Using Gamma Radiation for Degradation of Diazepam, Midazolam and Flumazenil in Wastewaters

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Abstract: *The growing development of the pharmaceutical industry and the high consumption of drugs, in recent years, have led to the delocalised input to the environment of a large number of pollutants. These products are mainly toxic substances, poorly biodegradable and persist in nature due to their high level of accumulation and low biodegradability. Examples of these are benzodiazepines, the most prescribed anxiolytics in the world that are in the list of emerging pollutants of interest due to the affectations that cause on reproduction, endocrine functions or photosynthesis of aquatic organisms. The concentration of these pollutants in the water bodies is in the order of hundreds of micrograms/liter, with values of removal of less than 10 % in waste treatment plants. The inability of conventional biological systems to eliminate toxic substances such as benzodiazepines imposes the implementation of new technologies like advanced oxidation processes. In the present work, the degradation of diazepam, midazolam and flumazenil in synthetic and real aqueous solutions of wastewater by the use of gamma radiation and its intensification with hydrogen peroxide and the Fenton reagent was studied. The best conditions for total radiolytic degradation of diazepam, midazolam and flumazenil were obtained at pH 3 and at an absorbed irradiation dose of 2500 Gy. The combination of gamma radiation and the addition of the Fenton reagent in synthetic matrices guarantees 100 % of degradation for both drugs and 95.7 %, 95.8 % and 89.6 % in real matrices of wastewater for diazepam, midazolam and flumazenil, respectively.*

Keywords*: Persistent pollutants, wastewater, gamma radiation, diazepam, midazolam, flumazenil*

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A Cost-Effective Virtual Reality Headset for Immersive Interactive Learning in Developing Nations

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Abstract: *Classroom lessons in the past have been taught on the blackboard, and as time progressed, the blackboard changed to the whiteboard which is being replaced by the smart board. This shows that technology is changing the learning environment of the classroom and lessons can no longer be taught by listening and writing alone as the 21st century learner has access to new material via the Internet every day. The ability to find information about new topics is now a simple task for new learners, and there is little need for traditional teaching methods owing to the lack of interactivity to suit their learning styles and keep them engaged in the classroom. One of the goals of Jamaica's "Vision 2030"seeks to stimulate students' interest and use of technology to teach challenging topics. The E-learning project has employed strategies to address these challenges by partnering with the University of Plymouth to offer a convenient way to learn the fundamentals for Mathematics on electronic devices. While this is a method that can be used to reinforce weak areas for students, it is more likely to be used in their own time. There are instances where more abstract topics require the use of simulations for students to interact with and gain a better understanding of the theory. Such instances could benefit by the concurrent use of interactive simulations to reinforce the points being taught. This paper proposes a simple cost-effective solution to further the use of interactive learning in developing nations by means of use of virtual reality headsets along with a mobile app designed for either a virtual lab experience or classroom setting by utilising free open-source software and recyclable materials. The mobile app would provide material on all subject areas, especially subjects that require experimental set ups. The proposed approach will allow students whose institutions do not have adequate resources to have a complete experimental experience and the opportunity to interact with advanced equipment, making the learning experience more interactive. The goal is to improve the interactive learning environment for students, thus increasing their knowledge base in a fun way.*

Keywords*: Vision 2030, E-learning, learning styles, mobile app, interactive lessons, simulation, recyclable, open source*

1. Introduction

Globalisation has caused changes in education worldwide, and a by-product is the need for adjustments in traditional methods employed in order to conform to the ever-changing environment of modern classrooms. "There is no greater context for educational change than that of globalisation, nor no grander way of conceptualising what educational change is about" (Wells et al. 1998). One major impact due to constant global change is seen in the learning styles of the current generation because of the increased access to new technologies. This has brought about an age of active learners who are more involved in their learning process, and prefer to be in control of their education. They require a more interactive learning environments because of the technological capabilities available to them via the Internet.

Owing to the constant changes in technology, increase in the online knowledge base, and its ease of access, 21st century learners must gain the knowledge and skills required to adapt to these changes because they are expected to meet higher academic standards. Modern education has been influenced by the integration of new technologies and concepts into the curriculum of secondary and tertiary schools to meet the requirements for these new learners. However, developing countries face a lack of financial resources, limited access to the Internet, and a lack of trained teachers who are on par with the new technologies in the education system provided by developed nations (Oliveira, 2004). The digital divide is a gap that exists between individuals with and without access to new technology (Rogers, 2001), and this is a challenge faced by developing nations. Some developing nations have taken measures to help reduce the digital divide, such as the Jamaican government, which has integrated free Wi-Fi hotspots to increase Internet access at several locations in the Corporate Area, including Devon House and Mandela Park, as well as putting Wi-Fi in schools (Smith, 2017). The government also has plans to increase the number of

locations with free Wi-Fi under the USFConnectJA project, and provide free Wi-Fi on Jamaica Urban Transit Company (JUTC) buses (Patterson, 2018).

In Jamaica, the slogan of the Ministry of Education is "Every child can learn, and every child must learn". In keeping with this statement, one of the goals of Jamaica's Vision 2030 mission is an education system that hopes to achieve world-class training and education for both students and teachers. The 2030 mission and the subsequent implementation strategies outlined by the National Standards Curriculum (NSC) facilitates the resolution of issues faced when educating modern students in a globalised learning environment. A range of solutions have been proposed which focus on the need for creative direction from educators as well as interactive programs which can engage the participants (Stennett, 2018). Solutions include a Mathematics application (app) made in partnership with the University of Plymouth to improve the Mathematics passes at the secondary level, and the National Standards Curriculum (NSC), which aims to equip students with the skill set for the constantly changing working world due to globalisation. NSC uses STEAM, which is an educational approach that incorporates Science, Technology, Engineering, Arts and Mathematics, to prepare today's learners for the working world by developing skills such as critical and creative thinking, problem solving and effective collaboration (Taylor, 2018). While these solutions introduce the use of technology in schools, the interactivity of the learning environment still needs to be improved to facilitate the needs of the modern learner.

"Virtual reality (VR) refers to immersive, interactive, multi-sensory, viewer-centred, three dimensional computer-generated environments and the combination of technologies required to build these environments." (Cruz-Neira, 2018). At every level of education, VR has the potential to make a difference, to lead learners to new discoveries, as well as to motivate, encourage, and excite. The learner can participate in the learning environment with a sense of presence, by being a part of the environment (Pantelidis, 2018). The use of VR headsets along with a mobile app designed for a virtual learning environment provides a simple and cost-effective solution.

Given the opportunity to shape the educational tools and materials to personalise and better suit the students' needs and the educator's perspective, the proposed solution of a recyclable cardboard VR headset paired with local curriculum-focused software content allows for unparalleled creativity in the classroom. Geared at interactive learning, students are able to design and redesign their headsets to their own liking, whilst teachers craft new laboratory experiments for the students to conduct and simulations, thus providing a more holistic experience of concepts being taught.

However, the usage of VR headsets in the learning environment can pose both health benefits and risks owing to the immersive multisensory nature of VR technology. The health risk of long exposure is VR-induced sickness, which exhibits a variety of symptoms such as dizziness, nausea, and eye strain (Nichols and Patel, 2002). By reducing prolonged student exposure, the number of possible cases of VR sickness can be limited.

The main focus of this initiative is to demonstrate the use of free open-source software and recyclable materials in order to provide a better learning experience and tackle the digital divide, while taking financial pressure off the country. A mobile app will be used as an educational tool to teach students different subject areas that require an understanding of more than the basic reading and writing skills. It will also provide the virtual space to carry out experiments, enabling students to have a more immersive understanding of complex concepts being conveyed as well as their applicability to real-world situations that they would otherwise be unable to access owing to financial or skill-level barriers to entry.

2. Method

The incorporation of this open-source software will enable the education systems in developing countries to achieve the integration of technology in schools by providing a simple and cost-effective solution to enabling interactive learning techniques and systems in the classrooms.

A qualitative research method was preferred to a quantitative one as there are multiple considerations that had to be included in the study, such as the suitability and validity of testing tools, ethical considerations, as well as its possible abuse and its effect on the physiology of the users. In addition, this would facilitate achieving the research goal with minimal discrepancies or concerns regarding the effectiveness of the design and implementation.

2.1 Hardware and Software Specifications

Each system consists of a VR headset constructed from fully recyclable materials, and was built to open-source specifications supplied by Google through a GNU General Public License. To allow for scalability and modularity, a specially designed mobile application was developed in the open-source cross platform game engine, Unity, to provide the user with an immersive, interactive laboratory or classroom experience.

2.2 Software Development

The development of the software is broken down into scenes, and each scene represents a level from which the user must progress to access the content. The three main levels are course selection, topic selection, and interactivity with the topic content. The flowcharts included below provide a modular view of each scene.

2.2.1 Level 1 Menu - Course Selection

The first scene brings the user into a classroom where they are greeted by the interface located on the chalkboard, and they are prompted to select the subject that they would like to explore (see Figure 1).

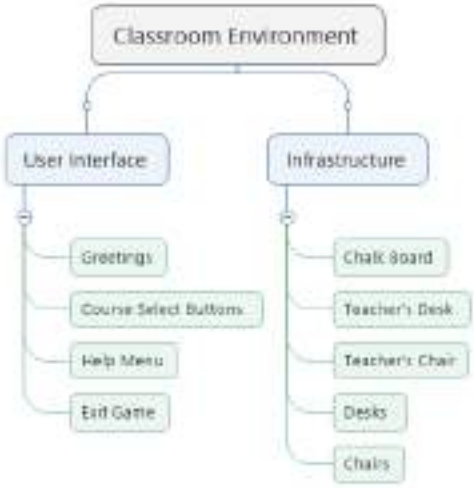

Figure 1. Level 1 Menu - Course Selection.

2.2.2 Level 2 Menu – Topic Selection

After the course has been selected, the user will be led into another classroom where the topics and the subtopics of the course will be located on the chalkboard. The user may then select the desired topic to be covered (see Figure 2).

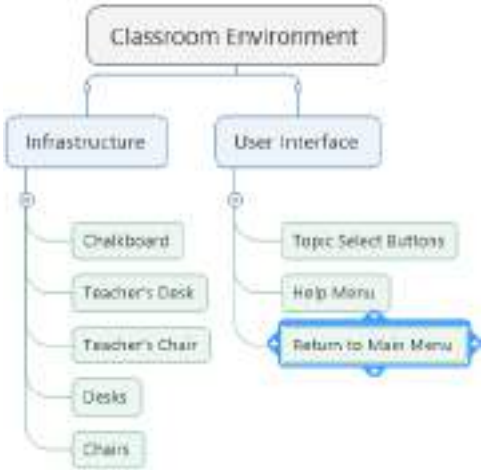

Figure 2. Level 2 Menu – Topic Selection.

2.2.3 Level 3 Menu – Interactive Topic Content

Once the topic or the subtopic has been selected by the user, the content with which interaction is to be made will become available (see Figure 3).

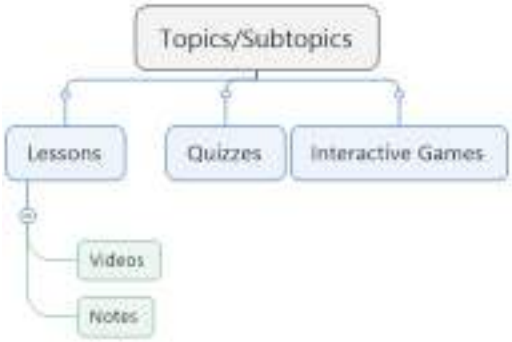

Figure 3. Level 3 Menu – Interactive Topic Content.

2.3 Future Work

The future development of the application will enable the integration of Bluetooth joysticks to increase the interactivity of the lessons. The application was primarily intended for secondary level students; however, with further developments, the course content would be tailored to tertiary level students and industry applications.

2.3.1 Intended User and User Selection

The intended user was expected to be relatively well acquainted with a national schooling curriculum, and should be competent in reading and comprehension along with an awareness of the fundamentals of the test lessons. A relatively small subset of 25–32 participants will be chosen based on their willingness to participate. During the first stage of the project, all participants will be over the age of 18 years and agree to participate in the experiment through a consent form. Test participants are not to be subjected to any further biases such as gender or economic class.

2.3.2 User Familiarisation

Before the testing begins, the users can interact and familiarise themselves with the system; however, this will be optional as the researchers concluded that it should not be required owing to the possibility of the students not receiving proper instructions prior to use. This is done in an attempt to simulate the possible scenario of some users receiving poor or no introduction to the system.

3. Results and Discussion

The topics chosen for this VR game were Mathematics, Physics, and Information Technology. The VR game creation was done using the open-source cross platform game engine, Unity. The current focus of the game development was based on functionality rather than aesthetics. In Unity, the project that was created used different functions that are built in the app. The use of different assets from the Unity Store and different packages allowed for the use of the VR element in the game. A package is a container that holds any assets, shades, scripts etc., which can be used in the project. In the initial setup, the Google cardboard VR package had to be imported into the project for use. The default camera for the project was replaced with the cardboard main camera to attain the split screen found in Google VR apps, and a selection tool was added to the cardboard main camera (see Figure 4).

A scene in Unity represents all of the different environments and menus involved in the game. The game switches from scene to scene in order to enable functionality and to access the content available. Scene one represents the course-selection aspect of the game and three different scenes were used as the topic selection. The room was created by inserting three-dimensional (3D) objects into the scene and scaling them accordingly to create the room, which was then made into a prefab. A prefab is an asset or combination of assets that can be used as a template in other scenes. The prefab of the room, the desks and the chalkboard were created and used in the other scenes for topic selection (see Figures 5 and 6).

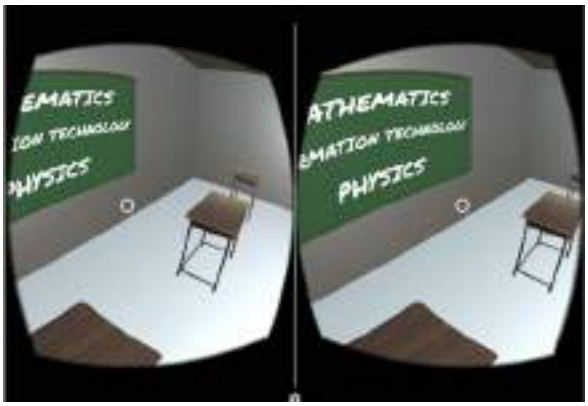

Figure 4: VR mode of the course-selection room.

Figure 5: View of the mathematics room scene.

Figure 6: Chalkboard view of the topics in the scene.

The topic selection was created using buttons in the user interface, text, canvas, and scripts. The canvas in Unity is for text creation, and it determines the location at which the text is displayed in the game. The canvas setting has to be set to world space so that any text written would be displayed anywhere in the game space once the text has been created. The script was written in the programming language C#. The script took the index number of the scene in the order that it was selected in the build settings. The script and the index number of the scene were applied to the button. Therefore, upon selection, the scene with the associated index applied to the button will be opened (see Figure 7).

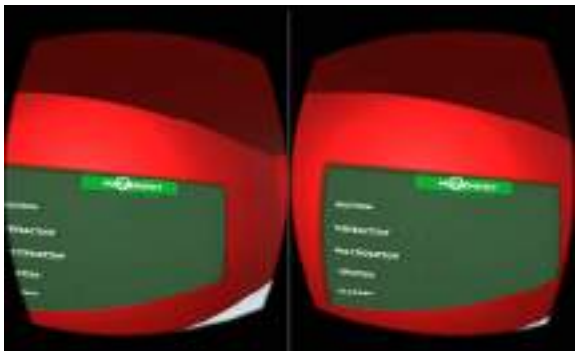

Figure 7: Button selection.

An asset is a representation of any item or object that can be used in the game or project. The asset for the desks, chairs and chalkboard in the classroom was imported from the Unity store, and was used to populate the room for the simulation of an actual classroom (see Figure 8).

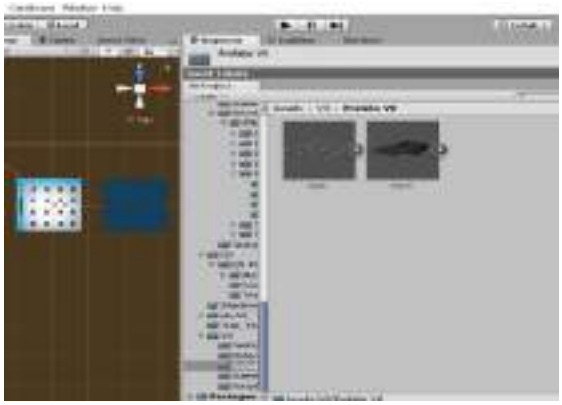

Figure 8: Prefab folder in the VR asset folder.

The interactive scenes in the game include video content on the fundamentals of hardware and software in information technology, as well as lessons on projectile motion in Physics. The video was linked to the cardboard main camera; therefore, if a user moves his/her head, then the video will move in the same way. The physics-based projectile motion game aims to help the students to understand and learn the concepts of different aspects of physics (see Figures 9 and 10).

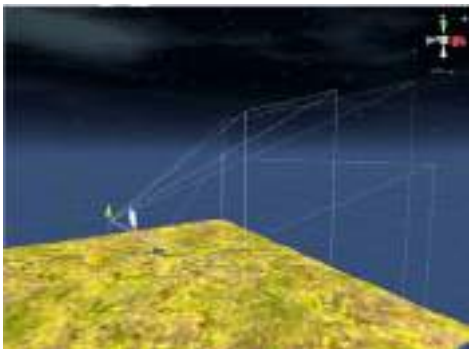

Figure 9: Camera linked to video_panel.

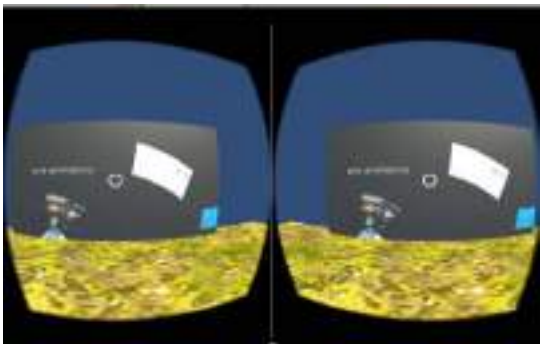

Figure 10: Video in VR mode.

In subsequent versions of the game application, ways of including more interactive games, such as quizzes, fill in the blanks, and 360 videos, etc. will be made available to the viewer.

4. Conclusion

In conclusion, this study proposes the incorporation of VR technology in the education system in developing countries. It is believed that this approach as well as additional stages planned for the future implementation of this application in schools will further enhance the interactivity of the existing learning environment, and will increase the application of ICT in the educational system. This application will also undergo further development to include the use of various forms of interactivity, such as 360° videos and quizzes, and by varying the content, its application can be expanded to not only the secondary level, but also the tertiary level.

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PET Technology: An Opportunity for Innovation in Radiopharmacy and Nuclear Medicine in the Caribbean

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Abstract: *The Positronic Emission Tomography (PET) is an innovating technology expanding around the world due to the availability of compact medical cyclotrons and automated chemical synthesis modules for the production of radiopharmaceuticals. With the inauguration in June 2018 of the first PET center in Lesser Antilles and the forthcoming availability of this technology in Cuba and the Dominican Republic, new roads are opening up for Caribbean health systems. This work analyses the main challenges for radiopharmacy and nuclear medicine in our geographical area. Among other aspects the main challenges in the near future are to develop and improve the diagnosis, treatment and health indicators of oncological, cardiovascular and endocrine diseases in the Caribbean basin, on the basis of a mastery of this new technology; to harmonise protocols for radiopharmaceutical synthesis and use of PET cameras; to set up and accredit quality systems for medical services and for the production of radiopharmaceuticals according to good manufacturing practices based on European and OIEA regulations; to guarantee the safe operation of the various technical systems according to the regulations of the national nuclear safety authorities, to guarantee reliable and safe operation for workers, and patients exposed to ionising radiation; to train health professionals in the provision of nuclear medical imaging and interventional radiology guided by PET; to define and structure the care path of the foreign patient requiring advanced medical imaging examinations; to define and deploy tele-expertise tools in the partner territories, to facilitate feedback and the level of expertise of specialists in the Caribbean Basin and, finally, to develop scientific research around topics on the development of new radiopharmaceutical products and personalised care offering through the creation of a Caribbean collaborative space. Then, we can confirm that the introduction of PET technology in the Caribbean is an opportunity for innovation in radiopharmacy and nuclear medicine for the well-being of our population.*

Keywords*: PET, radiochemistry, nuclear medicine*

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Catalytic Conversion of Carbon Dioxide to Methanol and Chemical Hydrogen Storage

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Abstract: *Catalytic conversion of carbon dioxide to methanol and chemical hydrogen storage are two fundamental green chemistry concepts. Carbon dioxide is a cheap, safe and renewable source of carbon. The conversion of carbon dioxide to methanol is regarded as a significant component of a methanol economy, as it is a liquid that can be easily stored and transported. Hydrogen is an attractive alternative to petrochemical resources because its combustion produces only water as a by-product. Unfortunately, the physical properties of hydrogen complicate its safe, efficient and economical storage. Our research group has discovered several classes of robust, air-stable, homogeneous ruthenium and iridium catalysts that facilitate the efficient conversion of carbon dioxide to methanol. The catalysts also facilitate efficient dehydrocoupling and solvolysis of ammonia borane to generate hydrogen gas. The discovery of the catalysts and their catalytic processes will be presented. Our progress towards the commercialisation of the technologies will be discussed.*

Keywords*: Catalysis, Green Chemistry, Hydrogen, Carbon Dioxide, Methanol, Ammonia Borane*

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The Effects of Wall Thickness and Raster Resolution on the Diametric Accuracy, Cylindricity, and Concentricity of Fused Deposition Modelled Sacrificial Patterns

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Abstract: *Additive Manufacturing rapid reproductive systems are gaining popularity within the manufacturing industry. One of the many benefits of such systems have been the exploration of building practical sacrificial patterns for investment casted metals. Methods such as, Castform and Quickcast, has been developed for selective laser sintering and Stereolithography apparatus technologies, respectively. On one hand, research has demonstrated significant cost savings, when additive manufacturing rapid reproductive systems are utilised for customised or small batch production of sacrificial patterns. On the other hand, the effect of many quality characteristics of additively manufactured parts are not fully understood or investigated. The purpose of this study was to investigate the effects of wall thickness and raster resolution on quality characteristics such as diametric accuracy, cylindricity, and concentricity. Since Fused Deposition Modeling (FDM) have been demonstrated by a number of experimental studies as a viable alternative to wax sacrificial patterns, this study explored the effects of wall thickness and raster resolution on diametric accuracy, cylindricity, and concentricity of FDM patterns. The results of the study indicated raster resolution had no effect on the measured quality characteristics, however, the ANOVA and Kruskal-Wallis tests indicated statistical significance (α=0.05) for wall thickness of cylindricity of a small diameter (0.5") and concentricity of two cylindrical features of diameters 0.5" and 1".*

Keywords*: Additive manufacturing, fused deposition modeling, quality characteristics*

1. Introduction

Manufacturers are constantly searching for methods of improving efficiencies. Improving efficiencies reduces overall costs and frees up much needed resources. This allows manufacturers to be more competitive by sharing those savings throughout the entire supply chain. Moreover, more efficient methods reduce time to product realisation. In addition, resources tied up in less efficient methods can become available for more efficient production processes. Presently, one of many methods of processing metals that is prevalent in the manufacturing and jewellery industries is investment casting or the lost wax process. Investment casting is one of the oldest metal processing methods still being used. Cast objects over 4,000 years old have been found, dating from ancient Assyrian, and Chinese cultures (Bruce et al., 2010), and the process is fundamentally unchanged. A wax sacrificial pattern is coated with a thick layer of refractory material. The wax is melted, and then molten metal is poured into the cavity to create the form.

Although the methods are unchanged, many studies indicate inefficiencies in traditional investment casting processes, especially for customised or small batch productions. A significant percentage of the investment casting cost occurs during the tooling of the patterns. Cheah et at. (2005) proposed that the tooling stage typically can range from 6 to 14 weeks. Further, specialised, highly skilled machinist are required for tool fabrication that can generate estimated costs as high as $30,000 per tool (Winker, 2010). Therefore, tooling is economical for large batch productions, as cost reductions can be realised through economies of scale. As a result, costs could be recouped from repetitive use of a single tool. Customised or small batch production, on the other hand, becomes challenging to some manufacturers utilising traditional methods of expensive tooling for investment casting. Without a doubt, the costs of inflexibility and expensive tooling are directly transfered to the customer and end user.

With the advent of additive manufacturing rapid reproductive systems, expensive tooling can be eliminated altogether and replaced by less expensive 3D printed sacrificial patterns. The patterns can be printed directly from computer-aided design (CAD) files, totally eliminating the tooling stage. Granting the cost savings from repetitive use of a single tool, the true benefits of additive manufacturing rapid reproductive systems become evident when customisation or small batch productions are needed. Dickens and Hopkinson (2003), in their experimental study of comparing three additive manufacturing technologies to injection molded wax sacrificial patterns, concluded that additive manufacturing rapid reproductive systems were more economical than traditional investment casting techniques of tooling, for production volumes in the thousands. The study compared cost savings of production of a small part, (less than 2" X 2" X 2") that resulted in volumes of less than 14000, as more economical for additive

manufacturing technologies when compared to injection moulded sacrificial patterns for investment casting. Grimm (2003), in an experimental evaluation study of additive manufacturing rapid reproductive systems for investment casting applications, noted that additive manufacturing has provided the advantage to manufacturers of cost-effective short runs with economic order quantities as low as one. In the experimental study, Grimm (2003) compares the dimensional accuracy and surface finishes of three Fused Deposition Modelling (FDM) systems. The Maxum, Titan, and Prodigy Plus were compared for dimensional accuracy of dimensions ranging from 0.25" to 4". Of the three systems, the Prodigy Plus resulted in the largest percent deviation of 0.6%, when compared to the Maxum and Titan systems of 0.37% and 0.47% respectively. Grimm further adds that additive manufacturing rapid reproductive systems are suitable for investment casting applications with little modifications to the standard foundry process. Since additive manufacturing rapid reproductive systems can be used as an alternative to tooling and injection moulding, little change is required to the existing investment casting process. Sacrificial patterns can be created from additive manufacturing rapid reproductive systems during the front end stages of investment casting, then integrated into the process with little hassle or modifications.

A survey of the literature regarding the application of additive manufacturing rapid reproductive systems for investment casting, favours the economic benefits associated with customised or small batch production. Additive manufacturing rapid reproductive systems replaces costly tooling, with patterns built directly from CAD files. The process is more efficient, eliminates wastes and facilitates rapid product realisation. Although, traditional investment casting practices utilise wax for sacrificial patterns, any material that can be flashed fired without damaging the ceramic shell, can be suitable for use as an investment casted sacrificial pattern (Chhabra and Singh, 2011). FDM technology deposits an acrylonitrile butadiene styrene (ABS) filament that pattern designs, and the majority of additive manufacturing rapid reproductive systems utilise a non-wax material for building parts. However, detailed studies conducted by Chhabra and Singh (2011) established that any material that can be heated, can also be extruded to create the part. After the layer hardens, a new layer is deposited. This process is repeated until the part is done. According to Sealy (2011), some of the advantages of FDM include minimal wastage, ease of support removal and ease of material change. FDM filament style spool allows for easy and quick exchange of material. The main disadvantages of FDM include limited accuracy due to filament size, slow processes and unpredictable shrinkages caused by the heating, and rapid cooling of the extrude head.

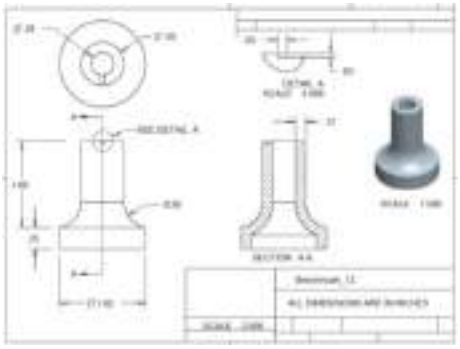
Despite the fact that non-wax patterns are stronger, more durable, and can better withstand finishing operations compared to wax patterns, issues such as shell cracking, incomplete burnout and residual ash remains a problem (Cheah et al., 2005). Non-wax patterns experience a greater rate of expansion than the surrounding ceramic shell, leading to shell fractures. Jacobs (1993), and Yao and Leu (1999) studied this phenomenon, and both concluded the design of thin walled sacrificial pattern geometries eliminated the effects of shell fractures as a result of solid geometry expansions. Jacobs (1993), focused his study primarily on Stereolithography Apparatus (SLA), and developed a QuickCast technique of replacing solids with triangular geometric patterns. Yao and Leu (1999), demonstrated that triangular geometric designs of sacrificial patterns eliminated induced thermal stresses. Their study demonstrated that a triangular geometrically designed sacrificial pattern, exerted no thermal stresses on the surrounding ceramic shell, due to the pattern melting and collapsing inwards during the burnout stage.

2. Methodology

The study consisted of a preliminary design. The purpose of the preliminary experimental study was twofold. One was to determine the smallest possible build diameter with good form and the other was to conduct a pilot test run of the study. The results of the preliminary experimental study showed that the smallest extruded diameter width was 0.015". A factor of 2 times and 4 times the minimum diameter were used to design the benchmark test specimens for the second part of the preliminary study. The design consisted of a 0.3" diameter cylinder of wall thickness 0.03" and another of wall thickness 0.06". A 0.3" radius fillet was also designed into the specimens. The results indicated extreme layer separation on the 0.03" diameter wall thickness specimen as observed in Figure 1. The separation was attributed to the amplification effects of layer cooling at a 0.03" diameter wall thickness. As a result of the observed phenomenon of layer separation at wall thickness of 0.03", the specimens were redesigned to incorporate better form geometries. Wall thickness of 0.06" and 0.12" were selected to construct two cylindrical feature of a base of 1" and 0.5" with a radius fillet of 0.3". The design of experiment comprised of four individual benchmark test specimens. The decision to use four benchmark test specimens, as compared to one panel consisting

Figure 1: Layer Separation of Pilot Test Build

of four specimens, was based in part to the printer's variability. The larger the benchmark test panel, the greater the variability of cooling rates amongst the material. Therefore, part warping is an inherent artifact of the prodigy plus™, particularly on large linear dimensions. To avoid part warping, four smaller benchmark test specimens were designed versus one large test panel of four specimens.



The benchmark test specimens were designed using Pro-Engineer (Wildfire Ver. 5). Figure 2 illustrates one of the two specimens. Three axisymmetric geometric features were designed. They included two cylinders of diametric dimensions of 0.5" and 1" and a fillet of radius 0.3". The specimens were designed with wall thicknesses of 4 times minimum (0.6") or 8 times minimum (0.12"). To distinguish the normal from the fine raster resolution setting, a notch of dimension 0.05" X 0.3" was designed for the fine raster resolution setting as shown in Figure 2, (detail A).

Figure 2: CAD Drawing of Benchmark Specimen

2.1 Design of Experiment

The following equation represents a model of the two factor experimental design (Montgomery, 2010).

$$y_{ijk} = \mu + \tau_i + \beta_j + (\tau\beta_{ij}) + \varepsilon_{ijk} \begin{cases} i = 1, 2, \dots, a \\ j = 1, 2, \dots, b \\ k = 1, 2, \dots, n \end{cases} \quad (1)$$

Where:

a = levels of factor A

b = levels of factor B

n = number of replications

μ= mean effect

τ_i = effect of ith level of factor A

β_j= effect of jth level of factor B

$\tau\beta_{ij}$ = effect of interaction between A and B

ε_{ijk} = random error

Figure 3: Build Plate and Code Scheme Position

The full factorial 2^2 design of experiment principles were used to guide the study. A two factor, two levels set of four benchmark test specimens were built and repeated 24 times in a random order. The coding scheme and build plate position references are illustrated in figure 3. Six plates of 16 specimens were built. Each build plate was allocated a unique build reference number ranging from 1 to 6, located on the upper right corner (see Figure 3). Randomisation of the build process was achieved by using Research Randomiser to generate 24 sets of 4 numbers per set. A total of 96 randomly positioned specimens were analysed for the study. Research Randomiser, version 4.0 was utilised to create random build position references for each benchmark test specimen

Table 1: Randomisation Coding System

Number	*Wall Thickness (1=0.06" / 2=0.12")*	*Raster Resolution (1=normal / 2=fine)*	*File Name*
1	1	1	Bench06_fine
2	1	2	Bench06
3	2	1	Bench12_fine
4	2	2	Bench12

Using the coding scheme depicted in table 1, each specimen was randomly placed on the build plate. To achieve maximum spacing, the pack was set to "un-restricted" in the preference menu, which allowed for tighter spacing of specimens. This in turn allowed more specimens per build plate, reducing the overall time to build.

Repetition and blocking for the study were achieved during part build. Each factor combination was repeated 4 times during a single plate build. A total of 16 specimens per plate were constructed. Six plates of 16 specimens each were built. Each plate build created a block. The study consisted of six blocks of 16 specimens, randomly placed for a total of 96 specimens (see Table 2). In this study, blocking was used to improve precision by eliminating nuisance variability in material and temperature. Since error within was significantly less than error between, each plate was classified as a block.

Table 2: Independent Factor Combination

Plate/Block	**Wall Thickness (0.06"/0.12")**	**Raster Resolution (normal / fine)**	**Interaction (Wall thickness and raster resolution)**
1	8 @ 0.06", 8 @ 0.12"	8 @ normal, 8 @ fine	4 of 0.06" & 4 of 0.12" @ normal and @ fine
2	8 @ 0.06", 8 @ 0.12"	8 @ normal, 8 @ fine	4 of 0.06" & 4 of 0.12" @ normal and @ fine
3	8 @ 0.06", 8 @ 0.12"	8 @ normal, 8 @ fine	4 of 0.06" & 4 of 0.12" @ normal and @ fine
4	8 @ 0.6", 8 @ 0.12"	8 @ normal, 8 @ fine	4 of 0.06" & 4 of 0.12" @ normal and @ fine
5	8 @ 0.06", 8 @ 0.12"	8 @ normal, 8 @ fine	4 of 0.06" & 4 of 0.12" @ normal and @ fine
6	8 @ 0.06", 8 @ 0.12"	8 @ normal, 8 @ fine	4 of 0.06" & 4 of 0.12" @ normal and @ fine

The results from the study were quantified through hypothesis testing by using the ANOVA test to determine statistical significant at a significant level of $\alpha = 0.05$. ANOVA required certain assumption to help improve the accuracy and robustness of the test. The assumption of normility was not satisfied due to the bimodal distribution of the dependent variables data. Therefore, to strengthen the overall results of the ANOVA test, the Kruskal-Wallis non-parametric test was also used to help validate the results from the ANOVA. Non-parameteric tests are less sensitive to following prescribed assumptions. The ANOVA provided an F statistic and associated p-value, while the Kruskal-Wallis provided a chi-square and associated p-value.

3. Results

Due to the fact that there was interaction between factors for the fillet radius variable ($F = 7.897$, $p = 0.006$), no further inferences were made at the shell thickness and raster resolution levels. The researcher recommends further investigation of the effects of shell thickness and raster resolution on geometric features such as, fillets, rounds, and chamfers.

Research Question 1 - Will the diametric accuracy of fused deposition modelling of the Prodigy Plus™ utilising ABS material, be affected by wall thickness or raster resolution?

The response consisted of a design of two cylindrical geometric features, each with three data capture points. Each cylindrical feature was measured at a prescribed top, middle, and bottom location. The parametric ANOVA

test for these measurements all agreed with a p-value greater than the defined alpha value of 0.05. Furthermore, the Kruskal-Wallis chi-square statistic test results supported the ANOVA results of p-values greater than alpha of 0.05. Since statistical significance was not present, it was concluded that at shell thicknesses of 0.06" and 0.120", and raster resolutions of fine and normal were statistically the same.

Research Question 2 - Will the cylindricity of fused deposition modelling of the Prodigy Plus™ utilising ABS material be affected by wall thickness or raster resolution?

The response consisted of a design of two cylindrical geometric features, with each of their measurements at a prescribed middle location. The parametric ANOVA tests for these measurements were varied. Raster resolution indicated p-values greater than alpha of 0.05 for both cylindrical features. However, the 0.5" diameter cylinder recorded a p-value smaller than alpha of 0.05 for the wall thickness factor. The larger 1" diameter cylinder recorded a p-value greater than that of the alpha of 0.05.

Furthermore, the Kruskal-Wallis chi-square statistic test results supported the ANOVA results for the 0.5" diameter cylinder for shell thickness and raster resolution ($X^2 = 12.761$, $p = 0.000$ and $X^2 = 0.052$, $p = 0.820$), and the 1" diameter cylinder for shell thickness and raster resolution ($X^2 = 0.001$, $p = 0.980$ and $X^2 = 0.256$, $p = 0.613$). Since statistical significance was present for the wall thickness factor of the 0.5" diameter cylinder, it was concluded that raster resolution was statistically the same on the cylindricity of 0.5" and 1" diameter cylindrical geometric features. In addition, when the wall thickness factor on cylindricity was examined, there was no statistical significance for the 1" diameter cylindrical feature, but, statistical significance existed for the 0.5" diameter cylindrical feature.

Research Question 3 - Will the concentricity of fused deposition modelling of the Prodigy Plus™ utilising ABS material be affected by wall thickness or raster resolution?

The response consisted of a design of two cylindrical geometric features with each of their measurements at a prescribed middle location. The parametric ANOVA tests for these measurements were varied. The concentricity form geometry compared the 0.5" diametric cylindrical feature to the 1" diameter cylindrical feature. The ANOVA results indicated a p-value ($F = 0.006$, $p = 0.940$) greater than an alpha of 0.05 for the raster resolution factor, but, a p-value ($F = 8.486$, $p = 0.004$) less than alpha for the shell thickness factor.

Likewise, the Kruskal-Wallis test results supported the ANOVA on the effects of raster resolution on concentricity ($X^2 = 0.015$, $p = 0.904$) and shell thickness ($X^2 = 8.084$, $p = 0.004$). It was concluded that the effects of shell thickness and raster resolution on the concentricity of 0.5" and 1" diametric cylindrical features, resulted in statistical significance for wall thickness but not for raster resolution.

3.1. Implications of the Results

Additive manufacturing technologies have presented both advantages and disadvantages as discussed in chapter 1. The ability to build virtually any shape using additive manufacturing rapid reproductive systems coupled with near net shape capabilities of investment casting, creates improved efficiencies for production of customised or small batch production.

The results of the study indicate to manufacturers who utilise fused deposition modeled sacrifical patterns for investment casting applications, that the effects of raster resolution on diametric accuracy, cylindricity, and concentricity was not statictically significant. According to the study, selecting a raster resolution of normal or fine did not effect the diametric accuracy, cylindricity, or concentricty of 0.5" and 1" cylindrical geometrc features. However, one key point recommended for future research, is to examine the effects of raster resolution on the time to build. As indicated earlier during the preliminary experimental study, it was noted that raster resolution seem to have an effect on time to build.

In the same way, manufacturers who utilise fused deposition modeled sacrifical patterns for investment casting applications, must consider the effects of wall thickness on quality characteristics such as diametric accuracy, cylindricity, and concentricity. According to the study, when building diametric cylidrical goemetric features, especially, with wall thicknesses of 0.06, and 0.120", particular considerations must be given to concentricity and the cylindricity of 0.5" diameter cylinder. It was observed that wall thicknesses of 0.06" amd 0.120" exhibited statistical significance on the concentricity of the 0.5" diameter to the 1" diameter.

Also, the wall thickness factor influenced the results of cylindricity of the 0.5" diametric cylindrical geometric feature. Therefore, in selecting apporpriate wall thicknesses consideration must be given to how various values can effect the overall concentricty and cylindricity of diametric features. The study did not consider wall thicknesses less than 0.60" or greater than 0.120". Also, wall thickness between 0.06" and 0.120" is recommended for investigation.

4. Recommendation and Future Research

A number of recommendations were identified for future research. Some were classified as additional controls that were not possible at the time of the study due to time constraints and scope management. Others were realised during the study and were recommended for future investigation and exploration.

The study was designed to investigate dependent variables of cylindricity and concentricity, particularly for their geometric form tolerances on cylindrical features. Although cylindrical features are common in part design and investment, casting such as, flanges, and gears, other geometric forms tolerances should be considered. The effects of shell thickness and raster resolution on other quality characteristics, such as, straightness and flatness should be explored and investigated. Determining how those factors influence straightness and flatness of non-axisymmetric geometric features will greatly add to the understanding, and improved accuracies of additive manufacturing and by extension, the investment casting process.

Defining the scope of any project requires a delicate balance of a number of constraints. The second recommendation is to explore additional cylindrical diameters. The study focused on two diametric values (0.5" and 1"). Diametric values greater than 1", lessor than 0.5" and in-between 0.5" and 1" should be considered for future exploration. As was noted during the study, the effect of wall thickness was statistically significant for the 0.5" diameter cylinder but not the 1" cylinder. Is it concluded, that based on the levels of wall thicknesses selected for the study, cylindricity is only affected if the cylindrical diameter is 0.5"? Or rather, based on the factor levels, there exist a maximum diametric value where statistical significance occurs for all values below.

The Prodigy Plus™ FDM is capable of printing, utilising two slice height factors of 0.010" and 0.013". The study was conducted with a layer slice height of 0.010". A duplication of the study at a layer slice height of 0.013" should be explored to further understand the effects of layer slice height on diametric accuracy, cylindricity, and concentricity.

In determining the concentricity of the two diametric features, the top 0.5" diameter cylinder was compared to the base 1" cylinder. The study indicated a statistical significance when the wall thickness factor on concentricity was examined. A few recommendations can be considered. Firstly, calculating concentricity based on the relationship of the 1" diameter cylinder to the 0.5" diameter cylinder. Secondly, building the specimen in an inverted orientation, where the 0.5" diameter serves as the base. In doing so, considerations must be given to the additional support material needed for the 1" diameter cylinder. This would result in additional material, time, and overall increase in costs. Although the change in build orientation possesses additional constraints, exploration is necessary and to some extent specimen count can be reduced.

No inferences were concluded at the factor levels due to interaction between the factors. Therefore, it is recommended to explore and investigate designs of multiple fillets, rounds, and chamfers, as these features are common in design and investment casting.

During the preliminary experimental study, the results of time to build seem to be influenced by raster resolution. Two specimens of 0.06" wall thickness, one of normal and the other of fine raster resolution and another two of 0.120" wall thickness, were compared for time to build and material usage. It was noticed the time to build was different for both wall thicknesses, as a result of the raster resolution setting. Since reductions in time can indicate reductions in costs, a recommendation to explore time to build especially pertaining to raster resolution, will further expand the knowledge and help improve efficiencies of additive manufacturing FDM processes.

The final recommendation deals with material selection of the Prodigy Plus™ FDM. This study consisted of building benchmark test specimens using a polymer ABS400 material. A number of experimental studies have concluded that an inherit challenge with using non-wax materials for sacrificial patterns is the thermal expansion. Thermal expansion normally results in ceramic shell fractures. Although thermal expansion of less than 0.35% has demonstrated no ceramic shell fracturing, this recommendation considers another method of removing sacrificial patterns from ceramic shells. Traditionally, investment casting uses a burnout process for removing sacrificial pattern from ceramic shell. As an alternative to burnout, specimens can be built of water soluble support material, which can be dissolved from the ceramic shell. All of the above recommendations can be applied to the water soluble material with further investigations of the proof of concept.

5. Conclusion

All in all, the study presents needed value to the existing body of knowledge. Due to the lack of understanding on the effects of shell thickness and raster resolution, especially on quality characteristics, such as, diametric accuracy, cylindricity, and concentricity, the results of the study are relevant and practical. Researchers and practitioners alike,

experience the benefits and added value of the study towards improving efficiencies of investment casted sacrificial patterns.

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Removal of 2-Nitrophenol, 2, 4-Dinitrophenal and 2, 4, 6-Trinitrophenol from Aqueous Solution through Adsorption on Cobalt, Nickel and Tungsten Ferrocyanides

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Abstract:*Cobalt, nickel and tungsten ferrocyanides were synthesised and characterised by elemental and spectral studies. Removal of 2-nitrophenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol from aqueous solution through adsorption on synthesised metal ferrocyanides were studied in the pH range 1.0 – 10.0 and at a temperature of 30 ± 1º C. The progress of adsorption was followed spectrophotometrically by measuring the absorbance of phenol solutions at their corresponding* λ_{max}*. The Langmuir type of adsorption is followed in the concentration range* 10^{-3} *M to* 10^{-4} *M for 2-nitrophenol, 2, 4 – dinitrophenol and 2, 4, 6 – trinitrophenol solutions. The 2, 4, 6 – trinitrophenol and 2 – nitrophenol were found to have maximum and minimum affinity with all three metal ferrocyanides studied. Nickel and tungsten ferrocyanides were found to have higher and lower adsorption capacity with all three substituted phenols. The phenols react with soil to reduce their fertility and decrease crop production. Phenol also produce bad odour in the environment. Therefore, phenols should be removed from our environment*

Keywords*:*Removal, 2-nitrophenol, 2, 4-dinitrophenol, 2, 4, 6-trinitrophenol, adsorption, metal ferrocyanides.

1. Introduction

The concentration of the chemical elements in the primordial sea is correlated with their biological behaviour Kobayashi and Ponnamperuma (1985). Further, it is assumed that divalent transition metal ions, which were in abundance in the primeval sea, would have formed complex compounds with the simple molecules readily available to them Egami (1975). It is therefore reasonable to assume that transition metal ions could easily have formed a number of stable and insoluble complexes with abundant CN^- in the primeval sea. The formed insoluble cyanometal complexes could have settled at the bottom of the sea or at the seashore, and might have catalysed a number of reactions such as condensation, oligomerisation, oxidation and interaction on their surfaces. The existence of metal ferrocyanides and metal ferrocyanides on the primitive earth has been reported by Arrhenius (1990). The metal ferrocyanides act as adsorbents (Viladkar et al., 1996; Viladkar et al., 1994; Alam et al., 1999; Ali et al., 2006), ion-exchangers (Baetsle et al., 1965; Baetsle et al., 1966; Malik et al., 1976; Saraswat et al., 1981) and photosensitisers (Tewari, 2005; Tewari, 2009) during the course of chemical evolution on primitive earth.

Phenol is a basic structural unit for a variety of synthetic organic compounds, therefore wastewater originating from many chemical plants and pesticides manufacturing industries contain phenols. Besides this, wastewater originating from other industries such as pharmaceutical, petroleum, tanning, textile, rubber, pulp and paper, gas and coke manufacturing and resin manufacturing also contain different types of phenols. In view of the wide prevalence of phenols in different wastewaters and their toxicity (Castillo and Bacelo, 1999) to human, animal life and environment even at low concentration, it is essential to remove them before discharge of wastewater into water bodies. Phenols also react with organic matters to reduce the fertility of soil. A number of methods such as biological methods (Kennedy et al., 1992), ion-exchange (Chan and Fu, 1998), photo-catalytic degradation (Alberici and Jardin, 1994) and oxidation with ozone / hydrogen peroxide (Mokrini et al., 1997; Koyama et al. 1994) have been used for the removal of phenols. However, these methods have shown low efficiency for the removal of trace level of phenols. Despite the availability of the above mentioned processes for the removal of phenols, the adsorption process is considered to be best as it can generally remove all types of phenols, and the effluent treatment is convenient because of simple design and easy operations.

The adsorption of phenols on a number of adsorbents has been examined by some researchers (Singh et al., 2008) reported liquid- phase adsorption of phenol using activated carbons derived from agricultural waste material. Adsorption of phenol, p-chlorophenol and p-nitrophenol onto functional chitosan was investigated by Li et al. (2009). Pan et al. (2008) studied adsorption and hysteresis of Bisphenol-A on carbon nanomaterials. Kinetics and isotherm studies for the adsorption of phenol using low cost micro porous $ZnCl_2$ activated coir pith carbon was

described by Subha and Namavivayam (2009). Adsorption of phenol on granular activated carbon from nutrient medium: equilibrium and kinetic study was reported by Dabhade et al. (2009). Yan and Quan (2009) investigated equilibrium and kinetic studies of phenol sorption by chitosan coated montmorillonite. Liquid phase adsorption of phenol by activated carbon derived from Hazelnut bagasse was studied by Karabacakoglu et al. (2008). Alzaydiene and Manasreh (2009) described, equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto activated phosphate rock. Studies on adsorption of phenols and 4-nitrophenol on Mg Al – mixed oxide derived from Mg Al – layered double hydroxide was reported by Chen et al. (2009). Wang et al. (2010) investigated adsorption of phenol on attapulgite – zeolite nano-structure adsorbent from aqueous solution. Evaluation of barley straw and its ash in removal of phenol from aqueous solution was studied by Maleki et al., (2010). Podkoseielny and Nieszporek (2007) described heterogeneity of activated carbons in adsorption of phenols from aqueous solution. Adsorption behaviour of chlorophenol on natural zeolite was reported by Rushdi and Bassam (2007). Phenol removal using Brassica Junsia hairy root: role of inherent peroxydase and H_2O_2, was investigated by Singh et al. (2006). Removal of phenol from water environment by surfactant-modified alumina through adsolubilisation was studied by Adak et al. (2006). Laser-induced photo-catalytic removal of phenol using in-type WO_3 semiconductor catalyst was described by Gondal and Seddigi (2006). Tris (2, 2-bipyridine) ruthenium (II) – clays as adsorbents for phenol and chlorinated phenols from aqueous solution was reported by Okada et al. (2005). Dabrowski et al. (2005) investigated adsorption of phenonic compounds by activated carbon. Impact of aging time on the dermal penetration of phenol in soil was studied by Abdel-Rahman et al. (2006). Arellano-Cardenas et al. (2005) described adsorption of phenol and dichlorophenol from aqueous solutions by porous clay heterostructure. Mahvi et al. (2004) reported potential of rice- husk and rice-husk ash for phenol removal in aqueous solution.

A literature survey indicated that adsorption of phenols on activated carbon and other adsorbents are well established, but no report is available on interaction of phenol and phenolic compounds with metal ferrocyanides. In view of this, an attempt has been made to investigate surface characteristics of the metal ferrocyanide-phenol system. In addition, present work describes removal of 2-nitrophenol (2-NP), 2, 4-dinitrophenol (2, 4-DNP) and 2, 4, 6-Trinitrophenol (2, 4, 6-TNP) through adsorptive interaction with cobalt, nickel and tungsten ferrocyanides.

2. Experimental Section

2.1. Chemicals

Potassium ferrocyanide, cobalt(II) chloride, sodium tungstate, nickel(II) chloride, 2-nitrophenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol, were obtained from BDH, Poole, UK. All chemicals were of Analytical Reagent grade and used without further purification. Solutions were prepared in double distilled water.

2.2. Synthesis of Metal Ferrocyanides

Nickel ferrocyanide was prepared by adding nickel chloride (500 mL; 0.1 M) potassium ferrocyanide (167 mL; 0.1 M) solution with constant stirring (Kourim et al., 1964). The reaction mixture was heated on a water bath for 3 h and kept as such at room temperature for 24 h. The precipitate was filtered under vacuum, washed several times with distilled water and dried in an air oven at 60º C. The dried product was grounded and sieved to 125 μm particle size.

Cobalt ferrocyanide was synthesized by adding (1 Volume, 0.5 M) potassium ferrocyanide and (2.4 Volume, 0.3 M) cobalt chloride and kept as such after gentle stirring over a period of 0.5 h at room temperature (Prout et al., 1965). The slurry of cobalt ferrocyanide was filtered under vacuum, washed several times with distilled water and dried. The resulting granules were dried and powdered to 125 μm particle size.

Tungsten ferrocyanide was prepared by adding potassium ferrocyanide (0.1 M, 200 mL) sodium tungstate (0.1 M, 400 mL) and HCl (1.0 M, 10 mL) with constant stirring (Kraus, 1955). The reaction mixture was then heated in a boiling water bath for 3 h. The product was left at room temperature for 24 h. The precipitate was then filtered under vacuum, washed with distilled water and dried in an oven at 60º C. The dried product was ground and sieved to 125 μm particle size.

2.3. Stability of Metal Ferrocyanides

Nickel ferrocyanide is an orange brown insoluble solid. It possesses octahedral structure with face centered cubic lattice of dimension 4.89 – 5.10 Å. Cobalt ferrocyanide is gray blackish in colour and similar in properties to nickel ferrocyanide. Nickel and cobalt ferrocyanides both have same ion-exchange capacity 6.05 meq. Cs /g. Tungsten ferrocyanide is a dark green colour amorphous insoluble solid. All three metal ferrocyanides showed no X-ray pattern.

All three metal ferrocyanides are found to be stable in acids (HCl, HNO_3, H_2SO_4, CH_3COOH) and bases (NaOH, KOH, NH_4OH) in the concentration range 0.1 – 2.0 M. Metal ferrocyanides are also found to be stable in salts (NaCl, KCl, LiCl, NH_4Cl, RbCl, CsCl, $BaCl_2$, $CaCl_2$, $MgCl_2$) solution in the concentration range 1.0 – 2.0 M.

2.4. Elemental Studies of Metal Ferrocyanides

Cobalt, nickel, tungsten hexacyanoferrate (II) complexes were characterised on the basis of elemental analysis. Cobalt, nickel, tungsten and iron were estimated by atomic absorption spectrophotometry on IL – 751Spectrophotometer (Vogel, 1978). Carbon, hydrogen, nitrogen analysis was performed on CEST – 118, CHN analyser (see Table 1).

Table 1.Elemental analysis of cobalt, nickel and tungsten ferrocyanides

Metal ferrocyanides	Percentage found				
	Metal	Iron	Carbon	Hydrogen	Nitrogen
CoFc	26.60	13.10	15.50	2.71	18.10
NiFc	31.30	14.80	20.30	1.50	21.40
WFc	52.71	7.27	9.31	1.67	12.07

Note.CoFc: cobalt ferrocyanides; NiFc: nickel ferrocyanide; WFc: tungsten ferrocyanide.

2.5. Spectral Studies of Metal Ferrocyanides

Infra-red spectra of the metal ferrocyanides were recorded in potassium bromide disc on Beckman IR – 20 Spectrophotometer. Cobalt, nickel and tungsten ferrocyanides revealed peaks around 3500 and 1600 cm^{-1} characteristics of water molecules / OH group and HOH bending, respectively (Lucchesi and Glasson, 1956). Two sharp bands at around 2070 cm^{-1} and 595 cm^{-1} are characteristics of cyanide and Fe – C stretching, respectively (Nakamoto, 1963). Another sharp band at 460 cm^{-1} probably shows the presence of a metal – nitrogen band due to polymerisation (Nakamoto et al., 1958) (see Table 2).

Table 2.Infrared spectral data of cobalt, nickel and tungsten ferrocyanides

Metal ferrocyanide	Adsorption frequency (cm^{-1})				
	H_2O molecules / OH group	HOH Bending	C ≡ N Stretching	Fe – C	Metal - N[a]
CoFc	3510	1600	2070	595	460
NiFc	3450	1635	2096	590	440
WFc	3510	1600	2000	620	490

Note. [a] metal – N band shows degree of polymerisation

2.6. Adsorption studies

2.6.1. Effect of pH on adsorption of phenols on metal ferrocyanides

The adsorption of substituted phenols on metal ferrocyanides at different pH (1.0 – 10.0) and 1 x 10^{-4} M adsorbate concentration was studies. A series of 15 mL test tubes were employed. Each tube was filled with 10 mL of substituted phenol solutions and adjusted to desired pH. The desired pH was maintained by dilute NaOH or HCl solutions. A 25 mg of metal ferrocyanide was added into each tube at room temperature (30 ± 1º C) and agitated for 6 h until equilibrium was attained. The equilibrium time and concentration range were, however, decided after a good deal of preliminary investigations. The content then centrifused, decanted and concentration of supernatant was measured spectrophotometrically using the Uvikonspectrophotomer (No. 922 Kontrom Instruments). The concentration of 2-NP, 2, 4 -DNP and 2, 4, 6-TNP were measured spectrophotometrically at 360, 360 and 382 nm, respectively. The amount of substituted phenols absorbed calculated by the difference in concentration before and after the adsorption.

2.6.2. Effect of concentration on adsorption of substituted phenols on metal ferrocyanides

The adsorption of 2-NP, 2, 4-DNP and 2, 4, 6-TNP on metal ferrocyanides as a function of substituted phenols concentrated (10^{-3} – 10^{-4} M) was studied at pH 7.0 ± 0.01 and room temperature 30 ± 1º C. A number of 15 mL test tubes were filled with 10 mL of phenol solution and adjusted to desired pH, sample of 25 mg of metal ferrocyanides

was added to each test tube and stoppered. The tubes were agitated for 6 h until equilibrium was attained. The content then centrifused decanted and adsorption of 2-NP, 2, 4-DNP and 2, 4, 6-TNP was measured spectrophotometrically at their corresponding λ_{max} 360, 360 and 382 nm, respectively.

3. Results and Discussion

3.1. Effect of pH on adsorption of substituted phenols on metal ferrocyanides

The adsorption of 2-NP, 2, 4-DNP and 2, 4, 6-TNP as a function of pH was studied over a pH range of 1.0 – 10.0 are shown in Figures 1, 2 and 3, respectively. The adsorption of 2-NP (pKa = 7.17), 2, 4-DNP (pKa = 3.96) and 2, 4, 6-TNP (pKa = 0.38) were found to be maximum near to their respective pKa values.pH was maintained as desired by using dilute HCl or NaOH Solutions. The percentage uptake of 2-NP, 2, 4-DNP and 2, 4, 6-TNP on cobalt, nickel and tungsten ferrocyanides are given in Tables 3, 4 and 5, respectively.

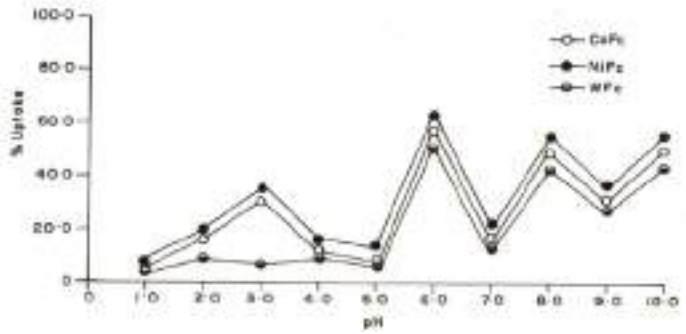

Figure 1. Effect of pH on adsorption of 2-NP on metal ferrocyanides.
Temperature = 30 ± 1 ° C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2 - NP = 360 nm.

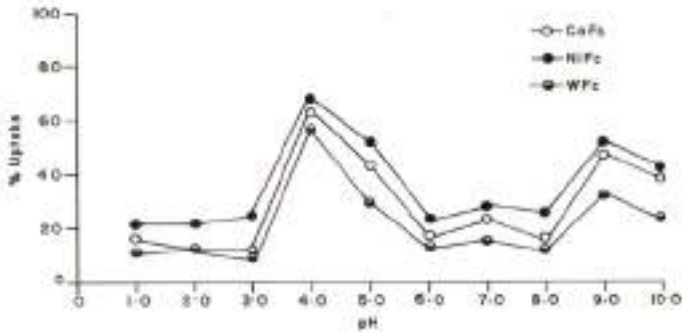

Figure 2. Effect of pH on adsorption of 2, 4-DNP on metal ferrocyanides.
Temperature = 30 ± 1° C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2, 4 - DNP = 360 nm.

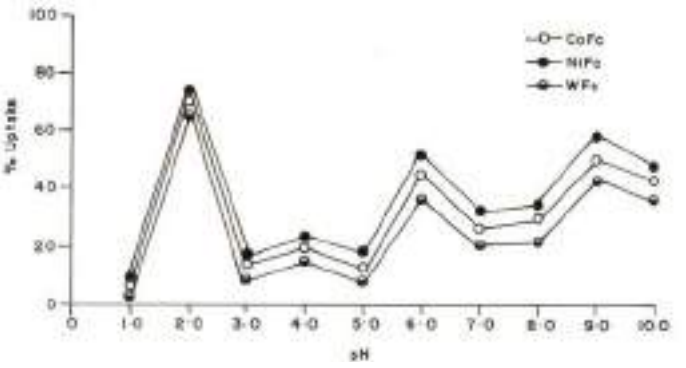

Figure3. Effect of pH on adsorption of 2, 4, 6-TNP on metal ferrocyanides.

Temperature = 30 ± 1 ° C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2, 4, 6 - TNP = 382 nm.

The percentage uptake was calculated by general formula

$$\% \text{ uptake} = \frac{\text{Differences in concentration of substituted phenols before and after adsorption}}{\text{Concentration of substituted phenols before adsorption}} \times 100$$

It is observed from Tables 3, 4 and 5 that 2-NP, 2, 4-DNP and 2, 4, 6-TNP has maximum adsorption at pHs 6.0, 4.0 and 2.0, respectively with all three metal ferrocyanides studied. It is also observed from Tables 3, 4 and 5 that 2, 4, 6-TNP and 2-NP has maximum and minimum adsorption, respectively with all three adsorbents.

Table 3.Percentage adsorption of 2-nitrophenol on metal ferrocyanides

pH	% adsorption		
	CoFc	NiFc	WFC
1	4.6	5.4	4.0
2	14.5	15.7	8.8
3	30.8	35.0	7.5
4	12.0	14.0	10.2
5	8.3	10.0	7.15
6	59.2	62.0	57.5
7	17.5	18.0	15.4
8	49.3	55.0	46.2
9	32.3	37.0	31.6
10	51.2	56.0	46.5

Note. Room temperature = 30 ± 1º C; amount of metal ferrocyanide = 25 mg :λ_{max} 2-NP = 360 nm; 2 - NP pKa = 7.17.

Table 4. Percentage adsorption of 2, 4-dinitrophenol on metal ferrocyanides

pH	% adsorption		
	CoFc	NiFc	WFc
1	16.6	22.0	12.0
2	13.5	22.3	12.0
3	13.0	24.0	10.2
4	62.7	67.7	59.9
5	43.7	55.5	31.6
6	16.7	23.4	15.0
7	23.5	27.0	17.6
8	18.5	25.9	13.0
9	47.0	53.3	32.0
10	37.6	43.2	23.4

Note. Room temperature = 30 ± 1º C; amount of metal ferrocyanide = 25 mg; λ_{max} 2, 4 - DNP = 60 nm; 2, 4 - DNP pKa = 3.96.

Table 5. Percentage adsorption of 2, 4, 6-trinitrophenol on metal ferrocyanides

pH	% adsorption		
	CoFc	NiFc	WFc
1	6.2	9.21	4.23
2	68.5	73.8	66.7
3	12.6	16.5	10.2
4	20.0	23.0	15.0
5	13.2	18.0	10.7
6	45.4	52.5	37.7
7	27.0	33.0	22.0
8	30.0	35.0	23.5
9	49.2	58.0	43.7
10	42.8	47.2	38.9

Note. Room temperature = 30 ± 1º C; amount of metal ferrocyanide = 25 mg; λ_{max} 2, 4, 6 - TNP = 382 nm; 2, 4, 6 – TNP pKa = 0.38.

Electron density of aromatic ring is strongly influenced by the nature and number of substituent present in it. The nitro group is electron withdrawing and reduces the overall electron density in the pi system of benzene ring. The nature of substituent is similar in all three adsorbates. The maximum and minimum adsorption in case of 2, 4,

6-TNP and 2-NP is only due to various number of substituent group. The minimum adsorption in case of 2-NP is also may be due to presence of intermolecular hydrogen bonding between ortho nitro and phenolic hydroxyl groups. The adsorption of substituted phenols on metal ferrocyanides may be due to presence of phenolic hydroxyl group, nitro group and benzene ring in substituted phenol molecule, which act as a site for interaction with metal ferrocyanides surface.

3.2. Effect of concentration on adsorption of substituted phenols on metal ferrocyanides

A neutral pH (7.0 ± 0.01) and room temperature 30 ± 1 ºC was chosen to run the adsorption of 2-NP, 2, 4-DNP and 2, 4, 6-TNP in wide concentration range. The neutral pH is physiologically significant, as most of the reactions in living systems take place in neutral medium. The desired pH was maintained by dilute NaOH or HCl solutions. The adsorption isotherms as phenol concentration versus amount adsorbed (mg / g) for adsorption of 2-NP, 2, 4-DNP and 2, 4, 6-TNP on cobalt, nickel and tungsten ferrocyanides are shown in Figures 4, 5 and 6, respectively.

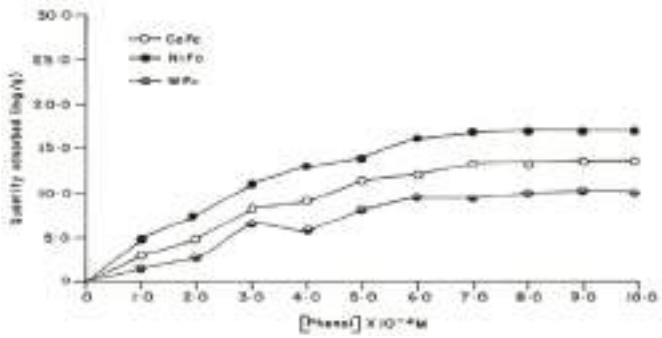

Figure 4. Adsorption isotherms of 2-NP on metal ferrocyanides .
Temperature = 30 ± 1 °C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2 - NP = 360 nm.

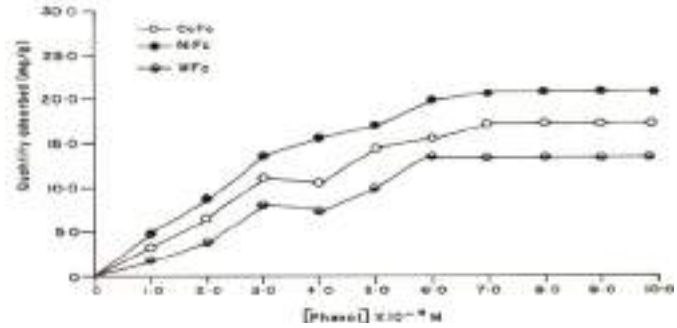

Figure 5. Adsorption isotherms of 2, 4-DNP on metal ferrocyanides.
Temperature = 30 ± 1 °C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2, 4 - DNP = 360 nm.

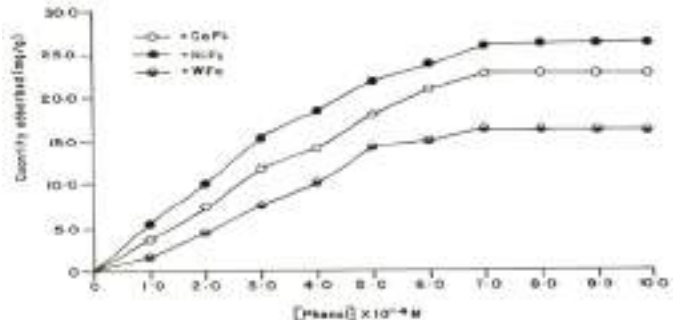

Figure 6. Adsorption isotherms of 2, 4, 6-TNP on metal ferrocyanides.
Temperature = 30 ± 1 °C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2, 4, 6-TNP = 382 nm.

Adsorption isotherms of 2 -NP, 2, 4-DNP and 2, 4, 6-TNP on metal ferrocyanides show that adsorption is fast in all cases isotherms are regular, positive and concave to the concentration axis. Slow adsorption gradually leading to constancy takes place at higher adsorbate concentration. In general, the adsorption curves were characterised by a gradual rise and a flattering at higher adsorbate concentrations. Further, more phenols are retained and their concentration increases and adsorption mechanism also become more efficient. The result is that affinity of metal ferrocyanides toward adsorption for 2- NP, 2, 4 -DNP and 2, 4, 6 -TNP follow the order

NiFc > CoFc > WFc

The present result also suggest that affinity of substituted phenols with cobalt, nickel and tungsten ferrocyanides follow the order.

2, 4, 6-TNP > 2, 4- DNP > 2-NP

Langmuir plots ($1/C_{eq}$ versus $1/Q_{eq}$) for adsorption of 2 – NP, 2, 4-DNP and 2, 4, 6-TNP on cobalt, nickel and tungsten ferrocyanides are shown in Figures 7, 8 and 9, respectively. Linear nature of plots showing the Langmuir type of adsorption in general. Langmuir plots exhibit the amount of substituted phenols adsorbed as a function of their equilibrium concentration. The trends of substituted phenols adsorption on metal ferrocyanides follow the Langmuir equation (Hertz et al. 1968).

$$1/Q_{eq} = (1/Q_0) + (1/C_{eq})\,(1/bQ_0)$$

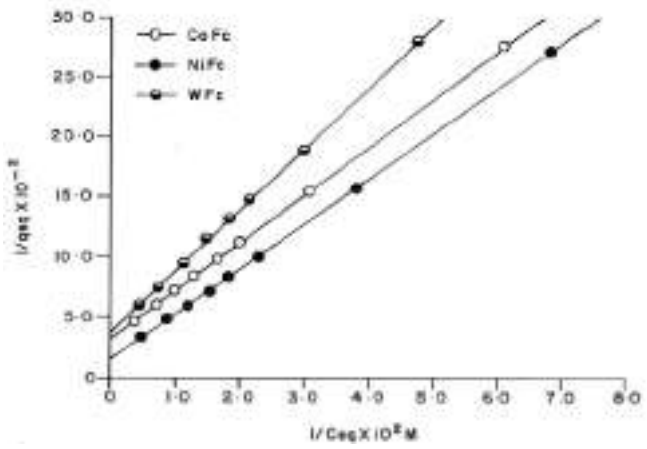

Figure 7. Langmuir plots of 2-NP on metal ferrocyanides.
Temperature = 30 ± 1 ° C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2–NP = 360 nm.

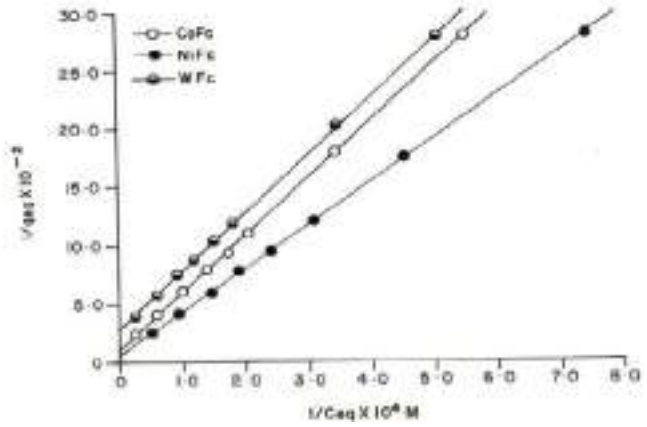

Figure 8. Langmuir plots of 2, 4-DNP on metal ferrocyanides.
Temperature = 30 ± 1 °C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2, 4–DNP = 360 nm.

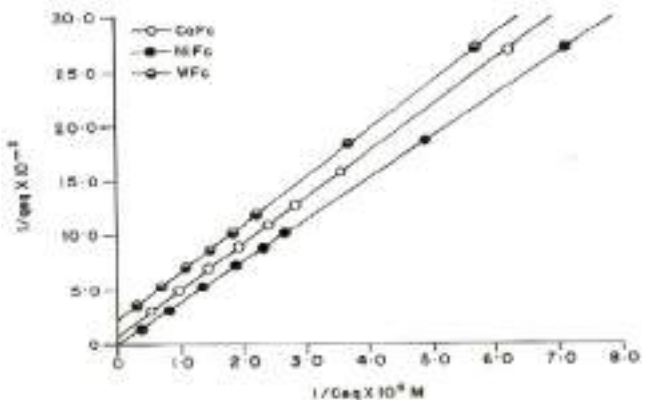

Figure 9. Langmuir plots of 2, 4, 6-TNP on metal ferrocyanides.
Temperature = 30 ± 1 ° C; pH = 7.0 ± 0.01; amount of MFc = 25 mg; particle size = 125 μm; λ_{max} 2, 4, 6 –TNP = 382 nm

where Qeq is the amount of solute adsorbed per unit mass of adsorbent, C_{eq} the equilibrium concentration of solute in solution, Q_0 the limiting amount of adsorbate that can be taken up by unit mass of adsorbent, b the constant related to equilibrium constant or bonding energy or enthalpy (ΔH) of adsorption (b α e - $^{\Delta H/RT}$, the parameter b reflects the steepness of the approach to saturation; more precisely, the b value is the reciprocal of concentration at which half of the saturation of the adsorbent attained). Actually, b is a constant, which is function of adsorption energy. The appropriate Langmuir constants b and Q_0 were calculated from the slope and intercept of Langmuir plots, respectively. The values of Langmuir constants are given in Table 6.

Table 6. Langmuir constants for adsorption of 2-NP, 2, 4-DNP and 2, 4, 6 -TNP on metal ferrocyanides

Substituted Phenols	Metal ferrocyanides	Particles size (μm)	Langmuir constants	
			b x 10^6 ($l\ mol^{-1}$)	Q^0 ($mg\ g^{-1}$)
2 – Nitrophenol (pKa = 7.17)	CoFc	125	75.01	33.33
	NiFc		46.01	58.82
	WFc		70.70	27.78
2, 4 – Dinitrophenol (pKa = 3.96)	CoFc	125	25.42	76.92
	NiFc		21.92	125.0
	WFc		54.08	38.46
2, 4, 6 – Trinitrophenol (pKa = 0.38)	CoFc	125	16.47	142.86
	NiFc		13.28	200.0
	WFc		51.22	47.62

Note. Room temperature = 30 ± 1º C; pH = 7.0 ± 0.01; amount of metal ferrocyanide = 25 mg; λ_{max} 2 - NP = 360 nm; λ_{max} 2, 4 - DNP = 360 nm; λ_{max} 2, 4, 6 – TNP = 382 nm.

Dolezal and Kourim,V. (1969) have reported a general formula of metal hexacyanoferrate(II) as M_2 [Fe $(CN)_6$], where M represents a transition metal ion. The M^{2+} ions are exchangeable cations, species [Fe $(CN)_6]^{4-}$ in metal hexacyanoferrate(II) exist with an octahedral geometry, where six CN^- ligands surrounds the central iron atom (Chandra et al., 1967). Due to strong field of the CN^- ligand, all six electrons become paired to give the electronic configuration t_{2g}^6. Although the CN^- ligand bound with Fe via 6 donation, there is sufficient back bonding from iron metal dπ orbitals to the CN^- ligand antibonding pπ orbitals.

Transition metal hexacyanoferrate (II) complexes usually have a polymeric lattice structure with [Fe $(CN)_6]^{4-}$ anions, where the outer transition – metal ion may be coordinated through the nitrogen end of the cyanide ligand. The adsorption of substituted phenols on metal hexacyanoferrate (II) is probable due to a substituted phenol interaction with the replaceable divalent metal ions present outside of the coordination sphere of the hexacyanoferrate (II).

4. Conclusion

The present research work has shown that metal ferrocyanides to be reasonable and plausible candidates in studies involving adsorption and removal of phenolic compounds from aqueous solution and waste water. Metal

hexacyanoferrate (II) complexes can be used for the removal of phenolic contaminants from agricultural soil and environment. The result on the present studies also show that the adsorption of substituted phenols on metal ferrocyanides is quite satisfactory. The most effective pH for the removal of 2 -NP, 2, 4 -DNP and 2, 4, 6 -TNP is found to be 6.0, 4.0 and 2.0, respectively. The adsorbents may be useful for the treatment of phenol bearing wastewater.

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Chiral Ruthenium Aminophospine and Phosphine Iminopyridine Complexes for Asymmetric Catalytic Transformations

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Abstract: *Asymmetric catalytic transformation is one of the most reliable methods for the preparation of chiral compounds and is widely used in the fine chemical industry. Catalytic transformation reduces or eliminates multistep processes that would otherwise require the use of harmful chemicals in the preparation of chiral compounds. Aminophosphine (P-N) is a privileged class of ancillary ligands with a unique combination of soft phosphorus and hard nitrogen centres, which can form a variety of transition metal complexes as potential catalysts for synthetically useful reactions. Herein, the catalytic applications of ruthenium complexes containing P-N and PNN ligand systems, namely (S)-8-(diphenylphosphino)-1,2,3,4-tetrahydronaphthalen-1-amine, [(S)THNANH$_2$], (R_c)-1-((S_p)-2-diphenylphosphino)ferrocenyl-ethylamine, [(R_cS_p)PPFNH$_2$], and (R_c)-1-((S_p)-2-diphenylphosphino)ferrocenyliminopyridine, [(R_cS_p)PPFNPy,] will be discussed. Suitable combinations of these aminophosphine ligands with ruthenium precursors afforded highly efficient systems for the asymmetric hydrogenation and transfer hydrogenation of selected ketones in 2-propanol. Ru-(S)THNANH$_2$ proved to be the most efficient catalyst for the asymmetric hydrogenation of selected ketones, whereas for asymmetric transfer hydrogenation Ru-(R_cS_p)PPFNPy was most efficient. The activities and enantioselectivities of the various catalysts will also be discussed.*

Keywords*: Aminophosphine, Phosphine iminopyridine, Catalyst, Ruthenium, Asymmetric catalysis*

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Characterisation of Trace Elements and Organic Compounds in Kingston, Jamaica

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Abstract: *Air Quality Standard (AQS) within first world countries in comparison to third world states, such as Jamaica are far advanced. The potential for Jamaica to establish an AQS, has come a long way and it has developed over the years. Through several initiatives, the National Environmental Planning Agency of Jamaica (NEPA) has been able to conduct air sampling routines most notable during a massive fire at the Riverton Deposal Waste Site in March 2015. The establishments of an Air Quality Index (AQI) consisting of thresholds for particulate matter below 10 and 2.5 micrometers ($PM_{2.5}$, PM10) are yet to be adequately accounted for. $PM_{2.5}$ and PM_{10} are hazardous due to their potential to travel into the cardiovascular system and cause adverse health impacts, hence the need for further research into the chemistry of these particulates. FIGAERO High Resolution Time of Flight Mass Spectroscopy and Proton Induced Mass Spectroscopy were completed at the University of Gothenburg in June of 2017. The highest reported concentration per filter was 42μgm^{-3}. Sulphuric Acid, Nitric Acid, Levoglucosan, Chloride, Nitrophenol, Hydrogen Cyanide, Benzoic Acid, IEPOX Sulphate are some of the compounds that were detected by HR-TOF-CIMS.PIXE analysis discovered the presence of Al, Si, Ca, Fe, As, Ti, V, Cr, Pb and other trace elements, Al and Si were present in the largest concentrations with at 1700 ± 60 ngm^{-3} and 3200 ± 50 ngm^{-3}, respectively. The development of a suitable air quality standard requires more detailed studies, with higher resolution sampling which would lead to a better understanding of $PM_{2.5}$ and PM_{10} particles in Jamaican ambient air.*

Keywords*: Air Quality, Particulate Matter, Climate Change, Aerosol, Analytical Chemistry*

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The Fatigue Resistance of RAP in Asphalt Concrete Mixes Using Two Different Binders

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Abstract: *Fatigue cracks in asphalt concrete are recognised as one of the most major distress mechanism in asphalt pavements. This type of deterioration must be understood and the causes of the distress must be identified. The objective of this study was aimed at evaluating the fatigue resistance of stone matrix asphalt (SMA) concrete mixtures using laboratory testing techniques. The SMA mixes were designed with different percentages of Reclaimed Asphalt Pavement (RAP) as well as virgin aggregates. Two binders 60/70 - Modified Bitumen (MB) and 60/75 - Trinidad Lake Asphalt (TLA) were used. The fatigue resistance of the asphalt concrete mix was evaluated using Stiffness Modulus and Indirect Tensile Fatigue tests. The laboratory tests showed that with increased RAP percentages there was a significant improvement in the Stiffness Modulus (SM) values and the virgin control mix with no RAP was out performed for both TLA and Modified Bitumen (MB). The peak SM was observed at the inclusion of 50% RAP. The results for the Indirect Tensile Fatigue Test (ITFT) showed the MB mixes of 5% RAP had the highest resistance to fatigue whereas the TLA mixes of 5% RAP showed the lowest resistance to fatigue. The mix of MB with 5% RAP performed significantly better than all other mixes. This study revealed that with the increase in RAP percentages resulted in an improvement in all mechanical properties. Also it was found that the mix containing 5% RAP showed high fatigue resistance when compared to the other RAP percentages and virgin control mix. The reduction of the use of virgin aggregates reduces the overall construction cost and increases the sustainability of the pavement infrastructure.*

Keywords*: Fatigue resistance, stiffness, stone matrix asphalt, asphalt concrete*

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Chemical Structure Investigation of Nutmeg (*Myristica Fragrans*) Shells and its Derived Carbon Sorbents and the Process Conditions for Producing Such Sorbents

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Abstract: *The Caribbean Island of Grenada is the World's number two producer of nutmegs (Myristica fragrans) and the only producer of any significance in the Caribbean. With an annual production of some 1,240 tonnes of nutmegs, 310 tonnes of nutmeg shells would be generated annually. These shells are essentially a waste material which presently have no commercial value. Being a carbonaceous material, it is hypothesized that these nutmeg shells could be successfully converted into activated carbon, yielding some 87 tonnes of activated carbon per year from Grenadian nutmegs. This could lead to the development of an industry producing activated carbon from nutmeg shells. If applications for this activated carbon could be found in Grenada, this would represent an application of Industrial Symbiosis - the development of techniques to turn apparent waste into industrial feedstocks. The benefits of the implementation of this could be twofold: the valorising a waste material thus providing an economic benefit to the island of Grenada, while at the same time tackling the environmental issue of the disposal of the waste shells. This paper highlights pioneering work done on characterising the chemical and surface structure of nutmeg shells and its derived carbon sorbents. The precursor and the produced nutmeg-shell chars and activated carbons were characterised using different techniques, such as infra-red spectroscopy, thermogravimetry, Raman spectroscopy and scanning electron microscopy. These characterizations were carried out to understand the structural behaviour and the surface morphology of the nutmeg char. Preliminary work has been carried out to determine the optimum process conditions for the manufacture of activated carbons from nutmeg shells, with absorptive capacity and surface area being objective functions. Possible applications - in Grenada and in the Caribbean - for nutmeg-shell activated carbon are explored.*

Keywords*: Nutmeg, Myristica fragrans, nutmeg shells, activated carbon, carbon sorbents, chemical structure, industrial symbiosis*

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PM $_{2.5}$ and Gaseous Pollution at an Industrial Site in Kingston, Jamaica

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Abstract: *According to the World Health Organisation (WHO), seven million premature deaths can be attributed to ambient air pollution annually. Aerosol particles and noxious gases contribute to air pollution especially when they exceed specified limits. In this study, aerosol particles smaller than 2.5 µm in diameter ($PM_{2.5}$) were collected for 24-hour periods at an industrial site along Spanish Town Road in Kingston, Jamaica between December 2013 and March 2104 to assess the air quality in the area. Gravimetrically the particle mass was determined, while the black carbon (BC) content was measured by light absorption and the elemental content with Energy Dispersive X-Ray Fluorescence (EDXRF), In February and March 2014, the concentrations of SO_2 and six volatile organic compounds (VOCs) were also determined with diffusive samplers. Spanish Town Road is the major commuter road in Kingston and along it, the main industrial area of Kingston is located, with a multitude of air pollution sources to which long distance transported pollutants are added and mixed. This makes it hard to distinguish the different contributions to the air pollution mix, but with statistical analysis of the results and prior knowledge in atmospheric chemistry, source categories can be determined. Of the analysed compounds, one of the measured VOCs, benzene, with an average concentration of 3 mg m^{-3}, was the only pollutant above the Jamaican national air quality standard. Several possible pollution sources were resolved and of those, traffic was found to be the major source influencing air quality in the area.*

Keywords*: Air quality, particulate matter, benzene, Spanish Town Road*

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Pincer Ligands Based on Pyridylcarbo(thio)amides Backbones as Effective Ancillary Ligands in Electro- and Homogeneous-catalysis

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Abstract: *Pincer ligands continue to generate interest owing to the unusual properties they impart on metal centers and consequently on the complexes they are involved in. In homogenous catalytic transformations, pincer ligands provide enhanced chemical and thermal stability which serve to minimise the leaching of the metal during the catalytic cycle. These ligands also offer the ability to fine tune the electronic and the steric properties about the metal center, thereby increasing the scope of their applications. Hydrogen is the leading candidate for a clean, renewable and high-energy–density source. As such, the search for catalysts that can facilitate the reduction of protons to hydrogen efficiently, is an area of current interest. Pincer ligands bis-N-(2,5-dimethoxyphenyl)pyridine-2,6-dicarbothioamide (**pdcta**), 6-(4,7-dimethoxy-2-benzothiazolyl)-N-(2,5-dimethoxyphenyl)-2-pyridinecarbothioamide (**pbcta**), N-(2,5- dimethoxyphenyl)-6-[(2,5- dimethoxyphenyl)carbamothioyl] pyridine-2-carboxamide (**pcta**), and 6-(4,7-dimethoxy-2-benzothiazolyl)-N-(2,5-dimethoxyphenyl)-2-pyridinecarboxamide (**pbca**) are a new family of pincer ligands that possess a combination of hard and soft atoms at the coordination site, namely NNS/O and SNS/O. These were synthesised using a three-step protocol and were characterised using combinations of elemental analyses, NMR spectroscopy and X-ray diffraction. Pincer complexes of Pd(II), Cu(II), and Ru(II) have been prepared and characterised using a variety of techniques. The application of the Pd(II) complexes of **pdcta** and **pbcta** as electro-catalyst for the reduction of proton to hydrogen in non-aqueous media, and as homogeneous (pre-)catalyst for the Suzuki-Miyaura cross-coupling of phenyl boronic acid and selected aryl halides will be discussed.*

Keywords*: Pincer ligands, electro-catalytic proton reduction, Suzuki-Miyuara cross-coupling*

Author's Biographical Notes:

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Advancing the Caribbean Energy Landscape – A Comprehensive Review of Electric Vehicles and Storage Systems

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Abstract: *This paper explores the burgeoning industries of electric vehicles (EVs) and storage systems within the Caribbean energy landscape. Renewable energy research and industry engagement are rapidly growing throughout the region, but integration of these systems fall short owing to aging infrastructure, burdened economies, and high investment costs. As international players are vying to rebuild the energy infrastructure and market within the region, many governments and utility agencies are turning to storage systems to ease the renewable energy transition. As an intermittent source of power, renewables such as wind, solar and hydropower are largely affected by climatic changes and stochastic weather events. Storage systems play a crucial role in these intermittent power cycles, feeding the grid in times of surplus demand and storing energy during surplus supply. The research delves into the CARICOM's turn towards EVs and other modern storage systems for modulating energy demands within the region, providing a current overview of both operational and proposed developments. Barbados leads the Caribbean with over 200 EVs on the road and over 50 publicly accessible charging points. Jamaica, having a more unique light-weight vehicle transport sector and below-average infrastructural support, was assessed as a brief case study for the integration of EVs. Results show that energy storage in the Caribbean is very much in its infancy. However, this looks set to change within the coming years, evidenced by the many advancements in renewable energy growth. Yet, Caribbean States need to further push policy development and increase power access points to see major modal shifts in energy systems.*

Keywords*: Renewable energy; climate change; storage; electric vehicles*

1. Introduction

The cost of petroleum in the Caribbean has been persistently high and volatile over the past two decades, though recent plunges in oil have provided some alleviation to over-burdened Caribbean economies. Current trends suggest stabilisation at much higher prices than the 2016 crash, and fluctuations will continue to affect renewable energy (RE) integration and investments (Shah *et al*, 2018; Dominković *et al*, 2018). In addition to high environmental costs, dependence on expensive imported petroleum products has led to serious inefficiencies in the power sector and has eroded competitiveness (McIntyre *et al* 2016). According to the US EPA (2016), the transportation sector accounts for 14% of global greenhouse gas (GHG) emissions, and nearly a quarter of global CO_2 emissions. Almost all (95%) of the world's transportation energy comes from petroleum-based fuels, largely gasoline and diesel, with the Caribbean being no different (US EPA, 2017). The transport sector in the Caribbean contributes upwards of 19% of total regional share of CO_2 emissions (Timilsina and Shrestha, 2008). Therefore, reductions of the fuel importation bill within the transport sector and consequent carbon and air pollutant emissions are paramount for governments in Caribbean and globally. The European Union (EU) and its member states, for example, are using vehicle and fuel regulations, substantial financial and non-financial incentives for consumers, the funding of infrastructure for alternative fuels, and other policies to replace petroleum with lower-carbon alternatives (Wolfram and Lutsey 2016). Implementing such efforts in the Caribbean must be complemented by major transitions in energy distribution, storage and regulation if the region is to see a harmonised and collaborative effort in building resilience and reducing fuel imports. The vulnerable nature of Small Island Developing States (SIDS) demands a more rapid energy transition, one that is also more conducive to investment.

The Caribbean is undergoing major shifts in RE integration, policy, and investments, with large potential for the mitigation of $C0_2$ emissions and global greenhouse gas (GHG) forcing (Ashtine 2018; Shirley and Kammen, 2015). The Caribbean Community (CARICOM) Energy Policy (CARICOM, 2013) encouraged member states to, among other points, develop comprehensive national energy policies that seek to increase the use of commercially viable and sustainable renewable energy sources and support such policies with action plans that propose concrete targets. Renewable energy targets amongst SIDS in the Caribbean are variable (Ochs *et al* 2015), with recent targets

of some oil-producing countries such as Trinidad and Tobago being as low as 10% by 2021 (EuroChamTT, 2018). While the costs for renewable generation continue to fall, integrating and effectively using these new resources, especially in regions with weak grid infrastructure, will require energy storage systems (ESSs) (Eller and Gauntlett, 2017). ESSs also serve to control frequency, voltage regulation, and ramping. Utility storage also solves the major problem of daytime over-production and evening surge demands of renewable sources such as Solar PV (Courvoisier, 2017a). Electric vehicles (EVs), like storage systems, play a unique role in modulating the grid distribution of power, and many SIDS are using these systems to buffer RE development and reduce fossil fuel dependence (Gay *et al* 2018).

This paper provides a comprehensive review of recent studies that explore the growth of storage system and electric vehicle integration in the Caribbean on isolated island grids. Furthermore, it explores the application of electric vehicles in vehicle-to-grid services and the growth of storage systems, highlighting the impact of these systems on RE integration and reduction of GHGs. The island of Jamaica is also briefly explored, acting as a case study for advancements in storage systems, and the role of its unique transport sectors as a model of increased electric vehicle adoption in the SIDS context.

2. The Growth and Potential of the Storage Systems and Electric Vehicles

2.1. Energy Storage Systems

In order to achieve regional sustainable development goals (SDGs) and the mitigation of pollutants and greenhouse gas emissions, a significant portion of new energy generation capacity in the Caribbean will likely come from renewable sources. However, the invariable nature of RE systems has been widely assessed and these systems, as standalone integrations, limit the ability of national grids in delivering steady power supplies to meet peak and baseloads in demand. Storage systems will play a key role in maintaining a steady power supply across the Caribbean, affording great RE integration despite aging grid infrastructure. The current energy landscape is prone to large curtailments in renewable sources during peak hours to prevent damage to national power systems. Storage is widely acknowledged today as an expensive option, particularly for Caribbean markets, but its costs are steadily falling and its value is improving (EASAC, 2017). Though very different in economies of scale and market readiness, SIDS are increasingly learning from, and working with, EU member states in terms of ESS deployment. Germany being a major world leader in complementing RE systems with well-integrated storage facilities (International Electrotechnical Commission, 2011). Energy storage deployments, particular to developing economies, can see growth > 40% annually in the coming decade, adding approximately 80 GW of new storage capacity to ~ 2 GW existing today (Eller and Gauntlett, 2017).

For the Latin America and the Caribbean, a significant portion of the new energy storage capacity expected to be deployed (see Figure 1), will likely come from remote power systems (Eller and Gauntlett, 2017). These include an 8 MW Lithium-ion (Li-ion) system developed by AES Energy Storage in the Dominican Republic, and numerous smaller ESS projects across the region. The Jamaica Public Service Company (JPSCO) is currently in the process to commission a 24.5 MW hybrid energy storage system consisting of both flywheels and Li-ion battery energy storage in Jamaica (JPS, 2018). Additionally, there are numerous storage projects to include: flywheel energy storage, underwater compressed air energy storage and smaller battery projects (Eller and Gauntlett, 2017).

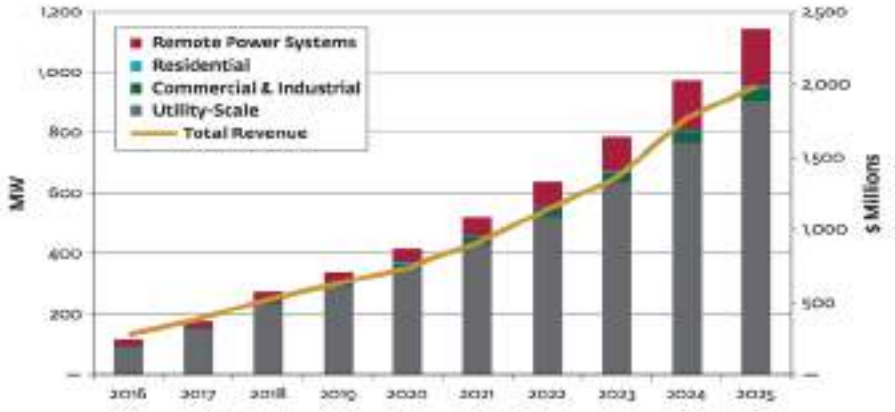

Figure 1: Projected Annual Stationary Energy Storage Deployments, Power Capacity and Revenue

by Market Segment, Latin America and the Caribbean: 2016–2025. Source: Eller and Gauntlett (2017)

A more comprehensive overview of storage systems across CARICOM member states, shows that storage system deployment is slow to progress, but is attracting major international financiers (see Table 1). Five of the 15 member countries have no storage systems accounted for, and as of September, 2018, only 7 operational and 11 proposed storage systems exist. Many of these systems are grid-tied, allowing for the communication with the national grid systems and the regulation of power supply and demand. Storage systems allow operators to secure energy during surpluses and return energy at times of deficit. Many of the listed standalone (micro-grid systems) also have hybrid systems which are backed-up by diesel generators to provide electricity when RE output cannot meet peak of baseload demands.

Table 1: Operating and Proposed energy storage systems (> 100 kW) across the CARICOM member states which have secured funding *

Country	Operating Systems	Proposed Systems	Main System Type(s)	Main Storage Type(s)	Total Installed Capacity (MW)	Minimum Accounted Costs (USD Millions)
Antigua & Barbuda	-	3	Grid-Tied	Battery	17.3	23.1
The Bahamas	2	1	Grid-Tied	Battery	14.5	8
Barbados	1	1	Grid-Tied	Battery	5	23
Belize	-	1	Standalone	Battery	0.3	2.7
Dominica	-	1	Grid-Tied	Battery	-	3-5
Grenada	-	-	-	-	-	-
Guyana	1	1	Standalone	Battery	1.3	1.3
Haiti	3	-	Standalone; Grid-Tied	Battery	0.9	0.5
Jamaica	-	1	Grid-Tied	Flywheel; Battery	24.5	21.6
Montserrat	-	1	Grid-Tied	Battery	1	-
St. Lucia	-	-	-	-	-	-
St. Kitts & Nevis	-	-	-	-	-	-
St. Vincent & the Grenadines	-	1	Standalone	Battery	100-250 (kWh)**	0.2
Suriname	-	-	-	-	-	-
Trinidad & Tobago	-	-	-	-	-	-
Confirmed Totals	**7**	**11**			**64.8**	**80.4**

* Data represent energy confirmed systems as of September, 2018. ** Recorded value in units of energy (kWh).

A major issue facing the storage industry is simply accounting for its growth and projecting future installed capacities based on ongoing RE developments in the region. The “Minimum Accounted Costs” column in Table 1 shows that these systems have installed costs (operational and proposed) of more than USD $80.4 million, with data being largely absent for many proposed systems. Many international players are key financiers within the region with organisations and government bodies such as The Rocky Mountain Institute, The Clinton Climate Initiative and The United Arab Emirates helping individual CARICOM states to fund major RE projects that are supported by storage systems.

2.2. Renewable Energy Systems Driving Change

The slow growth of storage systems across the Caribbean is placed into perspective when assessing the growth of RE systems throughout the region (see Figure 2). Countries such as Trinidad and Tobago have, to date, no RE systems over 100 kW installed, or any with confirmed funding in the pipeline. Other member states such as Guyana have more proposed projects than operational, suggesting bottlenecks in the implementation process, securing major financing for instance. Jamaica, stands out firmly amongst the other islands in terms of the number of projects, having 39 operational RE systems, with over 160 MW of installed capacity. In the CARICOM, only Suriname has a great installed capacity (~196 MW), even though only 6 hydropower plants are operational at the scale 100 kW and greater.

Many of the Caribbean’s RE projects have been implemented without storage facilities, but recent technological advances and pricing reductions have stimulated many regional utilities and projects to consider storage options, often adding storage to existing RE systems. Though focusing only on systems > 100 kW, it is important to note that the English-speaking Caribbean is largely lagging behind its sovereign neighbours. Cuba and

Dominican Republic alone account for over 74 operational projects, far exceeding CARICOM developments, albeit Jamaica. Despite the rapid advances of RE development in the Caribbean, the benefit of storage systems is just beginning to come online to support RE integration.

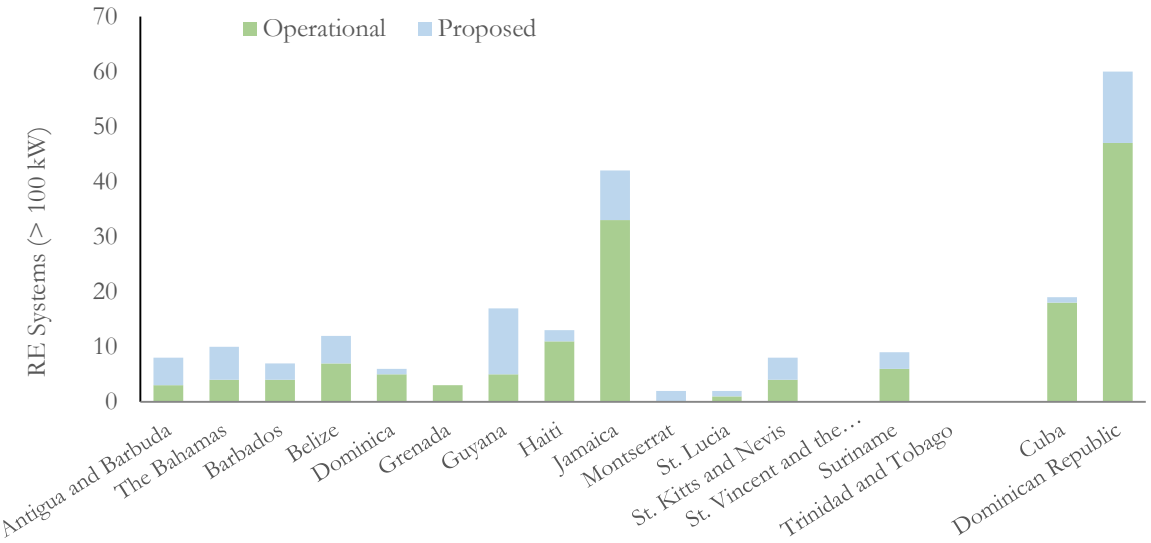

Figure 2: Operational and Proposed renewable energy (RE) systems (> 100 kW) across CARICOM with secured funding, including the independent Spanish-speaking countries of Cuba and Dominican Republic.

2.3. Electric Vehicles Globally

Previous studies (Coignard *et al*, 2018; Taibi *et al*, 2017; Li *et al*, 2017) provide a foundation for overcoming some of the major hurdles to EV and storage deployment in the Caribbean and globally, at present, and in the future. This is in support of CARICOM's Energy Use for Transportation Policy (CARICOM 2013), which among other objectives, aim to implement strategies to encourage fuel switching in the transportation sector and improve fuel conservation and efficiency in ground, marine and aviation transportation. Different authors employ varying methodologies to explain the characteristics, status and evaluation of EVs and ESSs. For example (Foley *et al*, 2009), in their case study of Electric Vehicles and Energy Storage in Ireland, examined a scenario of the potential contributions that the addition of 10% EVs, could make to the increased electricity generation from renewable energy sources to the all-island electricity grid. While Taibi *et al*, (2017) in their study of the impact of EV deployment on production costs in Barbados, explored EVs as a pre-calculated demand profile, an approach which explored three scenarios leading to three different demand profiles in order to assess the different impacts on production costs that EVs could have, depending on different charging profiles. Generally, in order to assess and report on ESS technologies, efficiencies and life cycles, as well as expose the issues and challenges of EV and ESS deployment, previous studies (Eller and Gauntlett, 2017; EASAC, 2017; McIntyre *et al*, 2016) rely on the most recent research from government, private business, academia, research institutions and peer-reviewed literature. It must be noted however that data on existing systems are very much limited and give a constricted overview of EVs across the Caribbean.

Given the environmental and economic challenges that the combustion of traditional fossil fuels is causing globally, countries are seizing the opportunity to integrate EVs into their vehicle fleets (Figure 3). By 2040, global markets can expect to experience 25% of the car fleet to be electrified (BNEF, 2017). California in the US has issued ambitious targets to decarbonise transportation through the deployment of electric vehicles (EVs), and to decarbonise the electricity grid through the expansion of both renewable generation and energy storage (Coignard *et al*, 2018). China's thrust into EV deployment is well documented; their broad commercialisation started with electric bicycles, but spread to public buses, and eventually to personal and other vehicles such as municipal service vehicles, street sweepers, and other transportation means (Earley *et al*, 2011).

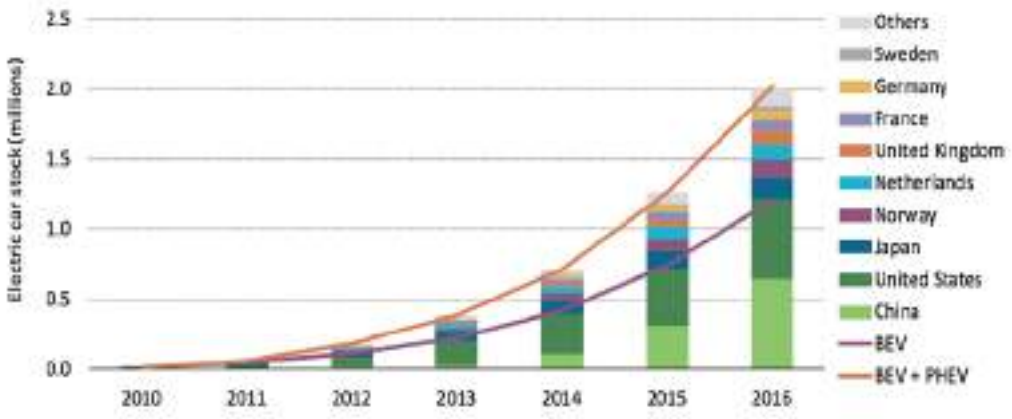

Figure 3: Evolution of the global electric car stock, 2010-2016. The electric car stock shown here is primarily estimated on the basis of cumulative sales since 2005. Source: IEA (2017).

2.4. Electric Vehicles in the Caribbean

Gay *et al* (2018) have recently published a comprehensive review of EVs and their feasibility for SIDS in the wider global context, giving particular focus to the Caribbean region. This review indicates that EVs can serve an important role in electricity storage, reducing fuel imports and even the potential for improving resilience to natural hazards in the region. With falling prices of Lithium-ion batteries, stronger international competition, and increasing demands for modal shifts in the transport sector, global changes in EV integration are filtering down to the Caribbean. Major international firms such as Tesla are already scouting the Caribbean to become a major supplier for the injection of their EVs (The Gleaner, 2016; The Cayman Islands Journal, 2016).

The highly vulnerable nature of SIDS, to climate change and volatile markets, are increasingly focussed towards the electrification of local fleets. CARICOM member states, like most SIDS, are progressively under political, environmental and economic pressures to alter existing transportation sectors and fuel economies. A closer look at fuel costs in the region (Table 2) shows a diverse range of prices for conventional fossil fuels and electricity. Trinidad and Tobago, a country with zero installed RE systems over 100 kW, has an average electricity cost of US $0.04 but the 3rd highest fuel imports in terms of GDP share (13.58%). Grenada is comparatively the most burdened with fuel prices, having 18% of their GDP spent on fuel imports, and a cost of electricity standing at more than ten times that of Trinidad and Tobago (US $0.43). With a CARICOM average of ~ 9% of GDP share going to fuel imports, EVs present much value for the transportation sectors across the region.

Table 2: Fuel and energy across CARICOM member states.
Source: Compiled from Ochs et al, (2015). Data for Guyana, Suriname, and Montserrat are not shown.

	Petrol (US$/L)	Diesel (US$/L)	Electricity (US$/kWh)	Fuel imports as share of GDP (%)
Antigua & Barbuda	1.29	0.98	0.37	5.76
Bahamas	1.15	1.20	0.32	11.35
Barbados	1.67	1.40	0.28	6.90
Belize	1.48	1.43	0.22	1.95
Dominica	0.87	0.75	0.38	7.79
Grenada	1.22	1.23	0.43	18.00
Haiti	0.92	0.71	0.28	5.32
Jamaica	1.22	1.21	0.32	9.00
St. Kitts & Nevis	0.94	0.43	0.25	3.99
St. Lucia	1.23	1.15	0.34	16.45
St. Vincent & the Grenadines	1.31	0.41	0.26	10.00
Trinidad & Tobago	0.59	0.36	0.04	13.58
Average	**1.16**	**0.94**	**0.29**	**9.17**

2.5. Vehicle-to-Grid Possibilities

The electrification of the transport sector, allows EVs a unique opportunity for the Caribbean region. Vehicle-to-Grid (V2G) services are being established in many developing countries as a form of decentralised storage, increasing the ability for national grids to be regulated and meet demands (Taibi and Fernandez, 2017). V2G, through the regulation of utilities, can smoothen energy profiles, meeting 'valleys' and 'peaks' in demand curves. Previous studies using island grids to investigate the integration of EVs show that careful modelling of charging strategies, regulation, and charging points, can adequately even out irregularities in power distribution, showing up to 50% reduction in mobility costs (Colmenar-Santos *et al*., 2017; Ioakimidis and Genikomsakis, 2018). With greater integration of EVs into transportation sectors, there is an enhanced opportunity to supply the grid with substantial amounts of power through bidirectional charging and communication (Waldron and Kobylarek, 2011). Additionally, it is important to assess the role that the public transportation sector can play in the integration of EVs, and its wider impact on the grid while operating as a regulated source of decentralised storage. With many Caribbean islands having aging public vehicle fleets (Gay *et al*., 2018), there is a great opportunity to revitalise this sector with EVs, complimenting policies for improved grid efficiency and distribution.

Caribbean countries are often plagued with power fluctuations and outages, often failing to provide enough spinning reserve to even distribute power. Outages become more important in the context of resilience to natural hazards, where downtime in national grids have substantial impacts on energy access and economic function (McLaren *et al*., 2017). EVs can be used in the region to effectively transform national grids to function more as 'smart grids' whereby the storage capability of EVs will allow for improved electricity supply. However, many systems in the Caribbean lack infrastructural efficiency and load-handling to allow the rapid growth of EV integration without addressing major limitations (see Section 2.6). Gay *et al*., (2018) state that utilities can encourage off-peak charging through incentivisation (preferential time-of-use rates for instance) to encourage EV owners and operators to effectively utilise the grid, preventing large fluxes in loading.

2.6. Major Barriers to Storage System Integration

Blechinger *et al.* (2015) gave a strong overview of the major constraints to RE development in the Caribbean. Much of these come as no surprise with top limitations including overcoming heavy capital investments, aged policies which bottleneck many RE projects, and the ability of the grid to absorb many of these RE systems without compromising distribution quality and regulation. Resource availability, magnitude, and system frequency are all considerations with RE integration in the Caribbean, and previous research has addressed the lack of ESSs as an important technical obstacle for electricity production from REs (Hall and Bain, 2008). The most significant hindrance to the deployment of storage in the Caribbean is the associated high prices, however, the region can see much larger growth as prices continue to fall (see Figure 4).

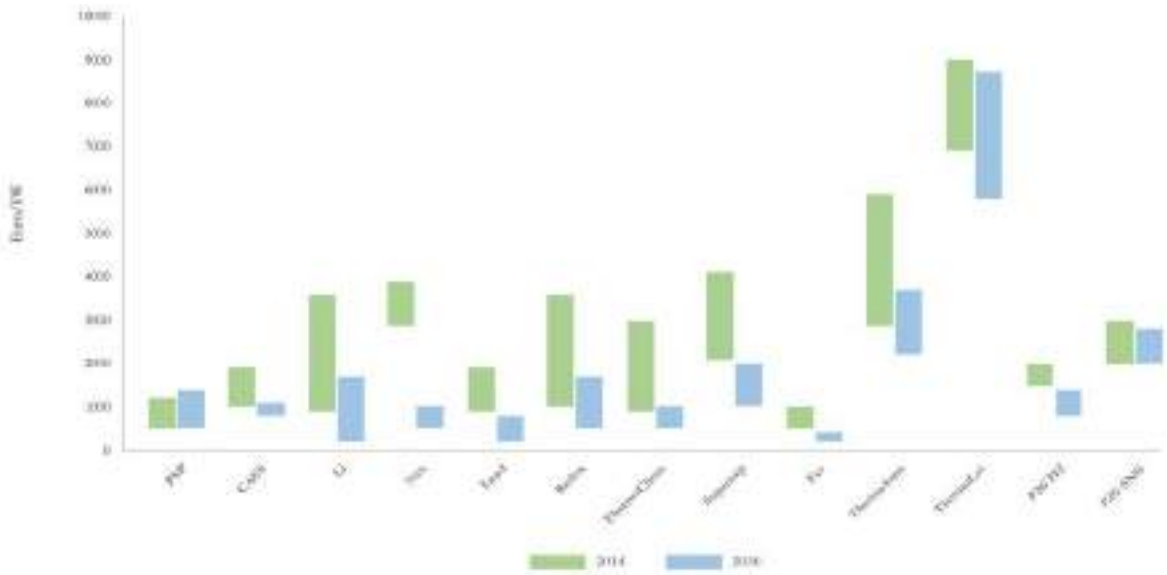

Figure 4: Specific cumulative investment costs (levelised) for major storage technologies for 2014-2030.
Source: Data sourced from PwC (2015)

For all listed systems, albeit Pumped Storage (PSP) systems which is a mature technology, there is a projected fall in the levelised costs by 2030, suggesting the Caribbean will undergo significant changes in the ESS landscape in the near future. Costs of lithium-ion batteries in particular have declined sharply in recent years due in large part to the growing market for electric vehicles and consumer electronics. The electrification of rural areas across CARICOM member states will see an increased deployment in micro-grid systems, utilising storage systems to complement RE resources. The savings experienced from increasing RE resources within off-grid rural areas can outweigh the current costs of adding storage systems (Norton Rose Fulbright, 2018) and the region will largely benefit from a continued decline in investment costs.

2.7. Major Barriers to EV integration

EVs are largely limited not only by cost, but by grid infrastructure and loading constraints. EVs can have an energy demand of ~ 10-100 kWh per charge and the cumulative charging on these vehicles can severely impact the grid and its stability (Gay *et al.*, 2018). Small CARICOM member states will be more prone to these limitations owing to the scale and capacity of grids which are often below 200 MW. The cumulative loading on the grid can be further compounded during the early stages of EV integration, where vehicles can be clustered in high-income regions and along major distribution centres, causing isolated loading points for the grid (Waldron and Kobylarek, 2011). Governments and utilities will need well-tailored policies and regulations to ensure that the initial phases of EV integration take these constraints into consideration. Preferential charging rates to capitalise on V2G systems feeding into the grid when demand is high or renewables are low will be some of the key incentives to effectively navigate EV users with existing systems. EV deployment can also be scaled in their models and charging capabilities to stabilise the system during transitory periods. With proper implementation and active engagement with the public and private sector, EVs can be used to benefit both utilities and EV owners.

Many CARICOM utilities are owned by major energy conglomerates and monopolies with major barriers to entry to the energy market. Thus, regional markets need to be conducive to EV integration and large-scale utility operators will need to be onboard with national energy planning strategies. These policy implementations are particularly difficult to introduce with the very limited transportation data available, stressing the need for further research into EVs and V2G technologies. EVs will also play a crucial role in meeting nationally determined commitments (NDCs), SDGs and other climate mitigation strategies through the reduction in GHGs. However, it is important to realise that economies of scale will force EVs to enter Caribbean markets than in the US and Europe, and government regulation of taxes and duties will enhance EV support and importation. The resale value, maintenance, and part-sourcing of EVs also causes many regional vehicle distributors to shy away from larger injections of these vehicles in regional transportation sectors.

3. Learning from Current EV Leaders in the Region

Barbados is leading the way for EV integration in the Caribbean. The share of RE in its electricity sector has been steadily increasing since 2010, primarily from solar PV. PV installations at the utility scale now stand at over 14 MW, and a new PV plant in Trents Plantation, St. Lucy (10 MW) has significantly contributed to their energy portfolio as of 2016 (Government of Barbados, 2017). The latter solar farm has the only operational storage system (Tesla battery systems) on the island at 5 MW installed capacity. Barbados now has ~ 10% share of RE for its electricity generation, resulting in an estimated emissions reduction of ~ 680 gCO_2e/kWh (Gay *et al*., 2018), with the new Government outlining a goal of 100% of RE supply by 2030 (Government of Barbados, 2017).

Megapower Ltd has begun a major push for the importation of EVs into Barbados, and to-date have deployed over 40 charging stations across the island (34 of which are publicly-accessible), with Nissan Leaf being the major EV of import (Gay *et al*., 2018). Edgehill and McGregor (2014) report that over 150 of these EVs were sold in less than two years of first importation in 2012. Charging stations at the present moment are not equally distributed across the island (Plugshare, 2018), but this is expected owing the national grid setup, major transportation hubs as well as loading factors affecting the grid. Gay *et al*., (2018) which have done a comprehensive case study of the Barbados EV injection, report that these Nissan Leafs have a cost of ~ USD $0.04/km which offer a savings of more than 50% over both petrol and diesel vehicles. They further report, using the Nissan Leaf's specifications, that with efficient drive habits, Barbados can see modal shifts in its transportation sector, making it one of the least emitting per km in the Caribbean (80 gCO_2e/km). Though further research is needed to see continued growth of the EV market in Barbados, its steady implementation is unique among CARICOM member states, and a much-desired model to follow within each island's economic context and frameworks.

4. A Brief Insight into Jamaica's Potential for EV Transition

The nation of Jamaica is dependent on fossil fuel importations (9% of its annual GDP, ~ USD $1.3 billion in 2015) and possessing a GDP-weighted climate vulnerability index value of 144 out of 192 as determined through a Worldwatch Institute study (Ochs *et al.*, 2015). Therefore, a clear, robust, incisive intervention was created in 2009 through, *The National Energy Policy*, which introduced smart policies as a key tactic to address crucial barriers for a sustainable energy transition. More so, a key policy recommendation of 20% commitment RE integration by 2030 was introduced, however, the Jamaican government has ambitiously raised this to 30%. Jamaica has made promising headway through numerous RE installations across the island and the commissioning of the 24.5 MW hybrid energy storage system. Jamaica has embarked on participation of the Global Fuel Economy Initiative (GFEI), which aims to promote global average automotive fuel economy. Through a comprehensive overview (Potopsingh, 2018), participation in GFEI is beneficial for Jamaica through fuel diversification and reduction in pollutant emissions. However, an even more ambitious investment through the potential implementation of EVs across Jamaica can significantly yield benefits both economically and environmentally.

Jamaica has experienced a significant increase (~ 350, 000) in the number of motor vehicles between mid-2014 to mid-2017, furthermore, light motor cars accounted for 70% while motorcycles accounted for 8% of the overall number of motor vehicles in 2017 (Potopsingh, 2018). EV intervention on an initial small-scale can target that 8% (~ 58,000 motorcycles) across Jamaica, hence such a scenario can yield substantial savings to the economy. A highly optimistic costing scenario can be generated at gasoline prices currently at JMD $140.00 (Petrojam, 2018), with the assumptions of motorcyclists refuelling at twice weekly (96 times yearly), for a 2.5-gallon average tank size. At such figures, the average motorcyclist consumes 908.16 litres/year accounting to USD $54.62 million in gasoline prices for the 58,000 motorcycles in Jamaica. These costs can be saved through EV intervention, at a full-scale transition, also accounting to reduction of roughly 121.8 kT of CO_2 emissions per year. Therefore, the possibility introducing EVs into the Jamaican road network is a tentative transition that requires in depth analyses into major road networks, grid stability, positioning of charging stations and a cost comparison of EVs to conventional motor cycles to create a competitive market price alternative. It is without a doubt, that Jamaica's recent upsurge in motor vehicle numbers are encouraging as a possible market for EV integration.

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Randy Koon Koon *is a Lecturer and renewable energy advocate at The University of the West Indies (UWI), Mona campus, Physics department. One year after completing his Ph.D. at UWI, St. Augustine in conjunction with the University of Saskatchewan (geothermal energy resource assessments), he has transitioned to academic duties at UWI, Mona campus. Dr. Koon has presented at conferences and published within journals, hence illustrating his understanding an appreciation for the importance of pursuing excellence through academic research publications. He plays an active role in curriculum development and research group activities, all focussed on alternative energy solutions within the Caribbean.*

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Anila Maharaj *has just completed a CCRIF internship with the Climate Studies Group at Mona, where she worked with Dr. Ashtine to assess the Caribbean's renewable energy progress. She recently completed her MBA programme at the Arthur Lok Jack Global School of Business, Trinidad and Tobago, with a particular focus to renewable energy systems.*

■

Residual Levels of Furan in Some Caribbean Foods Using Headspace Gas Chromatograph Mass Spectrometer (HS/GC-MS)

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Abstract: *Furan is a genotoxic food contaminant that has potential carcinogenic effects on humans. The recent discovery of furan in commercial foods has stimulated tremendous interest surrounding food safety. Furan has been reported to be prevalent in baby foods, coffee, soups and sauces at levels greater than 100 µg/kg, which is ten times the default maximum residual limit for pesticides in food. Unlike acrylamide – another recently discovered food toxicant, furan formation does not only generate from Maillard reactions facilitated by heat treatment, as it is also found in thermally untreated foods. Over 70 Caribbean food samples that were both commercial and home-prepared were selected for determination of residual levels of furan. A modified FDA method involving Headspace Gas Chromatography Mass Spectrometry (HS-GC/MS) was validated and utilised to quantify the levels of furan detected in a wide range of Caribbean foods, such as: coffee, milk products, soups, meats, fruits, pastries and snacks. Furan was found to be present in raw foods in the range of 0.7-18 µg/kg which is another difference between it and acrylamide which is not found in such foods. Residual levels of furan were detected in the other Caribbean foods within the concentration range of 0.1-1017 µg/kg compared to the reported acrylamide concentration range of 65-3640 µg/kg said to be found in such foods. The levels of furan present in each sample was determined by standard addition with recoveries in the range 94 - 113%. The numerous mechanisms by which furan may be formed and its volatility complicates analysis. As a result, the formation of furan in foods is not fully understood and there is limited research. The concentration of furan found in similar foods from other countries, the relationship between the concentration of furan found and the postulated precursors as well as the health implications from the findings will be discussed.*

Keywords*: Furan, Genotoxic, Carcinogenic, Caribbean foods*

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■

Assessing the Potential Impacts of Increasing Temperatures on Asphalt Binder Performance

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Abstract: *Global transportation sectors and pavement management systems are inexorably linked to asphalt binder performance. Historical variations in temperature, human population growth and the potential impacts of climate change have renewed the demand for sustainable bituminous pavements to combat intensified rate of defects. Trinidad Lake Asphalt (TLA) is natural semi-solid bitumen which can produce a binder material with high resistance. While, polymers display stabilisation benefits for refinery bitumen. This paper gives a comparative analysis of TLA and Rubber Latex Polymer (RLP) as modifiers of conventional 60-70 refinery bitumen. Traditional testing and the Dynamic Shear Rheometer (DSR) were used to investigate the rheological response of modified and unmodified binder blends after short-term ageing. There is considerable evidence that polymer modified blends indicate greater performance benefits for the test temperature ranges (40 °C – 50 °C) of the Caribbean.*

Keywords*: Trinidad Lake Asphalt, temperatures, bitumen, rubber latex polymer, DSR*

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■

Effect of Sample Mass on Particle Size Distribution in Predominantly Medium to Heavy Textured Tropical Soils

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Abstract: *Particle size distribution (PSD) is a fundamental soil property that is crucial in agriculture, engineering and environmental applications as well as in basic research such as in developing water release curves in flow and transport modelling. The accurate determination of PSD, particularly clay content, is especially critical in ascertaining the magnitude and rates of many physical, chemical and hydrological processes in soils. The accuracy of the hydrometer method for PSD, which relies on the settling velocity of soil particles in a soil suspension, could be affected by the density of the suspension, which in turn, depends on the initial sample mass and the texture of the soil. We investigated the effects of mass on clay content determination using the hydrometer method with soils of differing mineralogies and textures. The experiment comprised seven soils and four soil masses (10 g, 20 g, 30 g, 50 g) in a 7×4 factorial design replicated three times. Results showed a general trend of increasing estimates of clay percentages as the soil mass decreased from 50 g to 10 g. This implies that the widely used 50 g mass of soil in the hydrometer method underestimates the clay content in the predominantly medium to heavy textured soils, which are widespread in the Caribbean. We conclude that the accurate mass of soil sample for the determination of clay content in these soils is confounded by organic matter and salinity.*

Keywords*: Particle size distribution, soil texture, settling velocity, hydrometer method*

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Ananda Ramlochan *is a Master of Science student at the Department of Managment Studies at The University of the West Indies, St. Augustine. He holds a Bachelor's of Science degree in Geography (special) from The University of the West Indies, St. Augustine. His areas of research interest are sustainable energy management, conservational agriculture, food security and permaculture.*

■

Morphology of Third Instar Larvae of Three Species of Flies (Family: Sarcophagidae) of Potential Forensic Importance in Jamaica

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Abstract: *Crime is a major problem in Jamaica, juxtaposed to crime is the difficulties the legal system has solving violent crimes. Forensic entomology may prove to be helpful in certain criminal investigations. The most important piece of information that can be derived from forensic entomology is the postmortem interval (time since death). In the Caribbean, forensic entomology is a relatively new area of study. For it to be credibly used, there needs to be the establishment of a database for insects specific to Caribbean climatic conditions; as geographic location and temperature influence insect succession and development.*

The fly family Sarcophagidae is one of the most important colonisers of a carcass utilised in forensic entomology; however, there is a distinct lack of research pertaining to Sarcophagids. Generally, immature stages of flies are the most utilised in forensic entomology. The first step is species identification and larval morphology is an important tool in this process. Larval morphology is even more valuable for this family because it is incredibly difficult to distinguish Sarcophagids to the level of species using the adults. Presented here is a study of the larval morphology of a number of Sarcophagids of Jamaica using the light microscope.

Light microscopy allows for rapid identification which is useful in crime solving. The alternative methods include the use of electron microscopy or molecular biology; however, these are relatively expensive and time-consuming. The method presented here provides crime fighters with a rapid, low-cost method which can be carried out using equipment which is basic and readily available.

Several features showed potential for use in separation of the third instar larval instar of the species studied, these include the general appearance of the larvae, the structure of the cephalopharyngeal skeleton (shape of the mouth hook and the length of the ventral cornu), the appearance and morphometrics of the anal segments and posterior spiracles. However, only the shape of the posterior cavity and spiracles are presented here. The third instar larvae of three species were studied and all could be differentiated using this method.

Adult Sarcophagids were attracted using bottle traps baited with pig liver. These adults larviposited and larvae were collected and colonises (generation 2 and 3) reared at room temperature for morphological work. The posterior ends of the larvae from segments 9 or 10 were removed and mounted posterior end upwards to allow study using a light microscope at magnification X200 (posterior cavity) and X640 (posterior spiracle). The remaining anterior sections of the larvae were cleared in KOH and the cephalopharyngeal skeleton dissected out and measured at different points.

Presented in Figure 1 are drawings of the posterior cavity of the anal segment of three species of Sarcophagids. Peckia chrysostoma, Blaesoxipha plinthopyga and a third species yet to be identified (referred to as Unknown species). The shapes are distinct and easily recognisable using the light microscope. Future studies which will be needed in addition to this study, include rearing the flies at different temperatures to deduce temperature's effect on the developmental rate. Collecting fly specimens from different areas of Jamaica, to provide full knowledge of the diversity of the Jamaican fauna, as well as the geographical distribution of the species which also have forensic potential.

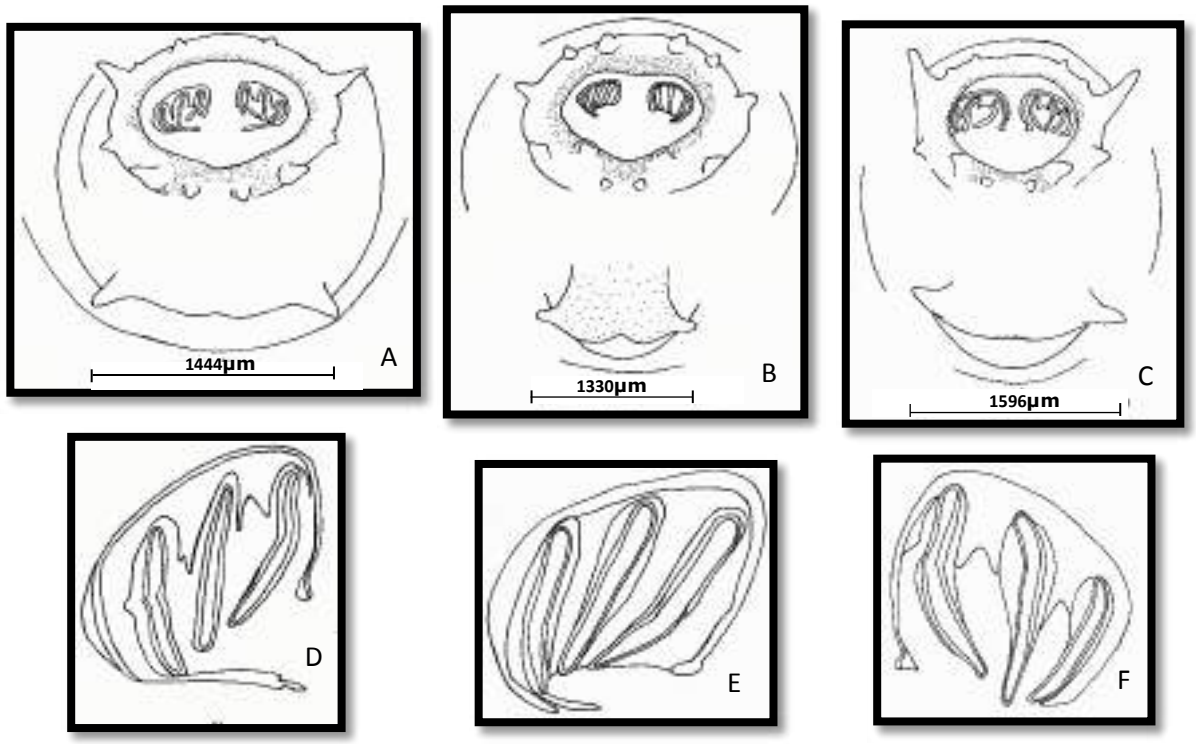

Figure 1. The posterior cavity and spiracle of Sarcophagid larvae: *Peckia chrysostoma* (A and D), *Blaesoxipha plinthopyga* (B and E) and unknown species (C and F). Scale bar for A-C shows the size of ventral papillae.

Keywords*: Sarcophagidae; 3rd instar larval morphology; forensic entomology; Jamaica*

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Rochelle S.H. Daley *is an MPhil candidate at The University of the West Indies, Mona. Her study focuses on the fly family Sarcophagidae, commonly known as flesh flies; under the title "The Morphology and Biology of Species of Sarcophagids of forensic importance in Jamaica." During the pursuit of her undergraduate degree, she fell in love with Entomology and was introduced to forensic entomology by Dr Eric Garraway; senior lecturer and entomologist. It is her intention to ultimately upgrade her MPhil research to a PhD.*

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■

On Well-Posedness of a Nonlinear Degenerate Dirichlet Problem with Very Irregular Data

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Abstract: *For the oil activities mathematical modelisation, regard to the domain size, the situation where the data are carried by neglectible surfaces requires the use of data measures. The exchange between the rock-shop and the outside are organised through the wells of injection and production, or are the result of the natural activity of oil slick expansion. As the size of the deposit is about hectometer and wells ones are about decimeter, it is not realistic to give conditions on boundary neglectible regions. The terms of sources and wells modelling requires the introduction of singularities, which raises analytical and numerical problems. The case of data measures had been studied by several authors. We propose a more general approach allowing to consider very irregular data, as for example distributions data. For that purpose, we work in the framework of the so-called generalised Sobolev algebras, constructed from the classical Sobolev spaces by Bernard and Nuiro (2005, 2012). To develop our method, we consider Ω an open bounded domain of IR^d, ($d>0$ is an integer) with a Lipschitz continuous boundary $\partial\Omega$, and we set the formal problem*

$$(P): \ -\Delta\Phi(u) + \Psi(u) = f \text{ in } \Omega, \quad \sigma(u) = g \text{ on } \partial\Omega,$$

where Δ is the well known Laplace operator, f and g are non-smooth functions. We assume that Φ, Ψ and σ are non decreasing real valued differentiable functions defined on IR such that $\Phi(0) = \Psi(0) = \sigma(0) = 0$, with continuous first derivatives which can vanish only on a finite set of discrete points of IR. To deal with the regularity problem, we introduce an auxiliary regularised problem, by means of an artificial viscosity method depending on a parameter ε. The resolution is based on the view of a family of mapping from a classical Sobolev algebra E into another F as a mapping from a generalised Sobolev algebra constructed from E into another constructed from F. Thus, we generalise a previously proven existence result, and prove a new uniqueness one. We also give some new behaviour properties of the solution and numerical illustrations.

Keywords*: Degenerate PDEs problem, Generalised solution, Sobolev algebra, Topology on generalised algebra, Maximum principle*

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■

Assessment of Temporal Rainfall Distribution in Trinidad and Tobago Using the Annual and Seasonal Precipitation Concentration Indices

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Abstract: *Temporal rainfall distribution has far-reaching hydrologic, economic, societal, and environmental consequences that directly impact water resources management, agriculture, forestry, tourism, sports, recreation, the construction industry, and ecological systems. Recently, several peer-reviewed studies using climate model simulations have reported that rainfall variability, the uneven temporal distribution of rainfall, is expected to increase robustly for various time scales ranging from daily and monthly to inter-annual and decadal over almost all land areas in response to anthropogenic greenhouse-gas induced global warming/climate change. The validity of these climate model results for Trinidad and Tobago was investigated using the annual and seasonal (dry and wet seasons) precipitation concentration indices. The precipitation concentration index (PCI) is a measure of the temporal distribution of monthly rainfall over a particular time period such as a year or season. The nonparametric Mann-Kendall and Sen's slope estimator statistical tests were used to determine whether there are monotonic positive or negative trends in the PCIs along with their statistical significance over the periods 1946-2017 for Piarco, Trinidad and 1970-2017 for Crown Point, Tobago. No statistically significant trends ($p>0.10$) were found in the time series data for annual, dry-season or wet-season PCIs in both Trinidad and Tobago. These results suggest that there has not been any statistically significant change ($p>0.10$) in temporal monthly rainfall distribution at these two locations and are thus inconsistent with climate model projections. Consequently, it is concluded that, at the monthly scale, rainfall variability has not changed in Trinidad and Tobago over the last several decades since the current global warming scare began in the 1980s. These empirical findings have practical implications such as support for the use of frequency analysis in the planning and implementation of appropriate operational strategies in the rainfall-sensitive sectors of the country.*

Keywords*: Temporal rainfall distribution, rainfall variability, global warming, climate change, dry-season rainfall, wet-season rainfall, precipitation concentration index, Trinidad and Tobago*

1. Introduction

Temporal rainfall distribution (or rainfall variability) has far-reaching hydrologic, economic, societal, and environmental consequences that directly impact water resources management, agriculture, forestry, tourism, sports, recreation, the construction industry, and ecological systems. Recently, several peer-reviewed studies using climate model simulations have reported that rainfall variability, the uneven temporal distribution of rainfall, is expected to increase robustly for various time scales ranging from daily and monthly to interannual and decadal over almost all land areas in response to anthropogenic greenhouse-gas induced global warming (Chou et al., 2007; Chou and Lan, 2012; Chou et al., 2013; Pendergrass et al., 2017; Konapala et al., 2017). The given explanation is that the water vapour content of the atmosphere has increased because of rising global temperatures resulting in the strengthening of the global hydrological cycle.

To the best of the author's knowledge, no previous research has been done to assess the validity of model projections of rainfall variability for Trinidad and Tobago. The objective of this study, therefore, was to investigate the validity of these climate model results to determine whether there have been any statistically significant ($P < 0.05$) changes, negative or positive trends, in intra-annual and intra-seasonal temporal rainfall distribution using the annual and seasonal (dry and wet seasons) precipitation concentration indices at Piarco, Trinidad and Crown Point, Tobago.

2. Data and methods

The monthly data used in the study were collected and provided by the Trinidad and Tobago Meteorological Service at Piarco, in Trinidad, 1946-2017 and at Crown Point in Tobago, 1970-2017. The Precipitation Concentration Index (PCI) proposed by Oliver (1980) was used to describe the variability (temporal distribution) of rainfall at a particular time scale such as annual, seasonal i.e. dry season and wet season. It is bounded by lower and upper limits of 8.3 and 100 respectively. A value of 8.3 indicates that monthly rainfall is the same for each month (perfect uniformity of rainfall distribution) while a value of 100 indicates that all the rainfall occurs in one month.

The PCI for the entire year (PCI_{annual}), January to December, is given by:

$$PCI_{annual} = \frac{\sum_{i=1}^{12}(P_i)^2}{(\sum_{i=1}^{12}P_i)^2} .100 \quad (1)$$

The PCI for the dry season ($PCI_{dry\ season}$), January to May, is given by:

$$PCI_{dry\ season} = \frac{\sum_{i=1}^{5}(P_i)^2}{(\sum_{i=1}^{5}P_i)^2} . \left(\frac{5}{12}\right) . 100 \quad (2)$$

The PCI for the wet season ($PCI_{wet\ season}$), June to December, is given by:

$$PCI_{wet\ season} = \frac{\sum_{i=6}^{12}(P_i)^2}{(\sum_{i=6}^{12}P_i)^2} . \left(\frac{7}{12}\right) . 100 \quad (3)$$

where P_i is the rainfall amount (mm) in the ith month of the year.

PCI values of less than 10 represent a uniform rainfall distribution (i.e. low precipitation concentration or variability), PCI values greater than 10 but less than or equal to 15 indicate a moderate precipitation concentration or variability; values greater than 15 but less than or equal to 20 indicate irregular distribution and values greater than 20 demonstrate a strong irregularity of precipitation (i.e. high precipitation concentration or variability).

The nonparametric Mann-Kendall (Mann, 1945; Kendall, 1975) and Sen's slope estimator (Sen, 1968) statistical tests were used to determine whether there were trends in the precipitation concentration indices, positive or negative, as well as their magnitude and statistical significance. The Mann-Kendall test determines whether a trend exists and the direction of the trend while Sen's slope estimator provides both the magnitude and direction of the slope.

3. Results and Discussion

3.1 Trinidad

Figure 1 shows the monthly rainfall for each year for the period 1946 to 2017 as well as the mean monthly rainfall for each month over the entire period. It is evident that although there is significant variation in monthly rainfall, there is a clear distinction between the dry season, January to May, and the wet season, June to December.

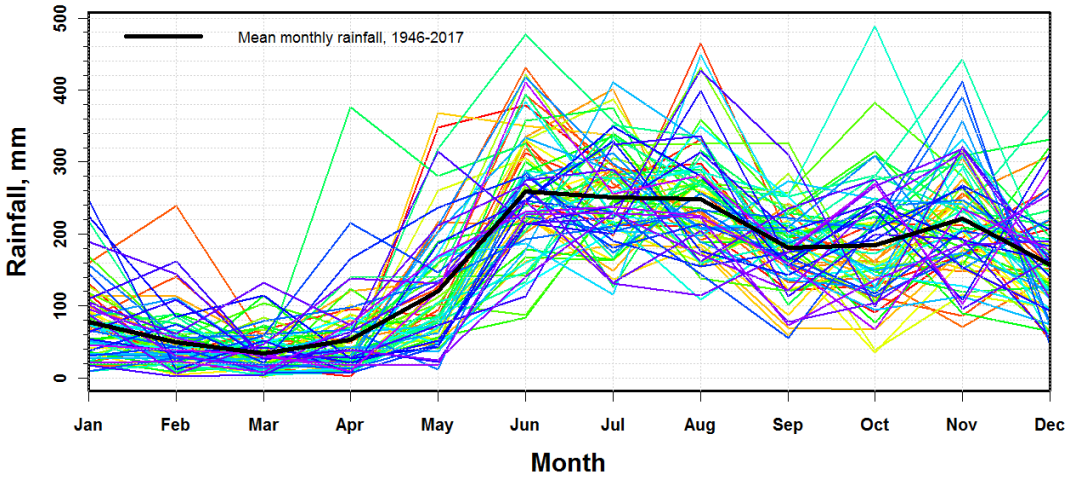

Figure 1. Monthly rainfall for each year at Piarco, Trinidad, 1946-2017

Figures 2, 3 and 4 show the time series plots of annual, dry-season and wet-season PCIs for Piarco, Trinidad, respectively along with their corresponding mean values shown by the red line. Table 1 shows the summary statistics for the corresponding PCIs. The annual PCIs range from 9.7 to 16.0 with a mean of 12.1 over the time period 1946-2017. The dry-season PCIs range from 8.7 to 27.0 with a mean of 13.1 while the wet-season PCIs range from 8.6 to 11.5 with a mean of 9.4.

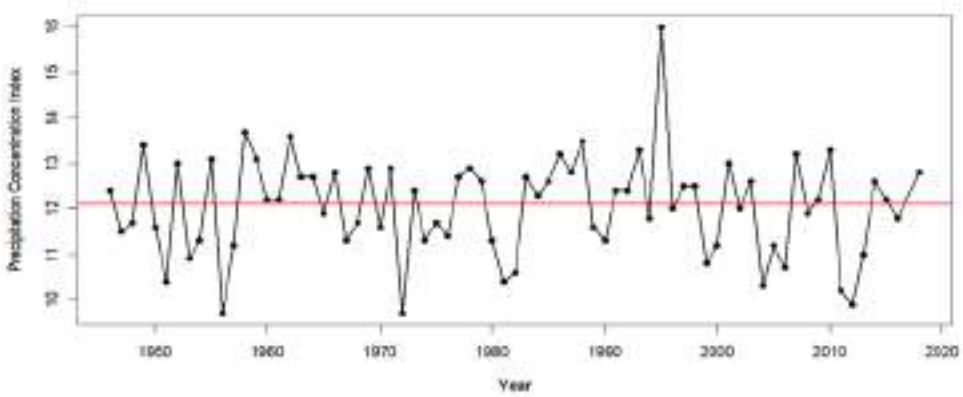

Figure 2. Precipitation concentration indices for annual rainfall at Piarco, Trinidad, 1946 - 2017. The red line represents the mean value over the period.

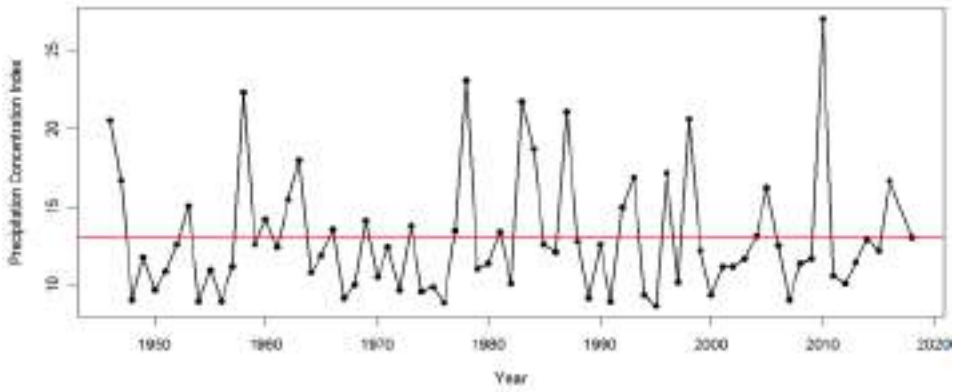

Figure 3. Precipitation concentration indices for dry-season rainfall at Piarco, Trinidad, 1946 - 2017. The red line represents the mean value over the period.

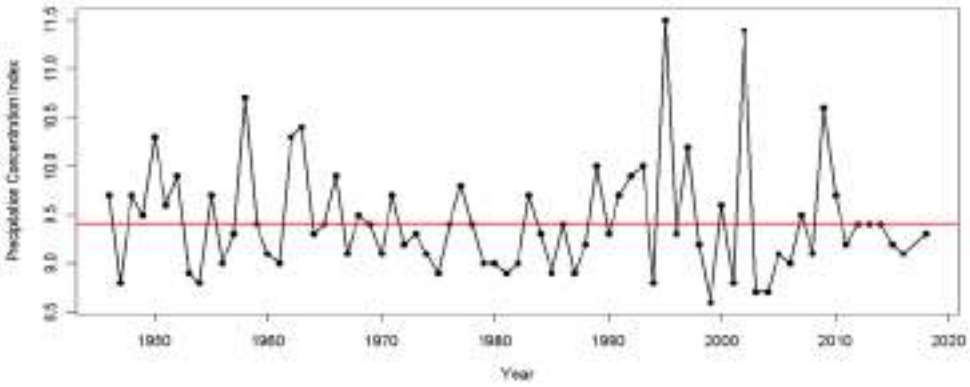

Figure 4. Precipitation concentration indices for wet-season rainfall at Piarco, Trinidad, 1946 - 2017. The red line represents the mean value over the period.

Table 1. Summary statistics of the PCIs for Piarco, Trinidad

Time scale	Min	Q1	Median	Mean	Q3	Max
Annual	9.7	11.3	12.2	12.1	12.8	16.0
Dry season	8.7	10.2	12.2	13.1	14.2	27.0
Wet season	8.6	9.1	9.3	9.4	9.7	11.5

Table 2 shows the statistical results of the Mann-Kendall and Sen's slope tests. For the annual PCIs, there is a small statistically insignificant (tau = -0.04, P = 0.63) slope of -0.0028, with 95% Confidence Interval (CI), {-0.0143, 0.0100}. For the dry-season PCIs, there is a small statistically insignificant (tau = 0.02, P = 0.77) slope of 0.0058, with 95% CI, {-0.0300, 0.0385}. For the wet-season PCIs, there is a small statistically insignificant (tau = -0.08, P = 0.36) slope of -0.0021, with 95% Confidence Interval (CI), {-0.0080, 0.0026}. These statistically insignificant slopes and the CIs which all include zero imply that the slopes of the three time series are not significantly different from zero. Thus, the slopes of the three time series are no different from their respective means.

These results clearly demonstrate that although there are pronounced fluctuations in PCIs from year to year, there are no statistically significant ($P < 0.05$) trends in the PCIs over the period 1946 - 2017. The PCIs for the three time scales can be viewed as random fluctuations about their respective means. Thus, there have been no statistically significant changes in the intra-annual or intra-seasonal temporal distribution of rainfall at Piarco, Trinidad over the period of the study.

Table 2. Statistical results of the Mann-Kendall and Sen's slope test for Piarco, Trinidad

Time scale	Kendall's tau	Sen's slope	95% CI	P-value
Annual	- 0.04	-0.0028	{-0.0143, 0.0100}	0.63
Dry season	0.02	0.0058	{-0.0300, 0.0385}	0.77
Wet season	- 0.08	-0.0021	{-0.0080, 0.0026}	0.36

3.2 Tobago

Figure 5 shows the monthly rainfall for each year for the period 1970 to 2017 as well as the mean monthly rainfall for each month over the same period at Crown Point, Tobago. Although there is significant variation in monthly rainfall, there is a clear distinction between the dry season, January to May, and the wet season, June to December.

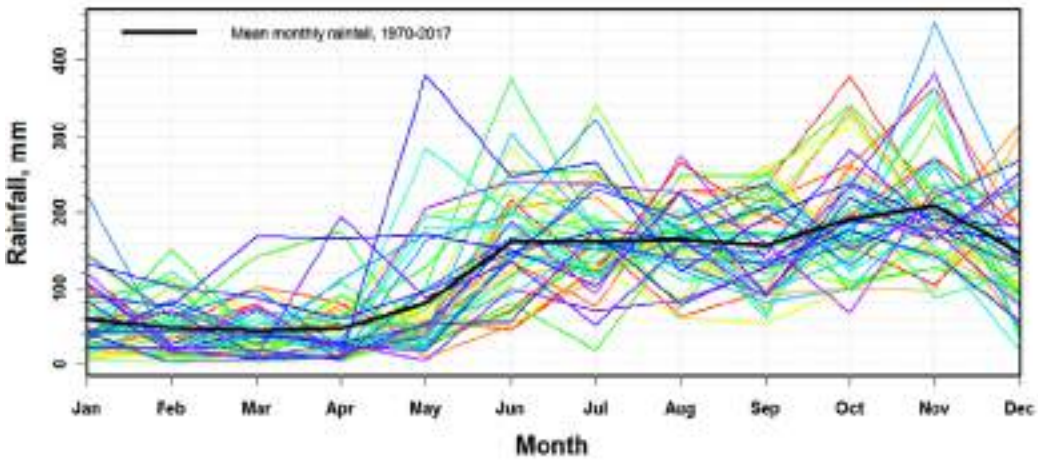

Figure 5. Monthly rainfall for each year at Crown Point, Tobago, 1970-2017

Figures 6, 7 and 8 show the time series plots of annual, dry-season and wet-season PCIs for Crown Point, Tobago, respectively along with their corresponding mean values shown by the red line. Table 3 shows the summary statistics for the corresponding PCIs. The annual PCIs range from 9.2 to 14.8 with a mean of 12.1 over the time period 1970 - 2017. The dry-season PCIs range from 8.6 to 31.3 with a mean of 12.5 while the wet-season PCIs range from 8.5 to 13.1 with a mean of 9.5.

Table 4 shows the statistical results of the Mann-Kendall and Sen's slope tests. For the annual PCIs, there is a small statistically insignificant (tau = -0.13, P = 0.20) slope of -0.0152, with 95% Confidence Interval (CI), {-0.0500, 0.0083}. For the dry-season PCIs, there is a small statistically insignificant (tau = 0.14, P = 0.18) slope of 0.0409, with 95% CI, {-0.0176, 0.1000}. For the wet-season PCIs, there is a small statistically insignificant (tau = -0.12, P = 0.25) slope of -0.0100, with 95% Confidence Interval (CI), {-0.0250, 0.0059}. The statistically

insignificant slopes and the CIs which all include zero imply that the slopes of the three time series are not significantly different from zero. Thus, the slopes of the three time series could be represented by their respective means.

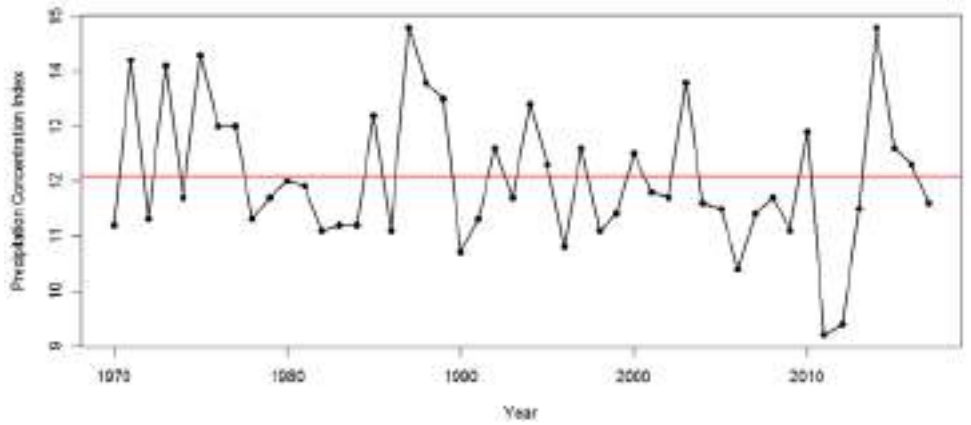

Figure 6. Precipitation concentration indices for annual rainfall at Crown Point, Tobago, 1970 - 2017. The red line represents the mean value over the period.

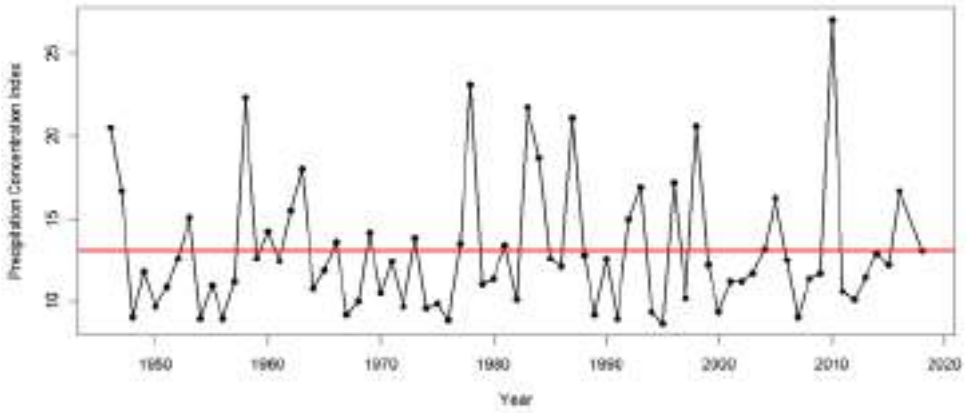

Figure 7. Precipitation concentration indices for dry-season Rainfall at Crown Point, Tobago, 1970 - 2017. The red line represents the mean value over the period.

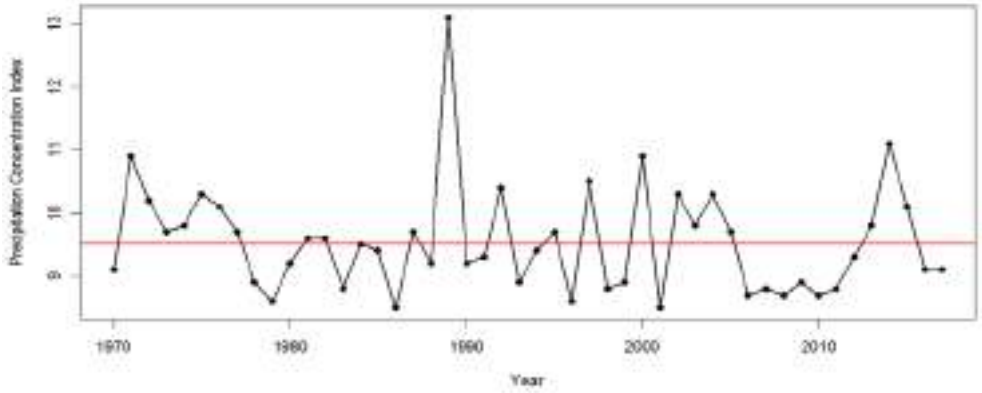

Figure 8 Precipitation concentration indices for wet-season Rainfall at Crown Point, Tobago, 1970 - 2017. The red line represents the mean value over the period.

Table 3. Summary statistics for the PCIs at Crown Point, Tobago

Time scale	Min	Q1	Median	Mean	Q3	Max
Annual	9.2	11.3	11.7	12.1	13.0	14.8
Dry season	8.6	10.0	11.5	12.5	14.1	31.3
Wet season	8.5	8.9	9.4	9.5	10.0	13.1

Table 4. Statistical results of the Mann-Kendall and Sen's slope tests for Crown Point, Tobago

Time scale	Kendall's tau	Sen's slope	95% CI	P-value
Annual	- 0.13	-0.0152	{-0.0500, 0.0083}	0.20
Dry season	0.14	0.0409	{-0.0176, 0.1000}	0.18
Wet season	- 0.12	-0.0100	{-0.0250, 0.0059}	0.25

These results clearly demonstrate that there are pronounced fluctuations in PCIs from year to year but no statistically significant ($P < 0.05$) trends in the PCIs over the period 1970-2017. The PCIs for the three time scales can be viewed as random fluctuations about their respective means. Thus, there have been no statistically significant changes in the intra-annual or intra-seasonal temporal distribution of rainfall at Crown Point, Tobago over the period of the study.

4. Conclusion

The time series data of annual, dry-season and wet-season precipitation concentration indices using monthly rainfall data collected at Piarco, Trinidad and Crown Point, Tobago were statistically analysed to assess whether the temporal rainfall distribution has changed over the last several decades. No statistically significant trends ($P < 0.05$) were found in any of the six data series. It is concluded that neither the intra-annual nor the intra-seasonal temporal distribution (variability) of rainfall has significantly changed at these two sites in Trinidad and Tobago. The use of frequency analysis is therefore appropriate in modelling annual and seasonal rainfall amounts for planning purposes.

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Temperature Effects on the Relative Stability of Ultra-High-Pressure Phases of Oxygen

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Abstract: *The phase diagram of solid Oxygen at terapascal pressures and several thousand degrees Kelvin has been studied with ab initio density functional theory within the quasi-harmonic approximation for the vibrational free energy. Our work extends previous theoretical studies done at zero temperature and shows that temperature has a dramatic effect on the sequence of phases. At low temperature, the transition from one-fold (molecular) to four-fold coordination takes place through two intermediate phases with two-fold coordination and space group I4/acd and Cmcm. Above 8000 K, we find that these two intermediate phases are no longer stable, and oxygen transforms directly from a molecular phase to a four-fold coordinated phase of space group Fmmm. We also find that the transition between Cmcm and Fmmm can be ascribed as a second-order transition driven by an electronic instability.*

Keywords*: Density functional theory, quasi-harmonic approximation, high pressure, solid oxygen*

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■

Solving Stochastic Multi-Objective Economic Dispatch Problems Incorporating CHP and Wind Power Units Using SDP Technique

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Abstract: *This paper has presented a semi-definite programming approach-based weighted sum in solving reformulated extended multi-objective models for economic dispatch problems incorporating CHP (Combined Heat and Power Production) and wind power units. In solving a stochastic multi-objective economic dispatch (MOED), the main objective is to come with a decision that will perform well on an average. The stochastic MOED problems are converted into their respective deterministic equivalents by taking the expectation of all the involved random variable assuming Gaussian distribution function while the wind energy conversion system involves Weibull pdf due to its high variability and intermittency. The multi-objective problems were reconverted as matrix to form semi-definite programming (SDP) relaxation problems and the system equalities and inequalities are entered into YALMIP (Yet Another Linear Matrix Inequality Parser), which is a linear inequalities parser. Simulation were performed on modified IEEE six and twenty units' networks with 2 cogenerations and 20 wind parks for each of the networks to determine the effectiveness of the proposed method and the results obtained from the SDP technique were compared with the results of other methods reported in the literatures.*

Keywords*: SDP, Stochastic MOED problems, CHP units, Wind power unit*

1. Introduction

Economic dispatch is defined as the optimal operation of power systems to produce minimum fuel cost by fulfilling the load demand and all other systems' operation constraints. Basically, in a real life economic dispatch of power generation, decision maker is faced with multiple goals. This case is considered to be multi-objective optimisation problem, in which several objectives are to be minimised or maximised simultaneously. Moreover, several methods reported in the literature involved in solving this problem are evolutionary in nature. Such methods are particle swarm technique, genetic algorithm, neural network etc. (Jubril and Adediji, 2015). The major limitation about these methods is in their mode of operation in solving optimisation problems which is based on random iteration. However, attainment of the ideal optimal solutions is not guaranteed in this case as they generate different solutions over several runs. Some related works to this study are hereby presented. Particle swarm optimisation technique has been reported in several cases for solving multi-objective economic dispatch (MOED) problem in (Azadani et al., 2008; Piperagkas et al., 2010; Wang and Singh, 2006; Lingfeng and Chanan 2008). Also, a wind dispatch model which involves both Gaussian and Weibull distribution approximations for the wind energy power conversion has been analysed in (Hetzer et al., 2006).

Semi-definite Programming (SDP) technique has been applied to solve stochastic multi-objective problem on Combined Heat and Power Dispatch CHPEED model presented in (Jubril et al., 2014). More so, SDP approach has also been used for power output control of a wind energy conversion system which is presented in (Jin et al., 2014). A multi-objective problem which involves high order polynomial of a fuel cost function with emission objective function have been solved using semi-definite programming (SDP) presented in (Jubril et al., 2013).

However, this research has considered joint probability distribution function in obtaining stochastic MOED problems incorporating both CHP and wind power units. Furthermore, this research reformulates and extends SDP application to the stochastic MOED problem incorporating wind power units due to its inherent advantages in achieving global optimal solution.

The remaining part of this paper is organised as follows; section II is the problem objectives, section III discusses explanation on the SDP technique and SDP relaxation and section IV is the simulation, analysis and the results and section VI is the conclusion.

2. Problem Objectives

The system comprises of thermal units, CHP units and wind powers units. The objective function for the total cost is formulated as follows which can be found in (Piperagkas et al., 2010);

$$J_1 = \sum_{i=1}^{N_p} C_i + \sum_{j=1}^{N_c} C_j(\theta_j, H_j) + \sum_{l=1}^{N_w} C_w\,(W_{av} - W_l) + \sum_{k=1}^{N_h} C_k(T_k) - \mu \times \Delta WC + WC_{max} \quad (1)$$

Where N_p, N_c, N_w, N_h, are the numbers of conventional power units, CHP units, heat units and wind parks respectively. WC = $WC_{max} - WC_{min}$ and $WC_{max} - \mu \times$ WC is the cost of wind power. However, μ is defined as follows (Piperagkas et al., 2010);

$$\mu = \begin{cases} 1 & WC \le WC(P_D)_{min} \\ \dfrac{WC(P_D)_{max} - WC}{WC(P_D)_{max} - WC(P_D)_{min}} & WC_{min} \le WC \le WC_{max} \\ 0 & WC \ge WC(P_D)_{max} \end{cases} \quad (2)$$

Where $WC = \sum_{l=1}^{N_w} WC_l$ is the running cost for wind power, the maximum and minimum bounds of the running costs for the wind power are denoted as $WC(P_D)_{max}$, $WC(P_D)_{min}$ respectively. At the upper limit, the wind system is unstable due to perturbation of the wind.

The expected stochastic objective cost function J_1 is further expressed as follows (Piperagkas et al., 2010)

$$\overline{J_1} = \sum_{i=1}^{N_p}\left\{\alpha_i + \beta_i P_i + \gamma_i(\bar{P}_i^{\,2} + V_{ar}(P_i))\right\} + \sum_{j=1}^{N_p}\left\{\alpha_j + \beta_j\theta_j + \gamma_i(\bar{\theta}_j^{\,2} + V_{ar}(\theta_j))\right\} + \delta_j\,\overline{H_j} + \theta_j\left(\overline{H_j}^{\,2} + V_{ar}(H_j)\right)\} + \xi_j + \sum_{k=1}^{N_p}\left\{\alpha_k + \delta_k P_i + \Theta_k(\overline{T}_k^{\,2} + V_{ar}(T_k))\right\} - \mu \times \Delta WC + WC_{max} + \sum_{l=1}^{N_w} k_p\,(W_{av} - W_l) \quad (3)$$

Where $V_{ar}(P_i)=V^2(P_i)\bar{P}_i^{\,2}$, $V_{ar}(\theta_j)=V^2(\theta_j)\theta_j^{\,2}$, $V_{ar}(H_j)=V^2(H_j)H_j^{\,2}$, $V_{\ ar}(T_k)=V^2(T_k)\bar{T}_k^{\,2}$, $Cov(\theta_j, H_j)=C^2(\theta_j, H_j)\bar{\theta}_j^{\,2}, \overline{H_j}^{\,2}$ and $V_{(),}C_{()}$ are the variance coefficients and correlation coefficients respectively. Where $Z_l = W_{av,l} - W_l$ implies the difference between the scheduled estimated wind power and the estimated available wind power. Using convolution integral for continuous functions f_w and g_l, the following equation is given:

The expected expression for $\overline{W_{av,l} - W_l}$ is written in Eq. (4) below (Piperagkas et al., 2010):

$$E(Z) = \int_0^{W_{r,l}} z\left(\int_0^{W_{r,l}} f_{w,l}(w)\,g_l(z-w)\,dw\right)dz \quad (4)$$

Where f_w and g_l are the weibull pdf for the available wind power and Gaussian pdf for the wind load respectively. Furthermore, substituting the variance and covariance values of all the involved random variables coefficients, Eq. (3) is expressed in deterministic form as;

$$\overline{J_1} = \sum_{i=1}^{N_p}\left\{\alpha_i + \beta_i P_i + \gamma_i(\bar{P}_i^{\,2} + V^2(P_i)\bar{P}_i^{\,2})\right\} + \sum_{j=1}^{N_p}\left\{\alpha_j + \beta_j\theta_j + \gamma_i(\bar{\theta}_j^{\,2} + V^2(\theta_j)\theta_j^{\,2})\right\} + \delta_j\,\overline{H_j} + \theta_j\left(\overline{H_j}^{\,2} + V^2(H_j)H_j^{\,2},\right)\} + \xi_j + \sum_{k=1}^{N_p}\left\{\alpha_k + \delta_k P_i + \Theta_k(\overline{T}_k^{\,2} + V^2(T_k)\bar{T}_k^{\,2})\right\} - \mu \times \Delta WC + WC_{max} + \sum_{l=1}^{N_w} k_p\,(W_{av} - W_l) \quad (5)$$

$$\overline{J_1} = \sum_{i=1}^{N_p}\left\{\alpha_i + \beta_i P_i + \gamma_i(1.04)\bar{P}_i^{\,2})\right\} + \sum_{j=1}^{N_p}\{\alpha_j + \beta_j\theta_j + \gamma_i(1.04)\theta_j^{\,2})\} + \delta_j\,\overline{H_j} + \theta_j(1.04)H_j^{\,2},)\} + \xi_j + \sum_{k=1}^{N_p}\left\{\alpha_k + \delta_k P_i + \Theta_k(1.04)\overline{T}_k^{\,2})\right\} - \mu \times \Delta WC + WC_{max} + \sum_{l=1}^{N_w} k_p\,(W_{av} - W_l)$$

The matrix transformation for Eq. (5) is expressed as;

$$\overline{J_1} = \text{trace}(X^T \Gamma X) + \Delta^{\mathrm{T}} X + \Omega + \delta_j^T \overline{H}_j - \bar{\mu}\Delta W + WC_{max} + k_{p,l}E(Z) \quad (6)$$

Where X is the vector variable represented in matrix form as;

$$X = [\overline{P_{i,}}\ \overline{\theta_j}, \overline{H_j}, \overline{T_k}];$$

$$\Gamma = blkdiag\left[(\gamma_1 \cdots \gamma_i);\ (\gamma_1 \cdots \gamma_j);\ (\theta_1 \cdots \theta_j);\ (\theta_1 \cdots \theta_k)\right] * 1.04;$$

$$\Delta = [(\beta_1 \cdots \beta_i);\ (\beta_1 \cdots \beta_j);(\delta_1 \cdots \delta_j)]^T;$$

$$\Omega = \sum_{i=1}^{N_w} \alpha_i + \sum_{i=j}^{N_c} \alpha_j + \sum_{k=1}^{N_k} \alpha_k$$

The correlation coefficient of each pair of random variables is taken as 0.3, the minimum and maximum wind power limits are considered to be 0.8pu and 0.3pu, respectively, the wind power underestimation $penalty$ is 30$/pu and the wind power price is taken as 120$/pu, 150$/pu and 180$/pu respectively (Piperagkas et al., 2010).

2.1 Expected emissions CO_2, SO_2 and NO_x

The expectation values of total emissions in ton/h of SO_2 and NO_x are given as follows by;

$$\overline{J_2} = \sum_{i=1}^{N_p} \left\{10^{-2}\left(\alpha_i + \beta_i P_i + \gamma_i(P_i^2 + V_{ar}(P_i)\right) + \zeta_i + \zeta_i \lambda_i \overline{P_i} + \frac{\zeta_i \lambda_i}{2}\ (\overline{P_i^2} + V_{ar}(P_i))\right\} + \sum_{j=1}^{N_c}\{(\vartheta_j + \eta_j)\overline{\theta_j}\} + \sum_{k=1}^{N_h}\{(\pi_k + \rho_k)T_k\} \quad (7)$$

where P_i is the power output generated by the thermal units, power produced by the CHP units is denoted as θ_j and the emission coefficients for the thermal units are α_i, β_i, γ_i, ζ_i, λ the emissions coefficients for the CHP units are given as ϑ_j, η_j are the emissions coefficients for the heat-only units are given as π_k, ρ_k respectively. The SDP relaxation conversion for the deterministic equivalent of Eq. (7) is presented in Eq. (8) below;

$$\overline{J_2} = trace(\overline{P_i}\Gamma\overline{P_i}^T) + \Delta^T X + \Omega_i + \zeta_i + \zeta_i\lambda_i\overline{P_i} + \frac{\zeta_i\lambda_i}{2}\ (1.04)\overline{P_i}^2 + \sum_{j=1}^{N_c}\{(\vartheta_j + \eta_j)\overline{\theta_j}\} + \sum_{k=1}^{N_h}\{(\pi_k + \rho_k)T_k\} \quad (8)$$

Where $\Gamma = diag[(\gamma_1 \cdots \gamma_i)] * 1.04;$
$\Delta = [(\beta_1 \cdots \beta_i)]^T;\ \Omega = \sum_{i=1}^{N_w} \alpha_i$

The stochastic expression of CO_2 emission is a linear power output equation presented in Eq. (9) (Piperagkas et al., 2010);

$$\overline{J_{2c}} = \sum_{i=1}^{N_p} \tau_i \overline{P_i} + \sum_{j=1}^{N_c} k_j \overline{\theta_j} + \sum_{k=1}^{N_h} \sigma_k \overline{T_k} \quad (9)$$

Where τ_k, k_j, σ_k are the coefficients of CO_2 emission.

The coefficients of cogeneration units emissions are given as $\vartheta_j = 0.00015$, $\eta_j = 0.0015$ and k_j=0.2 for SO_2 and CO_2 respectively, and for heat-only units, $\pi_k = 0.0008$, $\rho_k = 0.001$ and $\sigma_k = 0.4$.

2.2 Expected Power Loss

The power loss p_L order wise known as J_5 can be further expressed by applying the Kron's B-loss coefficients as;

$$J_5 = \sum_{i=1}^{N_p}\sum_{m=1}^{N_p} P_i B_{im} P_m + \sum_{i=1}^{N_p}\sum_{j=1}^{N_c} P_i B_{ij}\theta_j + \sum_{j=1}^{N_c}\sum_{n=1}^{N_c} \theta_j B_{jn}\theta_n \quad (10)$$

The Eq. (10) is further expressed in stochastic form which can be found in (Piperagkas et al., 2010):
Therefore, the matrix transformation for stochastic of Eq. (10) in its deterministic equivalent is expressed as follows;

$$\overline{J_5} = \sum_{i=1}^{N_p}\sum_{m=1}^{N_p} \overline{P_i^T} B_{im}\overline{P_m} + \sum_{i=1}^{N_p}\sum_{j=1}^{N_c} \overline{P_i^T} B_{ij}\overline{\theta_j} + \sum_{j=1}^{N_c}\sum_{n=1}^{N_c} \overline{\theta_j^T}\ B_{jn}\overline{\theta_n} + \sum_{i=1}^{N_p} 0.04\overline{P_i^T}P_i + \sum_{j=1}^{N_c} 0.04\ B_{jj}\overline{\theta_j^T}\theta_j$$
$$+ 2\sum_{i=1}^{N_{p-1}}\sum_{m=i+1}^{N_p} 0.09\ B_{im}\overline{P_i^T}\overline{P_m} + 2\sum_{j=1}^{N_{c-1}}\sum_{n=j+1}^{N_c} 0.09\ B_{jn}\overline{\theta_j^T}\ \overline{\theta_n} + \sum_{i=1}^{N_p}\sum_{j=1}^{N_c} 0.09\ B_{jn}\overline{P_i^T}\ \overline{\theta_j} \quad (11)$$

2.3 Problem Constraints

The total electric power generation is set to be equal the total electric power demand and the real power losses, given as follows (Piperagkas et al., 2010):

$$\sum_{i=1}^{N_p} \bar{P}_i + \sum_{j=1}^{N_c} \bar{\theta}_j + \sum_{l=1}^{N_w} \bar{W}_l = \bar{P}_D + \bar{P}_L \quad (12)$$

The expected values are obtained within these ranges of minimum and maximum limits set as (Piperagkas et al., 2010)

$$I^T P_i^{min} \leq I^T \bar{P}_i \leq I^T P_i^{max} \quad (13)$$

$$I^T \theta_j^{min} \leq I^T \bar{\theta}_j \leq I^T \theta_j^{max} \quad (14)$$

$$I^T H_j^{min} \leq I^T \bar{H}_j \leq I^T H_j^{max} \quad (15)$$

$$I^T T_k^{min} \leq I^T \bar{T}_k \leq I^T T_k^{max} \quad (16)$$

$$0 \leq \bar{W}_i \leq w_{r,l} \quad (17)$$

$$0 \leq \bar{\mu}_i \leq 1 \quad (18)$$

$$\sum_{l=1}^{N_w} \bar{W}_l = W_{max} - \bar{\mu}\, \Delta W \quad (19)$$

$$W_{max} - \mu\, \Delta W \leq \Delta W \leq \sum_{l=1}^{N_w} \bar{W}_{av,l} \quad (20)$$

Where the power limits for thermal unit and the CHP units are P^{min}, P^{max}, $\theta^{min}, \theta^{max}$ respectively, the rated power of wind turbines is w_r, H^{min}, H^{max}, T^{min}, T^{max} are the heat production limits of CHP units and heat-only unit. Details for the expected power and heat deviations objectives functions are available in (Piperagkas et al., 2010).

3. SDP Relaxation

A semi-definite programming (SDP) is a convex optimisation technique that converts a linear programming problem into its matrix equivalent form. The SDP approach maximises or minimises the linear optimisation problem subject to the constraint that are affine combination of symmetric matrices is Semi-Definite (Alli et al., 2017). Thus, SDP relaxations for minimising a non-convex quadratic function over a box are given below:

$$\min\left\{ \frac{1}{2} x^T P x + c^T x \right\}$$
$$subject\ to \quad 0 \leq x \leq e \quad (21)$$
$$X = xx^T$$

Where $x \in \mathbb{R}^n, P \in \mathbb{R}^{nxn}, c \in \mathbb{R}^n\ and\ e \in \mathbb{R}^n$ is the all-ones vector. Eq. (21) is non-linear polynomial (NP)-hard, if P is not a positive semidefinite. To achieve a global optimal solution for the problem in (21), it is best to relax it into a convex problem, which provides a tight lower bound on the optimal value with low computational cost. One best approach is to introduce a lifting variable X to replace quadratic term $x_i x_j$ but the valid semidefinite inequality $X \geq xx^T$ should be included to obtain an SDP relaxation. Therefore, (22) becomes;

$$\min\left\{ \frac{1}{2} \boldsymbol{trace}\langle \boldsymbol{P}, \boldsymbol{X} \rangle + c^T x \right\}$$
$$subject\ to \quad 0 \leq x \leq e \quad (22)$$
$$\begin{pmatrix} 1 & x^T \\ x & X \end{pmatrix} \geq 0$$

3.1 Randomisation of a Nonconvex Optimisation Problem

In this section, the semidefinite relaxation is used to produce a positive semidefinite or covariance of the matrix together with the lower bound on the objective (Aspremont and Boyd, 2003). However, if x is taken as a Gaussian

variable with x~N($x, X - xx^T$), the nonconvex QCQP will be solved by x "on average" over this distribution, meaning

$$\begin{array}{ll} min & \mathrm{E}(trace\langle P, X_0\rangle + 2{q_0}^T x + r_0) \\ subject\ to & \mathrm{E}(trace\langle P, X_0\rangle + 2{q_0}^T x + r_0) \\ & \begin{pmatrix} 1 & x^T \\ x & X \end{pmatrix} \geq 0 \end{array} \quad (23)$$

By sampling x over a sufficient number of times, a "good" feasible point can then be determined, which leads to keeping the best feasible point.

3.2 Weighted Sum Method

The weighted sum method involves a linear or convex combination of the objectives $f_i(x)$, $i = 1, \cdots, p$, details can be found in (Jubril et al., 2014). The scalar objective, $\emptyset(f, w)$ is obtained by multiplying every of the objectives $f_i(x)$ by a weight factor $w_i$which are then summed up expressed as follows:

$$\emptyset(f, w) = \sum_{i=1}^{p} w_i f_i(x) = w^T f(x) \quad (24)$$

Where the number of the objectives is denoted as p and

$$\sum_{i=1}^{p} w_i = 1, \ \ w_i \geq 0, \qquad i = 1, \cdots, p \quad (25)$$

The transformation of this vector optimisation to a scalar form can be represented as

$$\begin{array}{l} minmize\ \emptyset(f, w) \\ s.t \ \ x \in X \end{array} \quad (26)$$

Consider when p = 2, a bi-objective function, then Eqs. (25) and (26) respectively, reduce to

$$\emptyset(f, w) = w_1 f_1(x) + w_2 f_2(x) \quad (27)$$

and

$$w_1 + w_2 = 1, w_1, w_2 \geq 0 \quad (28)$$

Let the weight in Eq. (28) is set as λ, such that $w_1 = \lambda \ and \ w_2 = 1 - \lambda$, then the slope of the curve is formed as

$$tan\,\theta_w = \frac{1 - \lambda}{\lambda} \quad (29)$$

while the sensitivity of the slope is given as

$$\frac{d}{d\lambda} tan\,\theta_w = \frac{d}{d\lambda} \frac{1 - \lambda}{\lambda} = -\frac{1}{\lambda^2} \quad (30)$$

3.3 Introducing Weight Selection into the Weighted Sum Method

In Eq. (31), a uniform spacing of λ does not generate a uniform distribution of the Pareto set solutions. But the weight is parameterised with variable k in such a way that k is constrained on the surface of the oval shape; an improved uniform distribution of the solution set is obtained on the Pareto front. Setting (Jubril et al., 2014)

$$w_1 = \frac{{\lambda_1}^2}{{k_1}^2}, w_2 = \frac{{\lambda_2}^2}{{k_2}^2} \quad (31)$$

Putting Eq. (32) in (29), the ellipsoid equation becomes

$$\frac{{\lambda_1}^2}{{k_1}^2}+\frac{{\lambda_2}^2}{{k_2}^2}=1 \quad (32)$$

Where k_1 and k_2 denoted the axes of the ellipsoid. By normalising the expression in Eq. (33) that is, setting value of $k_2 = 1$ and $\lambda_1 = \lambda$, then the slope becomes

$$tan\,\theta_w = \frac{{k_1}^2-\lambda^2}{\lambda^2} \quad (33)$$

$$\frac{d}{d\lambda}tan\,\theta_w = -\frac{2{k_1}^2}{\lambda^3} \quad (34)$$

Setting $k_2 = 1$ means that the mirror axis of the surface of the ellipsoid is set to a unit value, where control weight selection k_1 is selected from a value greater than 1. The control of the curvature of the ellipsoid is achieved by varying the value of control weight selection k_1. Thus, a higher sensitivity is produced by the selection of the non-linear weight and the k_1 parameter determines further sensitivity improvement. The solution points can be examined in such a way that the clustered points can be distributed out by varying the value of control weight selection k_1 parameter; this will ensure an improved computational efficiency of the method (see Tables 1 and 2).

Table 1: The coefficient data for the thermal units

Gens	α_i	β_i	γ_i	P_i^{min}	P_i^{max}	α_i	β_i	γ_i	ζ_i	λ_i	τ_i
P_1	1.0	2.0	0.1	0.05	0.5	4.091	-5.554	6.490	2E-4	2.857	0.32
P_2	1.2	1.5	0.1	0.05	0.6	2.543	-6.047	5.639	5E-04	3.333	0.26
P_3	0.4	1.8	0.2	0.05	1.0	4.258	--5.094	4.586	1E-06	8.000	0.36
P_4	0.6	1.0	0.1	0.05	1.2	5.326	-3.550	3.380	2E-03	2.000	0.44

Table 2: The coefficient data for the CHP units

Gens	α_j	β_j	γ_j	θ_j^{min}	θ_j^{max}	H_j^{min}	H_j^{max}	δ_j	Θ_j	ξ_j
CHP_1	265	145	34.5	0.05	1.0	0	0.6	42	30	31
CHP_2	125	360	43.5	0.05	0.6	0	0.6	6	27	11
T_1	110	41	23	-	-	0	22	-	-	-

4. Simulation Results and Discussion

The proposed SDP method is tested on modified IEEE 6 and 20 units' networks with 2 CHP units and 20 wind parks for each of the networks to determine its efficiency. This paper has also considered the rated wind speed to be 15 m/s, cut-in wind speed is 3.5 m/s and the cut-out wind speed is 25 m/s. Thus, the SDP problem is converted into the primal/dual form by using YALMIP parser toolbox. Two main cases were investigated:

4.1 Case Study I: Modified IEEE Six Units

This paper has considered the simulation analysis conducted by (Piperagkas et al., 2010) for the case study I. A modified IEEE six units, 30 bus test system with 2 cogeneration units and 20 wind parks is considered. All the B-coefficients are given in per unit (p.u.) on a 100 MVA base capacity. The B matrix of the transmission loss coefficient is given by:

$$B_{ij} = \begin{bmatrix} 0.1382 & -0.0299 & 0.0044 & -0.0022 & -0.0010 & -0.0008 \\ -0.0299 & 0.0487 & -0.0025 & 0.0004 & 0.0016 & 0.0041 \\ 0.0044 & -0.0025 & 0.0182 & -0.0070 & -0.0066 & -0.0041 \\ -0.0022 & 0.0004 & -0.0070 & 0.0137 & 0.0050 & 0.0033 \\ -0.0010 & 0.0016 & -0.0066 & 0.0050 & 0.0109 & 0.0005 \\ -0.0008 & 0.0041 & -0.0066 & 0.0033 & 0.0005 & 0.0244 \end{bmatrix} \quad (35)$$

It is observed from the optimisation results presented in Tables 3 and 4 that lowest minimum total cost is obtained from SDP approach compared to a modified multi-objective particle swarm optimisation (MOPSO),

genetic algorithms and the weighted aggregation reported in the literature when only CHP units are considered and for the case of the power systems incorporated with the wind power units at wind power operation cost σ set to be 120$/p.u.

The effect of control weight selection k_1 can be observed in Figures 1 to 4 by performing fifty one (51) runs for each parameter value and different values for $k_1$were tested. It is noticed in Figure 1 that there is a close solution points on the Pareto front with control weight selection $k_1 = 1$ which results to waste of computational efforts. As the value of control weight selection k_1 is increased, the Pareto points were distributed out.

Table 3: Cost reduction incorporating CHP only considering a modified IEEE six units

GEN/OBJ	*SDP*	*MOPSO*	*GA*	*WA*
$\overline{P_1}$	0.0500	0.2980	0.4597	0.0500
$\overline{P_2}$	0.6000	0.4576	0.5290	0.6000
$\overline{P_3}$	0.5260	0.6519	0.4721	0.7737
$\overline{P_4}$	1.2000	0.7826	0.8623	0.7205
$\overline{\theta_1}$	0.4629	0.3468	0.4856	0.0600
$\overline{\theta_2}$	0.0500	0.1523	0.0699	0.0600
$\overline{H_1}$	0.0000	0.2422	0.3684	0.0000
$\overline{H_2}$	0.6000	0.2330	0.1507	0.2000
$\overline{T_1}$	0.2000	0.2972	0.2309	0.5000
$Cost$ ($/hr)	**1275.3**	**1305.0**	**1322.4**	**1303.6**
CO_2	1.0823	1.5960	1.7212	1.6001
NO_x,SO_2	0.1519	0.1272	0.1285	0.1361
$Power\ dev.$	0.5265	0.4784	0.5447	0.4882
$Heat\ dev.$	0.0268	0.0309	0.0292	0.0206

Source: Abstracted from Alli et al. (2017)

Table 4: Cost reduction incorporating both CHP and wind power units considering modified IEEE six units

GEN/OBJ	*SDP*	*MOPSO*	*GA*	*WA*
$\overline{P_1}$	0.0500	0.1991	0.2272	0.0500
$\overline{P_2}$	0.5121	0.3254	0.1667	0.6000
$\overline{P_3}$	0.0500	0.2283	0.4550	0.1783
$\overline{P_4}$	1.2000	0.7522	0.7536	0.8536
$\overline{\theta_1}$	0.2063	0.2812	0.4203	0.3562
$\overline{\theta_2}$	0.0500	0.1604	0.1380	0.0600
$\overline{H_1}$	0.0145	0.2049	0.2847	0.5139
$\overline{H_2}$	0.6000	0.2353	0.2322	0.2000
$\overline{T_1}$	0.1855	0.3039	0.2334	0.0361
$\overline{WP_1}$	0.0049	0.0426	0.1142	0.0440
$\overline{WP_2}$	0.0073	0.0017	0.0115	0.0050
$\overline{WP_3}$	0.0057	0.0280	0.0164	0.0050
$\overline{WP_4}$	0.0059	0.0155	0.1450	0.0050
$\overline{WP_5}$	0.0059	0.0582	0.0660	0.1320
$\overline{WP_6}$	0.0057	0.0120	0.0124	0.0050
$\overline{WP_7}$	0.0057	0.0175	0.0125	0.0050
$\overline{WP_8}$	0.0059	0.0666	0.0582	0.0050
$\overline{WP_9}$	0.0059	0.0627	0.0124	0.1000
$\overline{WP_{10}}$	0.0059	0.0296	0.0464	0.0050
$\overline{WP_{11}}$	0.0057	0.0346	0.0253	0.0450
$\overline{WP_{12}}$	0.0056	0.0088	0.0130	0.0050
$\overline{WP_{13}}$	0.0057	0.0581	0.0038	0.0990
$\overline{WP_{14}}$	0.0060	0.0162	0.0321	0.0540
$\overline{WP_{15}}$	0.2338	0.0076	0.0085	0.0050
$\overline{WP_{16}}$	0.0057	0.0603	0.0577	0.0050
$\overline{WP_{17}}$	0.2338	0.0274	0.0023	0.0050
$\overline{WP_{18}}$	0.2338	0.0395	0.0033	0.0720
$\overline{WP_{19}}$	0.0053	0.0901	0.0799	0.0050

$\overline{WP_{20}}$	0.0058	0.0786	0.0069	0.1190
$Cost\ (\$/hr)$	**1218.5**	**1257.1**	**1319.4**	**1288.4**
CO_2	0.8216	1.5339	0.5313	1.6000
NO_x,SO_2	0.1619	0.1327	0.1328	0.1418
$Power\ dev.$	0.7156	0.6122	0.6762	0.6515
$Heat\ dev.$	0.0276	0.0403	0.0412	0.0354
μ	$5.3653e^{-08}$	0.0084	0.2215	0.1500

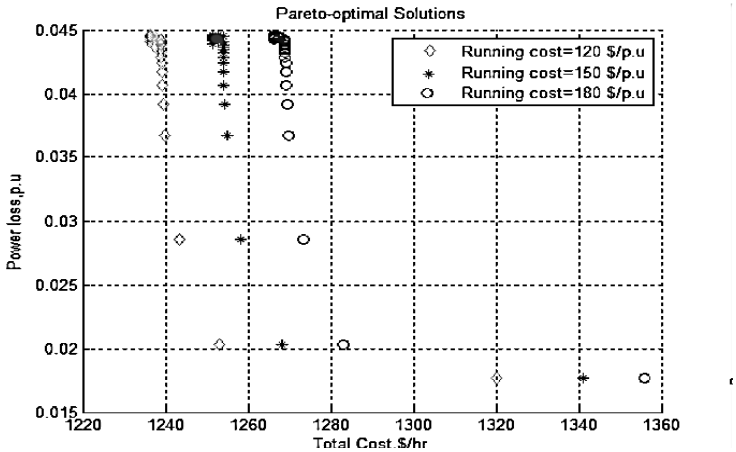

Figure 1: The effect of k_1=1 on the Pareto curve obtained for different running costs of wind power utilising a modified IEEE six units test system.

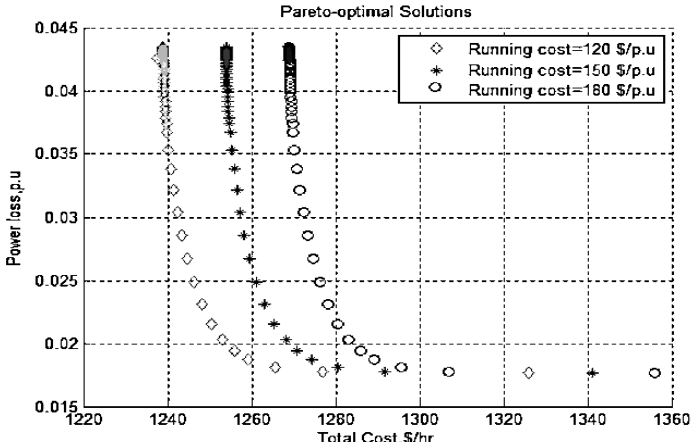

Figure 2: The effect of k_1=5 on the Pareto curve obtained for different running costs of wind power utilising a modified IEEE six units test system

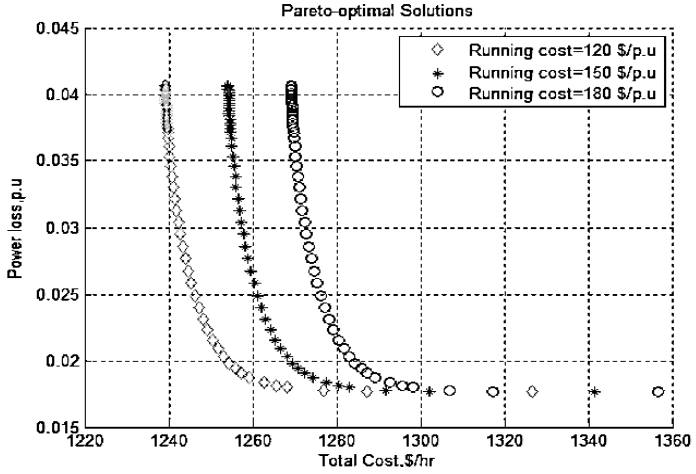

Figure 3: The effect of k_1=10 on the Pareto curve obtained for different running costs of wind power utilising a modified IEEE six units test system.

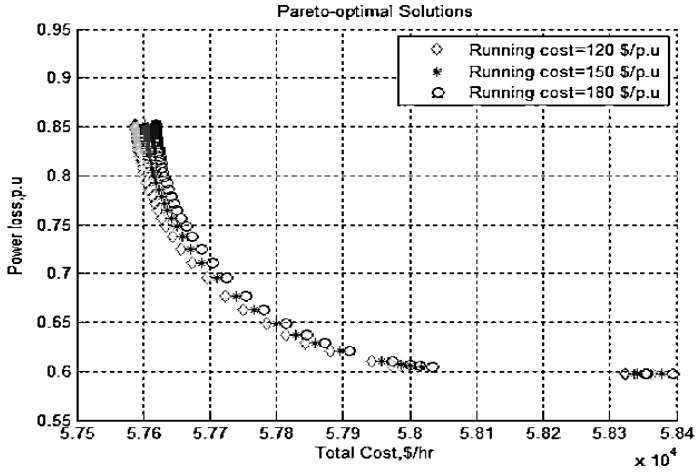

Figure 4: The trade-off between Power loss (p.u) and the total cost at different running costs of wind power at k_1=10, using a modified IEEE twenty units test system.

4.2 Case Study II: Modified IEEE Twenty-units' System

This case study consists of modified twenty thermal units with two CHP and twenty wind power units. The total load demand P_D supplies by the thermal system is given as 25.00 pu. The data for the IEEE twenty-units' network and the B matrix of the transmission line loss coefficient are also available in (Coelho and Lee, 2008)

5. Conclusion

The SDP method solves a stochastic problem by minimising the expectation of the multi-objective functions using the statistics of Gaussian pdf and Weibull pdf is employed in the characterisation of the stochastic wind data for the wind energy conversion system (WECS). It is clear that introduction of weight adaptation into the optimisation method produces more uniform distribution of the solutions points as the value of control weight selection k_1 increases. Simulations results have differentiated the running costs obtained by the system that includes both the cogeneration units and wind power penetration for various wind power prices by satisfying all the systems' constraints. The Pareto solutions presented using SDP approach for the multi-objectives formulation problem indicated that the decision maker has the ability to choose a suitable solution from a set of ideal optimal solutions in the multi-objective optimisation

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Peristaltic Transport of an Ellis Fluid in an Inclined Channel

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Abstract: *The flow of an Ellis fluid in an inclined channel driven by peristaltic waves is studied with low Reynold's number assumption. The effects of the wave amplitude, channel inclination and fluid parameters are observed for varying values of the time averaged volume flow. The wave type considered is sinusoidal and the flow parameters are calculated in the wave frame of reference and later converted to the stationary frame. It is observed that the axial velocity, which has a parabolic distribution at any instant of time, has a larger value at the periphery of the channel and a lower value at the centre of the channel for changes in the Ellis fluid parameters. The relationship between the time averaged volume flow rate and the pressure rise per unit wavelength is non-linear and becomes more obvious with increase in volume flow rate. However, for the Newtonian case, this relation is linear. The efficiency of the pumping and the frictional force at the wall are analysed for the varying fluid types and flow conditions. Reflux and trapping phenomena are investigated by plotting of the streamlines as well as the velocity field.*

Keywords*: Peristaltic pumping, Non-Newtonian fluid, Ellis fluid, lubrication theory*

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■

Dynamics of e-Rumor Models

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Abstract: *In recent years, with the new tools of communication (like, Facebook, Twitter, and WhatsApp), social networks became new kinds of propagation of rumors. In particular, in the case of fake news, this phenomenon is very dangerous for our societies, both from an economic and a political point of view. The first mathematical works on this subject highlighted a similitary between propagation of rumors and epidemics. Indeed, in the epidemic case, the population is in general divided into three groups, the one of susceptibles, the one of infected and the one of removed, whereas in the case of rumors, the population of a network contains the ignorants, the spreaders and the stiflers, that is those who know the rumor but do not spread it for the moment. This multi-dimensional diffusion, process is mainly driven by socio-psychological elements and its randomness has been pointed out. The transmission of information is done as the transmission of a disease but the parameters involved in the decision for a person to become a spreader are not the same than the ones leading a susceptible to become infected. In both cases, the transmission can only occur after a direct contact between a spreader (respectively, an infected) and an ignorant (respectively, a susceptible). However, the transmission depends on different parameters as characteristics of the information, demographic and socio-psychological factors, and external sources (respectively virulence of the epidemic, sensibility of the individual, subject or not to pathologies, genetic transmission possibility). In the present work, we propose first an e-rumor deterministic dynamical system, in which we take into account then the random perturbations leading a person of the social network to become or not a spreader by adding diffusion terms. From this last one, we determine the thereholds of extinction and persistence of the spreaders density.*

Keywords*: Deterministic and stochastic e-rumor models, extinction, persistence*

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Kendy Valmont *is a PHD student supervised by the two previous authors. Her thesis is based on stochastical optimal control theory related to problems of rumors propagation.*

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Rapid Propagation of Improved Cassava Varieties Using the Multiple Shoot Removal Technique

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Abstract: *Cassava (Manihot esculenta Crantz) can be rapidly multiplied by the multiple shoot removal technique (MSRT) which utilises little planting material for mass propagation. In this two-step process, two-node hardwood cuttings from stems of mature parent plants are put to sprout in well-watered potting medium. Once a shoot has reached 8 cm height, it is severed 1 cm from base and put to root in a humid environment. Under good conditions, multiple shoots sprout from each two-node cutting, are excised and put to root similarly. The MSRT was investigated with three improved cassava varieties recently introduced to Jamaican farmers, comparing shooting from cuttings from different parts of parent stems (nodal ages) in fertilised or unfertilised potting medium. Size of cuttings generally increased with nodal age. Sprouting of cuttings depended on variety; sprouting was better on cuttings from older nodal ages for the poorly-sprouting varieties. Fertilisation of the medium did not influence sprouting, but did increase rate of growth of the shoots that sprouted. Shoot growth rate was higher from the (larger) oldest nodal-aged cuttings after 7 weeks, suggesting that nutrient stores in the cuttings were being used in growth up to 7 weeks. The quality, especially nutrient status, of the cuttings was suggested to play an important role in sprouting and shoot growth. Of the cut shoots, 79% rooted successfully. The MSRT was demonstrated to have good potential for rapid propagation of cassava in Jamaica.*

Keywords*: Cassava, internode dimension, sprouting, shoot induction, two-node cutting, vegetative propagation*

1. Introduction

Cassava (*Manihot esculenta* Crantz) also known as mandioca, yuca or tapioca is a tropical crop known for its high starch content, and the fourth most consumed staple. The plant is a shrub with heights of 1 to 5 m according to plant age and variety. The whole plant may be used but its roots (tubers) are the most economic portion, which begin bulking and accumulating starch about 75 days after planting (DAP) (Alves, 2002). Cassava could be an important crop for food security as it is highly drought tolerant and the roots may go unharvested up to 24 months after planting (MAP) yet maintain palatability.

The cultivation of cassava has always been challenged by the availability of sufficient good quality planting material. Cassava is mainly propagated vegetatively using stem cuttings of 20 to 30 cm with 10-20 axillary buds, taken from plants at the time of tuber harvest. Because of the large size of planting material used, the number of propagules produced per plant is low compared to numbers of true seeds in other crops. True seed propagation in cassava is impractical due to uncertain and varying flowering of the plant and large varietal differences. Hence, a method for the mass propagation of cassava planting material was developed at the Centro Internacional de Agricultura Tropical (CIAT) in the 1970's (Cock, 1983). Two methods were developed to help avoid issues with the long crop cycle of 9-12 months, only after which the planting material traditionally becomes available. Leaf and bud cutting involves the use of planting material as young as 3 months old. The axillary bud is removed with the leaf at a node (each node has only one leaf and bud), the lamina reduced in size, and put in water to root under sterile humid conditions, then transferred to planting trays after roots are 1 cm long. This method may yield up to 60,000 traditional size cuttings from one cassava plant in 1½ years (Lopez, 2012).

The second method is known as the multiple shoot removal technique (MSRT) or shoot induction. Mature cassava stems are cut into two-node pieces which are allowed to shoot under good potting conditions. The subsequent shoots are excised and put to root, leaving behind a 1-cm stump with buds for re-sprouting, and the process continues until the two-node piece dies. Eight or more shoots may be obtained from each two-node cutting and the process requires less skill and care than when using leaf-bud cuttings (Lopez, 2012; Wholey, 1974).

This study explores factors affecting shoot induction and growth in the MSRT for three improved cassava varieties in Jamaica: use of cuttings from different parts of parent stems (nodal ages); fertilisation or no fertilisation of potting medium.

2. Method

Three mature stems (used as three replicates) were taken from 10 months or older cassava plants for each of varieties MCol1505, CM516, and CM849, removing the stem apex and cutting about 30 cm above the base. Plants were part of germplasm grown at the Bodles Research Station of the Ministry of Industry, Commerce, Agriculture and Fisheries, Old Harbour, St Catherine, Jamaica. Stems were 1.2 - 1.5 m long and were sectioned into four, from top (apical) to bottom (basal). Each section was categorised as a nodal age: ages one, two, three and four, respectively from top to bottom. The sections were cut further into smaller pieces with two healthy axillary buds (termed two-node hardwood cuttings). Eight cuttings were selected from each section per stem, to represent the nodal age; internode dimensions, length and diameter, were measured.

Cuttings were placed for 10 mins in an insecticide-fungicide dip. They were planted in 110 g of a sandy loam soil mix and arranged in a complete randomised block design (with three replicates) in propagation domes in a greenhouse at the Department of Life Sciences, UWI Mona, St Andrew, Jamaica. The domes were made from plastic sheets and PVC pipes, 180 x 120 cm by 60 cm maximum height, and positioned under a 'roof' of shade cloth. The pots were watered regularly to maintain the potting medium at, or close to, field capacity. High humidity was encouraged in the domes by the presence of three or four saucers of water. Relative humidity and soil temperatures were determined for a sample period (8 days in November 2015).

A complete fertiliser solution was applied from 40 DAP to the potting medium of four of the eight cuttings per variety and nodal age, and withheld from the other four. Thus there were three experimental factors and a total of 24 treatments: three varieties by four nodal ages by two fertilisation regimes (fertilised and unfertilised). Sprouting and the height of sprouted shoots from the two-node hardwood cuttings were recorded at intervals for 3 months.

Softwood shoots which sprouted from the cuttings and attained heights of at least 8 cm, were cut, leaving 1 cm at the base, and put to root in 350-cm^3 plastic cups in a medium of loamy soil, sand and commercial potting mix. The rooting environment was large cardboard boxes covered by clear plastic sheets that were placed under shade. Rooting shoots were kept in the boxes for 14 days followed by 7 days hardening in a greenhouse. Soil moisture was maintained by frequent watering. The growth rate (from measurements of height) and number of leaves of these softwood shoots were determined during the 3 weeks.

Data were analysed by ANOVA (and Tukey's HSD test for differences among means) using the statistical package SPSS Version 21 (with 5% as the critical probability and testing for validity of the parametric assumptions). Non-parametric data sets were analysed by the Kruskal-Wallis or Mann-Whitney tests.

3. Results

3.1 Microclimatic Conditions of Propagation Environment

Relative humidity (RH) tended to remain high in the daytime in domes (97.3% on average) and soil temperature was relatively constant. The domes were situated under a 'roof' of shade cloth in the greenhouse, so although the variation of light intensity was considerable, it was less than under open sky (see Table 1). The propagation environment used in a previous trial with the MSRT (carried out with similar methodology) was a mist house, with pots placed out of reach of the misters. In this microclimate, the daytime variation in RH and soil temperature was greater, while the range of light intensity was similar. However, the results for sprouting were equivalent to those in the domes.

Table 1. Microclimatic conditions of the propagation domes
(from measurements at 9 am and 1 pm over 8 days in November 2015).

Relative humidity (%)		Soil temp (°C)		Light intensity lux ×1000	
min	max	min	max	min	max
95.3	99.3	17.0	19.3	103.3	479.4

3.2 Dimensions of Two-node Cuttings

There was a trend for internode diameters to increase with increasing nodal age of the cutting, although differences were small and not quite significant (p 0.063) (see Table 2). Differences among varieties (p 0.516) and the

interaction of variety and nodal age (p 0.957) were not significant for mean diameter. There was a progressive increase in internode length with cutting age for CM516, and MCol1505 age 1 cuttings were 45% shorter than the older ages (p 0.022), but lengths were similar across the ages for CM849 (p >0.05).

Table 2. Internode dimensions (diameter and length) of cassava two-node cuttings of four nodal ages (numbered from apical to basal ends of parent stems) from three varieties set to propagate in plastic domes (means of three replicates with four cuttings per replicate).

Variety	Diameter (cm)					Length (cm)				
	at nodal age:				Var. mean	at nodal age:				Var. mean
	1	2	3	4		1	2	3	4	
CM 516	1.74	1.67	1.97	1.95	1.83	1.15	1.50	2.43	2.95	2.01
CM 849	1.76	1.86	1.91	2.16	1.92	1.43	1.35	1.25	1.45	1.37
MCol 1505	1.79	1.94	1.98	2.13	1.96	1.18	2.18	2.00	2.25	1.90
Standard error (se)	0.138					0.369				
Overall age mean (se)	1.76 (0.01)	1.82 (0.06)	1.94 (0.03)	2.08 (0.06)		1.25 (0.10)	1.68 (0.19)	1.89 (0.25)	2.22 (0.31)	

3.3 Sprouting Success of Two-node Hardwood Cuttings

There were variable results and poor sprouting percentages for some varieties (see Table 3). The significance of effects was tested using ANOVA on the arcsine-transformed percentage data (in degrees). Fertilisation was not started until 40 DAP and therefore differences were not significant between sprouting of two-node pieces grown in to-be-fertilised and non-fertilised medium (p 0.950, means of 29.2% for both, se 2.93) at 21 DAP. Almost all sprouting over the 3-month period occurred by 21 DAP.

Variety CM849 sprouted more often (significant at p <0.001) than the other varieties, 1.8 times than MCol1505 and 3.7 times than CM516. Generally, sprouting was lower for cuttings from younger parts of the stem: no sprouts were produced from nodal ages 1 and 2 for CM516 and fewer from nodal ages 1 and 2 for MCol1505. However, sprouting was similar across the ages for CM849 (see Table 3).

Table 3. Percentage sprouting of two-node cuttings at four nodal-ages in fertilised and non-fertilised growing medium for three cassava varieties in propagation plastic domes in greenhouse

Variety	Percentage sprouting at nodal-age:								Variety mean (se 3.58)*
	1		2		3		4		
	Non-fert.	Fert.	Non-fert.	Fert.	Non-fert.	Fert.	Non-fert.	Fert.	
CM 516	0.0	0.0	0.0	0.0	8.3	16.7	16.7	41.7	13.2
CM 849	66.7	41.7	66.7	66.7	58.3	66.7	41.7	41.7	48.7
MCol 1505	8.3	16.7	41.7	8.3	16.7	33.3	25.0	16.7	26.4
Nodal-age mean (se 4.14)*	22.6		27.7		34.1		33.2		
Overall mean*	29.4 (se 2.07)								

Nodal-age numbered from apical to basal end of parent stem; 21 days after planting; four two-node pieces per treatment; * signifies that mean and se were obtained from ANOVA on arcsine-transformed data, in degrees.

3.4 Effect of Fertilisation of Propagating Medium on Growth of Shoots from Two-node Cuttings

Fertilised cuttings generally produced taller shoots (see Figure 1) and greater growth rates (see Figure 2). Heights at 20 days after planting (DAP) were not significantly different (p 0.093) between the fertiliser treatments, but heights at 52 up to 95 DAP were significantly greater (p 0.025 and 0.006) for shoots from fertilised hardwood cuttings, by 1.4 times at 52 DAP, increasing to 1.7 times at 95 DAP (See Figure 1). Figure 2 suggests that the initial growth rate of all shoots was relatively fast for the first 20 days, after which growth slowed, then increased from 52 to 76 DAP,

by which time fertiliser was being applied to the selected treatments. In this period, shoots grew faster on fertilised than unfertilised cuttings by 1.7 times (p 0.005).

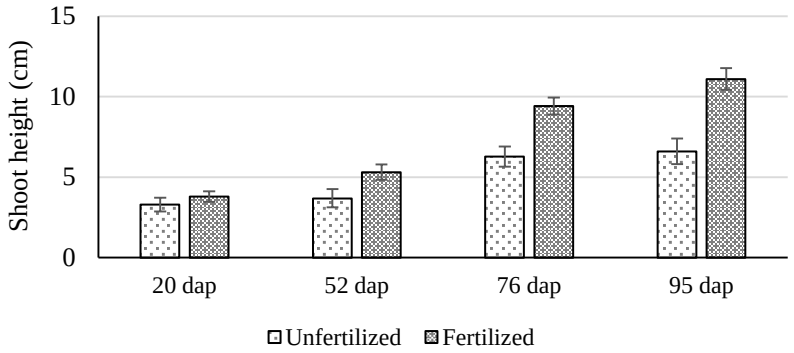

Figure 1. Plant height (cm) of shoots sprouting from fertilised and unfertilised two-node hardwood cassava cuttings in propagation domes in a greenhouse (dap, days after planting of cuttings).

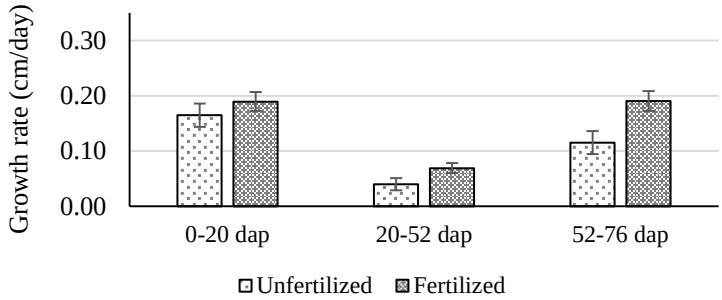

Figure 2. Growth rate (cm/day) of shoots sprouting from fertilised and unfertilised two-node hardwood cassava cuttings in propagation domes in a greenhouse (dap, days after planting).

3.5 Varietal Effect on Growth of Shoots from Two-node Cuttings

For the first 3 weeks, shoots of MCol1505 had the fastest growth rate (0.29 cm/day, p 0.022), dropping by about a third in the subsequent 4 weeks (see Figure 3). Rates were lower by about a half for shoots of CM516 and 849 in the first 3 weeks, but the three varieties had statistically similar rates for the next 10 weeks (averaging 0.07 to 0.17 cm/day) (see Figure 3). CM516 produced very few shoots overall and showed peak growth rate (0.30 cm/day) at 8-11 weeks, but these were shoots mainly from fertilised, age 4 cuttings, compared to shoots from a wider range of nodal ages, fertilised and unfertilised for the other two varieties.

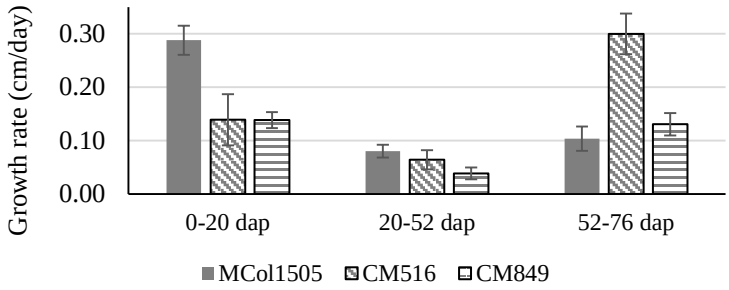

Figure 3. Growth rate (cm/day) of shoots sprouting from two-node hardwood cassava cuttings of three varieties in propagation domes in a greenhouse (dap, days after planting).

3.6 Effect of Parent Stem Nodal Age on Growth of Shoots

There was an effect of nodal age, manifesting especially at 52-76 DAP (p 0.006) (see Figure 4). Shoots on cuttings from basal (age 4) sections of parent stems had a higher rate of growth than those on cuttings of younger nodal age: 3 times as high as those from age 1 and 1.5 times as those from ages 2 and 3 cuttings (see Figure 4).

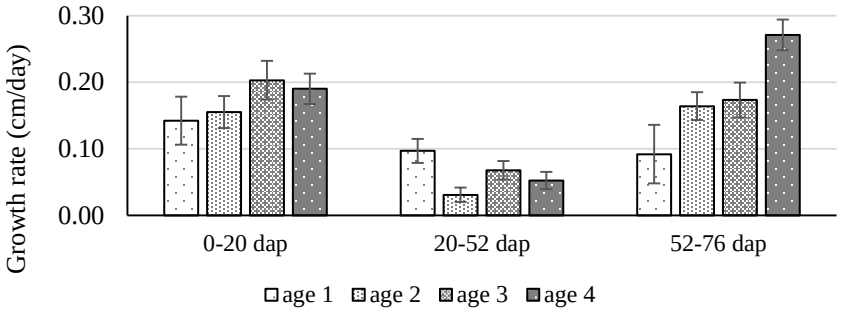

Figure 4. Growth rate (cm/day) of shoots sprouting from two-node hardwood cassava cuttings of four nodal ages in propagation domes in a greenhouse (dap, days after planting).

3.7 Rooting and Growth of Cut Shoots

Overall the rooting success of the softwood shoots was 79%, with approximately similar percentages for the three varieties, four nodal ages and both fertilisation treatments. Considering the numbers of rooted shoots, CM849 (due to the higher amount of sprouting from cuttings) produced most new plants (58% of the 76 total), followed by MCol1505 (24%) and CM516 (18%). Figure 5 illustrates the heights of rooting shoots from fertilised and unfertilised cuttings over 21 days, showing an almost constant increase in height. Shoots from fertilised cuttings maintained their significant differential over those unfertilised.

On average, 63% of the original leaves were lost from cut shoots by 9 DAP, but the remaining 37% (2.2 leaves) were retained up to 21 DAP. New leaves developed gradually, with about 2.0 mature leaves being produced at the shoot apex by 21 DAP. Although not individually statistically significant, shoots from cuttings of older nodal ages tended to have slightly more leaves than those from younger nodal ages.

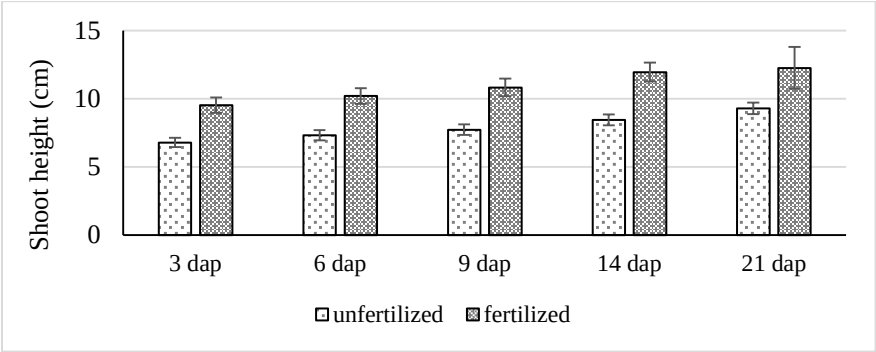

Figure 5. Heights (cm) of shoots during rooting after incision from fertilised and unfertilised two-node hardwood cassava cuttings in propagation domes in a greenhouse (dap, days after planting).

4. Discussion

The percentage of cuttings that sprouted depended on the variety and age of the part of the stem from which cuttings were taken, termed nodal age (see Table 3). Variety CM849 was most successful with shoots being produced from half of the cuttings, with no difference among nodal ages. In contrast, sprouting was very low (13% of cuttings) for CM516 and no shoots developed from cuttings of younger nodal age. Sprouting by MCol1505 was intermediate at 25% of cuttings; there was a small effect of reduced sprouting from younger nodal ages. These relatively low rates

of sprouting contrast with high rates generally reported (Cock, 1983; Lopez, 2012; Wholey, 1974; and personally observed elsewhere) and are likely to be due mainly to low quality parent stems. The importance of taking cuttings from high quality planting material is well-known, particularly in relation to nutrient content (CIAT, 2011; Lopez, 2012). The availability of nutrients for developing shoots correlates with nodal age, the older ages tending to have greater nutrient stores and better potential sprouting (Lozano et al., 1984; Wholey, 1974).

The size of the cuttings in this investigation did not show a consistent relationship with nodal age, although internode diameter increased with nodal age (see Table 2). On average, diameters of youngest aged cuttings were 15% smaller than those of the oldest age, representing the difference from top (apical) to bottom (basal) sections of parent stems. Differences in internode length depended on variety; lengths of older, basal cuttings tended to be greater than younger, apical cuttings for CM516 and MCol1505, but there was no difference for CM849 (see Table 2). It is concluded that the CM516 stems were of lower quality for planting than those of the MCol1505, while CM849 stems were of higher quality than both the former, but still not of optimum quality for use in the MSRT or for traditional propagation.

Results of our previous trial with the MSRT in a mist house (data not presented here) showed that supplemental fertilisation had no effect on sprouting and shoot growth up to at least a month after planting of cuttings (DAP), as reported by Lopez (2012). Sprouting shoots develop over this initial period using nutrients stored in the cuttings. Fertilisation of the propagating medium in this study started at 40 DAP and resulted in greater shoot height, and faster shoot growth from, 52 DAP (figures 1 and 2). Overall, growth of sprouts was initially fast and then slowed, apparently as nutrients were being used up from the cuttings (figure 2). After 52 DAP, the root system being produced by the cutting seemed to be able to take up nutrients from the potting medium and addition of the nutrient solution allowed more shoot growth. Good nutrient content of parent stems has been suggested to be just as important as fertilisation of the planted progeny (Cock, 2011; El Sharkawy, 2003; Lopez, 2012) for cassava plant growth and yield. The response of cassava plants to fertilisation in the field can give yield increases between 49-110% (Boateng, 2015).

There were varietal differences in growth of shoots from cuttings, with the highest rate from MCol1505 over the first 20 days, twice as much as for the other two varieties (figure 3). Rates were similar thereafter. Shoots from CM849 especially, but also MCol1505, developed from cuttings over the range of nodal ages, both fertilised and unfertilised. On the other hand, CM516 cuttings produced few shoots and only from cuttings of older parts of parent stems. By 52 to 76 DAP, most of these CM516 shoots were fertilised, age 4 cuttings and correspondingly showed a relatively high growth rate (see Figure 3).

The effect of nodal age on shoot growth was apparent by 52 DAP, after which shoots on cuttings from basal sections of parent stems grew faster than those on cuttings of younger nodal age (see Figure 4). Since the basal cuttings were larger, they were expected to have stored and be able to uptake more nutrients and be able to provide for greater growth than younger, smaller cuttings. Therefore, the importance of nutrient availability is shown for shoot growth as well as sprouting rates, as discussed above.

The successful rooting of 79% of the cut shoots was reasonably good, although we have found higher rates in other trials. Increase in shoot heights during rooting was constant and not affected by initial height (see Figure 5). As expected, a proportion of the original leaves was lost after cutting; successful rooting corresponded to retention of about a third and the development of new leaves from apical growth over three weeks.

The multiple shoot removal technique was successfully demonstrated in this study and can be used for rapid propagation of cassava. As for traditional planting, the use of good quality planting material is critical. The varietal and nodal age effects demonstrated here need to be confirmed with repeat trials of the MSRT using planting material that has been grown under standard conditions.

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Lisa R.S. Myers-Morgan *is Principal Research Director for the Research and Development Division, Ministry of Industry Commerce Agriculture and Fisheries, Jamaica; she has worked for over 22 years in several capacities, providing technical and policy advice to the agriculture Ministry and its stakeholders in plant health, food and nutrition security. She leads the Ministry's National Agriculture Research and Development programme, covering multidisciplinary crop and livestock research. Dr. Myers-Morgan possesses a Doctor of Plant Medicine Degree (University of Florida, Gainesville), Master in Botany and Bachelor in Natural Sciences majoring in Biochemistry (The University of the West Indies, Mona).*

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Muscadine Grape Skin Extract Decreases Proliferation of Prostate Cancer Cells by Affecting Proteins Involved with the Cell Cycle and the Androgen Receptor

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Abstract: *Prostate cancer, the sixth leading cause of cancer death worldwide is the leading cause of male cancer mortality in the Caribbean. Globally, men of African descent appear to be more affected by the disease at a younger age and are less responsive to available treatment options than other groups, making the discovery of new therapies a priority. The total ethanol extract (TE-MSKE) was prepared from the skin of the Muscadine grape. It was evaluated for anti-prostate cancer properties using the androgen-independent PC-3 prostate cancer cell line, which mimics late stage prostate cancer. Preliminary studies performed included cell viability and cell migration. At the mechanistic level, western blots provided vital information about some of the proteins and genes that may have been affected by the extract. The results found that TE-MSKE significantly inhibited cell growth, invasion and migration of the PC-3 prostate cancer cells. Also, following treatment of the cancer cells with the extract, the expression of HSP40, a protein involved in the activation of the androgen receptor was decreased. Additionally, Cyclin D1 and NFkB, proteins involved in cell cycle regulation were also decreased with increasing concentrations of the extract. TE-MSKE appears to offer the potential for development into novel and effective anti-prostate cancer therapies.*

Keywords*: Prostate cancer; PC-3 prostate cancer cells; cell migration, muscadine grape skin; NFkB*

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Trevor Alleyne *is a Professor of Biochemistry at the Faculty of Medical Sciences. He held the post of Deputy Dean, Basic Health Sciences from 2003 to 2007. Professor Alleyne has two broad areas of research. The first involves mechanistic studies, including bio-computing, of the enzyme cytochrome c oxidase. The second involves using Caribbean plants and natural products to discover novel treatments for cancer. Professor Alleyne is a Fellow of The World Academy of Science, President of the Trinidad Chapter of CAS and a past President of CAS.*

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Components of a Leaf Extract of an Exotic Caribbean Plant Inhibits Growth of PC-3 Androgen Independent Prostate Cancer Cells

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Abstract: *According to published data, the mortality rate for prostate cancer within populations of African descent is higher than that of other ethnic groups. Moreover, it has been shown that standard anti-prostate cancer drugs often fail to be efficacious as a long-term cure for castration resistant prostate cancer, highlighting the need for novel remedial strategies. In this study, the leaves of one plant indigenous to the Caribbean was investigated for its phytochemical profile and assayed for antitumour activity against PC-3 prostate cancer cells; this cell type mimics metastatic prostate cancer. Freshly picked green leaves of the plant were washed, dried for 72 hours and then blended in methanol to a very fine consistency. The suspension was allowed to stand at room temperature for 24 hours and then filtered. The resulting filtrate (the total methanol extract) was then fractionated using solvents of varying polarities. Thin Layer Chromatography confirmed that alkaloids, polyphenols, steroids and tannins were present in the leaves. Both the total methanol extract and one of its fractions (F2), significantly retarded the growth of the PC-3 androgen independent cancer cells, with excellent IC_{50} values of 6 and 0.05 µg\ml respectively. Morphology studies suggest that both the methanol extract and the F2 fraction deformed and killed the prostate cancer cells. Importantly, both preparations the total methanol extract and the F2 fraction inhibited cancer cell migration, an activity that is essential for the spread of cancer: Significantly also, both preparations exerted low toxicity towards normal prostate cells. Overall, these two plant preparations appear to be showing potential for use in the treatment of prostate cancer.*

Keywords*: Prostate cancer; metastatic prostate cancer; PC-3 prostate cancer cells; cell migration*

Authors' Biographical Notes:

Dunstan Arrindell *holds a Bachelor's degree with majors in Biochemistry and Zoology and a Master of Philosophy in Biochemistry from The University of the West Indies, St Augustine Campus. His research focuses on the anti-cancer potential of selected Caribbean plants. He is employed at the Biochemistry Unit of the Faculty of Medical Sciences, The University of the West Indies, St Augustine Campus and has a keen interest in the medicinal value of Caribbean plants.*

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Caribbean plants for bioactive agents, including anticancer compounds and antioxidants, climate change resistance and new uses in agriculture.

Trevor Alleyne *is a Professor of Biochemistry at the Faculty of Medical Sciences. He held the post of Deputy Dean, Basic Health Sciences from 2003 to 2007. Professor Alleyne has two broad areas of research. The first involves mechanistic studies, including bio-computing, of the enzyme cytochrome c oxidase. The second involves using Caribbean plants and natural products to discover novel treatments for cancer. Professor Alleyne is a Fellow of The World Academy of Science, President of the Trinidad Chapter of CAS and a past President of CAS.*

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Carbon Storage Change as It Relates to Land Use and Texture in a Tropical Forest Ecosystem

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Abstract: *Assessing anthropogenic impacts on carbon storage in terrestrial ecosystems is of great value for increasing the resilience of the soil natural capital and ecosystem sustainability of tropical Small Island Developing States (SIDS) that are known to be vulnerable to the impacts of climate change. We used historic air photos to assess land use/land cover changes and the natural capital project InVest model for carbon storage and sequestration to evaluate the carbon storage. We also presented a framework that examined the critical soil quality factors that determine soil ecosystem health for Aripo Forest Reserve and investigated the effect of texture on soil carbon content. Comparing 1969 and 1994 photos, there was an evident heavy disturbance in key areas of the forest reserves associated with quarrying and construction of pipelines with an estimated 5% of grassland area affected. This is an unsustainable rate of disturbance and must be curtailed. Carbon storage was reduced by 80157.93 mg of carbon in the Aripo forest reserve due to a reduction in forest extent and coverage because of land conversion activities encroaching into forested areas. Carbon storage in tropical forests generally is a function of forest extent and density. The InVest carbon storage and sequestration model is suited for the evaluation of carbon in tropical forest ecosystems. It has implications for soil natural capital as it provides information on the soil ecosystem that lead to changes in the provision of services to people. Planners should view it as effective tool for exploring alternative management decisions among sectors and services.*

Keywords*: Land use/land cover change, tropical forest, soil natural capital, carbon storage, ecosystem services*

Authors' Biographical Notes:

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Mark N. Wuddivira *is a Senior Lecturer and Head of the Department of Food Production, The University of the West Indies, St. Augustine. He has served as Deputy Dean and Acting Dean of the Faculty of Food and Agriculture. Dr. Wuddivira is the Treasurer of the Caribbean Academy of Sciences. He holds a Ph.D. in Soil Science and has published widely in high impact journals and book chapters covering areas such as precision agriculture, soil physics, soil structural stability, infiltration, runoff and erosion under intense humid tropical rainfall, soil water characteristic and hydrology in tropical ecosystems, soil and watershed geophysical imaging using electromagnetic induction.*

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■

Guyana-Suriname Energy Resources

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Abstract: *Deepwater exploration is continuing in the Atlantic Ocean on the classic passive margin of South America where Guyana-Suriname basin is the world's second-most prospective, underexplored offshore basin, with an estimated 13.6 billion barrels of oil and 32 trillion cubic feet of natural gas to be discovered. Esso E&P Guyana Ltd, the operator, holds 45 percent working interest, ess Guyana Exploration Ltd has 30 percent interest and CNOOC Nexen Petroleum Guyana Ltd. holds 25 percent of Stabroek Block, 120 miles offshore Guyana, 6.6 million acres (26,800 square kilometers), equivalent in size to 1,150 Gulf of Mexico blocks, Multiple prospects and play types represent additional multibillion barrel unrisked exploration potential. Eight significant discoveries at Liza, Payara, Snoek, Liza Deep, Turbot, Ranger, Pacora and Longtail hold gross recoverable resources estimated at over 4 billion barrels of oil equivalent with multi-billion barrels of additional exploration potential on the block. A ninth discovery at Hammerhead reinforces the potential of the Guyana basin. Liza Phase 1 development, sanctioned June 2017, is progressing, laying the foundation for first production in 2020. 17 wells will be connected to a floating production, storage and offloading (FPSO) vessel designed to produce up to 120,000 barrels of oil per day. Liza Phase 2 development will utilize a second FPSO with gross production capacity of 220,000 barrels of oil per day. Start-up is expected in mid-2022. Planning is underway for a third phase of development, targeted for sanctioning in 2019, with an FPSO designed to produce 180,000 barrels of oil per day, with first production in 2023. Up to five floating production, storage and offloading (FPSO) vessels may be producing over 750,000 barrels per day by 2025.*

There is potential for additional production from significant undrilled targets and plans for rapid exploration and appraisal drilling. A second exploration vessel, the Noble Tom Madden, will arrive in Guyana in October to accelerate exploration of high potential opportunities and will commence drilling at the Pluma prospect approximately 17 miles (27 kilometers) from Turbot. In April 2018, Hess acquired 15 percent interest in Kaieteur Block, located 155 miles (250 kilometers) offshore, adjacent to the Stabroek Block and covering 3.3 million acres (13,535 square kilometers). Seismic interpretation and evaluation of a future drilling program are planned for 2018. In 2016, Hess Suriname Exploration Limited, a wholly-owned subsidiary of Hess Corporation, acquired one-third non-operated interest in the Block 42 contract area, along the northeast margin of South America. Operator Kosmos Energy holds 33.3 percent working interest. Hess Suriname Exploration Ltd. and Chevron Corporation each hold 33.3 percent interest. 3-D seismic is being interpreted. Deepwater Block 59, to the north and contiguous to Block 42, was awarded to Hess and co-venture partners ExxonMobil and Statoil in 2017. Each has a one-third interest and Exxon is the operator, Seismic acquisition is planned in 2018.

In January 2016, Eco Atlantic signed a Petroleum Agreement and is party to an Offshore Petroleum Licence with the Government of Guyana and Tullow Oil for the Orinduik Block offshore Guyana. The 1800 km² Orinduik block lies in shallow water, 170 km offshore Guyana in the Suriname Guyana basin, adjacent to recent Exxon Mobil discoveries. Eco Atlantic holds a 40% working interest in a significant licence, 6.5 km from the world-class Liza oilfield. ExxonMobil and Hess confirmed that the deep-water Liza Field is officially the largest commercial find in South America in 50 years holding between 2.25 and 2.75 billion barrels of recoverable oil, one of a handful of billion-barrel discoveries in the last half-decade. Tullow Oil with a 60% working interest will be the operator and will pay Eco Atlantic US$0.4m and fully carry Eco Atlantic for approximately C$3m of the 2D and 3D survey for an initial 4 years work commitment.

In September 2017, Eco Atlantic subsidiary, Eco Atlantic (Guyana) Inc. entered into an option agreement on its Orinduik Block with Total E&P Activités Pétrolières, a wholly owned subsidiary of Total SA. Pursuant to the option, Total paid an option fee of US$1,000,000, at its sole discretion, to Farm-in to the Orinduik Block for an additional payment in cash of US$12,500,000 to earn the 25% Working Interest. The survey acquisition was completed on September 5th 2017. Processing is expected to take 2-3 months. The exercise of the Option must be made within 120 days of completion of processing of 3D seismic data. Following exercise by Total of the option, the Block Working Interests will be as follows: Tullow – 60% (Operator), Total – 25%, Eco Guyana – 15%.

Keywords*: Guyana, Suriname, oilfield*

Author's Biographical Notes:

Sally Radford *is Trinidad and Tobago's first female petroleum geologist. She is the first woman to win a Texaco scholarship to study geology at The University of the West Indies (UWI) in Mona, Jamaica, and the first West Indian woman to undertake oceanographic research. Dr. Radford did so aboard the research ship Atlantis II off Tobago whilst collecting seabed samples for her doctoral research. In that era, women were not allowed to work with men on ships or on rigs. Being on a rig was the highlight of her career. She was also part of the team that brought the first oil ashore from the Brent Oilfield in the UK.*

■

Students' Conceptions about Geothermal Energy in the Caribbean

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Abstract: *The increase in greenhouse gas emissions, global warming, fossil resource depletion and energy dependence bring the world in a common effort for renewable energy transition. The environmental and geological contexts of the Caribbean islands offer valuable opportunities for the development of renewable energies. In fact, those islands are located in subduction zone (Lesser Antilles) where the volcanic and geothermal activities provide useful resources for the geothermal energy exploitation. For example, 20 % of electricity in Guadeloupe comes from renewable energy, of which 5 % is generated by geothermal energy. Even if this percentage seems low, Guadeloupe is the only island of the Caribbean where the geothermal industry has grown since 1986 (Bouchot et al., 2010). Today, many islands as for example St Kitts, Dominica, Montserrat or St Lucia are exploring the possibilities for the development of their own geothermal production (Laplaige, Durimel, & Mompelat, 2013). At the same time, Guadeloupe is working for a geothermal center of excellence with the support of national and European funding. The increase of such projects and the demand of professionals in Guadeloupe and in the Caribbean require the development of a local education for this discipline.*

This paper aims to carry out a strategic and intelligent thinking for the construction of such education in the Caribbean context. In this purpose, and as one of the first steps of this research framework, a questionnaire survey has been conducted with a representative sample of 15-16 years old students from three Caribbean islands: Guadeloupe, Dominica and Martinique. Geothermal is very different in those three island. In Guadeloupe, geothermal industry produces around 5% of the electricity. In Dominica, geothermal has a well known potential that could supply neighboring islands with energy. Exploration drillings have been process since a decade but no production plant exist. In Martinique the resource is not as important as in Dominica and Guadeloupe, and the exploration studies realised in 2000 did not give away.

A total of 1,350 students were interrogated in different high schools, about their conceptions towards geothermal concepts (Clément, 2010; Forissier, 2003). The questionnaire was set up between October 2016 and Jun 2017. It includes open and closed-ended questions, and drawings, exploring their knowledge, opinions and experiences regarding the geothermal energy concept. Quantitative and qualitative analysis made with descriptive and statistical methods have revealed different results, depending on the island in question. Cross table and khi² test as well as multiple correspondence analyses were set up. Strong links and similarities between schools from a same island have also been demonstrated. Students from Guadeloupe convey conceptions related to the industrial, technologic and technical dimension of geothermal. Dominican students express conceptions linked with the industrial, economical and utilitarian aspect of the geothermal exploitation. Students from Martinique show an environmental and phenomenological point of view of the geothermal concept. Furthermore, it has also been demonstrated that students' opinions in Dominica, although broadly positive, are sometimes negative, and geothermal energy can be perceived as an annoyance.

As a first conclusion toward the development of a geothermal education in the Caribbean, this study reveals the importance of territory geothermal context for the construction of conceptions. These contextual specificities of conceptions should now be used to design a more efficient geothermal education. Furthermore, the study has revealed that sometimes, conceptions are strongly linked to contextual elements such as the geothermal plant or the volcano. Those conceptions could become obstacle for the learning if they are not taken into account during the teaching. Identification of alternative conceptions can be a support for the teaching and improve the learning process.

Keywords*: Education, conceptions, Martinique, Guadeloupe, Dominica, context, geothermal energy*

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Mazabraud Yves *is a geophysicist specialised in crustal deformation. His work focuses on the precise description of the earth's deformation patterns in order to emphasise the mechanisms at the origin of stress concentrations, using a variety of tools such as seismology, geodesy, field geology and tectonics. He also developed an expertise in geocognition and the study of geosciences related conceptions of students. He is an Assistant Professor at the Université des Antilles (Guadeloupe).*

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Underpinning Intercultural Competence within a Context-Effect Didactic Method

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Abstract: *Modern learning approaches and teaching methods put a special emphasis on unleashing each student's innovative and creative potential. On the grounds that children need to become actors of their own active learning (Piaget, 1958, Bonwell et al., 1991), new pedagogies for science education are being developed alongside technologies (Scott CL, 2015). Arguably, in the knowledge-based era that we live in, the understanding of cultural diversity is highly considered as a core value and a driving force for innovation (Bouncken et al., 2016). In this regard, the project TEEC (Educational Technologies for Teaching in Context - Technologies Éducatives pour l' Enseignement en Contexte, funded by the program ANR-FRQSC) lays the groundwork for designing a context-effects based learning approach, determined by the socio-cultural factors that influence one's learning, which fosters collaboration among students in Guadeloupe and Quebec. Within the framework of TEEC, synchronous and asynchronous technologies are being combined with authentic learning situations (Newmann et al., 1995), in order to observe children's understanding on different scientific objects in different disciplines: geothermal energy, sustainable development, linguistics, socio-history.*

This work outlines preliminary findings on two TEEC's in-situ experimentations, more specifically one focusing on sustainable development (object of study: sugarcane/maple syrup) and the other one on linguistics (object of study: folktales of Antilles/Québec). These specific topics, which embody a high sense of didactic interest, are of fundamental importance for both territories especially in dimensions such as society, culture and economy. In the first case, sugarcane is a core reference point in Guadeloupe, while maple syrup is a prominent element of Québec's culture. Our participants, elementary school students, undertook research investigations in their context, at then collaborated with their peers to draw conclusions on the notion, the existence and the manufacturing process of sugar. In the second case, folktales of Antilles and of Quebec are of different nature and follow different structure patterns. Students of primary school in Guadeloupe worked on a creole folktale entitled "Compère Zamba voulait tromper Compère Lapin" (Benzo, 2000) while the students of Quebec worked on a traditional folktale entitled "Rose Latulipe" (Aubert de Gaspé, 2006). During their research investigations, students improved their knowledge on folk literature and developed diverse conceptions around different specificities of the folktales. Their final production in collaboration was a common tale including elements from both regions.

After the completion of these experimentations, participants -children aged 10-12 years old- were asked to note the cultural context elements that they have encountered and retained from their exchanges with their peers. The evidence draws from their answers to their post-tests, by which is feasible to identify some facts that impressed them the most regarding their peers, their cultural exchange experiences and those two various contexts.

Keywords: *Context, cultural diversity, social interaction, virtual environment, primary school*

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Essential Oil Composition and Antimicrobial Activity of *Cannabis Sativa* Grown in Jamaica at Five Stages of Maturity

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Abstract: *Cannabis sativa is an herbaceous plant that has been used in food, medicines and insecticides. There is limited information on the essential oil of Cannabis sativa grown in Jamaica, despite ongoing research on the Cannabis sp. This study assessed the chemical composition and antimicrobial activity of Cannabis sativa essential oil on a weekly basis, as the plant matures from week eight through to week twelve. Oils were extracted from fresh female plants by hydrodistillation. Afterwards, the components were identified and characterized using Gas Chromatography-Flame Ionization Detector (GC-FID), Gas Chromatography-Mass Spectrometry (GC-MS) and Retention index comparison. Well diffusion, Disc diffusion and broth microdilution methods were utilized to screen the essential oils for their antimicrobial activity. As the plant matures, the percentage oil yield increases having β-caryophyllene, α- caryophyllene and β-myrcene as the main components. Some of the essential oils had antimicrobial activity against gram-positive bacteria.*

Keywords*: Cannabis sativa, essential oil, antimicrobial activity, gram-positive bacteria*

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Kellyann Clarke *is a graduate student at The University of the West Indies. She obtained a Bachelor of Science in General Chemistry with a minor in Education. Currently, Kellyann is pursuing a Master of Philosophy in Natural Products within the Chemistry Department, under the supervision of Dr. Roy Porter and Dr. Petrea Facey. Furthermore, Kellyann is an active participant in co-curricular activities. She is the secretary of the Chemistry Association of Graduate Students (CAPS) and member of the Panoridim Steel Orchestra.*

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■

Duration of Life Cycle Stages of Four Species of Blowflies (*Diptera: Calliphoridae*)

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Abstract: *Members of the family Calliphoridae have been used as evidence in forensic entomology cases to estimate the time since death (Post Mortem Interval=PMI). Five species of the said family have been reported in Jamaica, Chrysomya megacephala (Fabricius, 1794), Chrysomya rufifacies (Macquart, 1842), Cochliomyia macellaria (Fabricius, 1775), Lucilia cuprina (Wiedemann, 1830) and Lucilia lucigerens (James, 1971). Flies undergo several life cycle stages, each change taking a known time to be completed. For entomological evidence to be useful in legal investigations, knowledge on duration of each life stage is important, taking varying temperatures and locations in consideration, as these factors influence development of most insects. Limited information is available on duration of life cycle stages of species found in Jamaica. Therefore, the aim of the study was to determine the duration of each life cycle stage for species of Calliphoridae found in St. Andrew, Jamaica. Individual masses of eggs were collected from bait in the field and transported to the laboratory for rearing and examination. For rearing, eggs were placed on meat housed in plastic containers. Development was tracked by removal of larvae as soon as the eggs hatched and then every 6 to 8 hours until larvae were in the third instar. Eggs of four species, C. megacephala, C. rufifacies, C. macellaria and L. lucigerens, were collected and larval development studied. Egg hatch occurred between hour 8 and 10 following collection and change from first to second instar and second to third instar larvae each lasted 12 to approximately 20 hours after egg hatch. The third instar larvae lasted as low as 3 days but exceeded 17 days depending on species. Overall, life cycle stages ranged from 7 to 21 days depending on species. There were no significant changes in development with temperatures ranging from 23°C to 29.9°C. With knowledge on life cycle stages at varying temperatures, the presence of immature stages on corpses could be beneficial in criminal investigations in Jamaica.*

Keywords*: Calliphoridae, Forensic Entomology, Instar, Jamaica, Life cycle, Post mortem interval*

1. Introduction

Forensic entomology is the use of insects as evidence in legal investigations. Members of the family Calliphoridae have long been used in criminal investigations (Benecke 1994) and in many cases, have been reported as arriving the earliest to decomposing tissue (Bharti and Singh 2003; Chin et al. 2008; Eberhardt and Elliot 2008; Martinez, Duque, and Wolff 2007; Ortloff, Peña, and Riquelme 2012). The adult flies feed on blood and other liquid emanating from the corpse and use the tissue as a medium to deposit eggs and subsequently supply food for feeding larvae. Each life stage of an immature fly takes a known time to reach completion. Knowledge on the duration of each life cycle stage for carrion feeding flies can be used by an entomologist to calculate the length of time immatures have been on a body, that is the post mortem interval (Dix and Graham 2000). However, environmental conditions, mainly temperature strongly influence the development of arthropods (Ubero-Pascal et al. 2010). For insect evidence to be useful in criminal investigations, the duration of each life stage needs to be estimated in relation to temperature, specific to a locality, as only then will insect evidence be valuable.

Five species of Calliphoridae have been reported in Jamaica. These species include *Chrysomya megacephala*, *Chrysomya rufifacies*, *Cochliomyia macellaria*, *Lucilia cuprina* and *Lucilia lucigerens*. While data on development at various temperatures is available in other countries, only limited information is available for species found in Jamaica. As such, studies on development was carried out over a period, taking daily ambient temperatures into consideration.

2. Methods

Eggs oviposited by adult flies on pig heads in the field, were collected and taken to the lab for rearing. Eggs were placed on meat (pork or liver) in rectangular plastic plates 0.16 x 0.12 x 0.04 metres; the containers were lined with

moist paper towel and the covers perforated. To determine the duration of each life stage of respective species, larvae were removed from rearing containers at different time intervals during the rearing process. Removal of larvae was done immediately following egg hatch and then every 6 to 8 hours until larvae were in the third instar. Following this, larvae were removed daily until pupation commenced. To reduce moisture in the rearing containers, paper towel was changed until a daily basis. Adults were fed a diet of sugar solution or honey and water upon emergence for 3 to 4 days, after which meat was introduced as a source of protein for females for oviposition. Average daily temperature was obtained from the Shortwood Teachers College automatic weather station; this weather station is approximately 8 kilometres North-West of UWI, Mona campus.

3. Results

For all species, the shortest life stage was the egg, which hatched in less than 10 hours irrespective of daily ambient temperature, followed by the first and second instars; the third instar was the longest of all three larval stages, being only slightly shorter than the pupal stage which varied from 2 to 6 days. However, variation was observed for each life stage in all species.

3.1 Duration of Life Stages of *Chrysomya megacephala* at Two Temperature Ranges

When daily average temperatures ranged from 23.1 to 25.1^{0}C, the life cycle was completed in 8 days. Collection of eggs and hatching occurred on day 3 of the decomposition/rearing process. By day 4 second and third instar larvae were observed and by day 5 only third instar larvae were observed in rearing containers; this life stage was observed until day 8 (lasted approximately 4 days) when pupation commenced (approximately 3 days in length). Adults emerged on day 11 (see Figure 1a).

At average daily temperatures of 25.4 to 27.6^{0}C, the life cycle stage was completed in 8 to 11 days. Egg masses were collected on days 1 and 2 of the decomposition/rearing process. All 3 instars were observed on day 2 and by day 4 only third instar larvae were observed in containers and pupation commenced on day 5 (life stage lasted for approximately 5 days). The first set of adults emerged on day 8 and by day 11 only adults were observed in all containers (see Figure 1b).

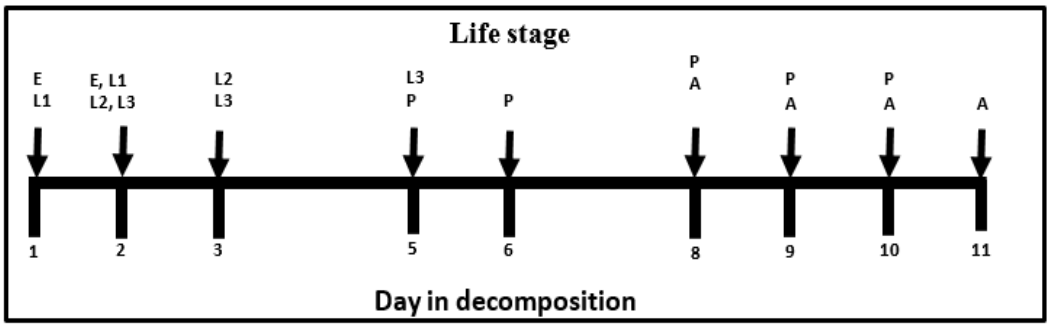

Figure 1a: Duration of life cycle stages of *C. megacephala* observed on different days of decomposition at temperatures ranging from 23.1-25.10C. E=Egg; L1= first instar; L2=second instar; L3=third instar; P= pupa; A=adult.

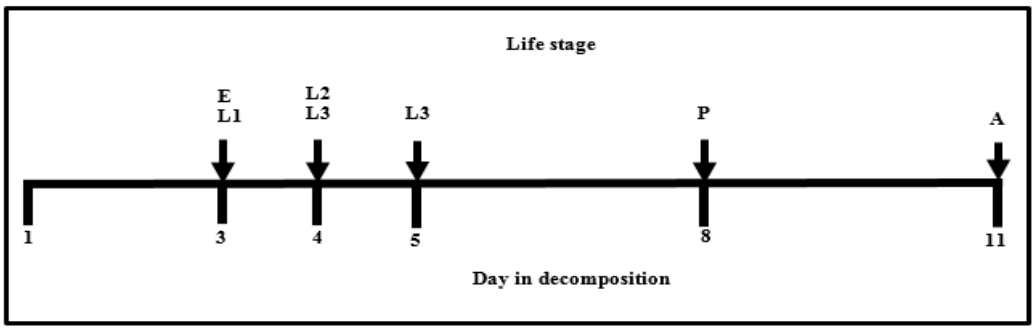

Figure 1b: Life cycle stages of *C. megacephala* observed on different days of decomposition at temperatures ranging from 25.4-27.60C. E=Egg; L1= first instar; L2=second instar; L3=third instar; P= pupa; A=adult.

3.2 Duration of Life Stages of *Chrysomya rufifacies a*t Various Temperatures

At average daily temperatures ranging from 25.4 to 27.6^{0}C, the life cycle of *C. rufifacies* was completed in 13 days. Eggs were collected on days 1 and 2, all the larval instars were observed on day 2 and by day 4 only third instars were present in rearing containers; larvae in the third instar were observed for approximately 6 days. Pupation commenced on day 8 and by day 10 adults started emerging (pupal stage ranged from 2 to 6 days). On day 14 only adults were present in rearing containers (see Figure 2a).

The life cycle of *C. rufifacies* was completed in 11 days at average daily temperatures ranging from 26.8 to 29.9^{0}C. Eggs were collected, and first instar larvae were observed on day 1 of the decomposition/rearing process. Only second instar larvae were observed on day 2 and by 3 there was a mixture of second and third instar larvae. Larvae were in the third instar for approximately 4 days after which pupae were observed-this stage lasted for approximately 5 days. All the adults emerged on day 12 (see Figure 2b).

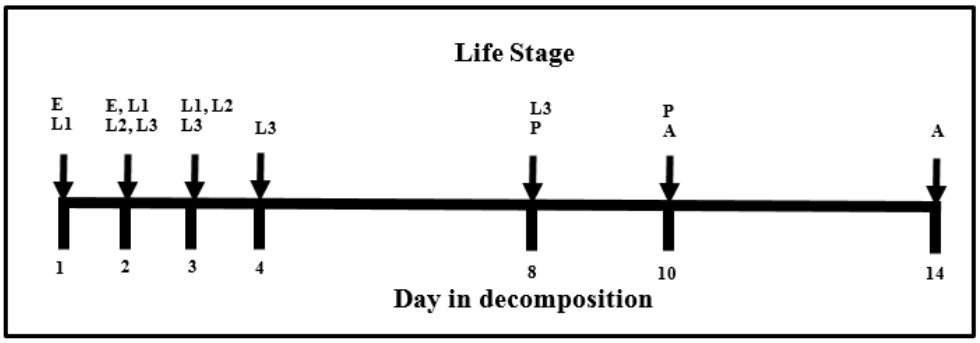

Figure 2a: Life cycle stages of *C. rufifacies* observed on different days of decomposition at temperatures ranging from 25.4-27.6^{0}C. E=Egg; L1= first instar; L2=second instar; L3=third instar; P= pupa; A=adult.

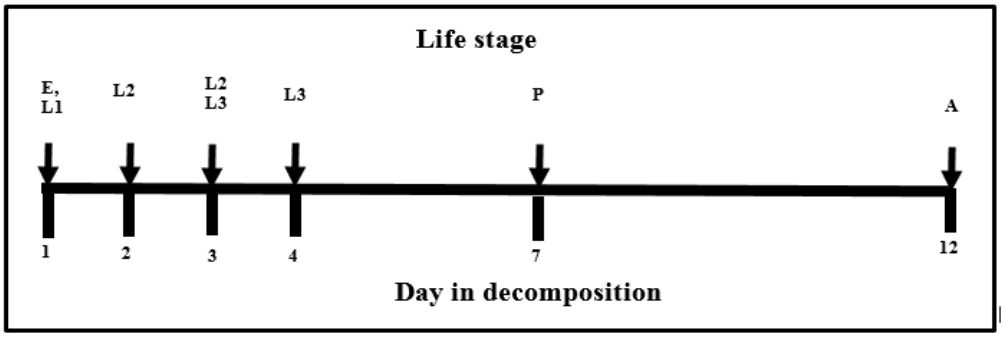

Figure 2b: Life cycle stages of *C. rufifacies* observed on different days of decomposition at temperatures ranging from 26.8-29.9^{0}C. E=Egg; L1= first instar; L2=second instar; L3=third instar; P= pupa; A=adult.

3.3 Duration of life stages of *Cochliomyia macellaria* at various temperatures

At average daily temperatures ranging from 25.4 to 27.6^{0}C the complete life cycle of *C. macellaria* was achieved in 13 days. Eggs were collected on days 1 and 2 of the decomposition/ rearing process. First instar larvae were observed on days 1, 2 and 3 (based on time of egg collection). By day 3 a mixture of all three instars was noted; only third instar larvae were observed on day 4 (stage lasted approximately 5 days). By day 8 pupae were observed in rearing containers and by day 10 the first set of adults emerged; by day 12, only adults were present in rearing containers (see Figure 3a).

At average daily temperatures of 26.8 to 29.9^{0}C, the life cycle of *C. macellaria* was completed in 9 days. Eggs were collected on days 1 and 2 and first instar larvae were observed on both days as well; second instar larvae

were observed on days 2 and 3 and by day 4 only third instar larvae were observed (duration of this stage was approximately 4 days). The pupal stage commenced on day 7 lasted for 3 days; adults were observed on day 10 (see Figure 3b).

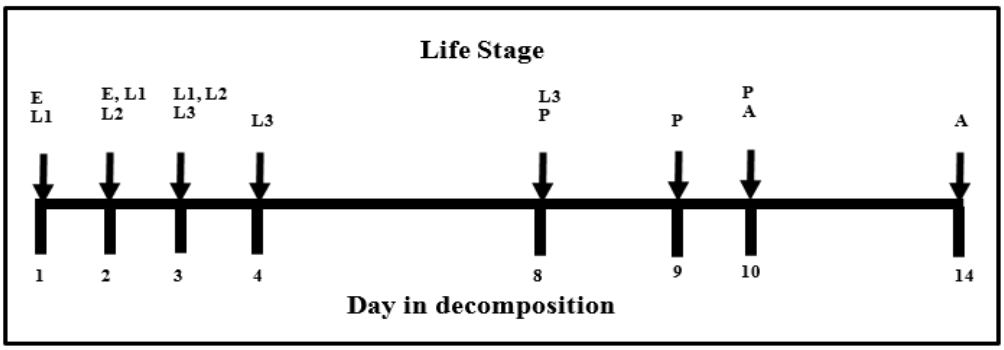

Figure 3a: Life cycle stages of C. *macellaria* observed on different days of decomposition at temperatures ranging from 25.4-27.6^{0}C. E=Egg; L1= first instar; L2=second instar; L3=third instar; P= pupa; A=adult.

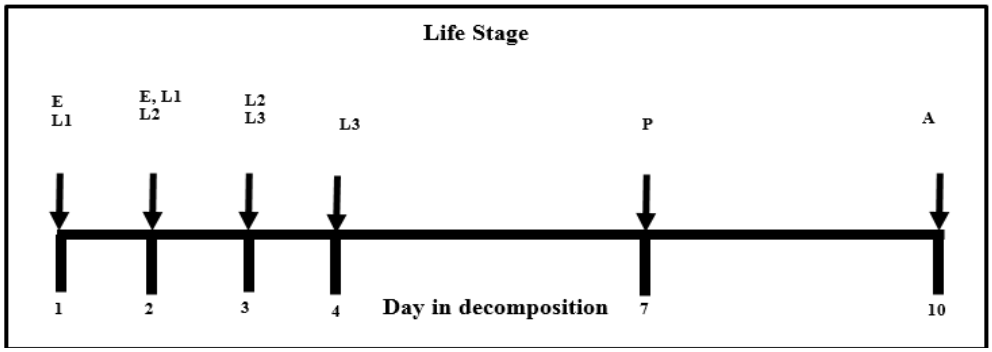

Figure3b: Life cycle stages of *C. macellaria* observed on different days of decomposition at temperatures ranging from 26.8-29.9^{0}C. E=Egg; L1= first instar; L2=second instar; L3=third instar; P= pupa; A=adult

3.4 Duration of life stages of *Lucilia lucigerens*

For the species *L. lucigerens*, no adults were observed but data was obtained on all the immature stages. Eggs were collected on day 1 of the process; additionally, first and second instar larvae were observed on that day (second instars observed close to day 3). By the end of day 3 only third instars were observed, and this observation was made up to day 17 when the first pupa was observed in rearing containers (third instar larvae lasted for 16 days). By day 22 only pupae were observed in rearing containers (see Figure 4).

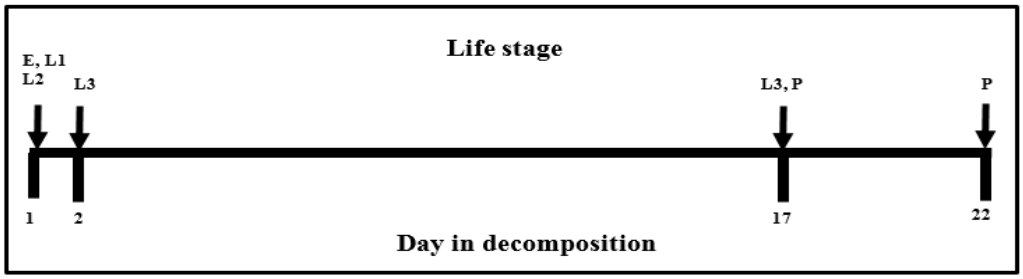

Figure 3: Life stages of *L. lucigerens* observed on different days of decomposition at temperatures ranging from 22.9-27.6◦C. E=Egg; L1= first instar; L2=second instar; L3=third instar; P= pupa; A=adult.

4. Discussion and Conclusion

Overall, the complete life cycle for species was shorter at higher temperature ranges. Temperature plays a major role in determining the rate at which insects undergo most physiological processes (Wall, French, and Morgan 1992). Bansode et al. (2016) found that the duration of the life cycle of *C. megacephala* reduced with an increase in temperature, and in a study by Bansode, More and Zambare (2016) it was reported that duration of life cycle stages of insects is decreased at lower temperatures. Egg hatch occurred in less than 10 hours for all four species at the varying temperatures during the study on development of Calliphorids. Researchers have found that egg hatch occur from hour 10 up to after 21 hours for different species (Bansode et al. 2016; Barros-Souza, Ferreira-Keppler, and Agra 2012; Shah, Ali Khan, and Ahmed 2015).

While the length of first and second instar larvae were similar for all species that of the third instar and pupae varied. In addition to variation in length of immature stages, there was variation in the time taken for each species to complete its life cycle. Barros-Souza, Ferreira-Keppler, and Agra (2012) reported similar findings. Bansode et al. (2016) reported variation in the length of the pupal stage which led to an overall difference in time taken to complete development. According to Donovan et al. (2006), growth rate of blowflies differs from species to species; this could be a possible reason for the variation in duration of life cycle stages that was observed among blowfly species that were reared under similar conditions throughout the study. The study showed that Calliphoridae in Jamaica respond differently to temperature; and variation was observed in the life stages and length of complete life cycle for all species. Further studies need to be conducted to gather information on temperature related impact on blowfly development specific to Jamaica, as only then estimations of PMI using insect evidence will be relevant.

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The Impact of Dibenzyl Trisulfide on Breast Cancer Cell Lines Derived from African American Patients and on Cytochrome P450 1 Enzymes

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Abstract: *Triple negative breast cancers (TNBC) lack the expression of the estrogen receptor (ER), progesterone receptor (PR) and overexpression of the human growth factor receptor 2 (HER2), thus carrying a poor prognosis. Dibenzyl Trisulfide (DTS) found expressed in the local plant, Petiveria alliacea (commonly known as guinea hen weed) has been shown to inhibit the growth of several cancer types. However, there is no known research on its impact on triple negative breast cancer cells derived from African American patients (AA-TNBC) nor on its impact on the activities of Cytochrome P450 1 (CYP1) family of enzymes which are associated with activating procarcinogens. This work, as part of an on-going ethnopharmacology-based bioactivity screening, was designed to fill this deficit. AA-TNBC cells lines, HCC1806 and MDA-MB-468, were treated with varying concentrations of DTS for 48 hours and cell viability was assessed using the Alamar Blue assay. Dose response curves were generated using GraphPad Prism5. DTS showed potent inhibition of the growth of HCC1806 and MDA-MB-468, producing IC_{50} values of 10.6 ± 1.2µM and 10.3 ± 2.0µM respectively. Furthermore, we found that DTS induced apoptosis in these cells. Activities of CYPs 1A1, 1A2 and 1B1 were potently inhibited by DTS yielding IC_{50} values of 1.68 ± 0.3µM, 1.9 ± 0.2µM and 1.29 ± 0.3µM respectively, with binding to CYP1A2 displaying irreversible enzyme kinetics. In addition to direct inhibition, DTS was observed to lower by more than half, the mRNA expression of CYP1 in both cell lines. As such, in-vivo evaluations of DTS as a potential candidate for treating AA-TNBCs and chemoprevention are warranted.*

Keywords*: Breast cancer, cytochrome P450, apoptosis, dibenzyl trisulfide, Petiveria alliacea*

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Shaniece F. Wauchope *is a MPhil Biochemistry student in the department of Basic Medical Sciences, University of the West Indies, Mona. Her research investigates the anticancer and chemo-preventive potential of the popular Jamaican plant Petiveria alliacea (Guinea Hen Weed) and the possible drug-herb interactions associated with its use. She has a BSc. (Hons) in Biochemistry (Major) and Food Chemistry (Minor) from the University of the West Indies. Mona*.

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Petreena S. Campbell *is from the rural district of Catadupa, St. James. She did her Bsc. in Biological Sciences at NCU and recently completed a PhD in Pharmacology at LLU. She has co-authored several manuscripts and published in several journals including Cancer Letters. She has a track record of mentoring future scientists and is the recipient of several awards including the prestigious AAUW International Fellowship. Her long-term career goal is to engage in team-based science, with a diverse cohort of individuals with competencies spanning basic sciences as well as population and clinical sciences, to provide more efficacious treatment options to cancer patients.*

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Maxine D. Gossell-Williams *is an Associate Professor of Pharmacology. She teaches and mentors research students in the Department of Basic Medical Sciences at the University of the West Indies. One of her proudest achievements is the development of the MSc Biomedical Research program, which prepares students to enter PhD programs through components that strengthen their knowledge base and ability to develop interdisciplinary approaches to innovative research. Her research projects focus on continuous sensitization of healthcare professionals to the importance of drug safety monitoring and reporting. Ongoing projects focus on pharmacovigilance.*

Rupika Delgoda *is a tenured, Senior Lecturer in the Faculty of Science and Technology and the Director of the Natural Products Institute (NPI), at the University of the West Indies (UWI), Mona. Following a D.Phil. degree in Pharmacology at Oxford University, U.K. and a post-doctoral research Fellowship in Biochemistry at the University of Leicester, U.K., she commenced her research in Jamaica at UWI in 2002. Her current research interests surround ethnopharmacology, safety and efficacy of Jamaican natural products. With the support of local and overseas grant funds, Dr. Delgoda has established dedicated research facilities for identification of natural products with cancer prevention and treatment leads and evaluation of potential drug-herb interactions.*

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Comparative Extraction Performance and Application of Sodium Alginate from Sargassum Seaweed

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Abstract: *Sargassum Seaweed is a member of the brown alga species originated from Sargasso Sea. Over some period of time, Sargassum has invaded the beaches of the Caribbean, prompting developments of its use. The present work focused on the extraction of sodium alginate from Sargassum Seaweed and its application to preparation of cosmetics. Various extraction methods were applied to extract sodium alginate from Sargassum and compared its extraction efficiency. The maximum weight percentage extraction was obtained with the modified standard protocol treatment containing 0.4% formaldehyde, 0.1 M HCl, 2% Na_2CO_3 and precipitation with ethanol. The extraction percentage range of alginate from these methods was 1 - 8%. The moisture content of the extracted alginate was also analysed by using standard methods and its content ranged from 61% to 96%. The extracted sodium alginate was applied to produce cosmetic products such as lotion and lipstick balm through a standard protocol. Characterisation of the extracted alginate was carried out using FT-IR spectroscopy to confirm its functional groups. This FT-IR spectrum was further compared with IR spectra of commercial sodium alginate and literature.*

Keywords*: Sargassum; Sodium alginate; Cosmetics; Extraction, FT-IR*

Authors' Biographical Notes:

Tiffany S. Husbands *completed her Bachelor's degree in Chemistry at The University of the West Indies (UWI), Cave Hill Campus, Barbados in the year 2016 where she conducted special research in Analytical Chemistry. Ms. Husbands used her creative nature to explore the wonders of Sargassum Seaweed, transforming the known nuisance into a profitable cosmetic product. Combining her knowledge of the main sub-disciplines of Chemistry, she discovered the overwhelming characteristics of the seaweed which landed her in the Nation News with the article "Weed Whacker" and in the Chill Magazine article "A Sargassum Solution".*

Srinivasa Rao Popuri *is a Senior Lecturer in The University of the West Indies (UWI), Cave Hill Campus, Barbados. His major research areas are Membrane Technology, Adsorption Technology, Microbial Fuel Cells and Resource Recycling of Electronic waste. He extended his research into the development of green polymers for antibacterial, water scaling and wastewater treatment applications. Dr. Popuri published a book, 48 journal articles in addition to the 52 conference presentations and received over 1500 citations to his publications. He received Young Scientist award for 2014 from The World Academy of Sciences (TWAS) – Caribbean Academy of Science (CAS) and Principal's Award for Excellence in Research from The UWI, Cave Hill Campus, Barbados.*

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Bivariate Distributions with Transmuted Conditionals: Models and Applications

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Abstract: *The class of transmuted distributions has received a lot of attention in the recent statistical literature. In this paper, we propose a rich family of bivariate distribution whose conditionals are transmuted distributions. The new family of distributions depends on the two baseline distributions and three dependence parameters. Apart from the general properties, we also study the distribution of the concomitance of order statistics. We study specific bivariate models. Estimation methodologies are proposed. A simulation study is conducted. The usefulness of this family is established by fitting two well analysed real lifetime data sets from engineering field.*

Keywords*: Conditional specification; concomitance of order statistics; transmuted distribution*

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Automated Pollen Recognition Using Shape, Texture Features and Logisboost Algorithm

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Abstract: *Analysing and counting pollen grain has many applications, such as chronological dating, climatology, allergy treatment, and even honey characterisation. In the last case, knowing pollen origins in this sweet substance can permit its singulation and a better valorisation. Due to the high number of pollen present in honey, manual analysis is a labour-intensive task. So, scientists have invented many automated methods based on physicochemical or image analysis. We propose an image processing-based method. This one had been tested on eight different Caribbean species. Forty images per species were used, and six features were extracted: area, perimeter, solidity, and standard deviation on luminosity, saturation, and hue. The recognition was done using the Iterative Classifier Optimiser method on the logisboost algorithm, and a recognition rate of 93.71 % was has been obtained. This study has proved that automated recognition of Caribbean pollen based on image processing is possible. Additional study will demonstrate the applicability of the method to a higher number of species and honey characterisation.*

Keywords*: Conditional specification; concomitance of order statistics; transmuted distribution*

Authors' Biographical Notes:

Endrick Barnacin *is a PhD student from the University of Antilles. He works on automated pollen recognition using image analysis and processing.*

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Dispersion of a Solute in Casson Fluid Flow under the Influence of External Body Acceleration

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Abstract: *In this paper, the pulsatile flow of a solute in a straight circular tube under the influence of external body acceleration is studied. The non-Newtonian nature of the fluid is taken into account by modelling as a Casson fluid. The equations governing the flow are solved using perturbation analysis. Due to the complexity of the resultant system of equations, the convection-diffusion equation is solved using a hybrid approach of analytical and numerical methods. In particular, the Crank-Nicolson finite difference numerical scheme is employed to derive numerical formulations for the exchange, convection, and dispersion coefficients respectively, as well as the mean concentration. The results are analysed with the aid of MATLAB software.*

Keywords*: Convection-diffusion equation, Casson fluid, MATLAB*

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■

Agriculture and a Knowledge-Based Economy – Gender: Missing in Action

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Abstract: *Agriculture, although often neglected in discussions and analyses on knowledge-based economies, epitomises the practical application of STEM - Science, Technology, Engineering and Mathematics. Similarly, gender issues through the lens of a knowledge-based economy are even less frequently analysed and addressed. Using qualitative data from Jamaica and the wider Caribbean, the presentation illuminates how, in practice, organic agricultural processes contribute to a knowledge-based economy, enhancing the 'green' economy, and supporting 'blue' economic development while contributing to mitigation of and adaptation to climate change. Interestingly, gender issues intersect all the above initiatives. The nature of this intersection presents the challenge of determining how to create effective actions, guide policy implementation, direct research and influence provision of services to the sector. Solving these questions offer solutions to the most effective approaches to reducing/ eliminating current and expected gender disparities, enhancing and increasing women's participation in applied STEM.*

Keywords*: Gender, agriculture, organic, knowledge-based economy*

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Making It Drier: How *Pinus Caribaea* Influence the Hydrology in Forested Tropical Watersheds

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Abstract: *In the tropics, there have been rapid declines in the extent of natural forest cover due to the pressures from agriculture, timber and urbanisation. The degradation or removal of the primary forest has resulted in different management responses to limit further land degradation. One such method is planting exotic species such as Pinus caribaea due to their high level of resilience. In many temperate forests, it has often been observed that the introduction of non-native species substantially alters hydrological processes including rainfall interception, infiltration, runoff and evaporation. While well recognised in temperate climates, such work is poorly described in the tropics and given the expected changes in climate forecasted for the region, the need for improved understanding of the hydrology in these forests are essential. A hydrological investigation on the impact of Pinus caribaea on water fluxes along steep slopes in Trinidad began in January 2018. Rainfall, throughfall, stemflow, litter interception was monitored weekly while changes in soil properties were assessed seasonally. Preliminary data shows that the pine forests intercept larger volumes of rainfall compared to natural forests despite having a less dense forest canopy. The infiltration rates and soil water repellency in the pine forests suggest that these non-native forests reduce water flow to deeper soil layers.*

Keywords*: Interception, infiltration, soil water repellency, hydrology, pine forest, tropical forest*

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Free Radical Scavenging Activity, Total Phenolics and Metabolites Identified in *Rivina Humilis* Berries

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Abstract: *Rivina humilis L belongs to the Petiveriacea family and is also known as pigeon berry, dog blood, dogberry or blood berry. The leaves of the plant are utilised in traditional medicine for the treatment of various ailments. The berries are however underutilised. Betalains are the pigments responsible for the red colour of the fruit. The free radical scavenging activity and IC50 value (inhibitory concentration) of the berries were determined utilising the 2,2-diphenyl-1- picrylhydrazyl (DPPH) assay and total phenolics by the Folin-Ciocalteu assay. The berry extracts were also analysed by Gas Chromatography Mass Spectrometry to identify metabolites present. R. humilis berries exhibit excellent free radical scavenging activity with an IC50 value of 4.93 mg/mL. The total phenolic content of R. humilis berries was 9.57 ± 0.03 mg GAE/g. Galactose was identified as the major carbohydrate in R. humilis berries. Other metabolites identified included citric acid and the triterpenoid, germanicol. R. humilis berries are a rich source of antioxidants and may be considered for commercial food applications.*

Keywords*: Rivina humilis, antioxidants, citric acid, galactose, germanicol*

1. Introduction

Rivina humilis L. belongs to the Petiveriacea family and is also referred to as pigeon berry, dog blood, dogberry or blood berry (Figure 1). The berries are safe for consumption but are currently underutilised (Khan et al., 2011). Betalains are natural water soluble nitrogen containing pigments that are responsible for the bright red colour of the berries. The pigments are stable at a pH of 4 – 7 and may be considered for use as a natural colorant in low acid and neutral foods (Cai et al., 2005). The total betalain content of *R. humilis* berries is 286.9 ± 19.2 mg/100 g fw (Khan et al. 2012). Betalains are further categorised as betaxanthins (yellow–orange) and betacyanins (red–violet). In *R. humilis* berries, betaxanthin (171.2 ± 11.1 mg/100 g fw) is present in higher concentrations than betacyanins (115.7 ± 8.8 mg/100 g fw) ((Khan et al. 2012). The betaxanthin, humilixanthin (5-hydroxynorvaline-immonium conjugate of betalamic acid) has been detected in extracts of the fruit (Strack et al., 1987). Other natural sources of betalains include red beets (betacyanins, 58-82 mg/100 g fw and betaxanthins, 35-48 mg/100 g fw) (Gasztonyi et al., 2001) and purple cactus pear (*Opuntia ficus-indica*) (Albano et al., 2015 and Stintzing et al., 2005).

The consumption of fruits and vegetables is associated with numerous health benefits. These include a reduced risk of chronic diseases such as cardiovascular disease, diabetes and cancer (Lui, 2003). This study was undertaken to investigate the free radical scavenging activity and total phenolic content of *R. humilis* berries. Metabolites present in the fruits were also identified by Gas Chromatography Mass Spectrometry.

Figure 1. *Rivina humilis*

2. Materials and Methods

Fully mature *R. humilis* (red variety) berries were freshly harvested from the Mona Campus of the University of the West Indies, Kingston, Jamaica (February 2018). Mature *Cissus sicyoides* berries were also harvested and their activity compared with *R. humilis* berries.

2.1 1,1-Diphenyl-2-picrylhydrazyl (DPPH) Radical Scavenging Assay

Berries were oven dried (65°C, 4 h, Gallenkamp Laboratory Oven OV-330, England), ground with a mortar and pestle and extracted with ethanol (80%) containing hydrochloric acid (1%) at room temperature. The free radical scavenging activity of berry extracts (1 mg/mL - 10 mg/mL) was determined utilising the DPPH assay according to the method of Brand-Williams et al., (1995). The reaction mixture consisted of berry extract (0.5 mL), absolute ethanol (3 mL) and DPPH (0.5 mM, 0.3 mL). The reaction was allowed to proceed in the dark for 15 min after which the absorbance was measured at 517 nm using a spectrophotometer (Thermo Scientific Genesys 10S UV-Vis). A mixture of ethanol (3.3 mL) and berry extract (0.5 mL) served as the blank. A control solution was prepared by mixing ethanol (3.5 mL) with the DPPH radical solution (0.3 mL). The DPPH scavenging effect (%) was calculated by using the formula:

$$\% = [1 - A_1/A_0]*100 \quad (1)$$

where:

A_1 = Absorbance of sample at 517 nm

A_0 = Absorbance of control at 517 nm

The concentration which showed 50% radical scavenging activity was calculated and reported as the inhibitory concentration (IC_{50}).

2.2 Total Phenolic Content

Total phenolic content was determined using the Folin-Ciocalteu assay with modifications (Singleton and Rossi, 1965). Dried berry samples (200 mg) were extracted with ethanol (2 mL, 80%) containing hydrochloric acid (1%) at room temperature. Extracts (100 µL) were reacted with Folin-Ciocalteu reagent (10%, 750 µL) and mixed for 5 min followed by addition of Na_2HCO_3 solution (6%, 750 µL). The solution was incubated at 22°C (1.5 h) and the absorbance measured at 760 nm using a spectrophotometer (Helios Omega, Thermo Fisher Scientific). A standard calibration curve of gallic acid (0-200 mg/L) was generated and the results expressed as mg gallic acid equivalents (GAE)/g dry weight.

2.3 Gas Chromatography Mass Spectrometry

Ethanolic extracts of the berries (10.0 mg/mL) were silylated with N-tert-butyl-dimethylsilyl-N-methyl-triflouroacetamide (MTBSTFA, 0.1 mL). Silylated samples (1 µL) were chromatographed on an Agilent HP6890 series Gas Chromatograph interfaced with a HP5972 Mass Selective detector. Silyl derivatives were eluted with helium carrier gas (flow rate 1.2 cm^3/min) through a DB-1701 column (30m × 0.25mm i.d.× 0.25µm film thickness, Agilent, Santa Clara, CA) in an oven programmed at 80°C for 2 min and increased at a ramp rate of 20°C/min up to 280°C for 10 min. Samples were injected at 250°C while the detector was maintained at 280°C. Constituents were identified by utilising the NBS75L library of mass spectra (match quality >90%).

2.4 Data Analysis

Samples were analysed in triplicate. The mean of the data and the standard deviation is reported.

3. Results and Discussion

The regular consumption of fruits and vegetables is recommended for a healthy life style and protection from chronic disease (Pem and Jeewon, 2015). Fruits and vegetables are excellent sources of bioactives with antioxidant and anticancer properties (Baby et al., 2017). Bioactives present in fruits include polyphenolics, flavonoids and tannins (Baby et al., 2017). Fruits are also a source of vitamins, minerals, sugars and fibers. Strawberries, blueberries, grapes and raspberries are popular berries that are consumed in North America and Europe. These berries do not readily grow in the Caribbean and are mainly imported with a high market value. In the tropics, several berries grow wildly that are currently underutilised. In the present study the antioxidant properties of *R.*

humilis berries which grow wild in Jamaica were investigated. Metabolites present in aqueous extracts of the fruit were also identified with the aid of gas chromatography mass spectrometry.

3.1 Free Radical Scavenging Activity

The free radical scavenging activity of *R. humilis* berries was investigated by use of the DPPH radical scavenging assay which is based on the ability of the DPPH radical to accept hydrogen or electrons from antioxidants. When reduced the DPPH radical changes colour from purple to yellow (Aksoy et al., 2013). This change in colour may be determined spectrophotometrically (Aksoy et al., 2013). The assay has several advantages in that it is rapid and the reagents utilised are environmentally friendly (Hangun-Balkir and McKenney, 2012).

In the current study, berry extracts were incubated for a period of 15 min. This shorter incubation period was necessary due to the rapid process by which *R. humilis* extracts decolourised the DPPH radical. Typical incubation times for the assay are from 30 min to 1 hr. This suggests the presence of high concentrations of antioxidants in *R. humilis* berries. The IC_{50} value for ethanolic extracts of *R. humilis* extracts was 4.93 mg/mL (Figure 2) which was approximately half that of *C. sicyoides* (11.73 mg/mL). This confirms that *R. humilis* berries are a more potent source of antioxidants than *C. sicyoides* berries. Hangun-Balkir and McKenney (2012) determined the IC_{50} values of several berries, namely blueberry (0.70 mg/mL), raspberry (0.80 mg/mL), blackberry (1.40 mg/mL), strawberry (5.60 mg/mL) and acai berry (>10 mg/mL) [14]. The free radical scavenging activity of resveratrol (4.70 mg/mL), a polyphenolic was also evaluated. The samples were incubated for a time period of 30 min. Of the samples investigated, blueberry was the most potent and acai berries the least (Hangun-Balkir and McKenney, 2012).

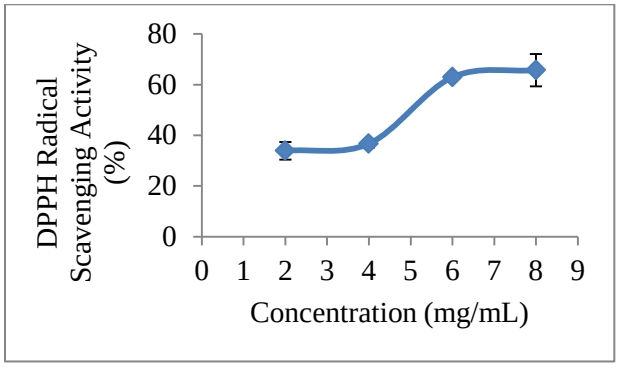

Figure 2. Free radical scavenging activity of *R. humilis* berry extracts

3.2 Total Phenolics

Berries are known to be among the best dietary sources of bioactive compounds (Skrovankova et al., 2015). The antioxidant properties of berries may be attributed to the presence of bioactive compounds which includes phenolics and fruit acids. The use of natural antioxidants in place of synthetic antioxidants is currently being explored by several food processing facilities. Antioxidants are utilised as a functional ingredient in a wide variety of products to reduce the occurrence of oxidative rancidity (Lorenzo et al., 2018).

Blueberries are an excellent source of antioxidants and possess a total phenolic content of 9.44 ± 0.03 mg gallic acid/g on a dry weight (DW) basis. Actual phenolics identified in blueberry extracts include gallic acid, vanillic acid, caffeic acid and cinnamic acid (Huang et al., 2012). The total phenolic content of ethanolic extracts of *R. humilis* berries was 9.57 mg GAE/g. *C. sicyoides* berries had a total phenolic content of 5.79 mg GAE/g.

3.3 Metabolites identified by Gas Chromatography Mass Spectrometry

Fruit acids are responsible for the tart taste of berries and also contribute to their antioxidant properties. Citric acid was identified as the predominant fruit acid in *R. humilis* berries (see Table 1).This is also the predominant acid present in blackcurrant, redcurrant, whitecurrant, loganberry, raspberry, strawberry and elderberry (Whiting, 1958). Citric acid is utilised as a food additive serving as an acidulant and also possessing antioxidant properties (Choe and Min, 2009). Its antioxidant properties are based on its ability to chelate metal ions. A smaller quantity of malic acid was also detected in *R. humilis* berries. Malic acid is the predominant acid in blackberry (Whiting, 1958).

Fruit peels and fruit cuticular peel are particularly rich in triterpenoids. Triterpenoids are polycyclic compounds that are derived from the linear hydrocarbon squalene (Reddy and Couvreur, 2009) and have been

detected in apples, grapes, olives, tomatoes, bell peppers and eggplants (Szakiel et al., 2012; Pensec et al., 2014; Bauer et al., 2004). In tomatoes, the level of triterpenoid triples at early stages of maturation with a subsequent decline as the fruit changes colour from green to red (Kosma et al., 2010). The triterpenoid germanicol was detected in *R. humilis* berry extracts. Germanicol has also been detected in tomatoes (*Lycopersicon esculentum* L) by the use of GC/MS (Bauer et al., 2004). Triterpenoids possess a myriad of medicinal properties which include anti-inflammatory, antiulcer, antibacterial and antiviral activities (Bishayee et al., 2011). They are currently being evaluated for use in functional foods and as chemo preventive agents (Bishayee et al., 2011).

Galactose is mainly associated with dairy products but is also present in fruits and vegetables. Tomatoes, dates, watermelon, persimmon, papaya and bell pepper are examples of plant sources of galactose (Gross and Acosta, 1991). Galactose was identified as the major carbohydrate in *R. humilis* berries (see Table 1). Other carbohydrates identified in *R. humilis* berries include arabinose, glucose, and myo-inositol. Cellobiose, galactose, mannose, arabinose, and xylose are structural sugars found in the cell wall of fruits (Gibeaut and Carpita, 1994). Xylonic acid, a five carbon sugar alcohol was identified in *R. humilis* berry extracts and is also present in papaya (Sanimah and Sarip, 2015).

Table 1. Metabolites identified in aqueous extracts of *R. humilis* berries

Metabolites	Percentage (%)
Fruit acids	
Glucaric acid	0.08 ± 0.0
Pentanoic acid	0.16 ± 0.1
Altronic acid	0.20 ± 0.0
Xylonic acid	0.45 ± 0.1
Phosphoric acid	0.55 ± 0.2
Succinic acid	1.14 ± 0.1
Citric acid	7.97 ± 3.1
Carbohydrates	
Arabinofuranose	0.30 ± 0.1
Arabinose	0.45 ± 0.0
beta-D-Glucopyranose	0.67 ± 0.2
Myo-Inositol	0.98 ± 0.3
D-Galactose	1.66 ± 1.0
alpha-D-Galactopyranose	11.06 ± 1.8
Fatty acids	
6,9,12-Octadecatrienoic acid	0.04 ± 0.0
alpha-Linolenic acid	0.31 ± 0.0
Stearic acid	0.37 ± 0.0
Linoleic acid	0.39 ± 0.0
Palmitic acid	0.51 ± 0.0
Oleic acid	0.62 ± 0.1
Triterpenoid	
Germanicol	0.53 ± 0.1
Ester	
Ethyl oleate	0.51 ± 0.1

Lipids play a protective role in nature and may be found in cuticular waxes, seeds and pulp of fruits (Klavins et al., 2015). Berries are a minor source of lipids (Celik and Ercisli, 2009). *C. sicyoides* berries contain 4.9 ± 0.5% lipid (Goldson Barnaby et al., 2017). Palmitic acid is the major fatty acid present in *C. sicyoides* which also contains stearic, oleic and linoleic acid (Goldson Barnaby et al., 2017). Linoleic and linoleic acids are the major fatty acids in red raspberries (Celik and Ercisli, 2009). Gamma-linolenic, linoleic, oleic, palmitic and stearic acids were detected in extracts of *R. humilis* berries (see Table 1).

4. Conclusion

R. humilis berries exhibited high free radical scavenging activity and high levels of total phenolics. Metabolites identified in ethanolic extracts of *R. humilis* berries included carbohydrates, fatty acids, fruit acids and a triterpenoid. Galactose was the primary carbohydrate and citric acid the major fruit acid. The triterpenoid germanicol was also detected in *R. humilis* berry extracts. *R. humilis* berries may be considered for use in the preparation of value added food products with potential utilisation as a nutraceutical and functional food. The authors have no conflict of interest to report.

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