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THE EXTRAORDINARY DESIGN OF THE BOMBARDIER BEETLE— A CLASSIC EXAMPLE OF BIOMIMETICS

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ABSTRACT

The innocuous looking bombardier beetle is one of the most remarkable creatures in the insect world. This tiny insect (1-1.5 cms long) is able to fight off any spider, frog, ant or bird that comes too close, by blasting the attacker with a powerful jet of hot, toxic fluid. Furthermore, the beetle can aim its weapon in any direction (even over its head) with pinpoint accuracy, and can reach distances of up to 20 cm with its spray. The bombardier beetle is rare in Europe but common in Africa, Asia and the warmer parts of the Americas, and in order to resist predators, forms a noxious spray by reacting small amounts of hydroquinone with hydrogen peroxide in a pair of combustion chambers in its abdomen, and in the presence of the catalysts catalase and peroxidase.

The beetle demonstrates irreducible complexity in the following systems: 1) the sensory mechanism which gives awareness of the approach of a predator, 2) the valve system that involves both inlet and exhaust valves working synchronously, 3) the chemical production of reactants hydrogen peroxide and hydroquinone, 4) the use of catalytic chemistry to eject a controlled explosive mixture, and 5) the moveable, flexible exhaust turret to enable ejection in any direction. These and others are systems which only work when each of the component parts are operating in harmony with others in a coordinated mechanism. For chemical systems the same point applies in principle. The overall chemical system will only operate correctly if each component chemical is in place in a prepared pathway.

This paper reviews the research of a number of authors (including Professor McIntosh) into the workings of the bombardier beetle spray system. Not only is this is a classic example of biomimetics (the study of design in nature and copying these designs and using them in engineering), but also tacitly underlines the necessity of design in the original beetle itself. The discovery that the McIntosh team made of sophisticated mechanisms in the beetle's structure and chemistry demonstrates the irreducible complexity in the design of the beetle.

KEY WORDS

biomimetics, biology, engineering, design, irreducible complexity, pulse combustion, valves, hydrogen peroxide

INTRODUCTION

The work of this paper is primarily concerning the physics of the beetle valve system and shows that it is irreducibly complex and marvelously *designed*. The production of hydrogen peroxide in the beetle is yet to be fully understood, but what is known shows the intricate sophistication of the beetle extends also into chemical system where interdependent chemical pathways defy the idea of a slow, evolving process.

This example of biomimetics shows clearly the evidence of design in the created world and underlines the truth of Rom 1:20 "For the invisible things of him from the creation of the world are clearly seen, being understood by the things that are made, even his eternal power and Godhead; so that they are without excuse". *The glory is to the God who made such an intricately designed system, including lowly beetles.*

THE WORKINGS OF THE BOMBARDIER BEETLE

The bombardier beetle (McIntosh 2007, Beheshti and McIntosh 2007a, Beheshti and McIntosh 2007b, McIntosh and Beheshti 2008 and see figs. 1 and 2) heats up a toxic aqueous mixture of quinones to above boiling point in a tiny combustion chamber less than 1mm in size by an exothermic chemical reaction and then sprays it from a moveable turret in its back end in any direction it wishes - even over its head. The beetle uses this mechanism for warding off attacks from spiders, frogs, ants and birds. The beetle forms the noxious spray (which is in a solution mainly composed of water) by reacting small amounts of hydroquinone with hydrogen peroxide in the combustion chamber (less than 1mm long) in the presence of the catalysts catalase and peroxidase. This exothermic reaction then produces benzoquinone and water, and heats up the solution to above boiling.

1. Combustion chamber with valve system

Pioneering work by Professor Tom Eisner of Cornell University (Aneshansley and Eisner 1999) showed that the mixture ejection is not continuous but is in fact a series of explosions similar to pulse combustion, whereby the reactants fill the chamber, react and are ejected, then more reactants enter and the cycle is repeated. This is done in the beetle's case at a frequency so high (400-500Hz) that it took a high speed camera operating at the kHz level to resolve the individual explosions. The results were astonishing as they showed that the audible note that the beetle makes when it is firing, and that can be heard by observers, is directly connected to the explosion frequency.

Aneshansley et al. (1969) measured the mass of the ejected liquid

Figure 1. African bombardier beetle

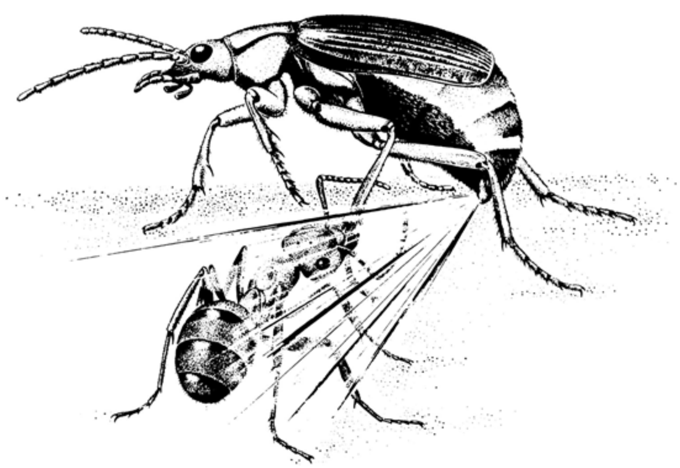

Figure 2. The beetle defence mechanism deters ants (shown), birds, spiders and frogs which may attempt to prey on the beetle.

and gases and found that it varied from 0.1 to 0.5 mg for a single discharge. While the reactant storage and delivery system is driven by muscle contraction, the reaction chamber is in fact rigid. Eisner and colleagues (Dean et al. 1990) reported spectrographic measurements of the discharge using seven beetles (45 discharges) and they concluded that the average discharge duration was 11.9 ms. The actual time elapsed was 2.6–24.1 ms, with 2–12 pulses per discharge recorded and thus a mean of 6.7 pulses per discharge. The frequency of the pulses is reported to range from 368 to 735 Hz, with the mean value at 531 Hz. The average velocity of the spray emerging from the tip of the beetle's abdomen was measured with a high-speed camera to be 11.63 m/s (ranging from 3.25 to 19.5 m/s), and the spray can reach as far as 20–30 cm.

Professor Eisner using electron microscopy was able to show that the beetle has twin combustion chambers (fig. 3) into which the combustible reactants are fed down a thin tube. This inlet tube is pinched under high pressure and acts as an inlet valve to stop the flow of reactants continuing during the combustion part of the cycle. Work with the team at Leeds (McIntosh and Beheshti 2008) also showed that there was also an exhaust valve which caused a membrane to lift at high pressure, so that there are in fact two valves controlling the ejection of the hot mixture of vapour and liquid (fig. 4). The ejected fluid is in fact primarily hot water and steam heated by the reaction of roughly a 25% mixture of the chemicals hydroquinone and hydrogen peroxide (Beheshti and McIntosh 2007a). And recent experimental work by another group at MIT (Arndt et al. 2015) led by Dr. Christine Ortiz has shown that the ejections are made with both of the twin chambers operating together. Furthermore a detailed analysis of the incoming glands carrying the reactants to the combustion chamber have now been made showing that the reactants come a reservoir chamber along fine tubes into the combustion chamber. The intricacy of these tiny parts of the system, all of which must be working to make the ejections take place, is an example of the irreducible complexity of the chemical burning and ejection process. All of this is completely independent of the digestive system of the bombardier beetle.

2. Chemistry

Much of the early investigations on the chemistry of the beetle were performed by Schildneckt (Schildneckt and Houlebek 1961). His work showed that hydroquinone and hydrogen peroxide were being combined to produce benzoquinone and water. The aqueous solution of reactants is stored in a reservoir, and is composed of hydroquinone ($C_6H_6O_2$) at a concentration of 25% and hydrogen peroxide at a concentration of 10% - concentrations assumed to be by mass, see Schildneckt and Houlebek (1961) and Aneshansley et al. (1969). Fig. 5 shows a schematic representation of the beetle's discharge apparatus including the reservoir and the reaction chamber. When the reservoir is squeezed, the mixture of reactants is introduced into the reaction chamber through a valve, which is opened in the first part of the cycle. Once the reactants are present in the chamber, the enzyme catalysts (catalase and peroxidases) are introduced from the combustor walls. An extremely fast catalytic reaction then takes place. While the hydrogen peroxide is decomposed with the help of catalase to water and free oxygen, the peroxidases play a role in the oxidation of hydroquinone. The reaction mechanism described by Aneshansley et al. (1969) can be described by the global chemical reaction:

$$C_6H_6O_2(aq) + H_2O_2(aq) \rightarrow C_6H_4O_2(aq) + 2H_2O(l) \quad (1)$$

and it can also be described in three most important decomposition steps:

$$C_6H_6O_2(aq) \rightarrow C_6H_4O_2(aq) + H_2(g) \quad (2)$$

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g) \quad (3)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad (4)$$

where "*aq*" means aqueous solution, "*l*" means liquid and "*g*" means gas. Note that equations (2)–(4) are not to be regarded as the breakdown of equation (1). Rather they represent the salient reactions of a much larger number of reactions, and the important point is that the sum of the enthalpy changes of equations (2)–(4) is equal to that of equation (1). The enthalpy of reaction at 25°C for equations (2)–(4) are $\Delta H_2 = +177.2$ kJ/mol, $\Delta H_3 = -94.5$ kJ/mol and $\Delta H_4 = -285.5$ kJ/mol respectively, with a negative sign meaning there is heat given off and a positive sign meaning that energy is used up. So equation (2) is considerably endothermic and uses up energy to get the hydroquinone to break up. Equation (3) though exothermic, is not exothermic enough to sustain the reaction of equation (2). Only when equation (3) comes into play and the reaction of Hydrogen with Oxygen takes place, is there a sufficient and self-sustaining cascade of energy available to not only provide the energy for the endothermic reaction of equation (2) but also extra left over to heat the rest of the water solution to make steam. So for the overall reaction [equation (1)], one can consider the equivalent enthalpy as the addition of these three salient reactions, i.e. $\Delta H_1 = -202.8$ kJ/mol which is more than twice as much as the energy per mole liberated by the hydrogen peroxide decomposition. The total heat released for 1 kg of solution is then 794.2 kJ/$kg_{solution}$.

Contrary to the assertions of Dawkins (Dawkins 1991) who argued for the gradual development of the beetle chemistry by proposing that gradually over the supposed generations of "beetle evolution" a primitive beetle used a richer and richer mixture of hydrogen peroxide with an appropriate catalyst, this is incorrect. He ignored the important role of the break up of hydroquinone [equation (2)] which given the initial heat of the hydrogen peroxide reaction then begins to liberate the hydrogen radical. His actual words were "In fact the hydroquinone does nothing at all. *We can put that on one side* …" It was a crucial error, as it is only by the presence of the hydrogen radical that the main hydrogen / oxygen reaction can take over with a much greater heat of reaction, and thereby cause the caustic mixture to come out with such ferocity and scalding temperatures in the face of a predator. The catalytic chemistry is not just causing the hydrogen peroxide to break down, but also preparing the very reactive hydrogen radical to be ready for the highly exothermic step with the free oxygen. This is a further irreducibly complex system which is to do with the chemistry itself. Hydrogen peroxide on its own is not going to make the chemical system needed. Neither will hydroquinone with H_2O_2 do anything unless there is a catalyst and a chamber where these catalytic reactions are contained. Only with a valve-controlled reservoir delivery system, a combustion chamber, the catalysts peroxidase and catalase, and an exhaust valve with a moveable turret plus sensory system to ascertain direction of the predator, can there be a machine gun like ejection device. Indeed the comparison to a machine gun is apt, since the beetle will keep a rapid sequence of ejections going for 5 seconds or so and then do this again a number of times if needed. Machines require design and involve raised free energy devices where energy pathways have to be constructed (McIntosh 2009, 2013) to make the system work. The design inference is both logical and the only reasonable approach to understanding the beetle valve and chemical mechanisms.

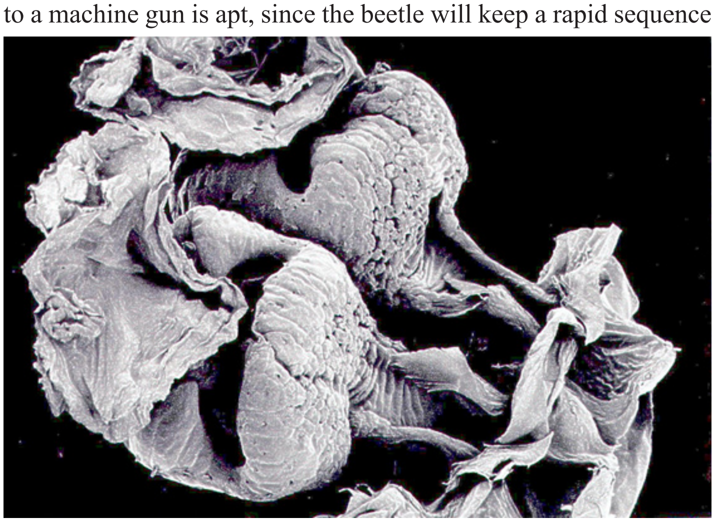

Figure 3. An electron micrograph showing the twin box-glove shape combustion chambers and nozzles in the *Stenaptinus insignis* beetle from a dissection by Eisner. Each of the combustion chambers has an inlet and exhaust valve. *Photo courtesy of Professor Tom Eisner.*

MIMICKING THE BEETLE VALVE SYSTEM

The investigations by the team led by Professor McIntosh have led to the building of an experimental rig mimicking the major physics of the beetle ejection system but not the chemistry. Rather than chemical heating as with the beetle, the experimental rig has

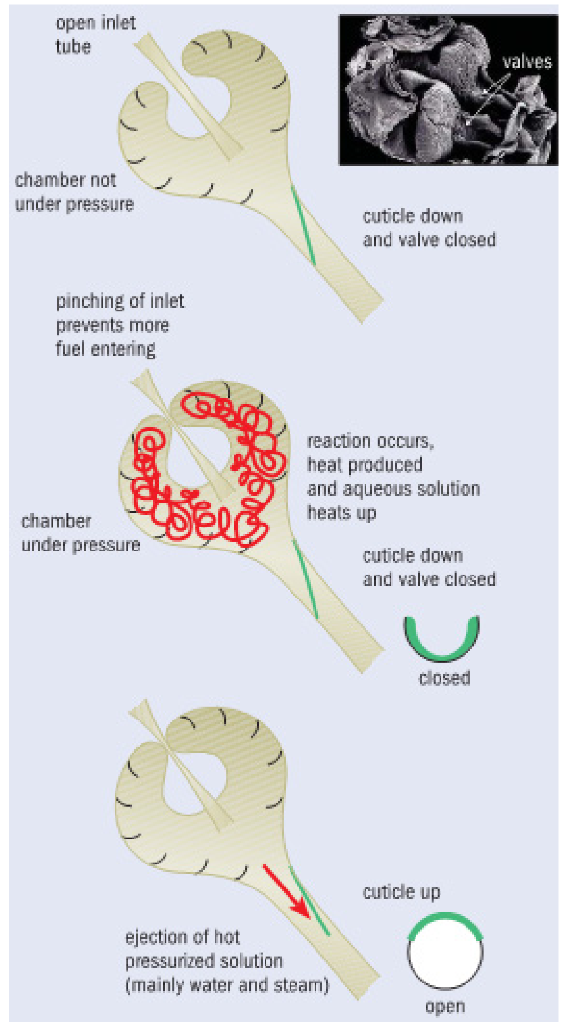

Figure 4. The cycle of vapour explosions in the bombardier beetle along with the ingenious inlet and pressure relief exit valve. When the combustion chamber is at low pressure, the inlet tube is open and the exit tube is closed by a membrane that sticks to the bottom part of the tube. This allows the reactants to enter the chamber. Insert shows the connection with Fig. 3 with the twin combustion chambers and nozzles from a dissection of a bombardier beetle. Once the chamber is under pressure (middle) the extremities of the 'boxing glove' like chamber pinch the inlet tube shut. As the chemical reaction in the chamber progresses, heat is generated and the pressure in the chamber increases until the exit membrane is forced to lift (see bottom picture), and the hot pressurized fluid is then ejected. Then the pressure in the chamber drops and the process is repeated until all of the reactants have been exhausted. *Figure from McIntosh and Beheshti (2008).*

been powered electrically and the inlet and exhaust valve system which is passive in the beetle, is actively controlled electronically. The results have been immediately impressive with a fast expulsion of water and steam which can only be achieved with a vapour explosion. What has been particularly encouraging has been the ability to control the droplet sizes and the frequency of ejection. The beetle can eject with an astonishingly small interval of approximately 2 msecs (which corresponds to a frequency of 500Hz – hence the distinct note that the beetle makes upon ejection). These larger experimental prototype rigs (with a typical chamber size of 2 cms) have reached a frequency of approximately 100 - 200 Hz. This is of great interest to industry because it has been found that the droplet sizes can be controlled by different chamber characteristics such as temperature and pressure of the chamber as well as the diameter of the outlet tube. The work has led to interest from industry with a raft of practical applications including fuel injectors, fragrance spray devices, fire extinguishers and pharmaceutical sprays.

Once the beetle valve system had been understood, the aim was to build first a theoretical model to indicate the level of importance of pressure to ejecting the mixture of steam and water (and in the case of the beetle the caustic chemicals as well). Then when this was understood the aim was then to build an experimental working model.

1. A computerized model

Having deduced the process behind the beetle's remarkable spray system, the next step was to deduce the role of pressure in producing the spray system both in the beetle and in the device which would eventually be built. To estimate the trigger pressure and other key characteristics, such as the temperature of the liquid and the diameter of the exit nozzle, a theoretical model of the combustion chamber was constructed using computational fluid dynamics (CFD). The model used a small cylindrical chamber measuring 0.6 mm in diameter and 0.3 mm in length, which is about the same size and volume (0.1 mm^3) as real beetle chambers. The cylinder was then joined to an exit nozzle 0.1 mm in length that could have any diameter in the range 0.1–0.5 mm.

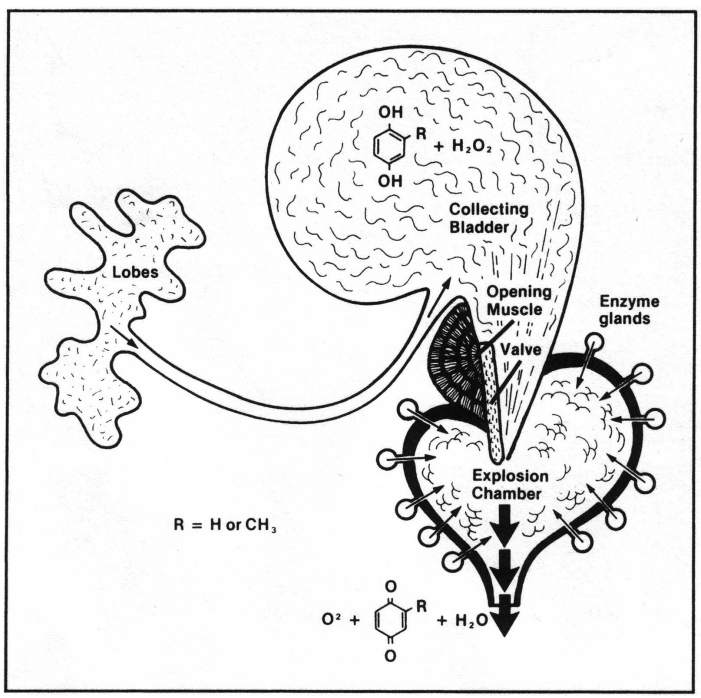

Figure 5. Explosion chamber of bombardier beetle. Hydrogen peroxide and hydroquinone react in the presence of the catalysts catalase and peroxidase, to yield benzoquinone and water. The overall reaction is exothermic and heats the aqueous solution which is ejected under pressure due to the valve system whereby the inlet valve closes under pressure and the exhaust valve opens at a prescribed pressure slightly above ambient.

The CFD simulations began with the water in the main chamber under pressure, and then the separation between the chamber and the exit nozzle was removed as an initial condition – thus simulating the exhaust valve. The simulation was run at a range of trigger pressures (1.15, 1.1 and 1.05 × 10^5 Pa), each of which has an associated saturation temperature – i.e. after the valve is opened, the liquid in the chamber is assumed to be at the saturation temperature for that particular trigger pressure. For example, for 1.1 × 10^5 Pa, the saturation temperature is approximately 105°C. The chamber was also modeled in a second computer experiment without the restricted exit valve, where the fluid is allowed to boil as soon as it is hot enough, and the results compared to the results where the exhaust valve was used. The model assumes that the flow is laminar based on the observed velocities in the experiments of Eisner (Aneshansley and Eisner 1999), and based on the velocities generated numerically here. Consequently, the Reynolds number is low and at its maximum is of the order of 100.

The important finding was that the flash-evaporation process is much more powerful than direct boiling without an exhaust valve. This is because the increased pressure exerted on the fluid significantly increases the ejection velocity. This reduces the time taken to squirt all the fluid out from over 10 ms without the pressure valve, to as little as 1 ms with it in place. The CFD model also managed to closely reproduce the velocities and timescales observed with real beetles for a trigger pressure of 1.1 × 10^5 Pa and a nozzle diameter of 0.2 mm. (Beheshti and McIntosh 2007b).

2. An experimental device

A. Description of experimental facility

The prospect of a spray technology where droplet size, temperature and velocity could be closely controlled, led to considerable interest from industry and the building of an experimental rig (a bio-inspired vapour explosion device) which mimics the important combustion chamber and valve system of the bombardier beetle.

Based upon the computer simulation work conducted, an experimental demonstration facility (fig. 6) was built, which implemented the principles of the liquid atomization method of the bombardier beetle and incorporated a Malvern laser to measure droplet sizes. The catalytic chemistry of the beetle was not copied in these experiments, and instead, the heating is done electrically. In a similar way to the bombardier beetle and the CFD simulation work, the core of this system is the chamber and valves, but with the electrical heat source. Unlike the bombardier beetle and the simulation work, the inlet and exhaust valves of the physical system are not opened passively by a buildup of pressure in the chamber, but instead the these valves are controlled electronically, resulting in an actively controlled pulsed spray. There are also other valves in the system, which control the refill flow into the chamber between ejections, similar to the chamber extremities which control flow into the beetle's chamber through an inlet tube. Opening or closing these valves and the inlet / exhaust valves then controls the flow of liquid (mimicking the bombardier beetle) and results in atomized spray generation. As with the beetle and the CFD simulation work, this is due to the formation (for a few msecs) of a closed volume of liquid at high temperature in the chamber just before the exhaust valve is opened. It is important for this high-temperature volume of liquid in the chamber to be closed off to allow the required temperature rise with minimal associated vaporization. This ensures that the chamber liquid temperature is allowed to rise above its boiling point and that a portion of liquid will flash evaporate once the exhaust valve is opened. This produces liquid atomization at much lower pressures than utilized in most liquid atomization devices (these generally use pressure atomization – forcing the liquid through small holes at high pressure) and is more energy efficient.

The fact that flash evaporation is used to achieve fast ejection of the water and steam, combined with appropriate control systems, means the system lends itself to a fine control of spray characteristics, particularly droplet size. This control is further improved by the decoupling of the exhaust valve from the chamber pressure. In an ideal system, there would be no vaporization of the chamber liquid during the heating phase; however, in practice, some vaporization will always occur. This is the major cause for the rise in chamber pressure seen in the bombardier beetle, which in that case triggers the opening of the (passive) pressure relief exhaust valve. Therefore in the bombardier beetle system, this limits the atomization level achieved, since the extent of flash evaporation will be roughly similar at each ejection. The liquid is heated a similar amount and exhausted at a similar time due to the correlation between chamber pressure and chamber temperature. As the exhaust valve on the experimental system is not pressure triggered, but actively controlled electronically, the extent of flash evaporation can be controlled to a much greater degree than that of the bombardier beetle.

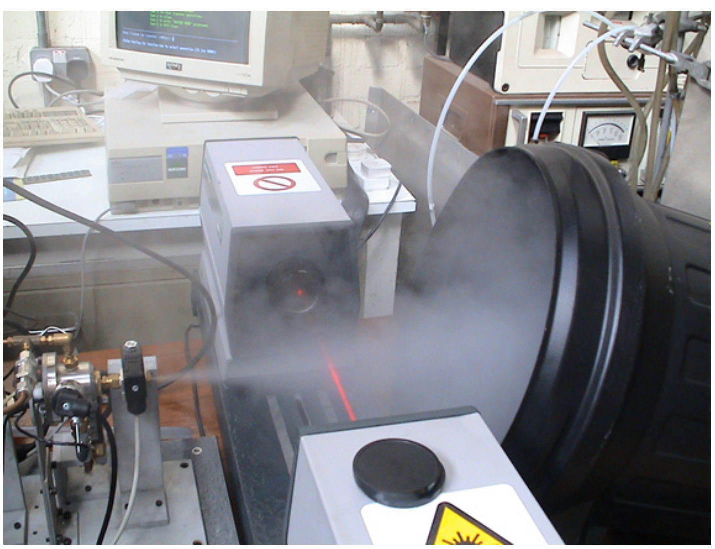

Figure 6 The experimental rig inspired by the bombardier beetle's combustion chamber. This facility is 2 cm in length and can fire liquid up to distances of 4 m. Shown also is the Malvern laser to measure droplet sizes. The facility can eject very fine mist with droplets 2 μm in diameter as well as much larger droplets 100 μm across.

B. Results from experiments

The physical scale of the first experimental system was considerably larger than that of the system found in the bombardier beetle. Whereas the bombardier beetle system has a chamber of approximately 1×10^{-3} m in length, the first experimental system has a much larger chamber, 0.02 m in length. This level of scaling is not limited to the chamber of the system and extends also to other parameters, such as the diameter of the feed and outlet tubes. The process in the experimental system however significantly increases the atomization of the liquid as it exits the chamber. The experimental system is not restricted to only atomizing very small liquid volumes like those found in the bombardier beetle, but also much larger volumes with a wider range of practical uses. Some key performance parameters are also scaled with the increase in chamber size, such as the throw ratio. A bombardier beetle can throw liquid 0.2 m, using a chamber 1×10^{-3} m in length. This gives a throw ratio of 200 where throw ratio is the distance of ejection divided by the chamber length. Comparatively, it was found that the chamber of 0.02 m in length on the experimental system could also achieve a throw ratio of 200, throwing a mixture of liquid and steam a distance of up to 4 m (Beheshti and McIntosh 2008, McIntosh and Beheshti 2008).

Initially single blasts of spray were explored and then repeated blasts. This required a computer-controlled system for opening and closing the inlet valve, the return valve and the exhaust valve. It was found that a wide range of droplet size and temperature of the spray could be achieved depending on the control of the valve system. The minimum droplet size was 0.002 mm and the largest droplet sizes are in the region of 0.1 mm. The temperature of the spray varies from a warm 45° C at a 20 cm distance from the nozzle for large droplets, to room temperature for the smallest droplets. The frequency of ejection on this first experimental facility could be varied from 1 to 20 Hz and the velocity of ejection is typically in the range 5-30 ms^{-1}. Later experimental facilities have readily reached a frequency of ejection of 100Hz.

One of the key features of the experimental facility is that it can produce a large variation in the characteristics of the spray produced. The type of spray produced is controlled by a number of factors including pressure and temperature in the chamber. Consequently, a range of spray characteristics can be achieved which is much wider than possible with other liquid atomization systems. Experimental work has shown that it can generate a very wide range of spray characteristics such as droplet size distribution, the ejection velocity of the spray, the mass ejection rate, and the temperature of the ejected spray. These features are described in more detail in Booth et al. (2012) and fgures 7 and 8 are reproduced here to show the different possibilities of droplet size distribution that can be achieved.

In summary, atomization is achieved by heating a liquid past its boiling point, and at a constant volume. This is suddenly allowed to vaporize though the rapid opening of an exhaust valve. This causes a flash evaporation of a portion of the liquid, which generates a very large force, which then ejects vapor and liquid out through the valve. The flash evaporation is such that as the liquid is rapidly

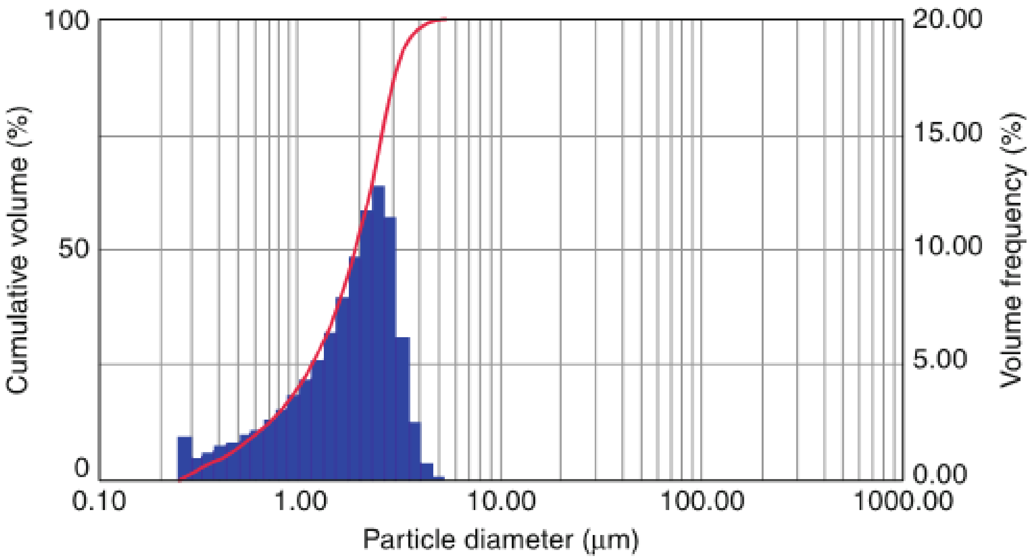

Figure 7 Typical droplet size distribution from experimental facility system set for producing the smallest droplets

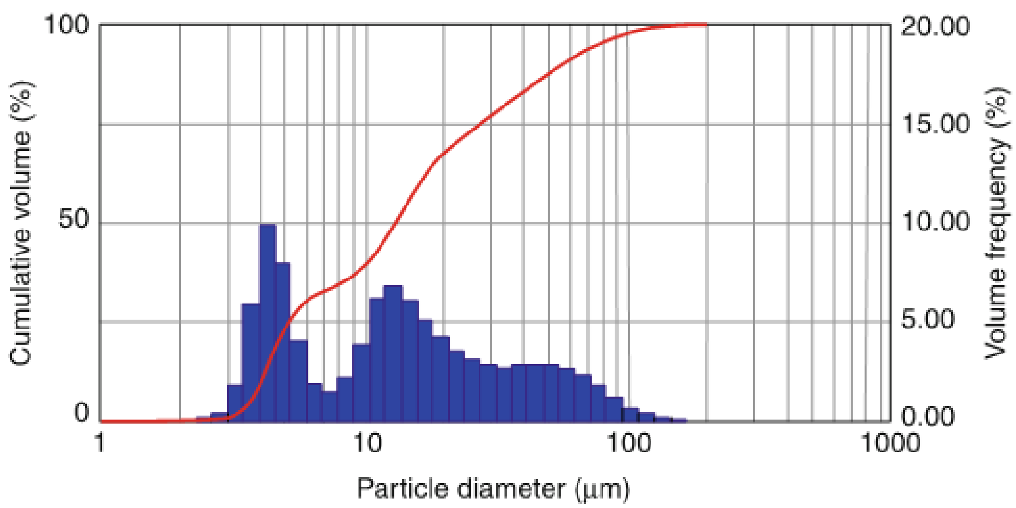

Figure 8 Typical droplet size distribution from experimental facility system set for producing a twin mode distribution of droplet sizes.

pushed out, large shear forces are generated on and within the volume of the liquid which repeatedly shatter it by overcoming its surface tension and viscosity in a cascade, producing a range of droplet sizes in the emanating spray. Many advantages of the liquid atomization seen in the bombardier beetle, such as high throw ratio, low chamber pressure, and overall energetic efficiency are also seen in the experimental system, despite it being on a much larger scale. The experimental system also expands upon the liquid atomization method by decoupling the exhaust valve from the chamber pressure, allowing more control over an already versatile system.

3. Biomimetic Applications

The experimental facility described here is a classic example of biomimetics where the study of naturally occurring systems inspires novel engineering technologies. There are a number of possible applications. This is primarily due to the wide range of spray characteristics which can be achieved using this novel approach, and because, other than the fuel application, all that is required is water. There are also related energy efficiencies inherent in the system described in this paper, and using water can replace environmentally unfriendly substances currently in use for aerosols and some other spray applications.

A. Fuel Injectors

A very important application is to fuel injectors, and this is one of the potential applications currently being pursued by Swedish Biomimetics 3000® Ltd. The liquid used for this application would be gasoline fuel, but the experiments using water show that the application will still be straightforward. The droplet size distribution in fig. 7 at the lowest end of the range of the system shows why this system is a potential fuel injector technology in that it can produce a fine mist of fuel droplets. Because very small droplet sizes can be produced, this results in droplets with a high surface area to volume ratio. Consequently this droplet size distribution is particularly suited to combustion applications, such as fuel injection, etc., as the larger overall surface area means that the fuel burns much more efficiently. Current fuel injectors primarily work on the principle of pressure atomization, where liquid is atomized by using high pressure to force it through a small opening to create a fine spray.

Generating these high pressures requires a significant amount of energy due to the large pressures used (over 1000 bar) to ensure proper atomization of the liquid. The beetle spray system requires substantially less energy to properly atomize the liquid, as all that is required is to heat the system to a relatively modest temperature.

B. Drug Delivery Systems

Another potential application of the ability to produce small droplet sizes is to the design of next-generation drug delivery systems. For many illnesses, the preferred method of drug delivery is directly to the lungs. This is best achieved using small droplet sizes (typically less than 10 μm) that allow the liquid to travel deep into the lungs, where it can be most rapidly absorbed into the blood stream. The inherent efficacy of inhaled therapeutic drugs makes this a key development area for this invention and could potentially provide a generic drug delivery system, with one unit being capable of delivering a wide range of drugs, or a personalized medicine device, which is built to satisfy a particular patient's unmet medical needs. Current investigations are also being made to address the pharmaceutical industry's need for innovative drug delivery systems for the administration of novel compounds, including, but not limited to, peptides and oligonucleotides. This would be a significant step forward in drug delivery technology. Other potential drug delivery applications of this spray facility include needleless injection and nasal drug delivery.

C. Consumer aerosols

A third possible application is for a consumer aerosol generator, primarily due to its technically advanced performance, but most importantly due to environmental benefits. Standard spray/ aerosol cans, as well as most medical inhalers, generally use volatile organic compounds (VOCs) such as propane and butane to generate the high pressures required to atomize the delivered liquid as it exits the can through the nozzle. Many think that these cause damage to the environment though this is not proven. But whether this is the case or not, the move is away from using VOCs which also have a safety risk at the point of use, as they are highly flammable. The advantage of the spray system described in this paper is that it has the capability of delivering consumer spray aerosols simply using water, and there is no other by-product.

D. Fire Extinguishers and Fire Suppressants

When the device is set for producing the larger range of droplet sizes, this is well suited to a fire-fighting system particularly as it has the ability to fire such a mixture of water and steam into the seat of a fire. Large droplets, maybe 100 μm, are effective at cooling the fire to a level below its reaction temperature, whereas small droplets evaporate very quickly and move oxygen away from the source of the fire – fire suppression. The spray can be made to comprise a distribution spanning these sizes and so having a range of droplets produced by one system would allow fires to be extinguished and suppressed efficiently as the fire progresses. Another significant feature of this system when producing droplets in this range is that it has a very high throw ratio, even for small droplets, and thus targeting is possible. As mentioned previously, the system has achieved a throw distance of up to 4 m under these conditions, which is a throw ratio with respect to the characteristic chamber length of 200. With larger chamber volumes, it is envisaged that an even greater throw distance can be achieved, which would be particularly relevant to fire-fighting applications. One application could then be for an individual firefighter carrying a limited supply of water as a back-pack, to target the seat of the fire in this way.

Recently in December 2017 some of the worst fires in living memory broke out in Southern California. Some of the most dangerous fires ever recorded were in the Santa Barbara area, with 1000 properties destroyed with subsequent mud slides in January 2018, as a direct result of the devastated area not being able to cope with subsequent rainfall. Consequently the need to contain the forest fires early on is essential, and the need to have targeted fire extinguishers is vital. The distinct advantage of the beetle inspired extinguishers is that one can literally shoot from a considerable distance and thus protect the fire-fighter.

MIMICKING THE HYDROGEN PEROXIDE SYSTEM

There are a number of other features not yet copied in the beetle. The sensory mechanism is not yet understood whereby the beetle knows where the attack is coming from without looking at the attacker. Another feature not yet copied is the moveable exhaust turret (the beetle can cause a spray to be directed forward over its head!). Another feature which is currently being considered by the authors is the remarkable chemistry of the beetle whereby it has the ability to make hydrogen peroxide (McIntosh and Prongidis 2010).

Di Giulo, Muzzi, and Romani (2015) in a most useful recent paper have shown the results of intricate dissections with high resolution scanning electron microscope images of the cuticular components of the defensive system of the bombardier beetle, analyzing also the fine structure of the glandular tissues in the defensive system. Shown clearly in their paper are the reservoir and the combustion chamber and the pygidial defensive gland systems which are connected to this defence mechanism. They found that the number of folds of the reservoir varies widely among genera and species. Quoting Di Giulo, Muzzi and Romani (2015) "… the only two openings of the reservoir are: (1) a small entrance opening, represented by the basal part of the collecting duct which fills the reservoir with hydrogen peroxide and hydroquinones; and (2) a wider opening into the reaction chamber which allows the passage of the stored chemicals, when permitted by a complex cuticular valve. The insertion point of the collecting duct is positioned almost in the middle of the tubular reservoir and represents the boundary between two functional parts: the distal part and the basal part. The distal part is shorter and wider, strongly bent downward, and blind ending: this represents the storage compartment. The basal part is longer and narrower, ending at the valve, and represents the more active dynamic compartment…"

These findings show that far from the inlet valve being simple, it is becoming evident that this itself has many parts, all of which work in harmony as another example of irreducible complexity. It has yet to be understood how the chemical system of the beetle produces hydrogen peroxide, but all the investigations, by a number of research groups, indicate that along with the mechanical systems already described, the chemical system is again an example of irreducible complexity. The formation of peroxides and quinones requires very specific chemical pathways to construct vital yet unstable intermediates.

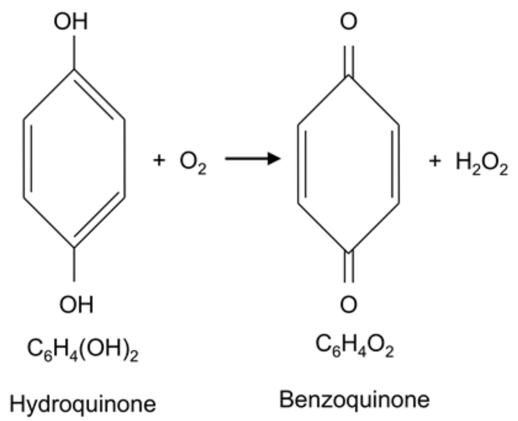

Figure 9 Oxidation of hydroquinone, which may be instrumental in producing hydrogen peroxide in the bombardier beetle.

One possible chemical route is that the beetle makes within itself a starting compound made of a quinol. This is prevalent in beetles as it is quinol compounds (e.g. anthraquinol $C_{14}H_{10}O_2$) and phenols (with only one hydroxyl attached to a carbon ring) which produce the variety of smells which play such an important part to insect existence. In this case we know that hydroquinone is involved, and it is suggested that the oxidation of the hydroquinone $C_6H_6O_2$ is taking place in the reservoir. Fig. 9 shows this diagrammatically in terms of a carbon ring diagram. This will be a slow reaction and in the absence of catalysts such as catalase and peroxidase, then the reverse reaction (whereby the hydrogen peroxide recombines with the hydroquinone to produce benzoquinone and water – that which takes place in the reaction chamber) is _not_ taking place in the reservoir or the connections to the reaction chamber. Di Giulo, Muzzi and Romani (2015) agree with McIntosh and Prongidis (2010) that the thin tube called the collecting duct or efferent duct (Eisner et al. 2001) is of a constant very small diameter (of the order of between 5-10 µm) but exceedingly long – possibly as long as 2×10^4 µm (2 cms). Such a thin tube may have its own catalyst to enable this oxidation reaction to occur.

POSSIBLE APPLICATION TO HYDROGEN PEROXIDE PRODUCTION

One of the main uses of hydrogen peroxide is the manufacture of "green" bleaching agents such as perborates and percarbonates for the paper and textile industries. Other significant uses include wastewater treatment, cleaning printed circuit boards, food bleaching with diluted H_2O_2 , cleaning wounds and hospital instruments with very diluted H_2O_2 , activation of land based gas turbines under fuel lean conditions by adding small amounts of H_2O_2 to the aviation fuel (Prongidis et al. 2012) and military uses for combustion.

Most methods of producing H_2O_2 today use a combination of hydrogenation and dehydrogenation reactions. It is a batch chemical autoxidation process involving two main stages – a hydrogenation reaction of anthroquinone over Ni or Pd catalysts producing anthroquinol, then secondly followed by an oxidiser reaction where the anthroquinol is turned back to anthroquinone and hydrogen peroxide. This method involves considerable energy expended in heating and cooling at each stage and condensing out the peroxide from the water – H_2O_2 mixture at the end of the process whereby the anthroquinone can then be reused for the hydrogenating part of the cycle. Laporte Chemicals first set up these methods in 1959 (Platinum review 1959) and they are now the most common method of production. Other methods are being considered using more direct routes of direct synthesis of hydrogen and oxygen (Samanta 2008) usually still involving a palladium catalyst.

The LaPorte method is costly and needs a considerable outlay in terms of capital expenditure in making the chemical plant as well as the heating and cooling control systems. Consequently the alternative that is used by the bombardier beetle is of considerable interest, since a method for producing a small amount of H_2O_2 could well have a number of advantages and applications, since it has the potential to be cheaper than the current production methods described above.

CONCUDING REMARKS

This paper has considered recent research into the workings of the bombardier beetle spray system. The workings display repeatedly both in the mechanics of the defence spray system and also in the chemistry, that irreducible complexity is involved in setting up interlocking systems – that is these systems will not work unless all the sub-systems involved are working in harmony together. This is particularly evident in the intricate twin valve system of the beetle, and the catalytic chemistry such that at exactly the right moment, the heating takes place in the combustion chamber prior to the exhaust system which, along with the moveable turret, is again an example of irreducible complexity. The inference of design is inescapable.

The investigation has also shown that this is a classic example of biomimetics and already the valve system is being copied in order to produce controllable spray systems for use in fuel injectors, drug delivery systems, consumer aerosols and fire extinguishers. Work is proceeding on seeking to understand the method by which the beetle makes small amounts of hydrogen peroxide. Such a valuable insight into the chemistry has major applications to many household and military uses for H_2O_2.

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