

## **Transcript of inaugural lecture by Prof Sanette Marx**

Date: 24 February 2022

Place: Crista Galli Venue

### **Slide 1**

I would like to dedicate this inaugural lecture to my husband, friend and soul mate, Riaan Marx without whose love and support none of what I am about to present to you would have been possible. Rest in peace my love.

### **Title slide**

The title of my lecture this evening is: Turning waste into products: A circular economy. I will try to speak as plainly as possible and hope that my lecture will be both informative and enjoyable to all. Let us start with some explanations of the words used in the title.

### **Slide 3**

The concept of a circular economy is not new. It is only now becoming a buzz word since humanity are forced to face the consequences of our easy lives. So the cycle begins with the input of raw resources, such as water, electricity, coal, crude oil and biomass to the processing industry that produces the edible and non-edible products we use every day. From these processes, waste is generated, and when we use the products, we generate domestic waste. This waste can either be landfilled, causing pollution or it can be re-used and processed to new products while recovering some of the resources, such as water and energy, for recycling back into the circular production system. The idea of course is to make our production processes more effective to reduce waste and re-use waste to maximise recycling. So why is waste suddenly a buzz word, what is the problem?

### **Slide 4**

To understand the problem, we need to understand the fundamental root cause. Many will tell you it is the use of fossil fuels that is causing global warming and all the associated disasters that we are confronted with on the news on a daily basis. They are not wrong, but they are wrong about the cause. It is not so much the use of fossil fuels as the amount of people using fossil fuels. If we take a look at the increase in global population, we see an increase from 1960 from approx. 3 billion to almost 8 billion in 2016. Looking over a longer period of time, we can see that global population as macro organisms is in the exponential growth phase. I refer you to the inaugural lecture of Prof Frans Waanders for conclusive proof of this statement.

If we look at the energy usage per capita, we see that individual person has not used more energy in 2016 than a person in 1960 however. If we look at the use of fossil fuels, we see a huge increase from 1960 to the early seventies when crude oil and fossil-base fuels were cheap. There is a slight decrease due to the first crude oil crisis in the early seventies and thereafter another increase as crude oil again became cheap and the innovation explosion in the 1950 to 1960 (due in a large part by WWII) that increased the use of fossil fuels in production processes. But by the early 80's, there was another crude oil crisis and an awareness of the impact of fossil fuel use started to surface. You can see the effect of this in the rapid decreased in fossil fuels and since around 1994 when the USA, Brazil and the EU switch in a large part to biofuels, fossil fuel use per capita has remain constant.

This all indicates of course as the world population increases, the use of energy and fossil fuels increase. The situation becomes more desperate though when looking at the increase in GHG emissions from organic waste as compared to the increase in global population. What thus tells us is that we as individuals are gradually producing more waste per capita. In fact, a person living in 2020 produced 33% more waste than a person living in 1960. If this trend is allowed to increase without intervention, GHG emissions from waste could be the grain of sand that eventually breaks the proverbial environmental camel's back. And this is why I have dedicated my research in finding an economically feasible way of re-using waste for energy and product applications.

#### **Slide 5**

The terrible effects of untreated organic waste are well known to us all. Every day, we are confronted with sewage and landfill effluent running into dams that supply our basic water needs. The presence of toxic, cancer causing chemicals in our water supply, our rivers and our dams is partly the result of untreated or poorly managed organic waste. You only need to stand next to the Hartbeespoort dam on a clear summer day to smell the pollution in the dam. We thus have an ethical obligation as chemical engineers to not only reduce the generation of organic production waste, but to also to come up with ingenious ways of re-using the waste to supplement natural resources and make them last longer and to preserve this precious plant on which we reside.

#### **Slide 6**

Do not be mistaken that nothing is being done about the global waste problem. There are several alternative to treat organic waste. The most popular is composting, but there is a limit to this since compost heaps also produce methane GHGs and are prone to spontaneous combust due to internal heat exothermic degradation reactions. Many industrial wastes are incinerated, and many informal settlements also incinerate waste to minimise contamination from dumped refuse. Some countries practice excellent landfilling where the methane gas is captured for use in biogas applications and the effluent is captured and treated to prevent soil and water contamination. There is also a huge waste recycling industry that recycle a large part of plastic, metal and paper waste. Unfortunately, of these methods is associated with either secondary air, soil and water pollution, or are too expensive to be widely and commonly practiced.

#### **Slide 7**

So this brings us to my research work over the last 15 years. First in establishing a biomass conversion research group at the North-West University and then building that group into an internationally recognised group for practical experience in hydrothermal liquefaction. Now for those who are unfamiliar with the term, hydrothermal liquefaction, or HTL for short is a process that mimics nature. As nature compresses organic material slowly and over long periods of time, organic matter is converted to coal and crude-oil deposits. Thus, meaning indirectly that where coal and crude oil deposits are found today, millions of years ago there must have been forests with lots of organic material. In the lab, we mimic this process by applying high temperature (280 – 360 °C) and pressure (90 to 150 bar) to organic materials (or what we refer to as biomass). The biggest advantage of this process is that the biomass can be processed wet, and sometimes we even need to add water as solvent during the process.

In this process, the biomass is liquefied into a range of different products, similar to what nature does. The amount of products and their quality depends very much on the quality of the organic feedstock so I am just giving average values here. The first product is a solid product we refer to as hydrochar or bio-coal. The energy value of this product is usually between 25 and 32 MJ/kg. To place that into perspective, some of the coal used by SASOL and ESCOM has an energy value of 16 MJ/kg and lower. The bio-coal can be upgraded to be used as a GreenCoal or it can be upgraded for use as a bio-adsorbent, but more about that later.

The second product is the bio-crude oil that has an energy value of between 29 and 40 MJ/kg. To put that into perspective, crude oil from the Arab countries generally has an energy value of 42-47 MJ/kg. The biocrude oil thus needs to be upgraded to be used as a transportation fuel or to be used in current refineries. Also, biocrude oils on average contain much less sulphur and nitrogen, leading to low emissions when used as bio-based diesel or petrol. And this is its biggest advantage. Biocrude oil usually makes up 10 to 25% of the products.

The third product is a biogas (usually 10 to 22% of the products) and consists mostly of carbon monoxide (CO<sub>2</sub>) and other light hydrocarbon gases such as methane and ethane. This gas can be cleaned to pure CO<sub>2</sub> and since it is generated at a high pressure, it can also be used to generate electricity using biogas compatible turbines.

The last product is the most interesting as we do not find it in nature, and that is the water-rich product that results from the moisture in the feed biomass. This product can make up as high as 60% of the products and contain valuable chemical building blocks such as alkali and alkali earth metals (Ca, Na, Mg, K, P and N) as well as phenolics such as cresols, guaiacol, vanillin and resorcinol, all chemicals used in the resin, hygiene, medical and food industries. Recovery of these valuable chemical building blocks is essential so obtain clean water that can be recycled back into the domestic water supply.

In summary, HTL is a process by which we convert organic materials (biomass) into energy products as well as chemicals to supplement or substitute current fossil-based products. So let me show you how we use this technology to build a waste-based bio-refinery.

## **Slide 8**

So, the first research question we asked ourselves is whether we can replace the water in the HTL process with primary sewage. This would not only minimise industrial use of clean water, but also provide an opportunity to use the HTL process as a means for treating primary sewage.

## **Slide 9**

A bit of pure science for the scientists in the audience. We recently published a paper on some of this work in Biomass and Bioenergy, but basically this is just to show the composition of the feed. Now obviously for safety reasons and due to service delivery protests, we could not get onto Tlokweng municipality's landfill sites to collect samples. We did however manage to get hold of the information on the general composition of the organic waste, which is similar to that in most cities. We use this to "make" our own municipal organic waste mixture to use in the experiments. The primary sewage we collected from the wastewater plant here at Potchefstroom. And this is the chemical composition of the feed we used in all experiments. So when I refer to the organic fraction of municipal solid waste, I mean this synthetic mixture.

## **Slide 9**

As you can see from this figure, there was not much difference in yield for the different products obtained from HTL of the organic waste with sewage. The gas yield looks slightly lower for when sewage is used as solvent, but it falls within the experimental error and thus the difference is not significant. If you look deeper into the analysis and look at the fatty acids present in the crude oil, you also see very little difference between the oil that was obtained using water as solvent in the HTL process and the oil obtained when sewage was used as solvent. In fact, the only difference seems to be that sewage resulted in more unsaturated acids and water in more saturated acids. And as we all know, unsaturated fatty acids is always good!

Looking at the overall comparison between the quality of crude oil and hydrochar obtained using the two solvents, we also see no significant difference. In fact, the only significant difference is seen in the total phenol content of the aqueous product and the overall carbon and nitrogen balance. Now firstly, the higher phenol content in the sewage-based crude aq. product was expected, because our bodies process some fibres while others end up in the sewage line. Since lignin fibre consist of phenols, it is understandable that replacing water with sewage would result in high phenol concentrations. So next when your dietitian tells you to eat more fibre, please comply and help us in collecting more phenols!

The most interesting result from this research was the very high carbon balance closure and lower nitrogen balance closure we obtained. To put this in perspective, the best power plant in the world currently has a carbon efficiency of 42%. The HTL process even with water achieves twice that, but with sewage it is even better. We did not expect the nitrogen balance result as we all know sewage contains urea that should add considerably to the nitrogen content of the products, but we did not see that.

## **Slide 11**

The conclusion from this work was thus that sewage does not have a detrimental effect of product yields and quality, and leads to a better carbon recovery for the process. It does however significantly affects the nitrogen balance and this is something that needs further investigation.

## **Slide 12**

This brings us to the second research question we asked ourselves, and that is if it is possible to upgrade the hydrochar to a coal-like product that can be used in ESCOM's boilers to lower the Power Utility's GHG emissions and improve their output.

## **Slide 13**

Do not get alarms by all the science on this slide. It basically only shows how we upgraded the hydrochar for use in GreenCoal formulations. We washed it with water to remove any water soluble impurities such as condensed salts. Then we activated the hydrochar using a hydrochloric acid solution (basically fancy pool acid) and then washed it again to remove all Chloride salts that might have precipitated in the pore structure. Then we dried it. The discard coal fines were obtained from SASOL's Twistdraai mine in Secunda.

## **Slide 14**

So we made up homogenised pellet mixtures containing different ratios of discard coal fines and hydrochar. And produced hand pressed cylindrical pellets with a diameter and width of 10 mm. Yes, we know industry used 25mm pellets and bigger, but we needed to fit the pellets into the Bayonette reactor setup to test its emissions. The important things to note here is that we added no  $K_2CO_3$  catalysts to the pellet mixtures, neither did we add a binder or used a wax coating to protect the pellets against moisture. Impact tests and water stability tests (not shown here) proofed the pellets to be robust in terms of not breaking apart easily on conveyer belts nor dissolving in wet weather. The pellets were cured (as is normal for any coal pellet) before used to test emissions.

#### **Slide 15**

So this figure shows the quality of the GreenCoal pellets on a Van Krevelen plot. You can see how well the GreenCoal pellets compare with other coal products in terms of its hydrogen to carbon and oxygen to carbon atomic ratios. The pellets obtained from using waste-based hydrochar were close in fuel properties to sub-bituminous coal that is mostly used for electricity generation in coal-fired power plants. The difference between the sub-bituminous coal and our GreenCoal is that the GreenCoal had a carbon content of approx. 56% carbon compared to that of sub-bituminous coal of on average 45%. Furthermore, the calorific value of the GreenCoal pellets were between 21 and 24 MJ/kg while that of sub-bituminous coal is between 19 and 26 MJ/kg. We could not determine the tendency of the GreenCoal pellets to coke and swell though.

#### **Slide 16**

The combustion emissions results were not quite as exciting as we had hoped for. We tested the emissions by combusting the GreenCoal pellets in a Bayonette-type reactor and measuring the emissions. As you can see, the nitrogen emissions are higher with an increase in hydrochar in pellet, and an advantage in lower sulphur emissions (6 times lower) is only gained at hydrochar ratios of 60% and higher. We could not measure particulate emissions, but calculations based on the proximate and elemental analysis showed a 60% reduction in particulate emissions for pellets containing only hydrochar.

#### **Slide 17**

Our research question had thus been answered, although the answer was not quite as we had hoped. We did manage to show that a stable, economically feasible pellet can be produced that reduces  $SO_x$  and particulate matter emissions when combusted.

#### **Slide 18**

The third question we asked ourselves is whether the hydrochar product can be upgraded to be used as an affordable bio-waste adsorbent. Adsorbents are like the activated carbon in some water filters you can buy from Pick & Pay that filters bad taste and contaminants from your water so it is safe to drink.

#### **Slide 19**

Since we are working on a bio-refinery concept, we decided to target the aqueous product from our HTL reactor as the wastewater stream to clean. The WHO limit for phenolics in safe drinking water is 0.001 mg/L and as you can see from the table, all concentration of all the phenolics in the water were higher than the limit. We thus need to purify this stream if we want to recover the water for

domestic consumption. Also, we wanted to see if it is possible to recover the phenolic components and AAEM from the hydrochar adsorbent once the water has been cleaned. The phenolic components were quantified by HPLC and the minerals were quantified by ICP-OES. The components of interest are vanillyl alcohol, that is used to produce guaiacol and synthetic vanilla, catechol, that is used in modern photography, phenol, which used in the production of Nylon and other material fibres, guaiacol which is used in the production of dental sedatives, resorcinol which is used in many beauty products, vanillin which is used to produce vanilla extract (the nice one from Woollies) and 4-Nitrophenol that is used to dye leather goods. I only listed the 4 metals present in the highest concentration in the aqueous product.

#### **Slide 20**

The first thing we needed to do, was to determine what the best way is to chemically activate the hydrochar. This is necessary to create active points on the surface of the char to which the components we wish to remove from the water would “stick”. From the figure, you can see that the HCL was lost the most carbon, which might be an indication that some phenolics were washed from the char during the activation process, which is a good thing! Also, the HHV of the hydrochar activated with HCL was the highest, although the difference was not significant. If we remove the large carbon bars from the graph, we can more clearly see that HCL also washed the most minerals from the hydrochar, which is of course the whole point of the chemical activation step. So we were happy with that.

#### **Slide 21**

After activation and preparation of the hydrochar, we tested its efficiency in removing the phenolic components from the aqueous product. And this is what is shown on this figure. As you can see, after 20 hours, we could remove 90% of most of the phenolics and more than 50% of vanillyl alcohol, guaiacol and resorcinol. We have also shown in another study that we can convert the guaiacol in-situ to vanillyl alcohol and enzymatically convert vanillyl alcohol to vanillin. I did not show those results here, because there is not enough time to show the results from all studies. Since vanillin is removed completely, it would theoretically be possible to completely remove all phenolic components.

#### **Slide 22**

This figure shows the adsorption of minerals and heavy metals present in the aqueous product. As you can see, most of the trace metals could be completely removed and K was the only metals with a removal efficiency lower than 50%. This was mostly due to the fact that K was present in the highest concentration.

#### **Slide 23**

This is just a comparison of components present in the aqueous product before and after adsorption treatment. I did not show the modelling, but anyone interested in how we modelled the data to obtain adsorption capacities using Henry's law for the metals and Freundlich for the phenolics are welcome to contact me afterwards. The high removal efficiencies (> 50%) and high adsorption capacities obtained indicated that it is possible to use hydrochar to completely remove low concentrations of phenolics and metals from the aqueous product to purify the water for recycling

into the domestic water supply. You can also see the actual % of each component recovered from the hydrochar for recycle back into the resource supply side of the circular economy model.

#### **Slide 24**

From this project we could proof that we can recover most of the phenolics from the aqueous product for recycle and re-use.

#### **Slide 25**

Leaving behind the hydrochar and aqueous products we are now going to look at what can be done with the biocrude oil. Specifically, we wanted to know what happens to the phenolic component in the oil product and if it is possible to upgrade the biocrude oil to a biodiesel that can be used in diesel trucks and farm vehicles to reduce the huge carbon footprint of fossil fuels in the agricultural sector.

#### **Slide 26**

This slide is just to show the experimental methodology of producing enzymatic biodiesel in the laboratory. The biocrude oil from the HTL of the MSW was recovered from the reaction mixture and filtered and dried to produce the oil you see here. To this we added lipase enzymes, Lipase enzymes are also found in laundry detergents (vanish). We determined the amount of fatty acids present in the biocrude oil through GC-MS analysis and then added methanol in different ratios according to the amount of FA present. We also looked at different reaction temperatures where the lipase is active as well as the total reaction time. After the reaction was completed, the lipase catalyst was recovered by filtration for re-use and the crude biodiesel was recovered from the glycerine using diethyl ether. The diethyl ether was then removed by vacuum distillation to obtain the final biodiesel product. The conversion of FA to biodiesel as well as the amount of FAMES present in the biodiesel product was determined using NMR spectroscopy.

#### **Slide 27**

As you can see from the results, the reaction time, temperature and methanol to oil ratio and almost no effect on the overall FAME content in the biodiesel with the highest yield obtained being 95.8%. The SANS 1935 standard for biodiesel demands a FAME content of 96.5%. Since the biodiesel as tested here have not been filtered or scrubbed yet as is the norm in commercial biodiesel production, getting to the required 96.5% would be relatively easy. The important thing to take away from these results is the fact that a stoichiometric ratio of methanol is good enough with enzymatic transesterification (I promise that is the last big word tonight!) to achieve a high FAME content. This is in contrast to traditional biodiesel production that struggles to get to 90% FAME content with a 1:6 ratio (excess methanol).

#### **Slide 28**

One of the biggest disadvantages of using lipase catalyst for biodiesel production is the high cost of enzymes. You can certainly feel it on your budget when you need to replenish your Vanish supply. To counter the high cost of the enzymes, we investigated the possibility of re-activating the enzymes using different solvents. The solvents were chosen based in their polarity and reports from literature. Most solvents performed well, except for DMSO. Acetone was the cheapest from the solvents used and thus we chose Acetone as the targeted solvent to regenerate the lipase catalyst.

## **Slide 29**

And here you can see the result of regeneration. After 4 cycles of regeneration and reaction, the FAME content was still above 80%, meaning that we can use the same enzyme up to 4 times before the conversion drops too low. Obviously there is still much work to be done here, but the basic concept had been proven. The biggest advantage of this biodiesel production method is that a) we can recover the enzyme and 2) we need much less methanol for complete reactions. This translates to a safer overall process and a considerable reduction in the downstream purification of the glycerine product. For every 1 kg of biodiesel produced, approximately 100 mL of glycerol is formed. You will shortly see why it was so important for us that we have a relatively clean glycerine product.

## **Slide 30**

So this research question we could answer positively, because we showed that we can produce high quality biodiesel with the added advantage of a relatively clean glycerine product.

## **Slide 31**

The 5<sup>th</sup> research question we asked ourselves was whether we can use the glycerine from the biodiesel production as a base to produce biodegradable polyurethane foam. Polyurethane foam is used mostly as insulation material, for example the pink stuff that we put in our ceilings to have cooler homes in summer and warmer homes in winter.

## **Slide 32**

Some of this work has been published and here is just a reference to that article. This is a sciencey slide showing the composition of the technical lignin we obtained. The Kraft lignin was bought from Sigma Aldrich, the lignosulphonate we obtained from the pulp and paper industry and the Organosolv lignin we extracted ourselves from sugarcane bagasse. Now lignin is like the glue that sticks vegetables together. It is the polymer in plant material that gives it strength. During the pulp and sugar making processes, the sugar polymers in sugarcane and wood are converted to paper and table sugar and lignin is usually left over as a waste product.

## **Slide 33**

We took the glycerine left over from the biodiesel production and used it as a solvent together with ethanol to liquefy the lignin into a polyol (a polyol is like a syrup that is used to produce polymers and resins).

## **Slide 34**

Of course, we had to “look” at the polyol to make sure of where the hydroxyl groups that will react to form the polymer foam are. And that is really all you need to know about this slide. The more important information is this, which shows the total hydroxyl content of the polyols and the ratio between primary and secondary hydroxyl groups. This is important because it affects how well the polymer is formed.

## **Slide 35**

Another publication from this work. Here you can see the composition of the formulations we used to produce polyurethane foam. And here are the final products from each lignin. Looking at the

colour of the blocks, maybe we should go with Think Brown instead of ThinkPink. Most of the produce polyurethane foams met the minimum requirements for polyurethane foam used as insulation material, but there is still a lot of work to be done in this field.

#### **Slide 36**

The overall and most important research question we asked ourselves was if we can put all of this research together to get an economically feasible waste-based biorefinery that uses primary sewage as solvent and the organic fraction of municipal solid waste as carbon source in a circular economy concept.

#### **Slide 37**

So this brings us to the overall objectives of my research career the last 10 years and more. Putting all of what you just saw together into a workable and economically viable waste-based bio-refinery. In terms of the UN Sustainable Development Goals, we are actively working on 6 of the Goals, including Clean Energy and Clean Water and Sanitation.

#### **Slide 38**

So this is our waste-based bio-refinery concept that ties into the circular economy. If we feed the same amount in weight of primary sewage and organic municipal solid waste (based on amount available in South Africa), we can convert it to products at 300 °C and a residence time of 20 minutes. Approximately 18 kton/hr of gas will form which consists mostly of CO<sub>2</sub>. About 14 kton/hr of biocrude oil will form that can be converted to 12 million L of biodiesel/hr. Approximately 28 kton/hr of hydrochar will be formed of which a portion is used to produce 32 kton/hr of GreenCoal while the rest is used to clean the 113 kton/hr of aqueous product and recover the phenolic components, organic acids and sugars present. From the biodiesel production process, we get approximately 1 million L of glycerine that can be used to produce 2 kton/hr of polyurethane foam. And this is just to show the connection between the different research questions and the bio-refinery.

#### **Slide 39**

If we add up the monetary value (based on a first Level economic analysis) we can see that the value of the products from HTL amounts to approximately \$1 million/day. The electricity is enough to run the entire plant off the grid, making the overall process economically viable.

#### **Slide 40**

These are some of the reference I used for some of the statement I made in this presentation.

#### **Slide 41**

And here are my contact details.

#### **Slide 42**

Now of course, none of this would be possible with many students that worked on different projects under my guidance as well as some colleagues from whom I learned research principles during my PhD study and during the time I built my research group. Also, specifically thank you to Gideon and Rene who were and am my laboratory managers and without whom no results would have seen the

light. Thank you from the bottom of my heart. To my PhD promotors, Prof Ray Everson, Prof Hein Neomagus, thank you for your patience in teaching me the true basics of research and being researchers to which I could look up to. I hope that I have made you proud of the researcher I have become.

#### **Slide 43**

These are the people closest to me who have always supported me. Who carried me when I was too tired, yelled at me when I was lazy and have been the best family anyone can be blessed with. All I can say is thank you and I love you. Soli Deo Gloria!