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Chemical Product Design In a Sustainable Environment

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From 2050 EU countries have decided to be climate neutral i.e. live by an economy with net-zero greenhouse gas emissions, which means that the EU countries shall abandon all fossil carbon raw materials from production of chemicals and generation of power. Many countries outside EU have similar agendas and this change will affect all previously given ways for production of commodities like polymers, pharmaceuticals and fuels and change the way other non-carbon products like e.g. cement in the chemical industry are produced. Traditionally chemical engineers have been trained in process technologies producing commodities like fuel, ammonia, polymers from crude oil and natural gas and e.g. cement using oil and gas as fuels for the kilns, following a mature protocol, where invention has been replaced with optimisation and efficiency.
If, however, future commodities after 2050 can no longer be made by using fossil basic materials a new paradigm must be followed, where commodities are made from generic processes in unit operations designed for specific processes with a new type of basic materials and will no longer follow purpose directed processes in purpose-built machinery.
The future life of the chemical engineer is changed due to a shift in raw material to more sustainable materials and in doing that the procedure of Chemical Product Design could be applied. In this work it is exemplified how this change can be affected in a rational way and shown with some practical examples e.g. how to make future fibres for textiles based on biomass derived raw materials. This simple analysis shows that in the future a replacement for the abundant polymer PET can be poly-lactate (PLA)
In the future of chemical engineering things might change radically in one particular way: Chemical product design as well as process design have focused on optimizing security in manufacturing and in this respect preferentially on the use of non-toxic basic material as well as economy. In the future sustainability will probably be the main parameter to optimize including safety, use of non-toxic materials and less attention will be paid on the economy, albeit, this will still be important.

1. Introduction

Chemical process industries are facing a disruptive change in their conceptual foundation. From 2050 the EU commission has decided to abandon all fossil carbon raw materials from production of chemicals and generation of power in order to invoke a climate neutral economy in Europe (Long term strategy brochure EU 2050). More countries have similar agendas and if this change come into effect globally it will affect all previously given ways for production of commodities like polymers, pharmaceuticals and fuels and change the way other non-carbon products in the chemical industry are produced. The concept of Chemical Product Design (CPD) has been defined to establish a foundation in the way chemical engineers are educated and work. Traditionally chemical engineers have been trained in process technologies producing commodities like fuel, ammonia, and polymers from crude oil and natural gas and e.g. cement using oil and gas as fuels for the kilns in effect following a mature protocol, where invention has been replaced by optimisation and efficiency.
This will change after 2050 if the directive of EU commission shall be the future norm. In the future, chemical engineers must develop a whole new concept of production to a shift in raw material that comply with a higher degree of sustainability and to implement that new guidelines for production are needed. One way is to apply the procedure of Chemical Product Design (CPD) (Cussler, 2006), which is based on the work done by several authors to give directions for future chemists to find optimal designs for both commodities and specialty

chemicals made with other raw materials than fossil carbon sources. This paper describes situations focusing on biomass generally and a number of cases where the principle might be used.
The procedure applied in CPD is based on four concepts (Cussler, 2006) and has been borrowed from other sectors of the whole manufacturing chain in industry like sales and management and production planning.

1. Need - what are the need to be fulfilled by the future chemical production?
2. Ideas- In what different ways can the product be made in order to fulfil the needs?
3. Selection- what ideas are the most promising?
4. Manufacture- How can we make the products in a sustainable and economical way?

In the future of chemical engineering things might change radically in one way. Chemical product design as well as process design have focused on optimizing security in manufacturing and in this respect preferentially on the use of non-toxic basic material as well as economy. In the future sustainability will probably be the main parameter to optimize including safety, use of non-toxic materials and less attention will be paid on the economy, albeit, this will still be important.

2. How can we implement Chemical Product Design (CPD) in a green translation?

Imagine making a textile fibre, a solvent for paints, a house or a polymer for a casing of electronics without any CO_2 footprint? These issues have very little in common except for the articulate need of making the products without producing any excess CO_2 or other greenhouse gasses to the atmosphere. When we can no longer use crude, natural gas or coal as raw material we must make precursors for basic commodities from other basic raw materials. In the four cases pointed out the answer can be use of biomass as the basic material.
Biomass is defined as the mass of living biological organisms in each area or ecosystem at a given time. Generally, that encompasses all living organisms, plants, insects, microorganisms, higher organized animals, but in this case, biomass is confined to plants containing ligno-cellulosic material. Now this is in common with the four examples given, that they should be manufactured from a material that leaves no extra CO_2 in the atmosphere, that for their proper design arguments must be made for the need of the products minimizing waste. Then the ideas that will comply with the need are chosen and then the best of these ideas are selected. Finally, decision is made how to make the products in a way compatible with the creed for sustainability both environmentally and economically.

3. The needs

Firstly this treatise is confined to cover cases where the basic requirement of future chemical products are that they should not increase the amount of CO_2 in the atmosphere, but rather help to reduce the already excess amount existing, then for this time the analysis will concentrate on how to create ideas of how this can be done and then the products are selected from a pool of ideas. Secondly, the need is established from a sustainability criteria, where all unnecessary products are excluded from the market e.g. determine what kind of polymers, is needed for our living by setting up requirements of a limited lifetime of products made from polymers in order not to have a situation where undegradable plastic is accumulated in the environment.
Basically, we can list a number of cases, where new products should replace products made from fossil basic material:

- Fuels: Fuels for transport and heating (houses and industry) are presently mainly made from oil, coal and natural gas. An urgent effort is needed to find sustainable CO_2 neutral replacements. This sector alone comprises about 81% of all consumption of basic energy supply and ensuing emission of CO_2 (Statista, 2018).
- Cement and bricks for housing: The most used basic materials for the building industry is still concrete, steel and bricks made from fired ceramics. Concrete alone stand for more than 8% of all CO_2 emissions globally and will have to be either replaced or made in a more sustainable way.
- Many solvents are made from crude oil, gas and coal. Non-toxic, non-fossil solvents for organic material e.g. dissolving polymers used for paints or for making cements or glue can be made from sustainable materials e.g. using the “sugar-platform” as basic material.
- Polymers for casings, food packaging, insolation, soft drink bottles, carrying bags, textiles etc. are all examples of commodities made from mainly non-biodegradable, fossil basic materials. Here again we need to find proper replacements from natural, CO_2 zero-emission sources.

- Large parts of fertilizer nitrogen are made from ammonia, which again has been made by the Haber-Bosch process, where the important reactant hydrogen is made from natural gas. We need to find a proper alternative for this process.

Generally, we can conclude that the most urgent need is to find a replacement for fossil fuel enabling acquisition of sustainable transport fuel, secondly it is urgent to find replacements for building material, that will not emit CO_2, and finally we could substantiate a replacement for polymers for e.g. textiles, where both the CO_2 footprint as well as major environmental problems like microplastic and huge water consumption play a considerable role.

So much for the need at the beginning. Next, ideas are created in the general case complying with the requirement of sustainability for any product produced.

4. Ideas

When the needs are identified, the next step is the generation of new ideas. Alternative way of production must be identified in at systematic and adequate way including both traditional methods and new methods that can ensure a sustainable production. In this section an example is given to illustrate the procedure.

Example: Textiles and apparels

As an example of creating ideas for sustainable chemical production, we can look at the situation for textiles, clothes, apparels, carpets etc. These items have until now predominately been made from synthetic fibres, as a report from the textiles industry shows (Truscott, 2018):
"The source of synthetic fibres and fabrics is the fossil fuel crude oil. It is estimated that 65% of all fibres used in the fashion industry are made from a synthetic material – mainly polyester (meaning for the most part PET (Poly-Ethylene Terephthalate) , but also nylon, acrylic, polypropylene and elastane. Around 98% of all future fibre market growth is expected to be in synthetic fibres, 95% of which is expected to be polyester" (Yang, 2014).
This is evidently not in accord with the sustainability goals of the EU commission in 2050.
Following a trend in production volume up to 2050 from the Market Report, 2018 (Truscott, 2018), the estimated volume of fibres will be a total of 245 mill. tons of fibres of which about between 55% to 70% will be synthetic if the production is not regulated.
Natural fibres for clothing are made of biomass except wool and silk, which is of animal and insects' origin respectively. All in all, natural fibres mainly comprise: Wool, silk, cotton, flax, hemp, bamboo, and rayon, which is a synthetic product made from cellulose, which again is a biomass basic material.
In the textile industry they amount to about 28% of the total production, the rest of fibres is synthetic made from crude oil derivatives.
Now the pertinent question regarding the need for new basic materials is: Can we find natural, renewable basic materials that can replace those of fossil origin? Do we have enough natural renewable materials to replace synthetic materials? The main part of the synthetic fibres are polyesters, like PET (Polyethylene terephthalate) amounting to 71% of all synthetic fibres and thus between 40 to 50 % of all fibres produced presently.
The monomer bis(2-hydroxyethyl) terephthalate can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a by-product (this is also known as a condensation reaction), or by transesterification reaction between ethylene glycol and dimethyl terephthalate (DMT) with methanol as a by-product.
The polymerization process is through a polycondensation reaction of the monomers that is done immediately after esterification/transesterification and with water as the by-product.
A "Green" replacement for fossil PET is already envisaged: Bio-PET e.g. made from bio-ethanol as shown in this diagram (Pang, 2016), where the two monomers from which PET is polymerized: Ethylene glycol (EG) and terephthalic acid (PTA) are made from a fermentation process of a sugar e.g. glucose (Syracusa, 2020).
(Figure 1)

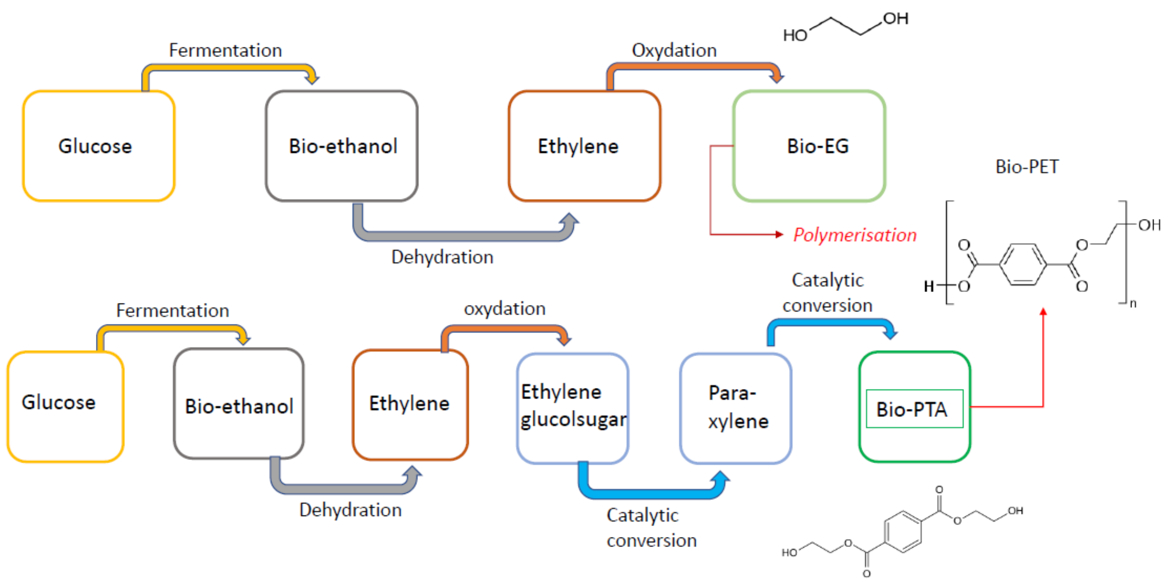

Figure 1: General scheme for Bio-Ethylene-glycol and Bio-PTA (Terephthalic acid) monomers production as monomers for Bio-PET polymerisation with molecular formulas for EG, Bio-PTA and Bio-PET.

The other most produced synthetic fibre is made of polypropylene (PP). The two main sources of propylene are as a by-product from the steam cracking of liquid feedstocks such as naphtha as well as LPGs, and from off-gases produced in fluid catalytic cracking (FCC) units in refineries (Stratton, 1983). However, PP can be made from glycerol with appropriate catalysers (Yu, 2017) as shown in Figure 2 and thus achieve a designation as non-fossil.

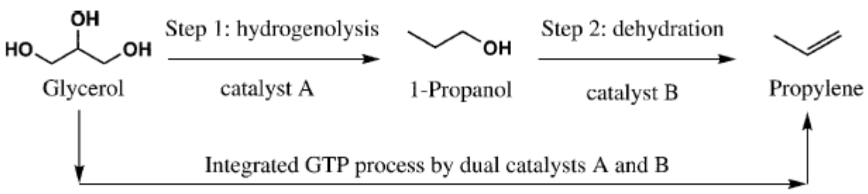

Figure 2: Catalytic conversion of glycerol to propylene

Another interesting alternative is bacterial cellulose (BC) made from food waste by *Acetobacter xylinum* (Römling et.al, 2015).
This microorganism forms a mat of cellulose on the boundary between the aqueous liquid containing the nutrient medium and air (which calls for a rather special fermenter in large productions). The nutrient medium most contain specific nutrients like certain amino acids and salts, but these might be available in many organic wastes. It is known that *K. xylinum* grows well in waste coconut and pineapple juice (Kongruang, 2008) but probably also in whey permeate. In the latter case this will be a voluminous and cheap source of feed. Many other sources originating from waste from food production are possible as stated in (Revin, 2018).
Adding to the list of natural fibres, one must be included, which is polyfuranoates. They are a relative new class of semi-amorphous polymers which can be produced by polycondensation. Polyfuranoates are semi-aromatic, fully transparent thermoplastics that can be easily moulded and thermoformed. A polyfuranoate that has gained a lot of attention and that is currently investigated for commercial use is poly(ethylene-2,5-furanoate) (PEF). (Eerhart, 2012). PEF is one of the most extensively studied biobased thermoplastic polyesters that is truly bio-based and recyclable, however, not biodegradable. It can be considered the furan-based analogue to poly(ethylene terephthalate) (PET) and could replace conventional polyesters in many applications. In fact, it is often considered the next-generation PET.
Perhaps the most appropriate replacement for PET and PP is PLA (Poly-Lactic Acid). PLA is a linear biodegradable aliphatic thermoplastic polyester derived from 100% renewable sources. (Farrington, 2006).
The monomer in PLA is lactic acid, which can be made by direct fermentation of sugars, preferentially hexoses like glucose or galactose. Hexoses can be made from hydrolysed starch originating from maize, wheat or any other seed containing starch. Sucrose from sugar beet or sugar cane are likewise good substrates (Farrington, 2006) and (Avinc, 2009).

According to Farrington properties of PLA are comparable to PET except for a few properties like melting temperature, which is lower for PLA and which might affect the use of a textile especially regarding cleaning and e.g. ironing, where the temperature has to be lower than on PET, but this can be amended by co-weaving the yarn with organic cotton or wool, which will still be renewable.
Collecting ideas in a mind map could look something like Figure 3. In the mind-map the most plausible candidates for a non-fossil raw material and finished fibres have been collected (Koronis, 2013). Included are those fibres that can readily be made into yarns for textiles and apparels and we can proceed to the next step in the CPD protocol: Selection.
So forth the analysis have identified ideas necessary for the CPD procedure. Next, a strategy needs to be found for selecting the candidate, which is the renewable textile fibre that will be leading the textile market in the future. Surely several fibres might find use because of the diversity in customer demand for a given type of clothes, whether we are dealing with work clothes or clothes for a social event of different kinds, but what we now will try to find is the fibre that complies with the many different utilisations where polyesters are used. As described above PET comprise about 40- to 50% of all fibres amounting to between 100 to 125 mill tons annually and the task now is now to find a proper polymer made from a renewable material that can replace polyester.

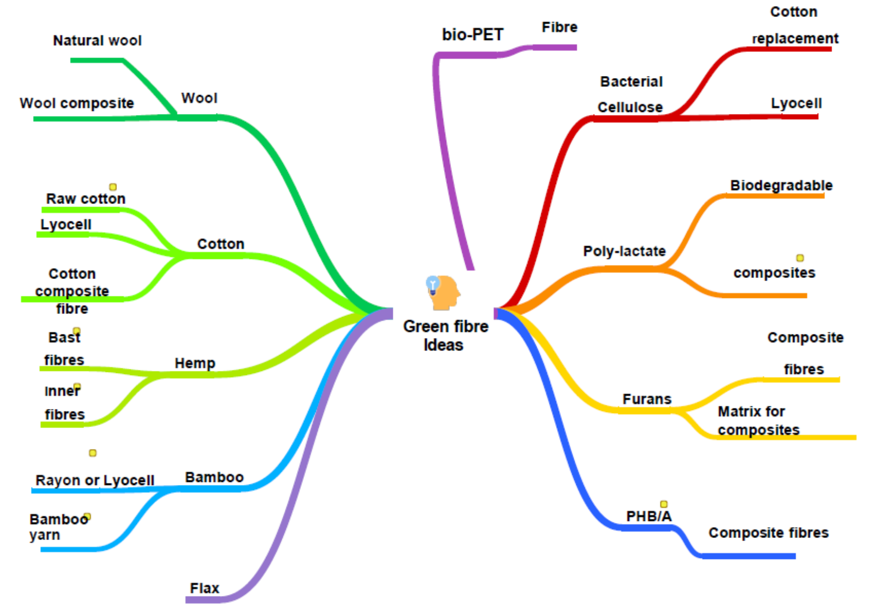

Figure 3: Most plausible green fibres and raw material for green textile fibres.

5. Selection

Selecting an appropriate fibre among the different renewable fibres of a biomass origin requires a judgement on sustainability based on objective criteria e.g. an LCA analysis stating GHG imprint, energy requirement for production and distribution and the choice of materials needed across the value chain of the product.
Another important criterion that must be satisfied is that the fibre can give an experience in clothes made from the fibre comparable to the experience of PET (terylene, dacron etc.), which translate into physical parameters describing PET.
And yet another very important issue must be considered: Environmental compliance i.e. in case of fibres, do they create problems when discarded? A major problem globally created by massive use of synthetic polymers in clothing is refuse from textiles in the form of micro plastic, which is now so abundant that it constitutes an environmental and a health problem.
For a future green textile to be accepted as sustainable in a very strict sense it must be biodegradable. This implies that the collection of ideas needs to encompass materials that are biodegradable besides being non-fossil.
Bio-PET and bio-PP complies with the non-fossil demand, but there is, however, one very important draw-back concerning Bio-PET and bio-PP. They are not biodegradable. The same concerns PEF. Albeit, a very good replacement for PET it is not environmentally compliant but will eventually end up in nature as a microplastic.
This leaves only the original natural polymers: Wool, silk and cotton and PLA as the plausible candidates for replacing PET. In the case of wool and silk they will probably not meet the demand for the necessary production

output, which is as stated above around 125 millions tons of fibres (replacement of synthetic fibres). Today the annual amount of silk comprises 110,000 tons (inserco.org, 2019) and around 1.160 million tons or of clean wool per year from a global herd of over a billion sheep (Intl. wool org., 2017), which shows that the compounded silk and wool production is far behind the requirement for fibres.
Cotton could replace polyester, but cotton have a major problem, when we employ a sustainability parameter to the screening procedure. Growth of cotton plants require enormous amount of water. For each kg of clean cotton yarn on average an amount of 10.5 tons of water is needed (Chapagain, 2006). Cotton is one of the crops that requires the most fertilizer for being economical. The pesticide consumption amount to 4 % of all pesticides globally and the amount of insecticides is about 10% of the global consumption (OTA, 2017). Cotton still occupies around 21% of the world market for textile fibres, but sees increasing competition on economy compared to synthetic fibres especially if cotton has to be grown in a more sustainable way (organic cotton), which means that if the renewable fibres bio-PET, PLA, PEF, or BC in the future can be manufactured at a price around the price of fossil polyester, they should be the fibres of choice for a PET polyester replacement.

6. Conclusion

The conclusion is thus that the best choice for a replacement for synthetic fossil fibres will be fibres made from PLA.
The next step in the Chemical Product Design protocol is to find appropriate specifications for the PLA production and the process according to that, where the raw material will be of organic biomass origin. Suffice it to say in this report that the abundance of raw material, which can in reality be any biomass containing cellulose, is present for that, but an analysis is beyond the scope of this narration.
The protocol used in the example with textile fibres can be extended to cover all future cases where a non-fossil replacement for production of chemical commodities needs to be found.

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