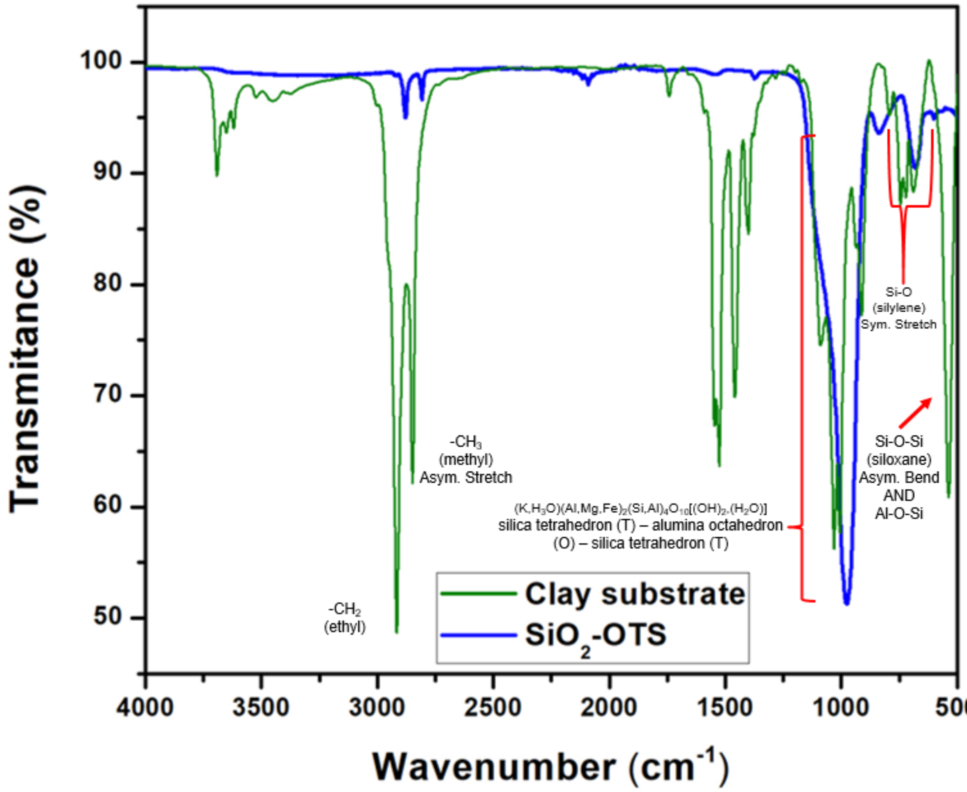


Fig. 28. FTIR analysis and comparison of functionalized SiO_2-OTS and substrate.

This sphere with spikes or "hairs" sticking from it, in figure 27, is what allows surfaces with the SiO_2-OTS particles to exhibit superhydrophobicity. Since these particles, which have been studied and used in other studies [9-22], keeps the SiO_2 particles properties and affinities it can be adhered to the same surfaces as untreated SiO_2 particles. As one can observe in figure 28, the FTIR analysis shows the energy groups of OTS and SiO_2 prior to being joined and once joined. The FTIR for our substrate, with is made of clay, can be observed in figure 29. Since SiO2, SiO_2-OTS and our clay substrate share energy groups through an FTIR analysis, these particles were chosen as the materials with which this investigation would work with. The amount of previous studies, along with the verification of these shared properties gives confidence in the ability to create a surface that can manifest hybrid properties.

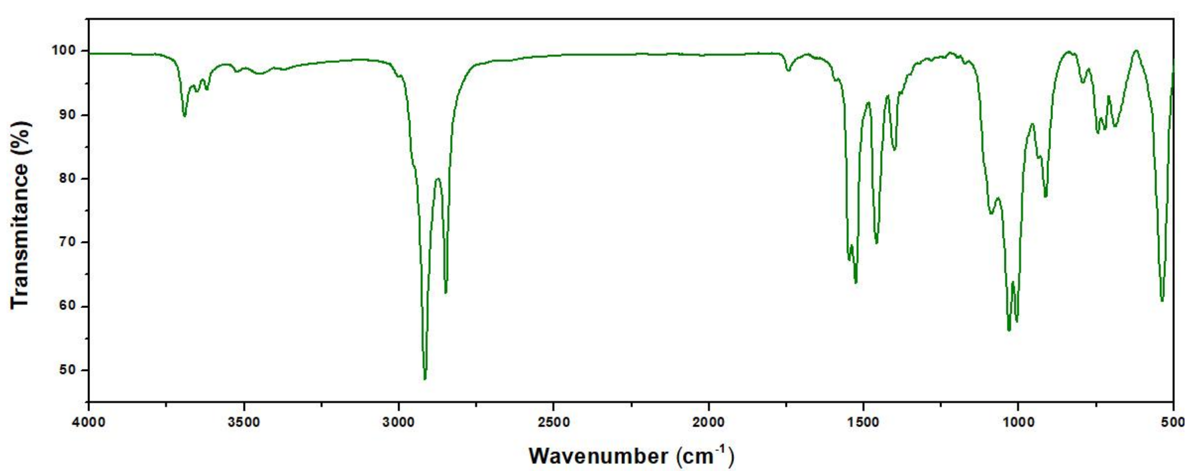


Fig. 29. FTIR analysis of substrate (clay roofing tile).

3. Composition of a Hybrid Surface

Dew enhancing properties have been identified to compose of hydrophobic and hydrophilic pairings [9-22]. These combinations tend to have the most optimal behaviors, where a hydrophobic majority surface with a pattern of small hydrophilic spots has been superior do to its capabilities to channel and drain water from the surface (making recollection easier) [9-22]. Understanding why such a combination is favorable and has a better performance over other surface treatments is crucial to create a surface with these dual properties. To understand, however, one must analyze what each type of surface characteristic is and how it can be achieved. The isolated behaviors, once understood, can then be paired with each other and the challenged of mixing and creating the surface can be faced.

3.1. Hydrophobic Properties

Technology is essential for the manipulation of particles and their properties. Studies have used a wide range of alternatives from physical to chemical to achieve materials and surface treatments that manifest hydrophobicity [9-22,41-69]. It is assumed that the mean by which particles are manipulated to manifest this property affects heavily on the efficiency with which the material or product manifest it [9-22,41-69]. However, there is no consistent nor standardized mean by which this property can be achieved as different particles and materials behave differently under circumstances and stimulation. Electrospinning, electrospray, chemical treatment, fusion, and many other alternatives have been used in studies to achieve their goals [9-22,41-69]. With such liberty, results are subject to experimentation through trial and error.

Artificial superhydrophobic surfaces have been prepared using various strategies including the generation of rough surfaces first and then modification with low surface energy molecules or roughening the surface of hydrophobic materials and creating well-ordered structures using micromachining and etching [43,45,120-124]. The creation of such surfaces and the degree of their contact angles has varied both on the particles used on the surface and the methods with which these particles are deposited or adhered. It is well known that the water contact angle (CA) (θ), $\theta<90^\circ$ and $\theta>90$ can indicate surface 'hydrophilicity' or 'hydrophobicity,' respectively, and when it is above 145 °, the word 'superhydrophobic' is sometimes used. Nature exhibits this phenomenon in 'lotus leaf effect' to harness the roll-off action for self-cleaning of leaves which has been attributed to a combined micro and nanoscale morphology of its surface [124–127]. Hydrophobic surfaces present the distinct behavior of preventing water molecules from adhering to the surface and "moving" or sliding off at low angles by gravity. However, hydrophobicity is an attribute that other elements or structures can manifest. This allows for many industries to use this behavior to separate water molecules from other molecules they wish. However, treating or giving this property to polymers or other particles has been a growing field of interest.

Recently, treatments by chemical and physical means in which particles are adhered to a surface have been common, but treating particles directly on an existing surface by altering their nanostructure has become more common. These are the most common alternatives by which hydrophobicity can be achieved as it's not a common characteristic or behavior among materials [9-22]. Out of both, chemical and physical creation or treatment of materials is the most common and frequently used do to the ease with which technology can allow us to manipulate particles. Altering the nanostructure of a surface is more complicated and less frequently used as it implies a greater degree of difficulty and results are not consistent. The nature of the materials itself influence heavily on the hydrophobicity, regardless of its nanostructure of particles. Thus, using chemical reactions or physical means to deposit particles with hydrophobic properties is more common. However, certain particles have manifested hydrophobic properties when decorated with other particles. This new development in the manipulation of particles and their properties has opened new opportunities for polymers and even “philic” molecules- such as SiO_2.

3.2. Hydrophilic Properties

Hydrophilic characteristics in materials is a common and natural behavior many particles and materials manifest. Organic compounds and certain other molecules present in the reality of our world are attracted to water or seek to absorb and retain as much of oxygen and hydrogen based molecules as possible. As such, hydrophilic properties are neither a mystery nor a rare occurrence. Natural fibers along with various plants and animals have molecules that are proficient at capturing water molecules [12]. As such, hydrophilic properties have only recently become an interest as their replication or creation on alternative materials such as polymers, metals or organic (earth based) materials.

New fields and industries are seeking to increase their efficiency by finding ways and alternatives with which they can capture water molecules for various industrial processes. However, this requires for hydrophilic properties to manifest in non-organic materials and to be compatible with the processes used. Special treatments or the complete manipulation of particles is required for such properties to manifest. Technology and methods previously mentioned (electrospray, force spinning, etc.) have also been integrated towards the creation of these materials [9-22,41-69]. By manipulating particles or joining new particles to these, nanostructures can be created where materials can now manifest these hydrophilic properties.

The manifestation of these properties are not so simple, especially over non-conventional surfaces or surfaces that have already gone through a surface treatment. For example, hydrophilic properties sought on a surface that has undergone a hydrophobicity treatment. As such, particles can only be deposited in a certain state and these will have to be later removed by other chemical means or a different method. Silicone Dioxide is problematic as its molecular structure is very defined and its hydrophilic nature is a well-documented characteristic [63-66].

3.3. Hybrid Surfaces

Inspiration from nature has led to the artificial replication of surfaces that manifest dewenhancing properties. However, achieving such a behavior has just recently been attributed to the combination of both hydrophobic and hydrophillic properties on the surfaces or on different elements that compromise a mechanism or assembly. These specialized adaptations on certain plants and animals like the stenocara beetle are the main source of inspiration for the creation of a hybrid surfaces. When its wings come into contact with humid air, water vapor condenses on the hydrophilic spots [13,25]. However, some specialized adaptations are more complex than others. The simplest and most appealing, which has led to various studies in recent years, is the Stenocara Beetle’s carapace which manifests dewenhancing capabilities efficiently.

A random array of smooth hydrophilic bumps present on the Stenocara beetle’s back (approximately 10 μm in size) [12,40] are hydrophilic regions surrounded by waxy areas. The hydrophilic areas are arranged in a hexagonal array [40]. Water collection onto the nonwaxy hydrophilic regions occurs by the beetle tilting its back wings into the fog and dew present in the wind direction. Any humidity incident upon the waxy hydrophobic regions is blown along the surface until it reaches a nonwaxy hydrophilic region. The droplets grow until they cover the entire hydrophilic bump, and then, under their own weight, they detach and roll downward into the beetle’s mouth. This naturally occurring microcondensation surface has been successfully mimicked in the laboratories [11,12,23-25]. As such, the scope of this study follows an already defined area of interest.

Studies that have successfully created hybrid surfaces mention “patterned surfaces” do further explain the appearance of the surfaces created [9-12]. Patterns commonly refer to arrays of bumps or protruding segments on the surface that follow a defined form and separations [9-12]. However, previous works have sued circular and square surface shapes for their arrays or “patterns” [9-12]. This work differs from these as it does not follow the common geometry used. Studies on the stenocara beetle have analyzed the creature's peculiar and “tailor-made” carapace to further understand the nature of its capabilities. The work of Guadarrama-Cetina et al. [40] was of particular interest for this work as it focused on an overlooked detail of the beetle's shell. As seen in figure 30-32, it is mentioned that the shell has a defined hexagonal shaped geometry where hydrophilic peaks rise. It is mentioned that these peaks allow for the microcondensation of droplets and these move water towards the hydrophobic, waxy surface of the rest of the shell that acts as “channels” to drain the water. As such, the present study proposed to work with a surface that closely resembles this feature and that a hexagonal geometry be used [40].

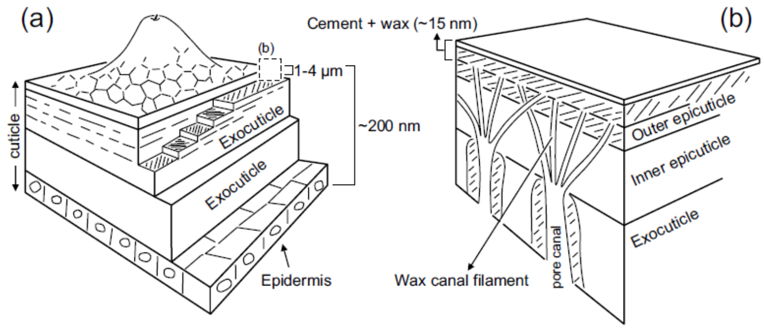


Fig. 30. Sketches of the stenocara carapace structure (a) General Cross-sectional view (b) Details of exocuticle and epicuticle [40].

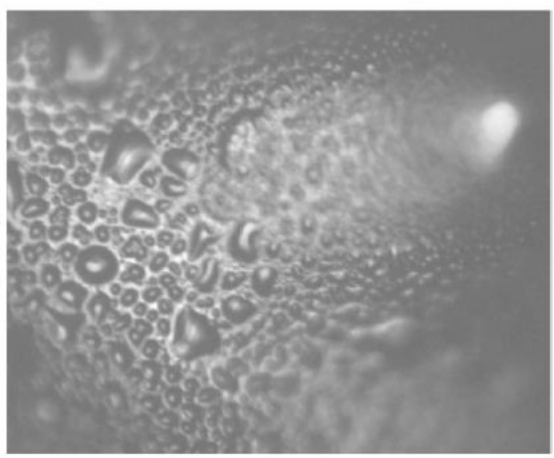


Fig. 31. Photograph depicting the localization and droplet growth locations on stenocara beetle carapaces [40].

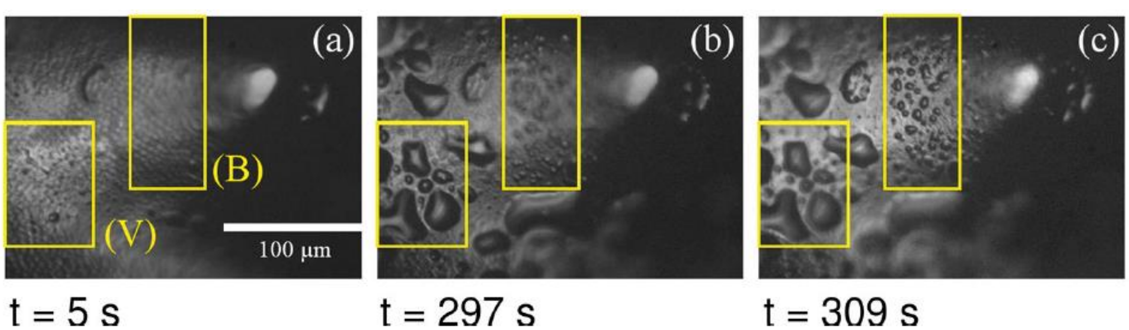


Fig. 32. Measurements of surface coverage by droplets of water between valleys and bumps of the stenocara beetle carapace [40].

Silicon Dioxide particles (SiO_2) treated with OTS (SiO_2-OTS) are to be adhered onto a solid surface by a method of particle deposition that ensures surface adherance. The particles seek to create a homogeneous hydrophobic or superhydrophobic surface by a combination of particle architecture and particle properties. However, to manifest the duality of behavior, the surface coated by SiO_2-OTS will undergo a second deposition to create hydrophilic patches or segments that will replicate the stenocara beetle's back behavior.

Chapter 5:

Simulations

The basis of research and science is to offer a robust and well documented work on observations, new ideas, new materials and anything and everything which tries to answer a question or offer a solution to a problem of our world and reality. However, this is easier said than done. As we have delved further into the mysteries of our universe and technology has allowed us to expand our capabilities and knowledge research has begun to require more specialized equipment, materials and environments. As such, science and research on a physical and experimental level have, thus, become expensive.

Much like the fields of medicine and biology, it has become too costly at a monetary, material and resource level to support and allow any and all physical trials of a hypothesis. It is here where the marvel of the digital world and computer science, which have grown exponentially in recent years. With computer sciences allowing computers to have more memory, computational power, become more compact and accessible, researchers have begun to migrate to these flexible and adaptable platforms to create their environments and experiments in a digital world. A world which has become a collaborative effort where companies and researches are constantly creating and improving environments (programs) that may imitate our real world [112-115].

With the digital world at hand and a wide range of platforms to choose from, one must define the limits, variables and conditions desired and from which to obtain data. Regardless of the advances of technology, it is still not possible to accurately represent and imitate the real world in a digital environment. As such, we must choose and create the specific experimental environment. We must design our experiments.

This means, there is a process with which we can ensure that our controlled and “fictional” environment is properly simulating the reality we wish to analyze. And everything starts with some research.

In this day and age, we are faced with a diverse selection of programs and platforms over which we can create simulations of our experiments in a digital and controlled environment. The most popular and recognized of these programs are: COMSOL Multiphysics, ANSYS, Siemens NX, MATLAB and Simio [112-115]. These programs have been constantly used in many research papers regarding the simulation of materials, fluids, aerospace, electrical systems and other similar physical and chemical reactions. However, not every program is adequate or accessible for every type of experiment or conditions to be considered. Such was the case for the current paper.

1. Defining the Simulation

Before one can decide on the program to run the simulation and acquire initial data, one must first understand and define the experiment conditions, environment and variables. As such, for the current paper, the first step was to understand the limits of the computer generated digital environment and what type of simulation could be run. As the main focus of this research is the generation of a hybrid hydrophobic/hydrophilic surface with a unique topology with dew-enhancing properties the variables and conditions had to be broken down. The most important aspect was the environment itself as dew-enhancing is the ability to micro-condensate water particles in the air. However, micro condensation or condensation is an ample subject with different theoretical approaches as mentioned in Chapter 2. Besides this, materials or the definition of material properties is an important aspect of this research. It is not necessary to delve into the mechanical, physical and chemical properties of a material, but a crucial aspect of condensation is the ability of materials to retain or dissipate heat, surface topology and other physical properties. As mentioned in previous chapters, the particles and substrate chosen were such do to an analysis of their physical properties and the affinity they have between each other and with water molecules. And finally, another variable or element relevant to our simulation are dimensions. Dimensions considered are millimeter and micrometers, thus a program capable to use these dimensions is favorable and required. However, there are more than just the individual variables that are required to mesh.

The overlap between the digital and the real world is always a difficult one. The digital world can't completely represent the real world and all of its "mechanisms". However, we can create different digital worlds that are more precise in imitating certain scenarios and behaviors in the real world. Regarding our specific scenario of "condensation of vapor or fog in the air" we need to assume and consider certain variables and conditions. For condensation, the equations mentioned in Chapter 2 considered were those that focused on the exchange of energy between water particles in the air and those in contact with the surface. Additionally, equations that focused on the convection of the surface, the growth of water droplets on the surface and those related to coalescence, surface tension and contact angles were also considered. Additionally, with an increase in interest in simulation of water condensation, water droplet growth and the impact of surface topology on water behavior in papers as Dupuis and Yeomans "Mesoscopic Modelling of Droplets on Topologically Patterned Substrates" programs that can employ Lattice Boltzman equations and Navier-Stokes Equations are attractive as well [95,96].

However, after defining the ideal program and consideration with which to simulate the possible experiments, the search of a platform that could fulfill most of or all of these desired parameters began.

2. Selecting the Simulation Platform (Software Program)

After some research, the programs available were ANSYS, COMSOL Multiphysics and MATLAB [112-115]. Considering the timeframe window for this thesis, MATLAB was discarded as it required a manual creation of the code that would calculate and simulate the experiment. The degree of difficulty and amount of time that would be invested in this labor was excessive. ANSYS and COMSOL are specialized and recognized programs for simulating a wide range of scenarios. From Microfluidics to phase change and Dual/Multi-Phase conditions [112,113]. However, ANSYS had the inconvenience of requiring a robust computer (hardware) to calculate and generate the simulation required. Additionally, ANSYS is a very open platform where the definition and modification of the equations was to be done manually [113]. Additionally, the generation of the data to analyze and compare different scenarios required a manual process as well. While ANSYS was a viable option, the INSTITUTO TECNOLOGICO DE ESTUDIOS SUPERIORES DE MONTERREY, where this thesis was developed, had a COMSOL Multiphysics license for use.

COMSOL MULTIPHYSICS is perhaps the most known and "go-to" option for simulations as it is a very friendly, robust and complete platform where many scenarios can be simulated. COMSOL works with packets or "equation banks" where certain equations are stored and considered and these can later be fine-tuned according to the simulation required and that one wishes to define [112]. However, it was not flawless. COMSOL proved to be a complex platform and the scenario and consideration to be made for my simulation on its platform required me to separate the simulation into different sections. These sections dissected the data and parameters into specific environments where the program would calculate and iterate results based on the variables declared and avoiding interference of "excess" data or data considered "irrelevant" according to the equations in the respective package and scenario selected (2D, 3D, one phase, Dual/Multi-Phase, etc). As the packages were examined in the licenses available, the package required for the simulation of a Multi-Phase environment of condensation and fluid mechanics was not present. Additionally, the computational power recommended for this simulation was not available. Hence, the simulation had to be analyzed once more and stripped further to use simpler, shorter simulation.

To explain the incident and importance of the definition of the simulation in a more colloquial way; the simulation desired and ideal would be to be able to set a piece with the proposed surface design in an open atmosphere where wind, humidity, temperature, solar time and the respective materials can be introduced and the simulation set to run for a full cycle of 24 hours. ANSYS allows for such a simulation, except that the water vapor and air would be a heterogeneous mixture in a confined space and the presence of the sun and it's cycle with time would not be considered or even be able to manifest. COMSOL, on the other hand, could simulate such an ideal scenario except for the influence of the solar cycle and time. As such, the simulation had to be simplified further. But not until the program SOLIDWORKS was used as a starting point.

SOLIDWORKS is a simulation platform that is very helpful for the analysis and understanding of systems, mechanical pieces and other physical elements that are subject to forces. As such, SOLIDWORKS allowed for such an ideal simulation to be established- except for its equation package that lacked a lot of the desired considerations. SOLIDWORKS's focus is on mechanical properties, material properties and similar, thus its equations for condensation or the representation of fluid mechanics is lacking [114]. There is little to no interaction between air and surfaces beyond simple exertion of force. Convection and condensation can be calculated but the package responsible for this tracks particles in a generalized form and does not take into consideration the equations responsible for drop growth, surface tension nor fluid mechanics themselves. However, as the simulation demonstrated, the computational requirements for such a desired simulation are excessive and the computer used collapsed and was damaged. Thus, the simulation had to be simplified further.

While defining the simulation to be used, an adequate and accessible simulation program was researched. While there is a preference for certain programs, it was decided to look freely on the internet for any other option that could be viable. The program Autodesk CFD came up among the search options. Autodesk CFD is a program specifically designed by AUTODESK for computational fluid dynamics and thermal analysis. Although fairly new, it has a sturdy equation package for both thermal analysis and fluid mechanics and the equations that bridge and correlate these with material properties [115]. Autodesk CFD became the flagship for the simulation I desired to generate and from which to acquire data previous to my physical experiments. And, knowing that the simulation ideally established was a stretch, the new and more simple simulations played and fit into the

Autodesk CFD program. But, the program is not a perfect environment as its equation packages work and can cover a broad range of scenarios and consideration do to certain pre-established conditions in its code.

3. AUTODESK CFD for Surface Micro-condensation

Autodesk CFD is the simulation oriented platform by Autodesk that focuses on the analysis of product behaviors and performance regarding to fluid flow mechanics and thermal conditions [115]. However, the program is not limited to simple interpretation of data and equations as the program (in its 2019 version) houses equations packages of partial differential equations that govern the flow, heat transfer, and associated constitutive terms. Being more specific, Autodesk CFD houses equations for:

- General fluid flow and heat transfer
- Turbulent flow
- Moist gas and humidity calculations
- Joule Heating
- Quick forced convection
- Compact thermal models
- General scalar transport equations
- Cavitation
- Rotating Devices
- Moving solids
- Particles Tracing
- Material and element properties
- PCB Property calculator
- Heat exchanger material device governing equations
- Erosion
- Free surface behavior equations [115]

Of these packages, General fluid flow, heat transfer, moist gas, humidity, general scalar transport and particle tracing are key for our simulation.

As mentioned in Chapter 2, there are many ways by which one can interpret, analyzes and calculate condensation. Mathematical models are very diverse and are adaptive tools. However, there is yet to be a single mathematical model to properly explain and simulate the condensation of water over a surface and (even more so) on a surface with topologies that grant hydrophobic and hydrophilic properties.

CFD uses a very efficient and elegant array of differential equations that mix and match to properly simulate most of the conditions and phenomenon desired in our simulations [115]. The equations of the program that were specifically used and that aided in acquiring the data desired to us were oriented towards fluid behavior and dynamics. As such, CFD covers a base and a series of equation packages to properly analyze a scenario with the appropriate equations.

3.1. Conduction, Convection, Radiation and Mixed

To begin, CFD uses three methods to calculate how heat is transferred [115]. In conduction, heat is transferred via molecular motion. The heat transfer rate is dependent upon the thermal conductivity. Convection heat transfer refers to heat being transported by fluid motion. Radiation heat transfer is an electromagnetic phenomena which is dependent upon the optical conditions of the radiating media. Conjugate heat transfer refers to the combination of 2 or all 3 of these modes of heat transfer. Thus, the initial base of the physical knowledge used by the program for our case defines the quality of the data acquired [115].

For the scenarios developed and analyzed, radiation and conduction are not a priority and the equations used to regard these are more generalized instead of properly analyzing their behavior. Since this work focused on dew-enhancing/condensation properties it is this effect that must be analyzed. Convection plays a crucial aspect in this as it is the behavior and interaction that fluid motion has with sources of heat or differences in these.

3.2. Natural, Mixed and Forced Convection

In natural convection, fluid motion is generated or at least dominated by temperature differences which affect the fluid properties, most notably the density. These flows are also referred to as buoyant-driven flows because the gravity term or buoyancy term in the momentum equations dominates the flow. Conversely, in forced convection flows, the temperature is dominated by the fluid motion and buoyancy or gravity has little or no effect. Mixed convection is a combination of these two, where fluid motion and buoyancy may both play a role. Natural convection frequently has no openings or no clearly defined inlets. Forced convection always has inlet region(s) and outlet region(s), as does mixed convection. Free convection is an un-enclosed or open natural convection problem. Do to the nature of our scenarios and the intended simulations we worked primarily with simultaneous mixed and free convection. Forced convection was not used or considered since we did not create scenarios where convection would be forced to happen. Additionally, free convection is an idealistic explanation towards the considerations maybe in a CFD simulation environment. Most simulation platforms require and demand defined and clear environments with finite dimensions in order to run and process data [112-115]. However, boundary conditions and certain variable definition are defined in a way in CFD where a partial free convection environment is created [115].

Thus, the CFD equations for convection are of vital importance. CFD considers a different approach with dealing with convection. Parting from the Boussinesq equations, CFD opts for low Mach number assumptions to decompose the pressure variables [115], thus, using the equation:

$$p = P_{ref} + \rho_{\infty} g_i x_i + \rho^* (\text{Eq. } 11).$$

Where:

Variable	Description
P_{ref}	Constant pressure specific heat
ρ_{∞}	gravitational acceleration in respective direction
g_i	enthalpy
x_i	thermal conductivity

Table 11. Definition of variables.

However, in CFD convection problems may be laminar or turbulent and, thus, the criterion used varies according to the type of convection used. However, the equations used in our scenarios are based and rely on the natural convection considerations. These use Grashof number as the parting point [115].

$$Gr = \frac{\beta g L^3 \Delta T}{v^2} (\text{Eq. } 12).$$

However, if CFD calculations struggle with this parameter it also opts for Rayleigh's number and Prandtl number as alternatives [115].

$$Pr = \frac{C_P \mu}{k} \text{ (Eq. 13.1).}$$

$$Ra = \frac{\beta g \rho^2 C_P L^3 \Delta T}{\mu k} \text{ (Eq. 13.2).}$$

Where:

Variable	Description
C_P	Constant pressure specific heat
μ	Absolute viscosity
ρ	density
k	thermal conductivity

Table 12. Definition of variables.

These equations interact with another base of physical concepts that are essential for the simulations done.

3.3. Film Coefficients

These concepts regard the behavior of fluids when these are considered as a thin film. In these cases, fluids do not hold all of their "bulk" properties. As such, special considerations must be made as how these bodies interact with other interphases, surfaces, etc. CFD calculates film coefficients (convection) in one of two ways [115]. The first way is to calculate the heat transfer residual. The heat transfer residual is calculated by forming the energy equation and substituting the last temperature (or enthalpy values) solution into the formed equations [115]. Thus, the heat transfer residual is:

$$h = \frac{q_{residual}}{\Delta T} \text{ (Eq. 14).}$$

Where the temperature differential is the one between the wall of the film and a near wall value (which must be predetermined). The second method CFD uses is to use an empirical correlation based on the Reynolds number [115]. To do this, CFD calculates Nusselt number.

$$Nu = \frac{hL}{k} \qquad \text{(Eq. 15).}$$

Where:

Variable	Description
h	Film coefficient
L	Length of surface
k	Termal conductivity

Table 13. Definition of variables.

Since the Nusselt number is a ratio of convective to conductive heat transfer the correlation that is used by CFD modifies this equation internally into an expression that ties into the expressions for film coefficients [115]:

$$Nu = CRe^a Pr^b \text{(Eq. 16)}.$$

There is a singularity, however, on how Nusselt and Reinolds are calculated in CFD. CFD considers and recognizes that Reinolds and Nusselt are dependent on a length and are dependent on dimensions [115]. However, it differentiates Nusselt and Reinolds to the degree that, even in the correlation where Reinolds number is used to calculate Nusselt number, these are different with different lengths [115].

3.4. General Fluid and Heat Transfer

The governing equations for fluid flow and heat transfer are the Navier-Stokes or momentum equations and the First Law of Thermodynamics or energy equation defined as [115]:

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} + \frac{\partial \rho w}{\partial z} = 0 \quad \text{(Eq. 17.1)}.$$

For the continuity equation. Which can be further expanded to:

$$\rho\frac{\partial u}{\partial t} + \rho u\frac{\partial u}{\partial x} + \rho v\frac{\partial u}{\partial y} + \rho w\frac{\partial u}{\partial z} \text{(Eq. 17.2)}.$$

$$= \rho g_x - \frac{\partial \rho}{\partial x} + \frac{\partial}{\partial x}\left[2\mu\frac{\partial u}{\partial x}\right] + \frac{\partial}{\partial y}\left[\mu\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)\right] + \frac{\partial}{\partial z}\left[\mu\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right)\right] + S_\omega + S_{DR} \text{(Eq. 17.3)}.$$

For the X-Momentum Equation and similarly for the Y-Momentum Equation:

$$\rho\frac{\partial v}{\partial t} + \rho u\frac{\partial v}{\partial x} + \rho v\frac{\partial v}{\partial y} + \rho w\frac{\partial v}{\partial z} \text{(Eq. 18.1)}.$$

$$= \rho g_y - \frac{\partial \rho}{\partial y} + \frac{\partial}{\partial x}\left[\mu\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right)\right] + \frac{\partial}{\partial y}\left[2\mu\frac{\partial v}{\partial y}\right] + \frac{\partial}{\partial z}\left[\mu\left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right)\right] + S_\omega + S_{DR} \text{(Eq. 18.2)}.$$

And, the Z-Momentum Equation.

$$\rho\frac{\partial w}{\partial t} + \rho u\frac{\partial w}{\partial x} + \rho v\frac{\partial w}{\partial y} + \rho w\frac{\partial w}{\partial z} \text{(Eq. 19.1)}.$$

$$= \rho g_z - \frac{\partial \rho}{\partial z} + \frac{\partial}{\partial x}\left[\mu\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right)\right] + \frac{\partial}{\partial y}\left[\mu\left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right)\right] + \frac{\partial}{\partial z}\left[2\mu\frac{\partial w}{\partial z}\right] + S_\omega + S_{DR} \text{(Eq. 19.2)}.$$

It is noted that the two source terms $S\omega$ and S_{DR} are for rotating coordinates and distributed resistances. Thus, CFD takes the equation for these as [115]:

$$S_\omega = -2\rho\omega_i \times V_i - \rho\omega_i \times \omega_i \times r_i \text{(Eq. 20)}.$$

$$S_{DR} = -\left(K_i + \frac{f}{D_H}\right)\frac{\rho {V_i}^2}{2} - C\mu V_i \text{(Eq. 21)}.$$

Where "i" refers to the global coordinate direction (u, v, w momentum equation).

3.5. Enthalpy and Energy Equations

Additionally, CFD uses an equation package for enthalpy. This is of great importance because energy change and energy equations are excellent towards explaining the behavior of particles between different phases. In other words, energy equations are the foundation for multi-phase flow calculations and behavior [115]. Thus, it is both a surprise and great aid that the program uses the following equation for precisely these type of simulations (multi-phase flow)- the basis of the simulations to be done.

$$\rho\frac{\partial h}{\partial t}+\rho u\frac{\partial h}{\partial x}+\rho v\frac{\partial h}{\partial y}+\rho w\frac{\partial h}{\partial z}=\frac{\partial}{\partial x}\left[k\frac{\partial T}{\partial x}\right]+\frac{\partial}{\partial y}\left[k\frac{\partial T}{\partial y}\right]+\frac{\partial}{\partial z}\left[k\frac{\partial T}{\partial z}\right]+q_V\,(\text{Eq. }22).$$

However, do to the computational demand of these equations and considerations, CFD makes a change in its multi-phase calculations. A temperature based formulation is used for moist gas flows with a special treatment of the specific heat to account for the phase change. Thus, CFD considers that for steam/water flows, the enthalpy is the energy of both the vapor and liquid phases. And, further into this criteria, for compressible flow, the energy equation is written in terms of total temperature [115].

$$\rho C_p\left(\frac{\partial T_0}{\partial t}\right)+\rho C_p V_i\left(\frac{\partial T_0}{\partial X_i}\right)=\frac{\partial}{\partial X_i}\left[k\frac{\partial T_0}{\partial X_i}\right]+q_V+\mu V_i\left[\frac{\partial^2 V_i}{\partial X_j \partial X_j}+\frac{\partial}{\partial X_i}\frac{\partial V_j}{\partial X_j}\right]+\frac{1}{2C_p}\frac{\partial}{\partial X_j}\left[k\frac{\partial}{\partial X_j}\left(V_j V_j\right)\right]+\Phi\quad(\text{Eq. }23).$$

Φ is the dissipation function and CFD uses Einstein tensor notation for the total energy. However, the last three terms are only considered in compressible flows. And the general variables considered are the ones on Table 14 [115].

Variable	Description
C_p	Constant pressure specific heat
gx,gy,gz	gravitational acceleration in respective direction
h	enthalpy
k	thermal conductivity
p	pressure
q_V	Volumetric heat source
T	temperature
t	time (sec)
u	velocity component in "x" direction (length/sec)
v	velocity component in "y" direction (length/sec)
w	velocity component in "z" direction (length/sec)
μ	viscosity
ρ	density

Table 14. Definition of variables.

As previously mentioned in the equations, CFD uses a temperature based formulation for moist gas flows. However, when humidity and moisture calculations are involved, the equations change once again as CFD considers the previously mentioned equations with a variable specific heat [115].

$$\rho\frac{\partial C_pT}{\partial t}+\rho u\frac{\partial C_pT}{\partial x}+\rho v\frac{\partial C_pT}{\partial y}+\rho w\frac{\partial C_pT}{\partial z}$$

$$=\frac{\partial}{\partial x}\left[k\frac{\partial T}{\partial x}\right]+\frac{\partial}{\partial y}\left[k\frac{\partial T}{\partial y}\right]+\frac{\partial}{\partial z}\left[k\frac{\partial T}{\partial z}\right]+q_V(Eq.24).$$

3.6. Moisture and Humidity

Additionally, CFD uses a separate equation to track the moisture in a fluid. This is the reason why the humidity equation package differs from the previous equation package that uses energy equations. CFD uses an additional partial differential equation to solve for a scalar quantity which represents the mass fraction of the moisture (in either liquid or vapor phases) [115].

$$\rho\frac{\partial f}{\partial t}+\rho u\frac{\partial f}{\partial x}+\rho v\frac{\partial f}{\partial y}+\rho w\frac{\partial f}{\partial z}=\frac{\partial}{\partial x}\left[D\frac{\partial f}{\partial x}\right]+\frac{\partial}{\partial y}\left[D\frac{\partial f}{\partial y}\right]+\frac{\partial}{\partial z}\left[D\frac{\partial f}{\partial z}\right]\quad \text{(Eq. 25)}.$$

CFD takes the solution of these two equations and supports itself with the steam tables (for example from M. D. Koretsky, "Engineering and Chemical Thermodynamics", John Wiley & Sons, 2004 [128]) to calculate the quality (vapor fraction) of the moisture [115]. With the quality and the mass fraction of the moisture, the mass or mixture fraction of the condensed water is calculated. However, once again, due to the computational demand of these equations, CFD simplifies some of its criteria. The properties of the moist fluid are calculated assuming a homogenous mixture [115]. Thus, the equation is simplified immensely to:

$$\rho=(1-f)\rho_{air}+f\rho_{moisture}\text{(Eq. 26)}.$$

The equation package for particles traces is a very useful tool in CFD and any simulation program or platform. It allows to track and acquire data of a "single particles" as it moves and changes in the environment it is placed in. This equation package uses Langrangian equations in CFD, but does not differ between massless particles, particles with a user defined mass or particles with negligible mass [115]. As such, the generalized Lagrangian equation used is:

$$\frac{dx_P}{dt}=v\quad \text{(Eq. 27)}.$$

Where the variable x_P is the particle's position vector and v is the local particle velocity. However, since massless and mass defined particles do not behave the same way, CFD uses an additional set of equations to accurately simulate their behavior. Newton's Second Law is used to acquire the velocity for these particles with mass [115]:

$$m_P\frac{dv_P}{dt}=F_D+F_b\quad \text{(Eq. 28)}.$$

The variables considered are explained in Table 2. CFD does expand the necessary equations [115].

Variable	Description
m_P	Particle mass
v_P	Particle velocity
F_b	Bouyant force
F_D	Drag Force

Table 15. Definition of variables.

So:

$$F_D = \frac{1}{2}\rho_f A_P (v_f - v_P)|v_f - v_P| C_D \quad \text{(Eq. 29)}.$$

$$F_b = m_P g \quad \text{(Eq. 30)}.$$

Where:

Variable	Description
ρ_f	Fluid density
A_P	Particle area. User input of particle radius
v_f, v_P	Fluid and particle velocity vector
C_D	Drag Coefficient

Table 16. Definition of variables.

Where:

$$C_D = \frac{24}{Re}(a + bRe^c) \text{(Eq. 31.1)}.$$

$$Re = \frac{\rho_f |v_f - v_P| 2R_P}{\mu_f} \text{(Eq. 31.2)}.$$

Variable	Description
Re	Reinolds Number
R_P	Particle radius
μ_f	Fluid viscosity

Table 17. Definition of variables.

3.7. Scalar Transport Equations and Scalar Values

Now, the Scalar transport equation package is a rather complex one to understand and which was not required to its complete extent in our simulations. However, it was required since our simulations required information on the scalar values for water particles. This is considered a passive scalar and an incompressible fluid in CFD, thus, it is governed by the equation [115]:

$$\frac{\partial f}{\partial t} + u\frac{\partial f}{\partial x} + v\frac{\partial f}{\partial y} + w\frac{\partial f}{\partial z} = \frac{\partial}{\partial x}\left[D\frac{\partial f}{\partial x}\right] + \frac{\partial}{\partial y}\left[D\frac{\partial f}{\partial y}\right] + \frac{\partial}{\partial z}\left[D\frac{\partial f}{\partial z}\right] \text{(Eq. 32)}.$$

Where:

Variable	Description
D	diffusivity (length^2/sec)
f	passive scalar
t	time (sec)
u	velocity component in "x" direction (length/sec)
v	velocity component in "y" direction (length/sec)
w	velocity component in "z" direction (length/sec)

Table 18. Definition of variables.

This was really the only equation used for our simulation. However, there is an important part of the scalar equation package that was crucial in our simulations. Defining the Boundary Conditions. CFD takes into account 6 types of boundaries for which conditions must be imposed on the scalar equation: inlets, outlets, no-slip walls, symmetry lines, slip walls and periodic boundaries [115]. For inlets, the value of the scalar should be specified, even if the value is zero. At outlets, symmetry lines, slip and no-slip walls the scalar equation uses a natural boundary condition of a zero gradient normal to the boundary. At periodic boundaries, the scalar at one boundary is enforced or translated to the corresponding point on the other periodic boundary. Thus, the proper behavior of the scalar values can be tracked and represented by the program.

It is with these equation packages that Autodesk CFD was chosen to be the simulation platform. It offered robust and quick methods by which complex scenarios and conditions could be simulated regarding multi-phase fluid flow and behavior. Although it simplified some equations for the sake of computational resource demand, it still uses proper criteria and equations to produce results that are accurate to reality. Additionally, it had compatibility with the environment and material designs done in SOLIDWORKS making the process of running simulations faster [114,115]. Simulations began with confidence.

4. Simulated Scenarios

The scenarios simulated were simplified versions of our ideal scenario. This was due to the computational demand that such an initial simulation required. From this starting point, simpler simulations were established, targeting specific objectives. Additionally, the simulations were separated into groups- each focused on offering information regarding a more general objective or hypothesis. Using the platform of Autodesk CFD, we were able to set these scenarios accordingly.

The first group of scenarios were focused on providing information and data on whether the intended proposal for the surface topology was an acceptable and offered some kind of improvement over the more conventional proposals. As mentioned in previous chapters (mention cual despues) the conventional surface topologies used by researchers are either square shaped or circular/elliptical. This is believed to be because these basic shaped are easier to produce as a topology against the proposed hexagonal design. However, since paper such as (mention) have shown that the Namibia dessert beetle has these topologies, and this creature is the inspiration for many biomimicked dew-enhancing surfaces, this research considered that such a specific design is not because of chance nor casualty. Besides, the creation of masks in order to properly create films in specific designs and locations is a technology that is now commonly used and that has many options on how to do so. Thus, we initially created 3 surfaces of 20 x 20 cm in size and 1cm in height with their corresponding protruding designs by 1cm, as seen in figure 33.

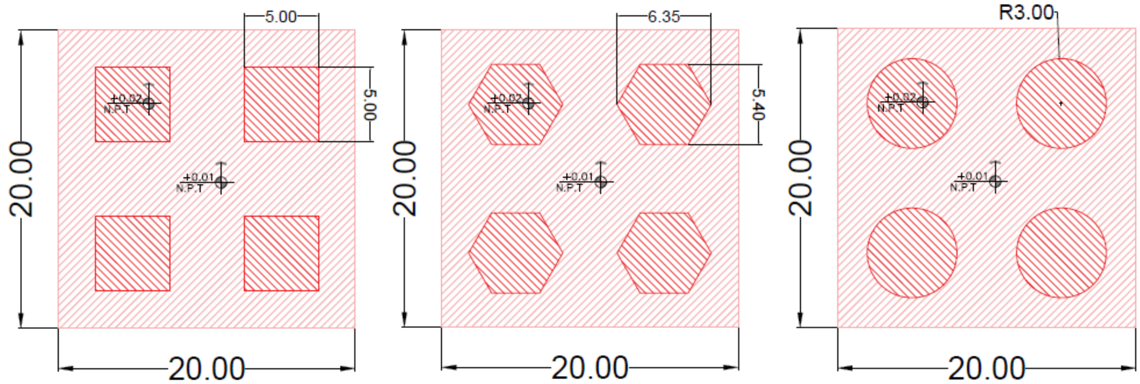


Fig. 33. Dimensions and Design for surface topologies tested in simulations.

These pieces were enclosed (an CFD requirement) in a space of 120cm x 80cm x 80cm. Essentially, this enclosure was to be able to mimic both an atmosphere and the physical experimental environment we designed were our pieces would be enclosed in a container of similar proportions. The pieces were identified as square, circle and hexagon, according to the morphology of the topology designed and consisted of an array of 4 pieces of these on the surface, as seen in figure 33. Additionally, all pieces were placed flat at the bottom of the enclosed space. According to how the CFD program works. The enclosed space in which the pieces were encased would be defined as the medium while the pieces themselves would be identified as the materials or pieces.

The second group of scenarios were focused on providing information and data on whether there is a significant difference on the dew-enhancing efficiency of the surface topology between a protruding morphology or a concave morphology between the hydrophobic and hydrophilic segments. The difference between these (numerically speaking) is a positive height differential at a micrometer scale and a negative height differential at a micrometer scale. Since the height is so small it may not cause a significant difference. However, if it did cause a difference then more information on the efficiency of the dew-enhancing properties of these hybrid surfaces can be acquired. This is important as papers as (mention which) have created different surface topologies where some have favored concave hydrophilic areas, others concave hydrophobic areas and others protruding hydrophilic areas. Additionally, this is important because it would help define the process by which the hybrid surface can be produced. Thus, 2 surfaces were created of 20 x 20 cm in size and 20 micrometers in height. One of the pieces had the protruding hexagonal design (our proposed surface geometry) with a height of 10 micrometers. The other piece had a concave hexagonal design with a depth of 10 micrometers. Figure 34 shows this simulated environment.

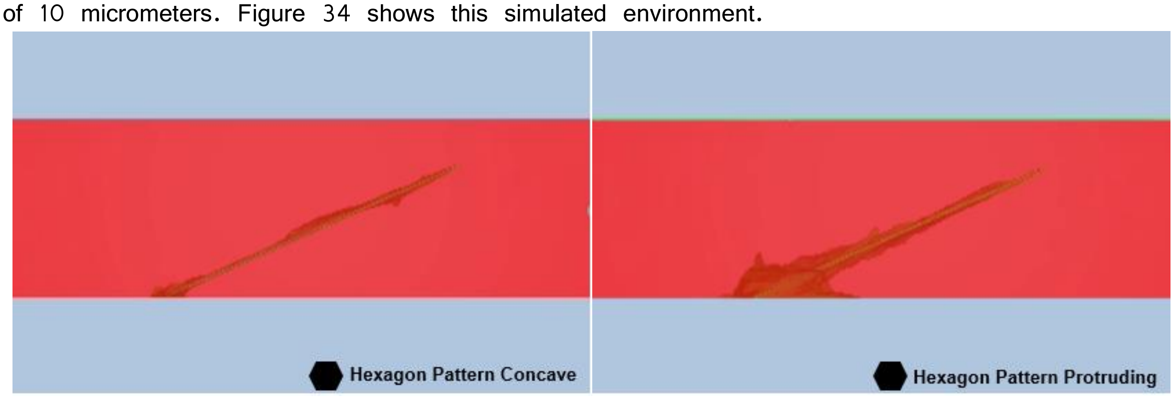


Fig. 34. Preparation of simulations between concave and protruding topology set at a 24° angle.

These pieces were enclosed in a space of 120cm x 80cm x 80cm. The pieces had a surface design and morphology much like the previous group of simulations except that both designs had a hexagonal geometry, but one was protruding and the other concave. Additionally, all pieces were placed at a 24° angle, which is the functional angle at which the stenocara beetle places itself to optimize its dew enhancing capabilities and it is an angle similar to the one at which rooftops are placed to allow water trickling. This can be appreciated in figure 34. The enclosed space in which the pieces were encased would be defined as the medium while the pieces themselves would be identified as the materials or pieces.

Inside the CFD program, the medium was defined as moist air, set at an ambient temperature of 30°C, with 50% Relative Humidity, at 1 atm. of barometric pressure and thermal conductivity and dissipation values and considered that it is capable of change over time (variable). The material for the geometry was established as dried Clay-Brick. However, more conditions were established according to the scenario developed. These were defined as follows in tables 19-21 and figures 35-37:

Table 19. Definition of conditions for simulation scenario 1.

Scenario 1: Wind Current	
BC	Inlet (S) and Outlet (N) with wind at 8m/s
BC	Wind Outlet defined as Pressure 0
IC	Temperature 30°C, 50% RH
C0	Surface at 25°C
Mat.	Clay Roofing Tile
Mat.	Moist Air Medium

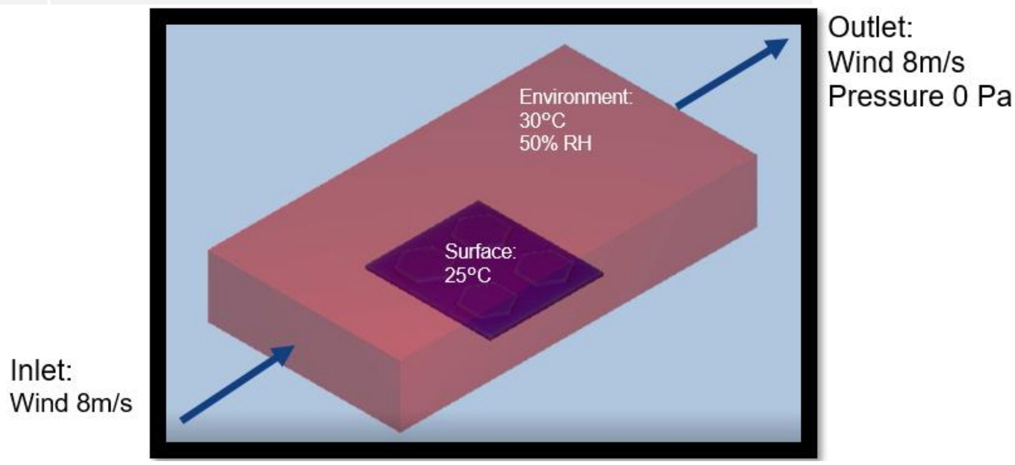


Fig. 35. Visual representation of defined environment for scenario 1.

Table 20. Definition of conditions for simulation scenario 2.

Scenario 2: No Wind	
BC	All laterals of medium space are Outlets
BC	Outlets defined as Pressure 0
IC	Temperature 30°C, 50% RH
C0	Surface at 25°C
Mat.	Clay Roofing Tile
Mat.	Moist Air Medium

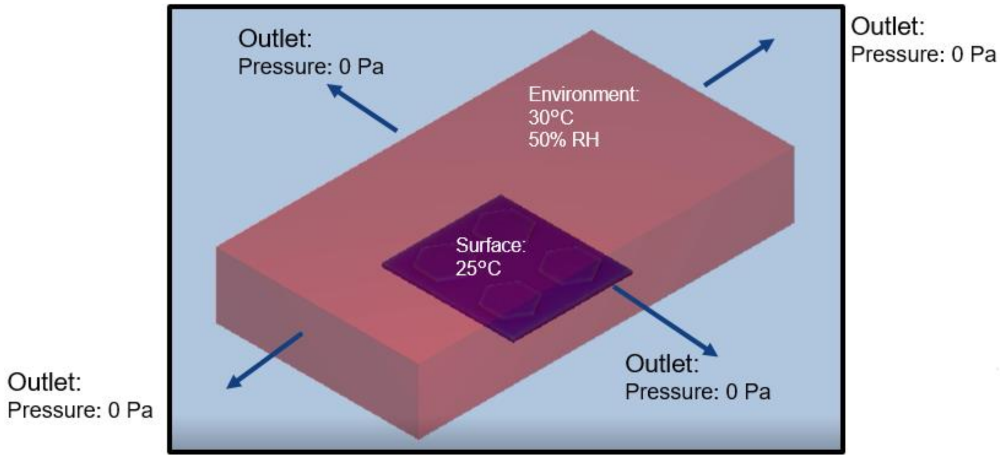


Fig. 36. Visual representation of defined environment for scenario 2.

Table 21. Definition of conditions for simulation scenario 3.

Scenario 3: Realistic	
BC	All laterals of medium space are Outlets
BC	Outlets defined as Pressure 0
BC	Surface defined as Hydrophobic with 5μm roughness
BC	Hexagons defined as Hydrophilic with 0μm roughness
IC	Temperature 30°C, 50% RH
CO	Surface at 28°C
Mat.	Clay Roofing Tile Substrate
Mat.	Hydrophobic Silica Glass
Mat.	Hydrophilic Alumina

Fig. 37. Visual representation of defined environment for scenario 3 .

The values and variables for which the simulations were run were primarily: Temperature, Scalar Value, Relative Humidity, Temperature, Percent Liquid and corresponding constitutive and continuity variables. Simulations were run as transient (changing in time) tracking and considering the time variable. CFD considers this as an unitless time variable and uses only internal interactions and output iterations. It was established that the simulations would run for 500 output iterations with 2 internal saved outputs. This means that each simulation ran for a total of 1000 iterations. More iterations are possible but require more time in generating results unless the computational resources are increased. For this thesis, 1000 iterations took a time of 20 hours. Increasing the amount of iterations would cause for longer calculation time and possible problems to the computer used. Additionally, CFD demands the use of resources continuously while it runs simulations and if these simulations were to be stopped by software malfunction, hardware malfunction, the computer turning off, resetting or having other programs or users demand computational resources would cause the calculations to take longer or become corrupted and losing all of the data in it.

5. Data and Models

CFD uses different methods, models and tools by which information and data can be extracted from the simulations. While all simulations run were saved and used as animations and videos, what each of these is presenting and how to interpret it is crucial. For our objectives, 1 method, 2 models and 3 tools were used to acquire data [115]. The method, although simple, was by time-lapse measurements, where data could be tracked and presented to us according to its value or condition at that point in time. The models used were 3-D particle mapping and 2-D surfaces [115]. The 3D models were used in 2 of the 3 tools. One tool allows us to work with the complete volume and reality of the simulation were all the data of the specific variable (previously mentioned) we desired to analyze would be presented. The other tool is called "Volume Analysis" where CFD track and creates a "body" of the array of values that exist in our defined volume of the desired variable we wish to analyze. This shows us the behavior of the variable as a moving and solid free-surface body. The last tool which is simply the 2-D surface analysis allows us to take infinitely small planar cuts of the volume with our material where we can analyze and observe how the desired variable data behaves. These work as figures 38 and 39 show.

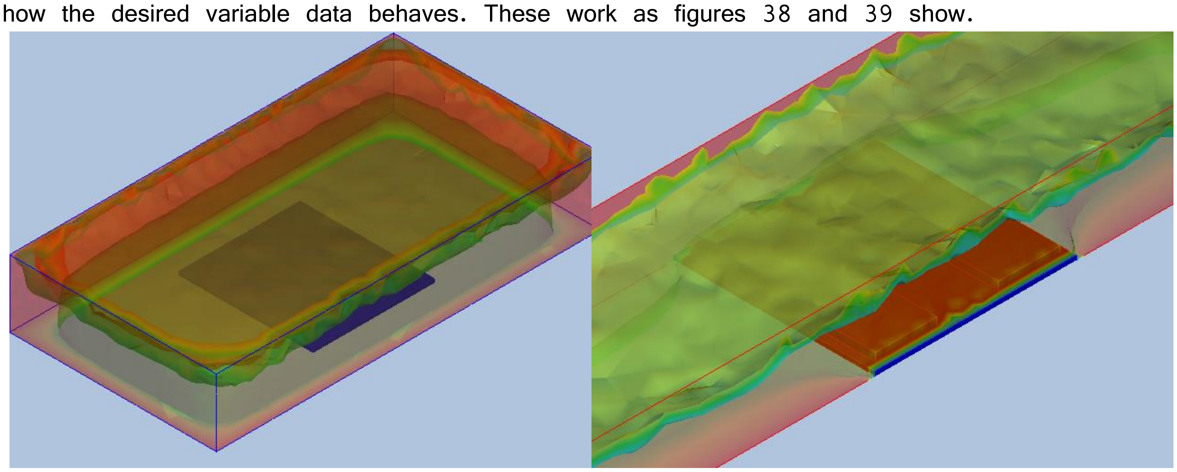


Fig. 38. Visual representation of the volume tool to analyze data offered by CFD program [115].

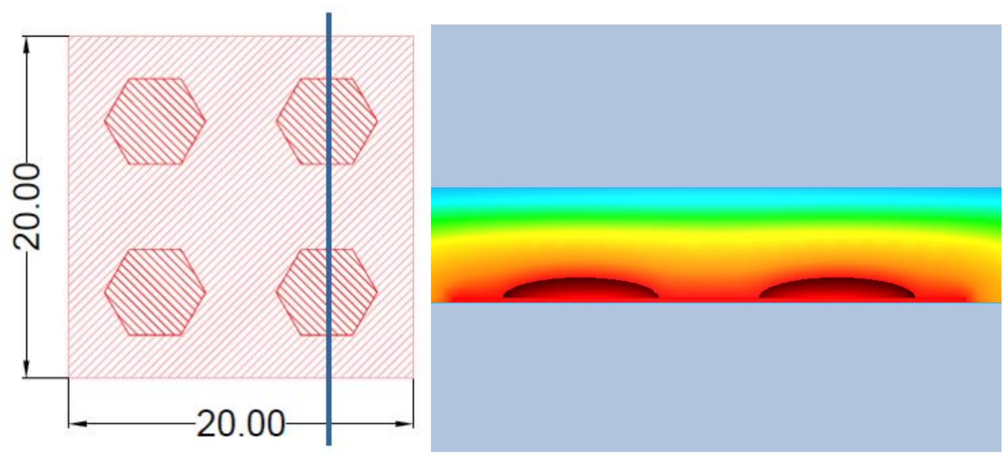


Fig. 39. Visual representation of the 2D surface tool to analyze data offered by CFD program [115].

It is with the aid of these tools that our results and their analysis was possible. CFD was, consistently, a useful platform.

Chapter 6:

Methodology

Simulations are assets by which we can glimpse at certain conditions and results of a particular situation. It is a vision of a future and reality. In that sense, to make such a future a reality then experimentations must be made in order to confirm this possible vision. However, prior to experiments for this work, the material or surface over which we will experiment and obtain data must be created.

Defining the creation of a hybrid surface is a series of processes that are composed of various steps of preparation. For the current work, understanding and basing ourselves on previous works allowed to define a proper methodology [9-18,79]. The order followed will be explained in detail as there were consideration made and conditions established in order to create all the surfaces for experimentation.

For this work, various pieces with different conditions were created. This was done so in order to verify data, hypothesis and to acquire as much data possible once experimentations began. Regarding the creation of the surface, the different segments of its creation had different set of conditions in order to find the most efficient surface that could be created. Each will be explained thoroughly.

Understanding the creation and process for a hybrid surface, then a process can be established to create it. Similar to previous studies as mentioned before [9-18,79], the creation of a hybrid surface will be done through the interaction and adhesion of SiO_2-OTS particles to a clay substrate over which SiO_2 hydrophilic particles will be adhered to create the localized surface geometry.

1. Particle Deposition

Silicon Dioxide particles (SiO_2) treated with OTS (SiO_2-OTS) are to be adhered onto a solid surface by a method of particle deposition that ensures surface adherance. The particles seek to create a homogeneous hydrophobic or superhydrophobic surface by a combination of particle architecture and particle properties. However, to manifest the duality of behavior, the surface coated by SiO_2-OTS will undergo a second deposition to create hydrophilic patches or segments that will replicate the stenocara beetle's back behavior. The second deposition will be assisted by a mask that will ensure that the hydrophilic SiO_2 particles deposit or adhere in the specific desired locations. The creation and use of a mask will be discussed later.

Common methods used for the deposition of particles are: Crop coating (Drop Casting), Dip Coating and Spray Coating [9-18]. Out of these, Drop coating was chosen as the methodology to use. Dip Coating requires too much material for each deposition and generates (thus) too much waste. Additionally, Dip Coating does not offer control over the rate at which the surface is created nor of the concentration of particles adhering. Spray Coating was not used as the equipment necessary for proper deposition and control of the rate of deposition was not available. Drop coating can be done by using micropipettes that come in a wide range of capacities. For the creation of the surface of this research, two micropippetes were used. One micropipette was used at a capacity of 500μL and a second one was used with a capacity of 10μL. The micropippete with greater capacity was used to create the superhydrophobic surface. The smaller micropippetes was used to create the hidrophillic hexagonal arrays over the hydrophobic surface. In this method, we were able to have control over the rate of deposition.

2. Particle Functionalization

The method used for the functionalization or "decoration" of SiO_2 particles with OTS particles followed a well-defined sequence that was used similarly in other papers [9-18,79]. OTS was used in a liquid state and it was mixed with Toluene in SiO_2 particles were mixed at a concentration of 1.5g of OTS for every 40g of Toluene. To this mixture SiO_2 particles are mixed in at a concentration of 2g. The mixture was placed under a sonic tip at 35% amplitude, 42kHz for 3 minutes in order to mix the different particles together and have an adequate dispersion. This mixture is later left at ambient temperature for 1 hour. The mixture is placed in a ceramic melting pot which has a parchment on its base to serve as a base. The base will serve as a base where the particles will deposit. This mixture is later placed in a furnace at 100°C for three (3) hours. The temperature and time are in order to evaporate all the liquid chemical components of the OTS and the Toluene. Upon extraction, what is left is a clump of fine powder that are the functionalized SiO_2 particles with OTS (SiO_2-OTS).

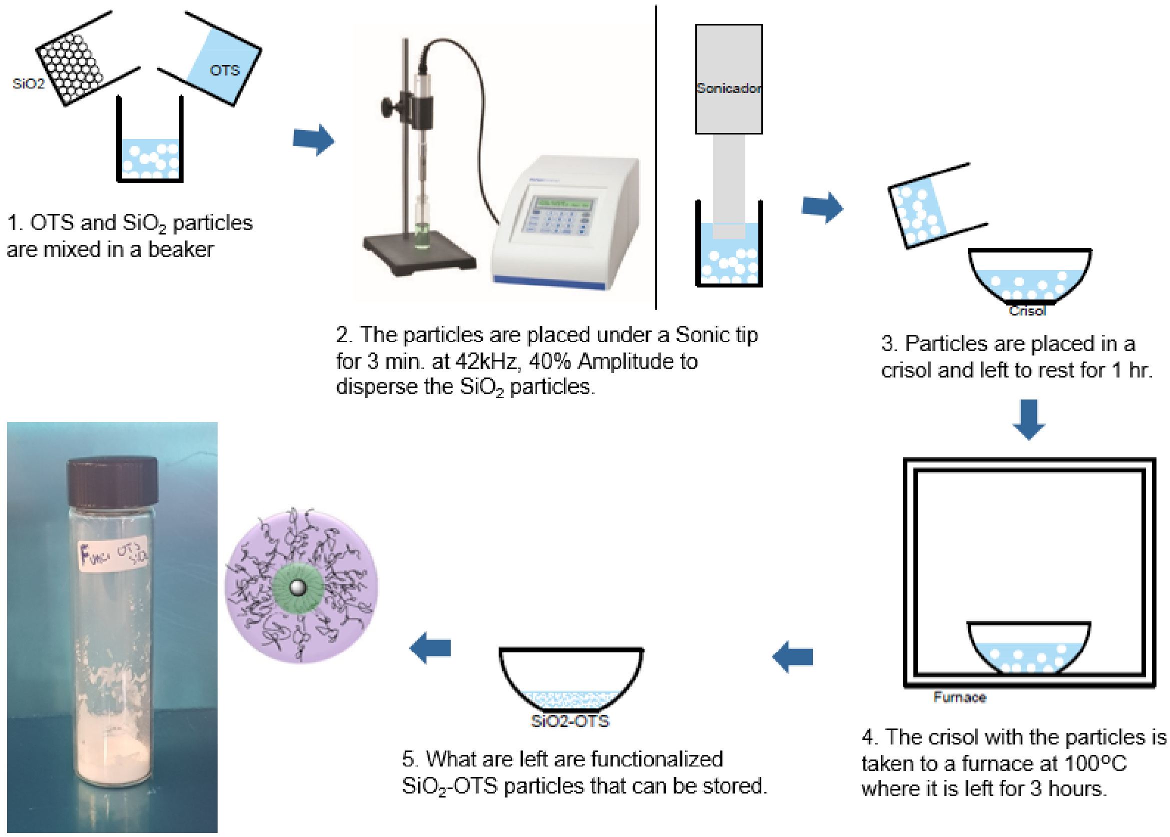


Fig. 40. Visual representation of the process by which SiO_2 particles were treated an functionalized with OTS.

3. Hydrophobic Surface

The hydrophobic surface created was created by also commonly known methods used in other studies [9-18,79]. The method used was Drop Coating, as mentioned previously. However, in order to create the surface we need to prepare the substrate. The preparation of the substrate required it to be cut into pieces of 2.50cm by 3.00cm (2.5 x 3 cm) and placing each piece in a furnace for 4 hours at 100°C. This is done in order to evaporate all water from the substrate and ensure a dry surface. The pieces are left at room temperature for 8 hours once extracted in order to allow them to cool down. This way, the particles will not be influenced by residual temperature. Once the substrate is prepared, the creation of the hydrophobic surface can be made. However, the particles must be prepared as well in a stable medium before being deposited.

SiO_2-OTS particles are used to create the hydrophobic surface. The particles are mixed with Toluene at a 5% concentration and are placed in a sonic bath to ensure proper dispersion. As toluene was originally used in the functionalization of the particles, it is a medium in which the particles can properly disperse but not dissolve or bond. This allows for a stable medium we can work with. The ultrasonic bath was used for 30minutes after which the glass beaker in which the mixture was placed is removed. Using a micropippete with a 500µL capacity we begin to deposit the mixture with dispersed SiO_2-OTS particles over the substrate. 500µL cover the surface of the substrate completely and each 500µL are considered a layer. A total of 12 substrates are prepared and divided into 2 groups of 6 each. One group was dried at ambient temperature and another group was dried in a furnace at 80°C for 5minutes after each layer was deposited. The drying in furnace was done in order to evaporate the most amount of toluene in between layers, raising the energy levels of the particles and making them gain more adhesion strength both to the substrate and with the next layer. Thus, each group has 6 pieces as different layers of depositions were used. Depositions were done in 1 layers, 2 layers, 3 layers, 5 layers, 8 layers and 10 layers. In between each layer the corresponding drying process was used for 5 minutes. After the last layer, the pieces were all placed in a furnace for 1 hour at 80°C in order to allow the evaporation of the toluene from the surface.

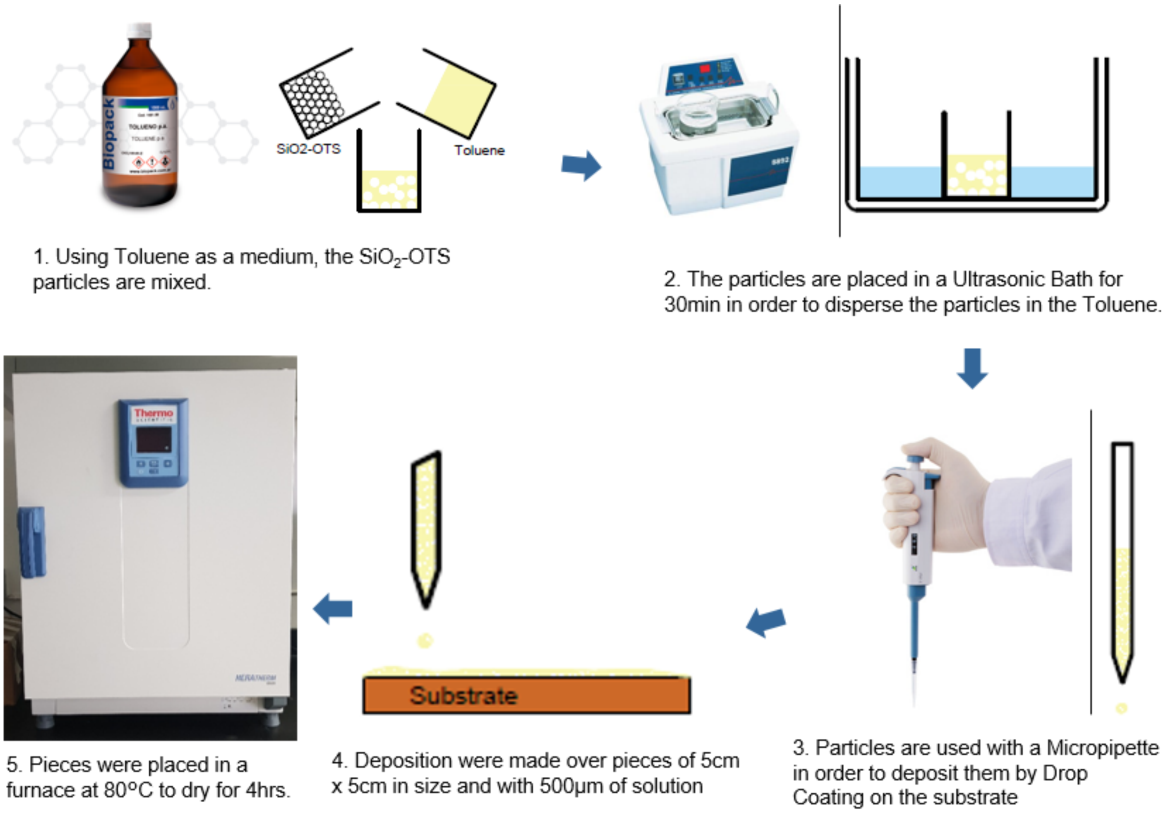


Fig. 41. Visual representation of the process by which SiO_2-OTS particles are deposited over our substrate and the creation of each layer is achieved.

4. Creation of a Mask

Other studies have created hybrid surfaces by using methods that range from deposition of particles over a surface to etching [9-18,79]. Do to the particles we chose (SiO_2), the method that was most appropriate to create the hybrid surface was to deposit our other (hydrophilic) particles over our already hydrophobic surface. Being both particles similar (SiO_2 and SiO_2-OTS), the method that would prevent damage to the original surface while still allowing adequate deposition and adherence was by using a mask. The mask is a concept in which the particles to be deposited would be identified as "painting" particles and an additional layer would be placed between the existing surface and the "painting" particles. Figure 42 shows the process that other studies have used that exemplifies accurately the use of a mask. The mask is a layer made of a material that will not damage the existing surface and will separate the new "painting" particles from the majority of the surface. This mask has a design where there are slits or "holes" where the "painting" particles will deposit over the intended surface. For this work, the mask created had a hexagonal geometry array. Each hexagon was 0.5cm in width and height and each had a separation between each other of 1.5cm. The mask created was 1mm in thickness and the material used was Chavat Industrial Modelling Clay ®. The design for this mask was the same as in figure 43.

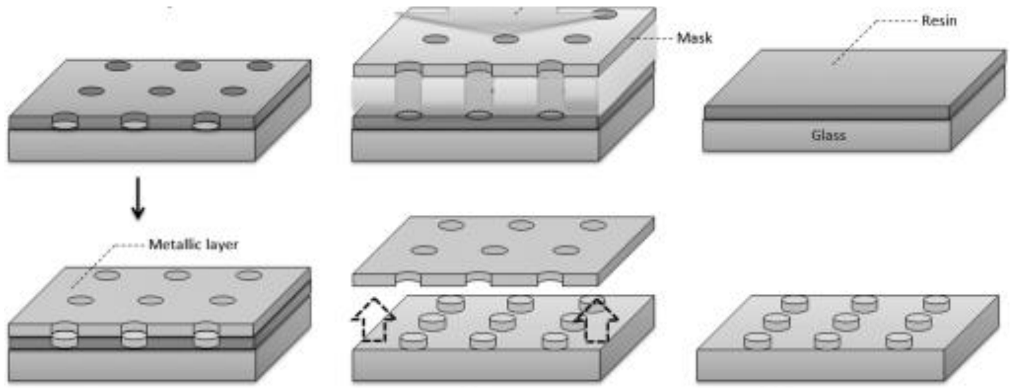


Fig. 42. Process and method by which masks are used [129].

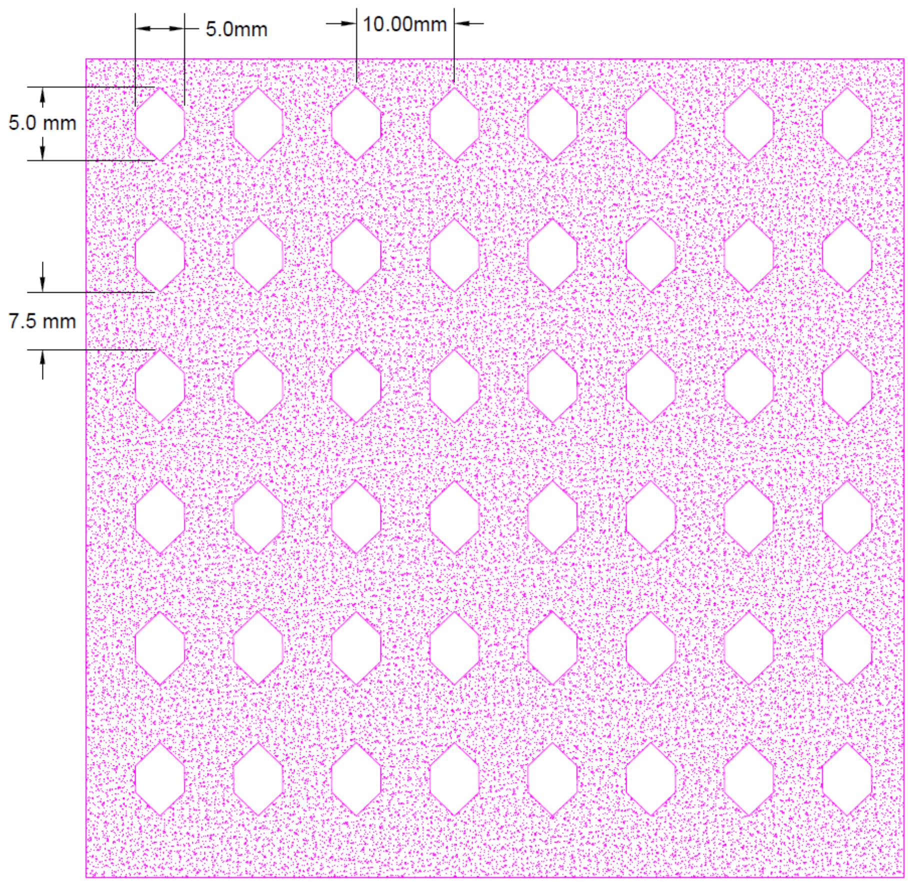


Fig. 43. Dimensions, design and proposal for the mask to be used.

Chavat Industrial Modelling Clay was used for it is also a clay-based material, it presents affinity with our surface material (SiO_2-OTS), and it is a material that can retain its shape while still becoming malleable when exposed to temperatures over 65°C. Thus, it was a material that could create a proper seal with our hydrophobic surface and easy to work with. The cuts and design for the geometry were done using a laser cutter that was available for use at Instituto Tecnologico y de Estudios Superiores de Monterrey (ITESM), Campus Monterrey. The laser cutter had a precision of 0.01mm and the cuts were made at a rate of 30mm/s with a max power of 60% and a minimum of 40%. Since our material is sensible to temperature, the piece of clay was placed over wooden bases to give it height. As the cuts were made, the cut pieces would fall and, thus, prevent fusion between the cut piece and our mask- leaving cleat cut pieces.

5. Hybrid Surface Creation

Creation of our hybrid surface was done by placing our substrate pieces with a treated Superhydrophobic surface (SiO_2-OTS) in a furnace at 60°C. The furnace was not closed and the temperature was chosen for two reasons: (i) Isopropyl Alcohol evaporates can evaporate at room temperature and higher temperatures accelerate its evaporation rate, and (ii) our mask can begin to fuse with our substrate at temperatures higher than 60°C as it becomes completely malleable at 65°C. With the piece in place, the particles were prepared. The particle preparation takes 30min and the pieces were left in the furnace at 60°C this time so their surface temperature could be close to these 60°C.

For the creation of the protruding hydrophilic segments and arrays over our superhydrophobic surface, this work used SiO_2 particles do to their naturally hydrophilic nature and affinity with our SiO_2-OTS superhydrophobic surface. However, we could not use Toluene as a medium since our substrate had originally been dispersed in Toluene. Using Toluene as a medium over our superhydrophobic substrate would cause an etching effect and the loss of effect of the superhydrophobic surface. Hence, the medium chosen this time do to its volatility (easy to evaporate) and sharing properties with toluene to serve as a medium for SiO_2 particles was Isopropyl Alcohol. Our SiO2 particles were mixed at a 5% concentration in Isopropyl Alcohol in a glass beaker. The mixture was placed in an ultrasonic bath for 30min, after which it was removed and taken to the furnace where the substrate pieces were left. With the furnace open, and the substrate pieces inside, the mask was placed over each substrate and using the micropipette of less capacity (10μL) our mixture was deposited over each opening of the mask. After each layer, the mask was removed and placed over the next piece. This was repeated for all pieces, removing the mask after each layer. After the last deposition, the pieces were left 1 hour in the furnace at 60°C. Once removed the hybrid surface was obtained.

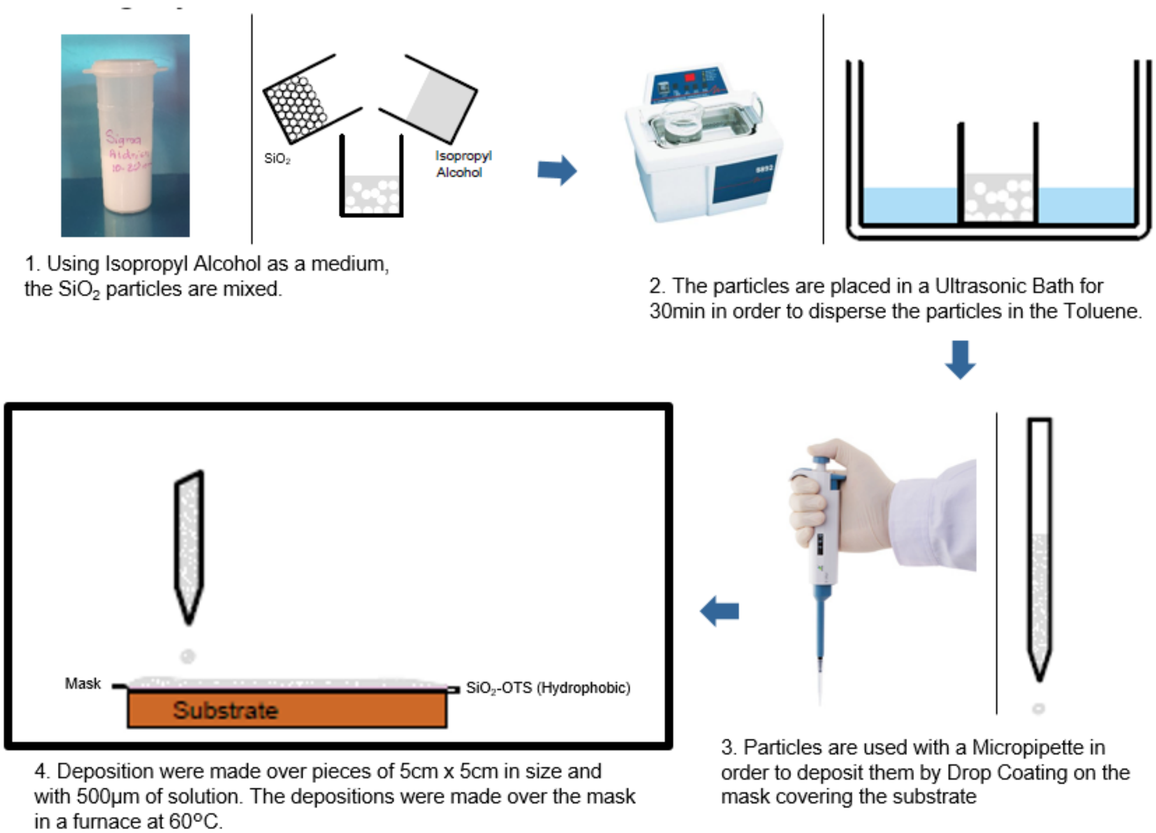


Fig. 44. Visual representation of the process by which SiO_2 particles are deposited over our treated superhydrophilic surface and the creation of the hydrophilic segments is achieved for the hybrid surface.

Chapter 7:

Experiments

Experimentation is the basis for acquisition of data. For the present work, however, there were two phases of experimentation: Preliminaries and Experimentation. The preliminary experiments were done prior to even our simulations. The focus of the preliminary stage was to acquire data in order to generate the simulations and define an efficient surface geometry. The experimentation phase properly tests our surface's behavior and characteristics. Each offers very different information necessary to properly evaluate the results of our surface.

1. Preliminary tests

The preliminary tests done consisted of a series of tests in a smoke tunnel and a wind tunnel. Both equipment were used in ITESM facilities. The tests were done with a total of 4 pieces for the wind tunnel and 8 pieces for the smoke tunnel. These pieces were created using PLA plastic and 3D printers. The 3D printers used were also in ITESM facilities. The dimensions required for the smoke and wind tunnels were pieces that had to be a maximum 7cm max in height, 5cm in width and 10cm in length. Our pieces were all on the limit of these maximums. The 4 pieces used in the wind tunnel were used in order to measure the aerodynamic properties of their design, and observe the lift force that wind would have on these pieces. Pieces were all perforated and mounted on a screw that went inside the wind tunnel, securing the pieces in the center of the tunnel. The 4 pieces used were characterized as:

Table 22. Identification of the tested pieces in wind tunnel.

#	Description
1	Beetle-back Shape
2	Flat Tile Shape
3	Flat Tile Shape with increased height
4	Flat Tile Shape, Double Dimensions

They were tested in the wind tunnel at 3 velocities and the lift force at each wind speed was measured. The 3 wind speeds were always at 8 meters per second (m/s), 14 meters per second (m/s) and 18 meters per second (m/s). The lift force was measured in Newtons (N) by a weight system that is incorporated on the wind tunnel. This can be observed in figure 45.

Fig. 45. Testing of the pieces created with PLA plastic in the wind tunnel.

The smoke tunnels tests used 8 pieces and their evaluation or performance was not quantitative, but qualitative. The smoke tunnel chamber has slits on one side from which smoke lines pass through and create “stream lines” that allow a clear visualization of the behavior of wind on a surface and how aerodynamic the piece is. To mount the pieces a piece of clay was used. The clay was fixed to the base of the smoke tunnel and the test piece was mounted on the clay. The pieces had different orientations but were always centered in the smoke tunnel machine. The pieces were characterized as:

Table 23. Identification of the tested pieces in smoke tunnel.

#	Description
1	Beetle-back Shape
2	Flat Tile Shape
3	Beetle-back Shape 4 Piece Array
4	Flat Tile Shape 4 Piece Array
5	Beetle-back Shape, Realitis Half Size
6	Flat Tile Shape, Realistic Half Size
7	Beetle-back Shape 4 Piece Array, 24° Angle
8	Flat Tile Shape 4 Piece Array, 24° Angle

The pieces were placed in the smoke tunnel machine and video footage was taken on how the smoke (stream) lines behaved once they interacted with the surface design and geometric shape. The angle of 24° (degrees) was chosen since it is the angle at which the stenocara beetle places itself to condense water.

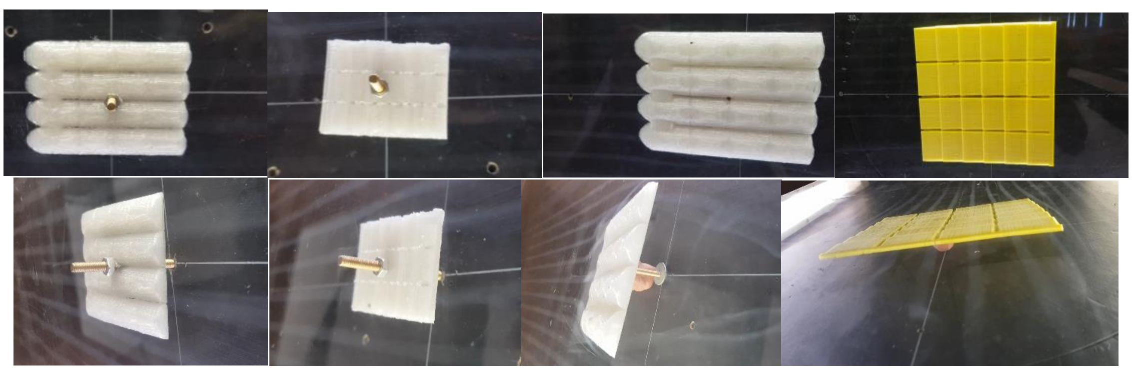


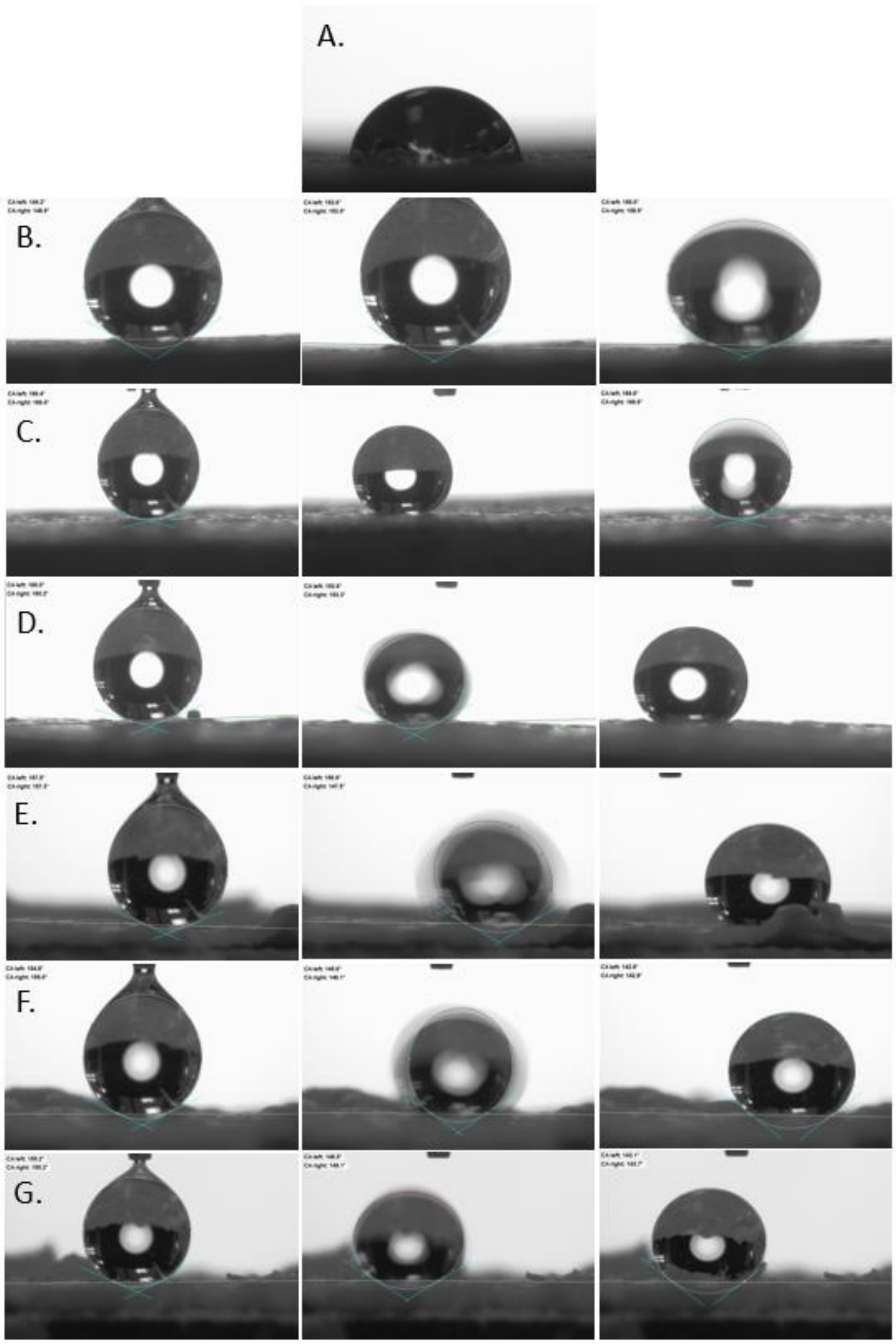
Fig. 46. (Top)Testing of the pieces created with PLA plastic in the smoke tunnel.(Bottom)View of the wind behavior on the pieces by the smoke streams.

The preliminary test offered information necessary for the simulations. However, they did not offer information relevant to the hybrid surface's behavior. As such, the hybrid surfaces had to be created in order to properly characterize it and its properties.

2. Contact Angle Tests

After the successful deposition of the hydrophobic surface, the hydrophobic or superhydrophobic behavior had to be properly confirmed. For these tests, the twelve pieces were used and an additional thirteenth piece was taken which was an untreated clay tile piece. The Contact Angle tests were made with a Contact Angle machine that ITESM has in an investigation installation called PIIT. The pieces were set on the machines mounted base and a syringe with water was used to gradually create a droplet of water that would come in contact with the created surface. The tests were done one piece at a time and 3 drop tests were done per piece. Each drop was done at a different point of the surface and the software of the machine was used to record the behavior of each drop. This was done since some drops rolled on the surface, so video recordings in slow motion had to be done to analyze the drop's behavior.

In the cases that the drop rolled on the surface, 3 measurements of the Contact Angle were done. Passing frame by frame with the video recording, a first measurement was done when the drop makes contact with the surface. The second measurement was done the moment the drop begins to roll. The third measurement varied since some drops stopped at some point in the surface and others simply rolled off. Those that stayed on the surface had the last measurement done at that point, while the ones that rolled off had a second measurement done while they were rolling. An average was taken from these reading and was reported as the Contact Angle of that drop. In total, each surface created had 9 measurements done on them as 3 measurements were done per drop and 3 drops in different locations of the surface. Of the video footage, pictures were extracted and the video footage was extracted itself from the software for future, additional analysis.



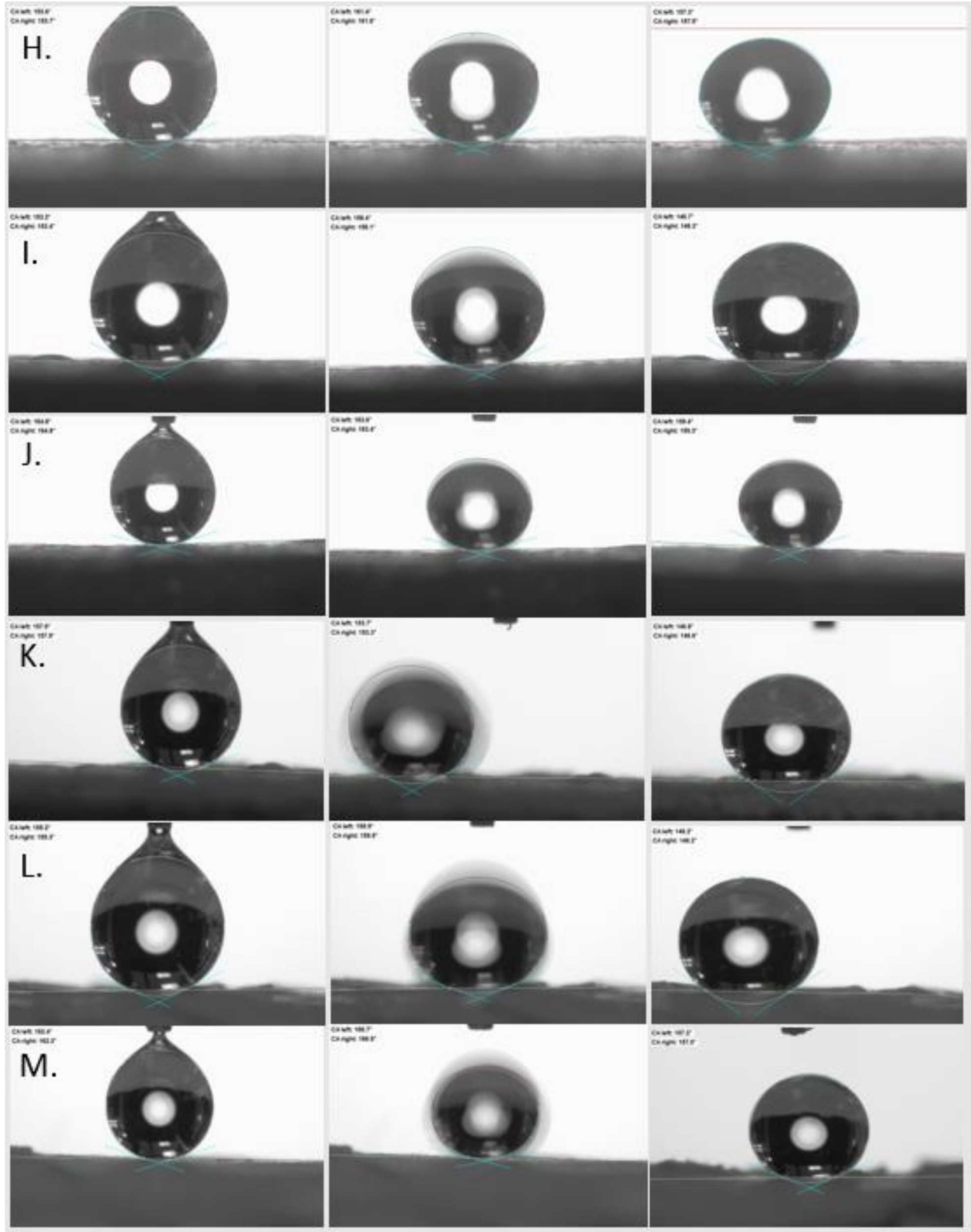


Fig. 47. Images of Contact Angle tests done on substrate with different layers of depositions. (A) Measurement done on the original untreated clay tile. (B) Measurements done on substrate with 1 layer of depositions dried in a furnace at 80°C. (C) Measurements done on substrate with 2 layers of depositions dried in a furnace at 80°C. (D) Measurements done on substrate with 3 layers of depositions dried in a furnace at 80°C. (E) Measurements done on substrate with 5 layers of depositions dried in a furnace at 80°C. (F) Measurements done on substrate with 8 layers of depositions dried in a furnace at 80°C. (G) Measurements done on substrate with 10 layers of depositions dried in a furnace at 80°C. (H) Measurements done on substrate with 1 layer of depositions dried at ambient temperature. (I) Measurements done on substrate with 2 layers of depositions dried at ambient temperature. (J) Measurements done on substrate with 3 layers of depositions dried at ambient temperature. (K) Measurements done on substrate with 5 layers of depositions dried at ambient temperature. (L) Measurements done on substrate with 8 layers of depositions dried at ambient temperature. (M) Measurements done on substrate with 10 layers of depositions dried at ambient temperature.

3. ConFocal Tests

From the Contact Angle tests, some pieces were discarded as they were found to be inefficient and to present weak superhydrophobic properties. However, how the superhydrophobic surface was created and how its surface heriarchitecture and geometry manifested was not visible. Thus, an additional equipment found in the investigation installations of the PIIT, of the ITESM, was used. The equipment used was a Confocal Microscope with which the surface roughness, geometry and heriarchitecture could be measured and observed. The Confocal was used on 9 pieces:

Table 24. Identification of the tested pieces in the Confocal Microscope.

#	Description
1	Untreated Tile
2	1 Layer Deposition, Ambient Dried
3	1 Layer Deposition, Furnace Dried
4	2 Layer Deposition, Ambient Dried
5	2 Layer Deposition, Furnace Dried
6	3 Layer Deposition, Ambient Dried
7	3 Layer Deposition, Furnace Dried
8	5 Layer Deposition, Ambient Dried
9	5 Layer Deposition, Furnace Dried

The process to use the Confocal machine was as follows. The machine required to be turned on and the software run, after which the machine had to be calibrated. The calibration is both mechanical and in software. The mechanical calibration is do to mounted x-y movement base and it is done automatically by the program. The software calibration is do to the resolution and color hue in order to ensure image quality and proper visualization. This last calibration was done manually in the software by settings task bar and manually selecting and making sure that the color hue was correct. After this, the pieces were mounted on the base, under the confocal lens and the readings could begin. The Confocal used had lens of magnification: 10x, 20x, 50x and 100x. The Confocal readings were 13 per piece using the 10x magnifying lens. The first reading was a 3D mapping of the surface, the second and third reading were planar cuts of the surface to visualize the surface geometry and heriarchitecture. One planar cut was done horizontally and the other was done vertically. The horizontal cuts were done at the center of the piece, another an offset upward and the third an offset downward from the center. The same was done with the vertical cuts except that these were done with offsets towards the left and the right from the center. The other readings were to analyze the roughness of the surface. These reading were done in 2 different orientations (vertical and horizontal) and at 3 different points per orientation.

The need and advantage of the Confocal tests was that it allowed a better visualization and clearer understanding of how the surfaces differ with each other. Additionally, it gives information in micrometers (μm) of the roughness each surface had, how constant or variable this roughness is, how the surface geometry looks like and whether the surface has abnormalities. The last was of great importance as some surfaces manifested clumps of concentrated particles that creates peaks and valleys in the surface geometry.

From this first series of tests, more surfaces were discarded and the Confocal was used one last time to properly compare the pieces with the most efficient contact angle. For this work, we found that this was between the pieces that had 2 layers of deposition. For these two pieces, one dried at Ambient temperature and the other dried in a Furnace, the Confocal 100x magnifying lens was used to analyze with greater precision the roughness of the surface. Various horizontal and vertical reading were done and a 3D mapping too in order to properly compare the differences and behavior of the formation of roughness of the surface. This was done so to further understand the nature of the superhydrophobic properties manifested and how it relates to the surface roughness or geometry.

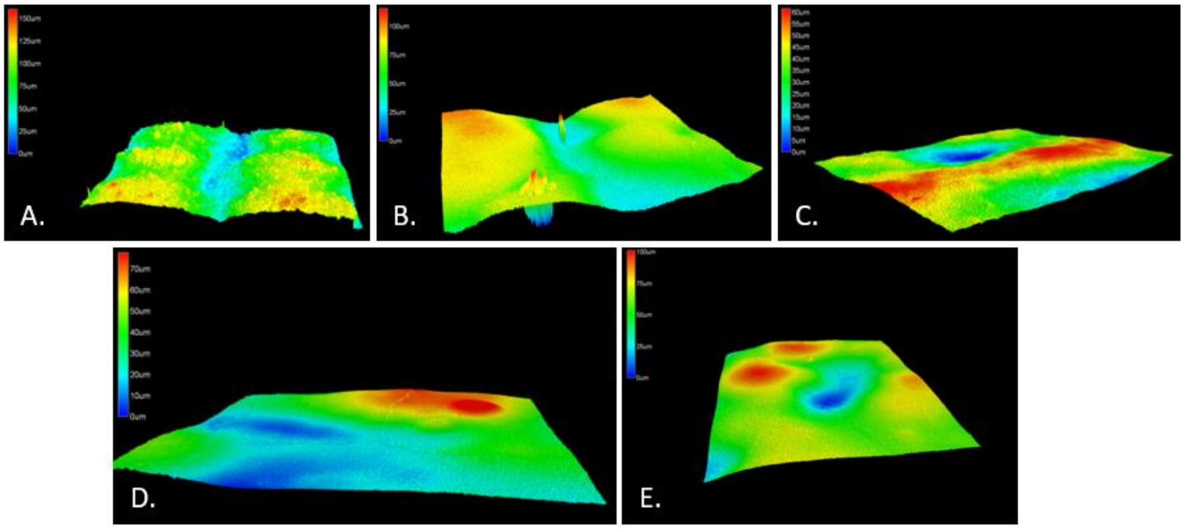


Fig. 48. Images of Confocal Microscope readings done on substrate with different layers of depositions. (A) Original surface of clay roofing tile untreated. (B) Substrate with 1 layer of deposition dried at ambient temperature. (C) Substrate with 2 layer of deposition dried at ambient temperature. (D) Substrate with 1 layer of deposition dried in a furnace at 80°C. (E) Substrate with 2 layer of deposition dried in a furnace at 80°C.

4. Condensation Chamber

A condensation chamber was fabricated using acrylic in order to observe and measure the capabilities of dew-enhancement of the hybrid surfaces created. The condensation chamber has an inlet and an outlet. The inlet is from where moist air will be introduced by means of a fan and a glass beaker with boiling water. The water vapor from the boiling water will enter with air into the chamber and create a small and controlled water cycle. The outlet is mainly to allow the flow of air. The pieces were set on a designed base at the center of the container were they would be at a 24° angle and a glass beaker would be placed at the lowest end of the base to measure the amount of water condensed and harvested by each piece. Each piece would be introduced one by one and exposed to environmental conditions of 50% Relative Humidity (RH) and 30°C. While the chamber held these conditions consistently, the pieces were used in 2 different timeframe experiments. Initially, pieces were placed in an environment as previously mentioned for a time of 12 hours, after which the system was shut down, but the pieces weren't removed. Not removing the pieces would simulate a cooling segment of time in which the chamber (through its outlets) would slowly cool down and lose its humidity. This is a condition similar to day and night cycles. The second experiment was oriented and done identically to the conditions of our simulations. A condensation chamber with consistent conditions of 50%RH and 30°C for 24 hours, after which the pieces would be removed. The amount of water recollected would be measured both by volume (with the help of graduated cylinders) and the efficiency of these pieces would be measured by scaling them to more manageable units ($L/m^2/day$).

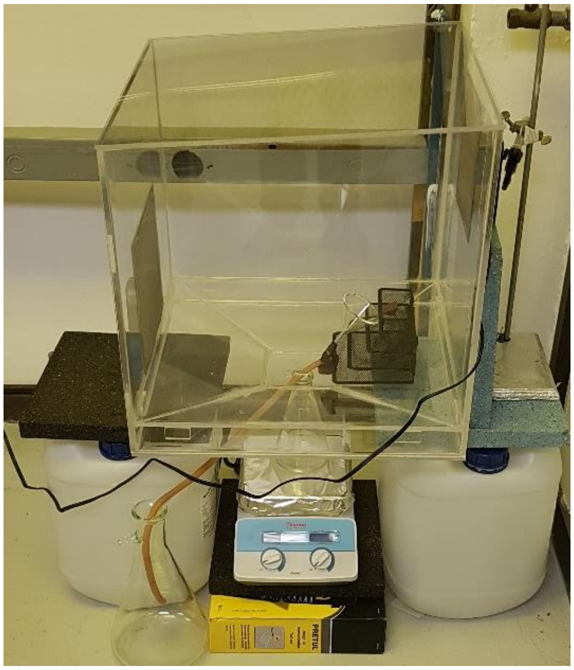


Fig. 49. The condensation chamber created and mounted for experiments analyzing the dew-enhancing efficiency of created hybrid surface pieces.

Chapter 8:

Results

The results obtained from each test were clear and require little explanation. However, the simulations offered information that is very subject to interpretation. The simulations were very close to reality and the conditions established were such to allow for very precise information and emulation of reality. However, the behavior of the pieces and the information recollected require proper interpretation in order to understand what is happening. The information gathered from real tests is physical evidence, so it requires minimal explanation. As such, our results will view the results from the experimental phase first and the simulations will be analyzed in depth as the last section.

1. Contact Angle Tests

From the Contact Angle tests we observed that all our surfaces had superhydrophobic properties as their Contact Angle was superior to 145°. However, we observed that there was not a clear improvement in our surface's properties as more layers were deposited. Quite the contrary, the more layers were added, the surface became more unstable and began to lose superhydrophobic properties. This was visible as droplets actually sunk or cracked the surface with their weight and (at 10 layers) the droplets were even coated by SiO2-OTS particles as they made contact with the surface. Thus we were able to conclude that the limit after which the surface become too unstable to be functional are 3 layers of deposition. However, among the 1, 2 and 3 layer depositions, there was a difference between those dried in the furnace and those dried at ambient temperature.

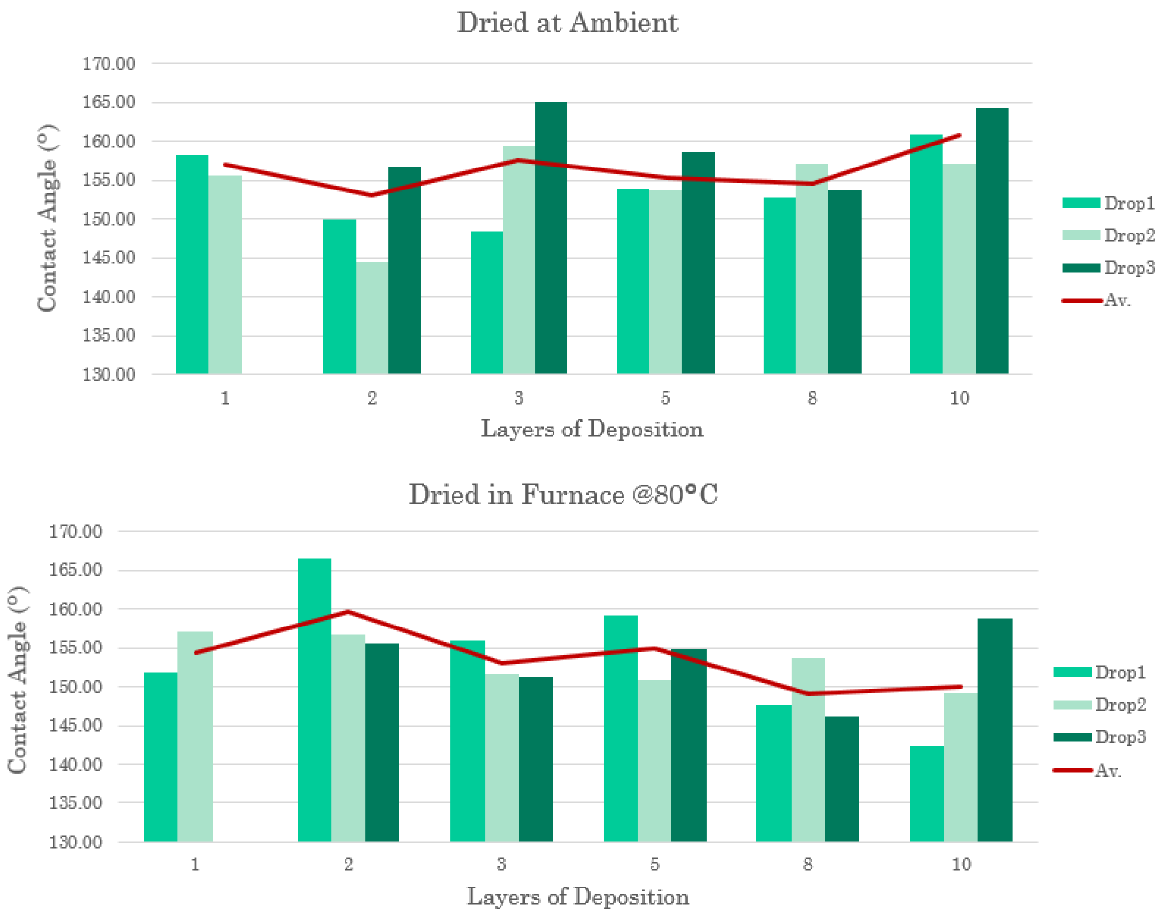


Fig. 50. Graphs of the various contact angle tests done and the angles registered.

The particles dried in the furnace showed the most efficient and highest superhydrophobic property out of the remaining, stable surface group. At 2 layers, our surface dried in the furnace manifested a 160° Contact Angle. This was the highest value recorded which is an average of the different drop measurements made. After this value, the surface dried at ambient temperature with 3 layers manifested also a 160° Contact Angle. However, since these contact angles after the 2 layers of deposition surface require more material and more layers to reach the superhydrophobic property manifested by this surface, they are less efficient and not favorable for our surface creation. As such, a superhydrophobic surface with SiO2-OTS particles over a clay substrate can manifest superhydrophobic properties with a Contact Angle over 160° with only 2 layers of deposition and dried in a furnace at 80°.

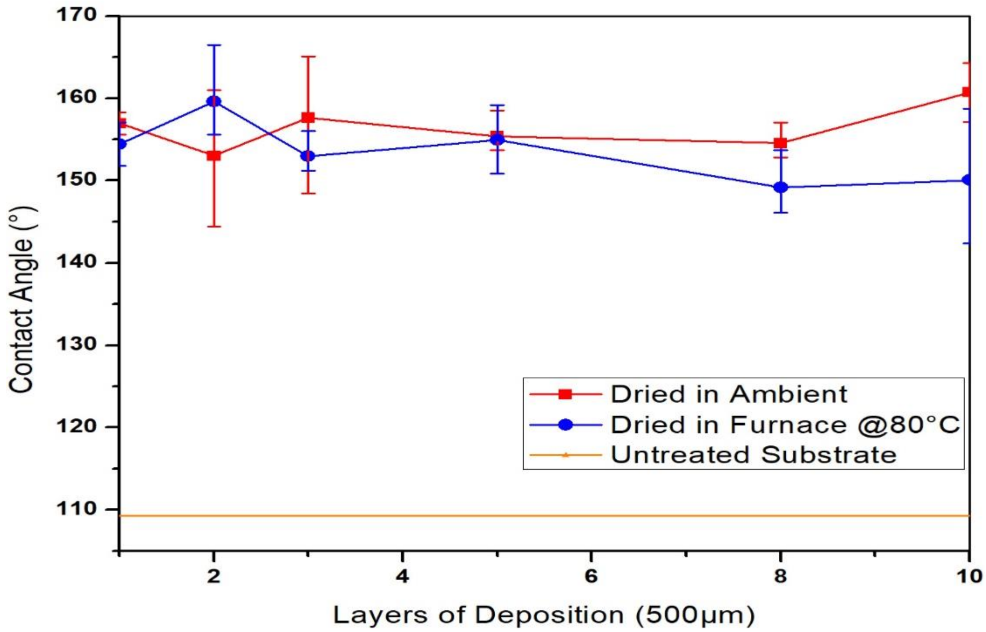


Fig. 51. Graph comparing the different methods of drying and the contact angles registered.

2. Confocal Tests

The Confocal tests offered a wide range of information regarding the surfaces created and how the different layers affected these. At a start, the untreated clay-tile surface manifested a very irregular surface, with distinctive peaks and channels. This initial geometry is not visible or sensible to touch. As such, it was observed that this geometry remained the same at only 1 layer of deposition for both drying processes. Additionally, it was observed that the clay tile's grains were still visible and present on the surface even with the SiO2-OTS particles adhered. At 2 layers of deposition this surface geometry begins to be covered by the SiO2-OTS particles and a homogenous surface can be created. However, the surfaces dried at ambient temperature manifested peaks and channels that imitated the original tile's surface while the surface dried in the furnace showed a more homogenous surface. The same effect happened with the 3 layers of deposition pieces.

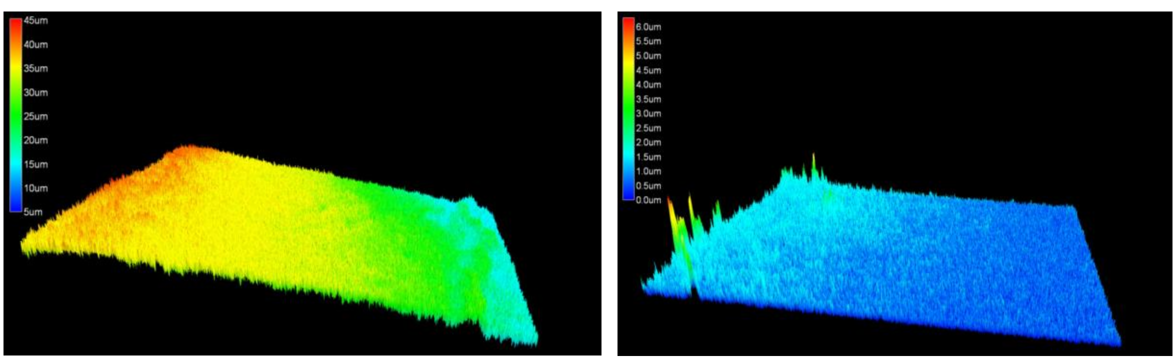


Fig. 52. (Left) The surface roughness of the substrate treated with 2 layers and dried in a furnace at 80°C. (Right) The surface roughness of the substrate treated with 2 layers and dried at ambient temperature.

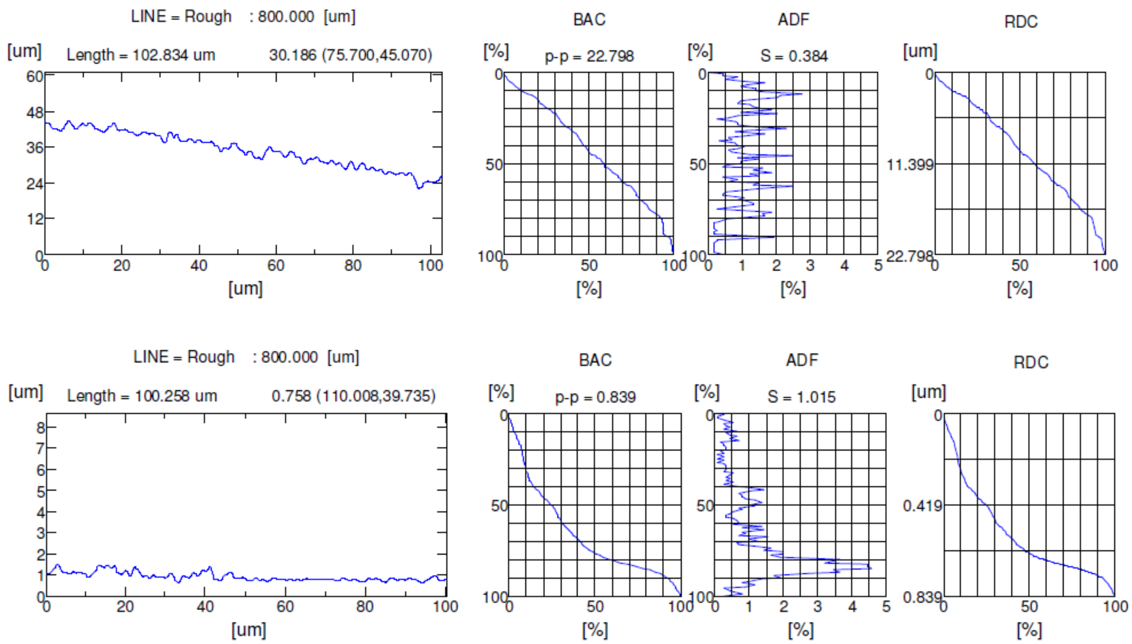
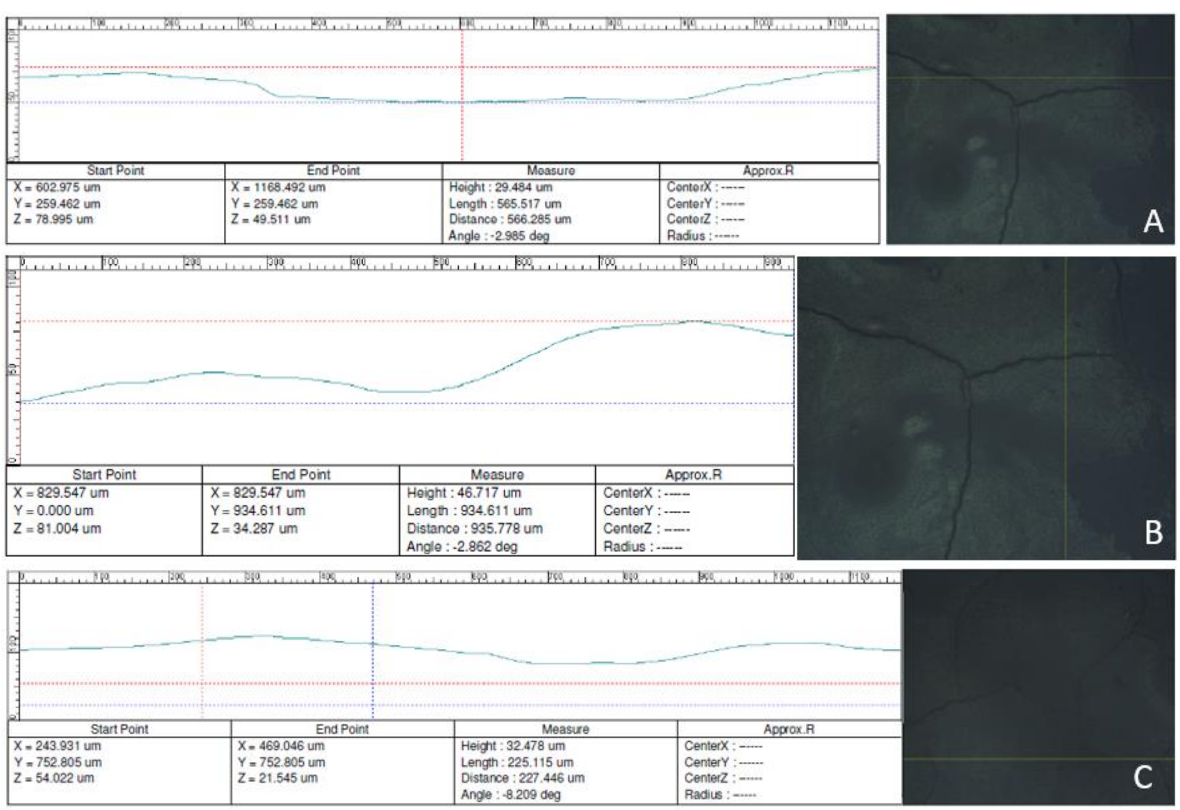


Fig. 53. (Top) Graphs offering a profile of the surface roughness dried in a furnace at 80°C, the variability of this roughness and how consistently the surface manifests roughness. (Bottom) Graphs offering a profile of the surface roughness dried at ambient temperature, the variability of this roughness and how consistently the surface manifests roughness.



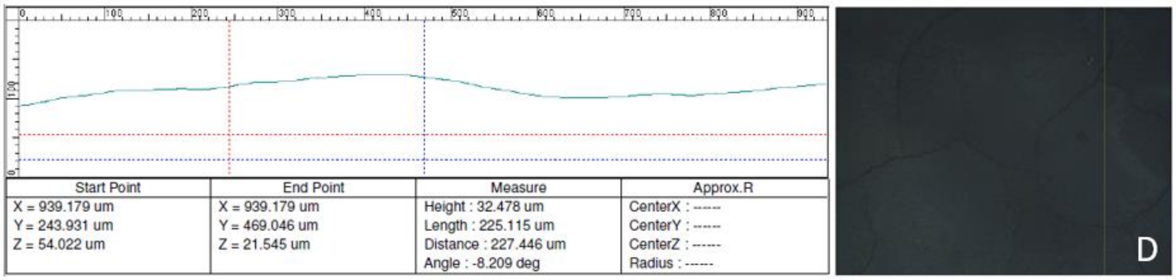


Fig. 54. (A) Profile of the surface topology of the substrate with 2 layers of deposition dried at ambient temperature, horizontally. (B) Profile of the surface topology of the substrate with 2 layers of deposition dried at ambient temperature, vertically. (C) Profile of the surface topology of the substrate with 2 layers of deposition dried in a furnace at 80°C, horizontally. (D) Profile of the surface topology of the substrate with 2 layers of deposition dried in a furnace at 80°C, vertically.

Analyzing the surface roughness offered more information. From our Contact Angle teste we found that the furnace dried pieces could have a range of superhydrophobic properties while the ambient dried surfaces were very consistent in their behavior. With the Confocal tests for roughness we found that the furnace dried pieces had a varying surface roughness with high variance. The pieces dried at ambient temperature had a low variance and very consistent roughness. The furnace dried pieces had a mean roughness of $\sim 6\mu m$ with a max height difference between a peak and valley of $\sim 13\mu m$, and a mean separation between peaks of $\sim 0.12\mu m$. The ambient dried pieces had a mean roughness of $\sim 4.5\mu m$ with a max height difference between a peak and valley of $\sim 8\mu m$, and a mean separation between peaks of $\sim 0.5\mu m$. Hence, there is a correlation between superhydrophobicity and surface roughness, as stated in other works and even mathematical concepts [93]. Thus, the pieces dried in the furnace can manifest superior superhydrophobic properties that the other pieces, making them more suitable and a better option for our hybrid surface. Additionally, drying in a furnace made the surface more homogenous and covered the original surface geometry with peaks and channels. With this surface characteristic, these pieces are also a better option in the creation of a clear hybrid surface with only a surface geometry between hydrophilic and superhydrophobic surfaces manifesting.

3. Simulations

3.1. Scenario 1: Moist Wind

This scenario considered a wind flow of 8m/s making contact with our surface that was placed flat on the lower limit of our simulation space. The information most relevant acquired was the percent liquid, scalar value, relative humidity (RH) and wind velocity. The combination of this information allows an understanding of the possible behavior of condensation and how the geometry of each surface affects the effects of condensation and the behavior of liquids.

Percent liquid is the relation of volume between liquid water and the medium. However, it is also calculated as where liquid water concentrates over a surface and where this liquid water is moving. For this simulation, it was observed that this percent liquid had a strong correlation with relative humidity (RH) and the scalar variable, but it had an opposite behavior with the scalar. It was observed that our environment of 50% RH, had an increase of its value when in contact with all the geometric forms in the surfaces. However, the square shape surface geometry presented a lower level of RH contrary to the hexagonal array and the circular array. Thus, the square shape was the least efficient as it showed to be unable to condense and retain liquid water effectively. Between the circular and hexagonal array it was observed that the circular array had a better behavior towards increasing its surface RH, but it showed lower levels of liquid water on its surface and, instead, showed in a timelapse that the RH and liquid were slowly moving from the point of contact with the wind to the location where wind had difficulty reaching. This caused streaks to form which can be interpreted as liquid water and water vapor being dragged away and off the surface. This was paired with the wind velocity over the surface, where the circular array had a very aerodynamic design. This causes the surface to be sensible to wind speed and strength, as well as lacking enough nucleation points on its surface to properly retain water and prevent it from escaping. The hexagonal array did not present this problem and instead showed that liquid water was always kept on its surface. This liquid water can be interpreted as becoming a film that is constantly sliding off the surface but the hexagonal array has enough nucleation sites do to its surface area design to keep condensing more water and keeping that film. This was also paired with the scalar values to confirm such behavior. The scalar value is the relation in mass of water and a medium (water is not differentiated as liquid or gas). As such, the Scalar variable is useful in properly following the trajectory of water in a medium and understand if condensation or evaporation is happening or if a film/fluid body is formed. In this scenario, the scalar variable created screen in both square and circular arrays. These “screens” resemble division of behavior of the surface where on one side condensation is happening, on the other evaporation is happening and in others where a film or fluid body was created. However, in the hexagonal array, these screens are also formed, but progressively stabilized over the surface. This stabilized “screen” supports the interpretation that a fluid body or film of water is consistently created on the hexagonal surface, meaning it is efficient in condensing water and keeping it.

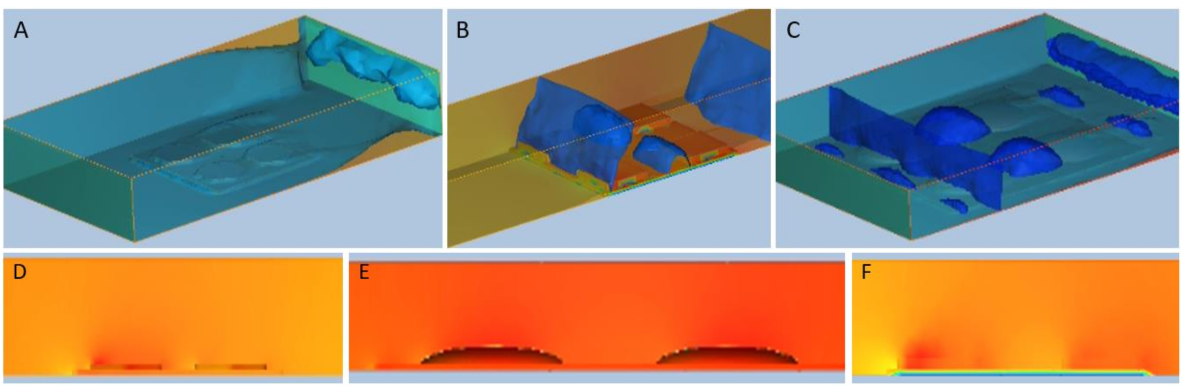


Fig. 55. (A) Volume analysis of the behavior of humidity in the medium of the hexagonal surface geometry. (B) Volume analysis of the behavior of humidity in the medium of the square surface geometry. (C) Volume analysis of the behavior of humidity in the medium of the circular surface geometry. (D) Profile of the behavior of the relative humidity in the medium on the hexagonal surface geometry. (E) Profile of the behavior of the relative humidity in the medium on the circular surface geometry. (F) Profile of the behavior of the relative humidity in the medium on the square surface geometry.

The hexagonal array had a superior behavior towards condensing and keeping water on its surface.

3.2. Scenario 2: No Wind

In this scenario an open medium with no wind is considered. Its initial, environmental and boundary conditions were established in order to imitate a natural atmosphere. It is also similar conditions to the condensation chamber. The most relevant information acquired were the RH, percent liquid and scalar variable. It is worth mentioning that small wind currents were created as a consequence to the constant temperature and energy exchange between the medium and the surfaces.

In this scenario, the square array stood out from the rest as it manifested an inconsistent percent liquid in the medium as a whole. To be more exact, the surface had an increase in percent liquid (liquid water present on it), but the medium had more water and this water simply escaped by other means. This was different from the circular and hexagonal arrays as these manifested a completely saturated medium and surface where “bodies” of percent liquid descended from the inlet at the top of the container onto the surfaces. This peculiar behavior observed in the simulation is interpreted as the condensation of liquid water on the surfaces of these arrays. The scalar value was used to confirm such a phenomenon and it showed the same behavior, except in all pieces.

The scalar variable evaluated manifests “screen” and a clear movement of water on the surfaces. The screen shows where water is moving, making contact with the surface and how it behaves. This screen is very similar between the circular and hexagonal arrays, but different with the square array, where the screen never comes in contact with the surface. In the circular array, upon contact the “screen” is constantly moving over the surface and sliding off it. This was interpreted much the same as the first scenario, the last of nucleation points or clear limits causes the condensed liquid water to escape the surface and simply roll off with ease, causing water to be lost. In the hexagonal array, the “screen” also moves over the surface but at a less pronounced rate and it never slides off. Instead water seems to move and be trapped (in the most part) in the central area created between the 4 pieces of protruding hydrophilic properties. Thus, the hexagonal array was more efficient in retaining liquid. This was also visible in the planar cuts used to track the behavior of scalar value. The simulation showed how water seemed to condense on the hexagonal array but never leave the surface, while the circular array had clear and distinctive rolling off the surface. A quick confirmation with RH showed that the circular and hexagonal pieces had a clear condensation or concentration of RH on their surface (higher than the ambient RH), but the circular array showed to be affected by the small wind currents formed by the exchange of heat and energy between the surface and medium, causing RH to move and be lifted off the surface. This can be interpreted as the loss of humidity or water droplets from the surface.

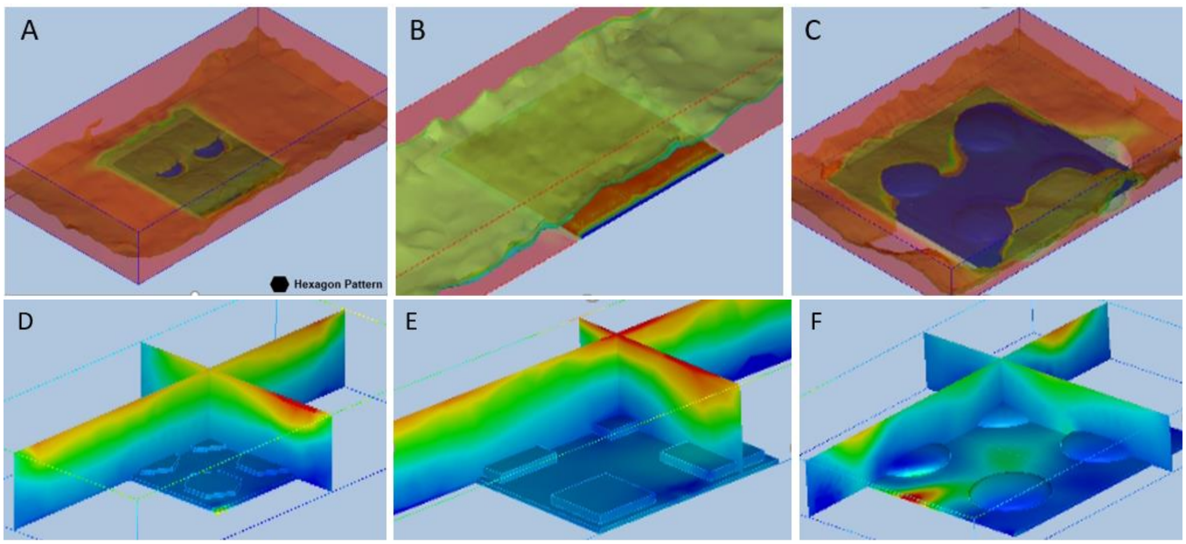


Fig. 56. (A) Volume analysis of the simulated occurrence of condensation by the scalar parameter in the medium of the hexagonal surface geometry. (B) Volume analysis of the simulated occurrence of condensation by the scalar parameter in the medium of the square surface geometry. (C) Volume analysis of the simulated occurrence of condensation by the scalar parameter in the medium of the circular surface geometry. (D) Profile Analysis of the simulated occurrence of condensation by the scalar parameter in the medium on the hexagonal surface geometry. (E) Profile Analysis of the simulated occurrence of condensation by the scalar parameter in the medium on the square surface geometry. (F) Profile Analysis of the simulated occurrence of condensation by the scalar parameter in the medium on the circular surface geometry.

The hexagonal array had a clear superior behavior in being able to condense water and reach a point of saturation (creation of a film). Water is not lost by other means except the excess of water formed.

3.3. Scenario 3: Realistic at 24°

Using only the hexagonal array this simulation tried to offer as much information as possible regarding the behavior and capabilities of the surface and (hence) hexagonal geometry in harvesting water effectively. Additionally, two scenarios were tested in order to confirm the most efficient surface design: protruding geometry or concave. The conditions of the environment were set similarly to scenario 2, so the only change were the surfaces themselves. In this scenario the most effective data obtained was the scalar value. While the relative humidity and percent liquid were still part of the data, along with others, they do not offer such a clear understanding of the surface behaviors. The program, Autodesk CFD, can simulate the behavior of fluids and this feature was visible in this scenario.

The scalar variable did not create “screens” in this situation. In this scenario, the thickness of the surface along with the definition of materials and surface geometry caused the scalar value to behave imitating a thin film of water. As scalar value analyzes and tracks the relation of mass between water and a medium, the simulation gradually showed how a film and bodies of water fluid were created over the surfaces. These bodies gradually grew in size in both cases and progressively began to drip by the superhydrophobic parts of the surface with assistance of the 24° angle slope. However, there was a clear difference between the protruding geometry and the concave geometry. The concave geometry manifested the scalar fluid manifesting in the concave hidrophilic areas and gradually and slowly dripping down. However, this dripping is in low quantities and manifests occasionally. The protruding geometry manifested how scalar fluids were created on the area of the hydrophilic protruding geometries and began to drip down the surface. This effect was consistent as the protruding pieces lost most of the fluid scalar created on it, which allows for another fluid body to manifest and the trickling effect to occur again. This continuous effect causes the program to simulate a constantly condensing and draining fluid. Although there are limitations to the program and the accuracy in the behavior of the body of water through scalar values, it is visually clear the difference in behavior and effectiveness between both surfaces.

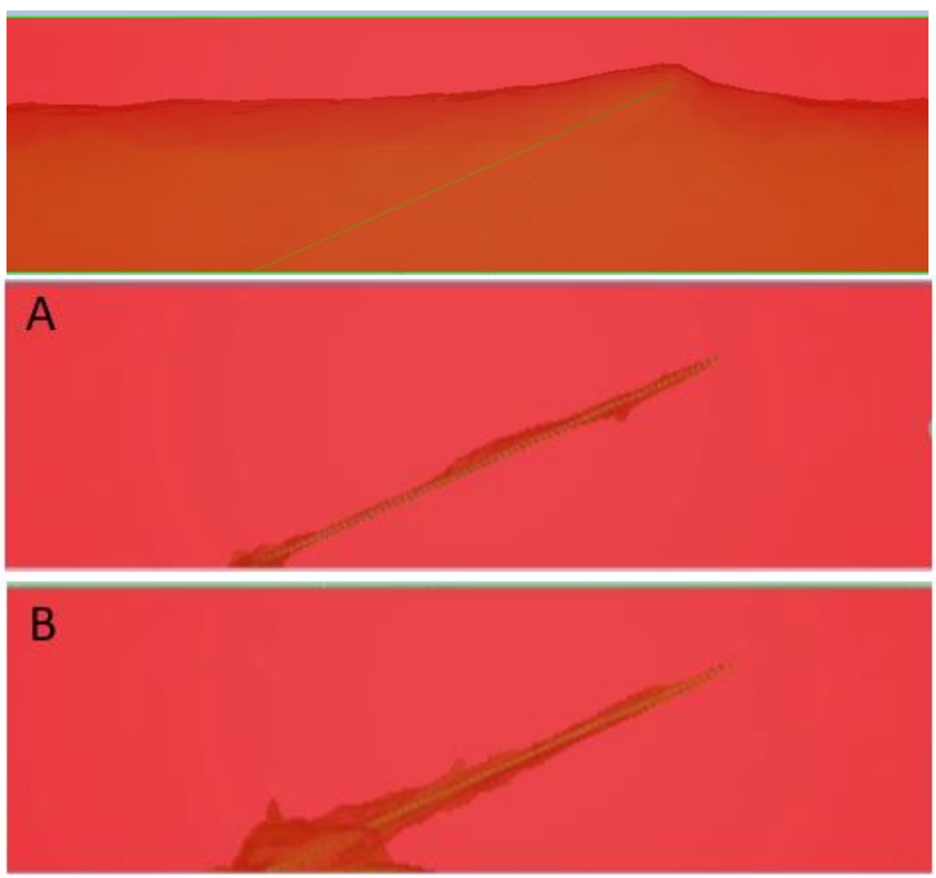


Fig. 56. (Top) Initial conditions for both simulations. (A) Computer Fluid Dynamics (CFD) simulated by the occurrence of condensation in the medium by the scalar parameter with a concave topology of the hexagonal geometry. (B) Computer Fluid Dynamics (CFD) simulated by the occurrence of condensation in the medium by the scalar parameter with a protruding topology of the hexagonal geometry.

The surface with protruding geometry has a superior behavior and performance against the concave geometry. This piece was also the one most similar to the stenocara beetle's own "tailor-made" shell design. Hence, this final simulation offers a couple of conclusions that have been supported by the previous simulations.

4. Condensation Chamber

Tests for the condensation chamber were run until 10 studies for the 12hr cycle and 10 studies for the 24hr cycle were achieved. With these results, graphs were generated with the average amount of water harvested. These results would assist us in evaluating the efficiency of our surface created and compare against other systems that are functional through-out the world.

Measurements were done until the end of every cycle (24 hours) by extracting the graduated cylinder that had vegetable pigmentation placed inside it to help properly identify and "read" the results of the experiments. Additionally, the pieces extracted were carefully placed in a mat at room temperature and left to dry naturally without assistance nor use of cloth or any physical mean. This care was taken in order to prevent damage to the generated hybrid surface and be able to use the pieces for more tests. The pieces used for both experiments were the same, being them used initially for the 12hr cycle tests and then for the 24hr cycle tests.

Fig. 57. Conditions inside the chamber of RH (%) and Temperature (°).

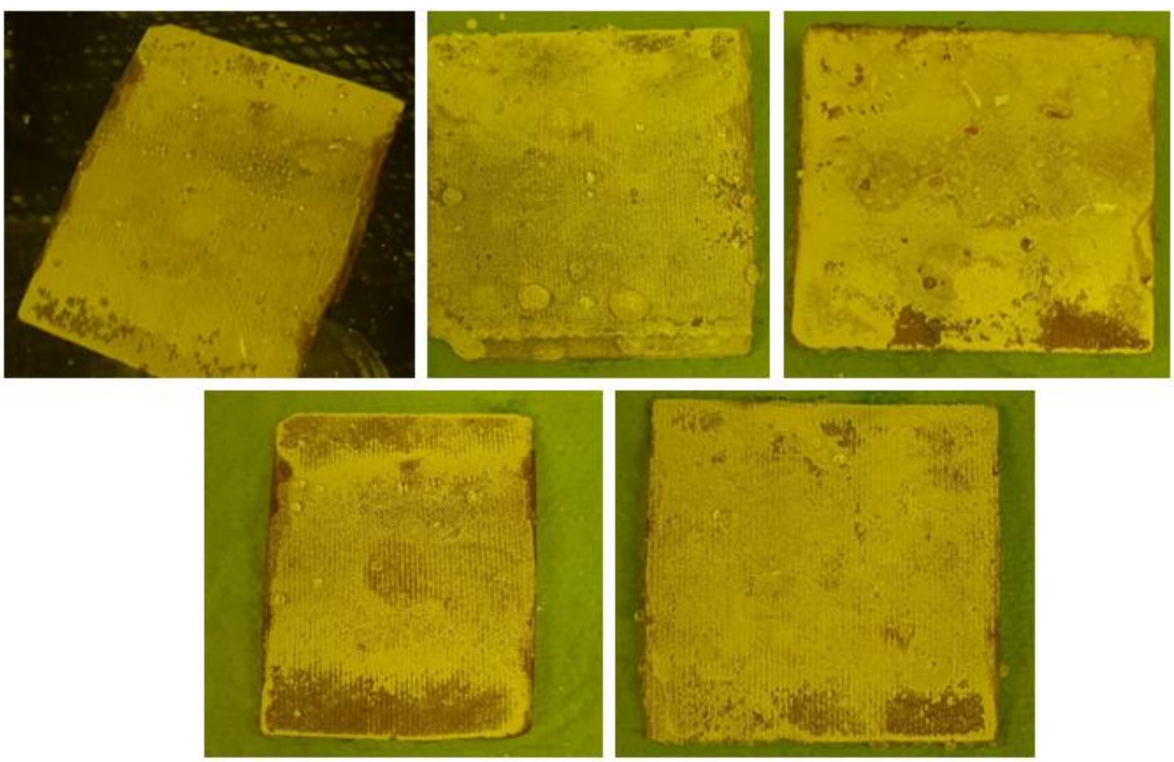


Fig. 58. Treated tiles with hybrid surface extracted from condensation chamber after cycles.

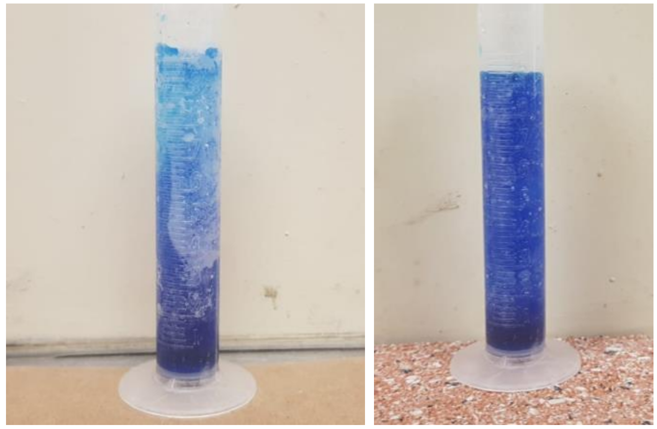


Fig. 59. Example of water recollections from the condensation chamber.

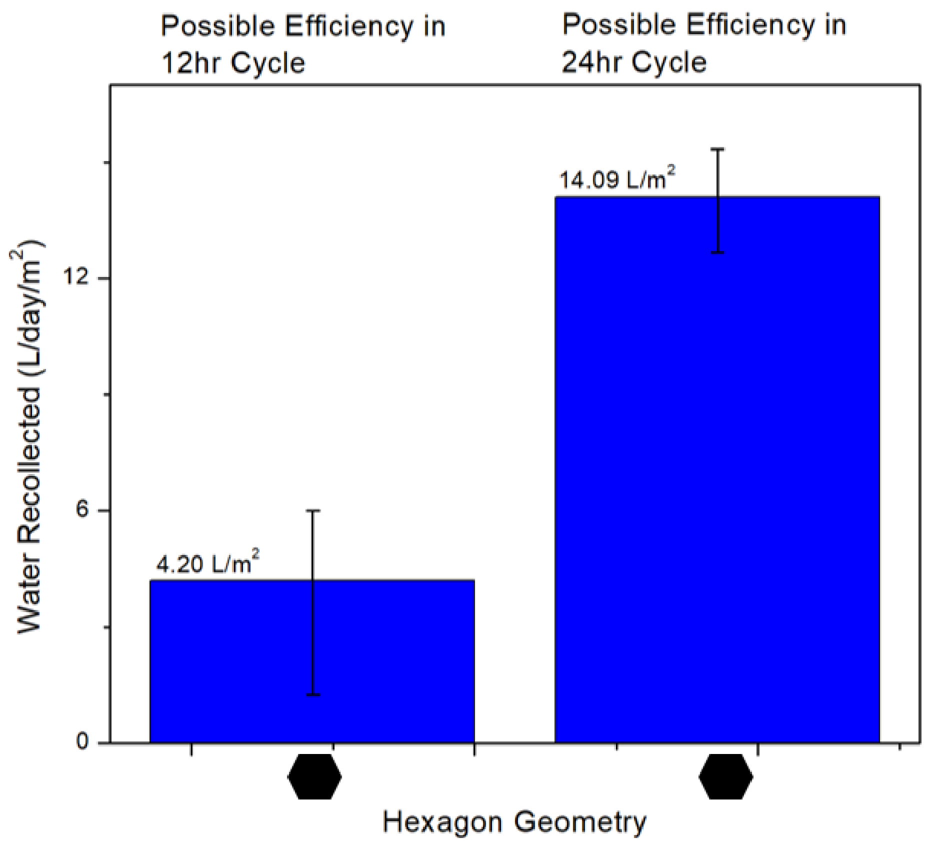


Fig. 60. Graphs on the performance of the developed hybrid surfaces at each cycle.

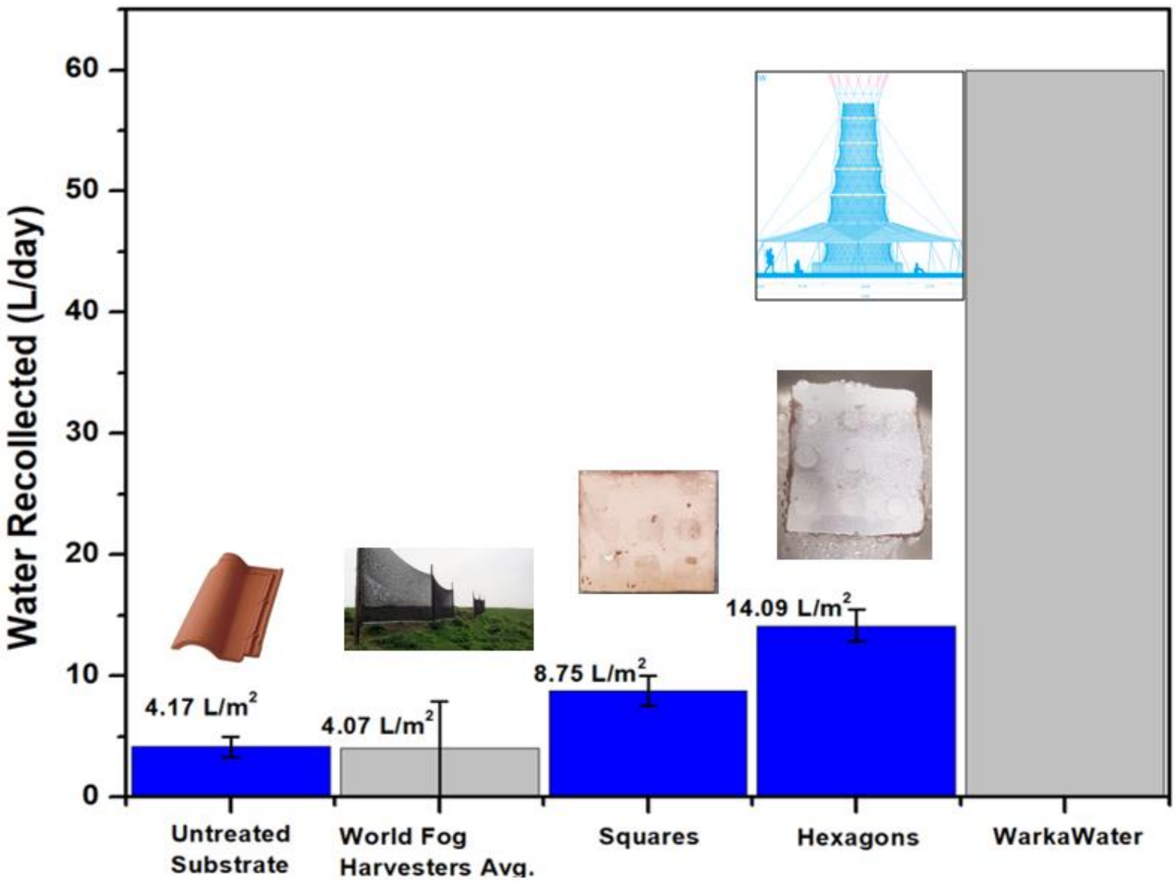


Fig. 61. Comparative graph between the different systems that passively recollect water from the humidity in the environment and/or from fog [31,33]. It is noted that the correct dimensions or surface area of WarkaWater are not specified, only its water harvesting (L) per day.

Chapter 9:

Conclusions

From the extensive work done both on surface development and simulations, conclusions can be drawn towards the behavior, performance and efficiency of the surface created. Additionally, these conclusions can be drawn further towards the future as this technology answers a problem that is growing in severity each year. This technology competes with various proposals that are different from it in many ways, but it has its advantages that making worth considering. And, more than considering, it can be implemented with ease.

1. Simulations

From the simulations it was concluded that the hexagonal geometries for the surface topology offer a better performance towards manifesting dew enhancing properties. Paired with the adequate surface treatment to create a hybrid surface where the Hexagonal peaks are hydrophilic on a hydrophobic surface, the new surface can passively collect water through condensation.

In greater detail, it was observed that hexagonal surface geometries manifested a consistently better behavior towards the condensation of water, its recollection and its draining. These three behaviors are essential for surfaces oriented towards water recollection. From the simulations it was observed that the square geometry offers contact points and resistances for air. This allows for nucleation and condensation to occur. However, square geometries lacked a proper method by which to recollect this water and water is consistently lost either by wind drag or droplets rolling off. This prevents a sufficient amount of water recollection; it is inefficient. Circular geometries, on the other hand seem to offer greater means for retaining water and draining it. However, circular geometries seem to lose water with ease by wind drag and, additionally, do not have adequate dew-enhancing properties. The circular geometry is very aerodynamic, causing droplets that form on hydrophilic segments to quickly coalesce towards the hydrophobic segments. This seems beneficial, but poses an inefficient result as (through observation) it was analyzed that these circular geometries never reach a point of saturation and tend to drop off in droplet formation (nucleation). Its very aerodynamic design causes less nucleation spots to occur. The hexagonal geometry, in the end, has the best combined behavior as it consistently (with or without air) reached a point of saturation while still condensing consistently. What this means is that the hexagonal geometry manages to condense water and recollect it until a thin water film forms on the surface. Additionally, it allows proper drainage as more condensation occurs and new droplets forms and these new droplets join the water film created which simply slides off slowly. This causes a slow and consistent cycle of water being drained and new water droplets joining the thin water film. Thus, hexagonal geometries offer a greater amount of nucleation points.

An additional variable that was analyzed was the topology of these geometries. Of this, protruding topologies prove to be superior in dew-enhancing behavior. The protruding topology not only offers more contact area for the wind/air to interreact and cause nucleation of water droplets, but it also allows for droplets of water that coalesce and begin to be drained to have a clear path. Additionally, the drainage of water by protruding topologies is more efficient as water is not "trapped" and coalesces at the moment that it exceeds its own surface tension (or Gibbs energy). This efficient relation prevents the protruding pieces to be soaked or covered by a thin film of water that would prevent or hinder more water condensation, by instead letting droplets rolls off once they reach their critical point.

With both ends of simulation (virtual experimental environment) and physical experiments, this work offers an answer to the hypothesis stated and the problem it faces. It is possible to create a hybrid surface on a clay-based substrate with dew enhancing properties that can harvest water from the humidity in the environment passively.

2. Experiments

From the various experiments and tests done, it was observed that there was a clear and consistent behavior that determined the most efficient path to create the hybrid surface proposed by this study. From figures 26, 28 and 29 it was observed from the FTIR analysis that our particles shared functional groups. This would allow a proper adsorption of our intended particles on the surface or substrate desired (clay tiles). However, more than this simple observation, it was observed from our various tests that the method of Drop-Casting and the use of a mask are facile and effective methods by which a hybrid surface with superhydrophobic and superhydrophilic properties can be created.

It was confirmed that SiO2 particles can be treated with OTS to create a superhydrophobic surface over a clay-based substrate, such as a Clay Roofing Tile. It was also concluded through this work that untreated SiO2 particles can be adhered to this superhydrophobic surface to create a hybrid Superhydrophobic-Hydrophilic surface. Additionally, it was concluded that the deposition of these particles offers the best performance when there is a “curing” process between depositions and when the treated surface has 2 layers. This “curing” process was done by placing the tiles in a furnace at 80°C. This curing process offered a homogeneous surface, covering the original clay tile’s surface geometry, and surface with greater roughness variance and depth. This last enhances the superhydrophobic behavior of the surface.

Hexagonal geometries for the surface topology offer a better performance towards manifesting dew enhancing properties. Paired with the adequate surface treatment to create a hybrid surface where the Hexagonal peaks are hydrophilic on a hydrophobic surface, the new surface can passively collect water through condensation. The condensation chamber gave us information on the efficiency of these surfaces created. The efficiency, following a 12 hour time sequence recollects an average of 4.20 $L/m^2/day$; which is competitive with other fog-basking or humidity harvesting systems of water [5,21,29,31,32,118]. In a window time of 24 hours with continuous humidity, the surface developed was more efficient that these by harvesting an average of 14.09 $L/m^2/day$. Thus, our hypothesis can be answered.

It is possible to create a hybrid surface on a clay-based substrate with dew enhancing properties that can harvest water from the humidity in the environment passively with efficiency.

3. Future Work

Although conclusions were drawn, there were areas of opportunity found during the experimentation and simulation of this work.

Drop Coating may cause irregularities to form since deposition drops are large and can concentrate particles in locations. This can affect the quality of the surface and of the hybrid effects. Experiments with other deposition methods are an option.

It was observed that the mathematical equations and models used by the simulation program and in research are limited. These equations that seek to explain condensation are not fit nor accurate for microfluidics or nanometric dimensions. A new mathematical model can be developed.

While the surface was successfully created there is not a clear idea on the lifetime of such a surface. It is understood that its exposure to climate and adversary conditions will deteriorate it, but not at the rate of such deterioration. Thus, a method to properly measure the adhesion strength of the particles to the surface can be used according to ASTM norms D3359-17, D2370 and D4060. With this method, one can measure the lifetime of surfaces such as this one and find better ways to improve their adhesion.

This work was done with the idea to apply this technology to the real world. However, the experiments made and information gathered was not scaled for industrialization. Additionally, industrializing this technology has not been considered in this work. The industrialization of this technology to meet market demands and allow for existing surfaces found in our urban reality and rural realities to start generating water for their inhabitants is still an open field.

With this idea, it can be also considered that the particles and process used in this work can be modified or changed completely to meet market demands, reduce prices or find a more facile method to create these hybrid surfaces.

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Curriculum Vitae

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