

### 1 - Why does the genetical manipulation to obtain GMO normally involve DNA instead of RNA.

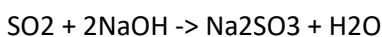
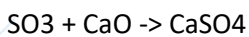
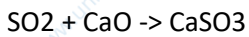
A GMO, or genetically modified organism, is a plant, animal, microorganism, or other organism whose genetic makeup has been modified in a laboratory using genetic engineering or transgenic technology. This creates combinations of plant, animal, bacterial and virus genes that do not occur in nature or through traditional crossbreeding methods. This is a technology that involves inserting DNA into the genome of an organism. To produce a GMO plant, new DNA is transferred into plant cells. Usually, the cells are then grown in tissue culture where they develop into plants. The seeds produced by these plants will inherit the new DNA. The characteristics of all living organisms are determined by their genetic makeup and its interaction with the environment. The genetic makeup of an organism is its genome, which in all plants and animals is made of DNA. The genome contains genes, regions of DNA that usually carry the instructions for making proteins. It is these proteins that give the plant its characteristics. For example, the colour of flowers is determined by genes that carry the instructions for making proteins involved in producing the pigments that colour petals. The DNA contains the genes, while the RNA transcribes the genes into messages that dictate proteins, which in turn determine specific traits in a plant or animal

### 2 - Discuss the term "Renewable Resource" and give an example of its use in energy generation and chemical synthesis.

Renewable resources are defined as resources that can be rapidly regenerated through natural processes. The key word in this definition is "rapidly". Also oil is produced naturally, but the amount of CO<sub>2</sub> released in the atmosphere once burned was fixed by plants and biomass 10<sup>6</sup> years ago. Meaning we are emitting in the atmosphere "new" CO<sub>2</sub> that isn't balanced by the ability of nature to fix it through photosynthesis. Renewable resources produce clean energy, meaning less pollution and greenhouse gas emissions, which contribute to climate change. There are some challenges associated with using renewable resources. For instance, renewable energy can be less reliable than non renewable energy, with seasonal or even daily changes in the amount produced. Renewable resources include biomass energy (ethanol), hydropower, geothermal power, wind energy, solar energy. Solar power arrives from the sun by electromagnetic radiation. It can be used directly for heat and converted to electricity for other uses. It is a nearly unlimited source, it is renewable, and largely, non-polluting. Key concepts in solar energy capture, including direct and diffuse irradiation, collector angles, spacing, tracking and concentration. Hydropower is one of the oldest renewable resources and has been used for thousands of years. With hydropower, the mechanical energy from flowing water is used to generate electricity. Hydroelectric power plants use the flow of rivers and streams to turn a turbine to power a generator, releasing electricity. Geothermal heat comes from the heat generated deep within the Earth's core. Geothermal reservoirs can be found at tectonic plate boundaries near volcanic activity or deep underground. Geothermal energy can be harnessed by drilling wells to pump hot water or steam to a power plant. This energy is then used for heating and electricity. Wind energy generates electricity by turning wind turbines. The wind pushes the turbine's blades, and a generator converts this mechanical energy into electricity. This electricity can supply power to homes and other buildings, and it can even be stored in the power grid. Bioenergy or biomass refers to organic material from plants or animals. This includes wood, sewage, and ethanol (which comes from corn or other plants). Biomass can be used as a source of energy because this organic material has absorbed energy from the Sun. This energy is, in turn, released as heat energy when burned.

### 3 - Why is it so important to reduce the presence of sulfur derivatives in fuels and how are generally removed from them?

Gasoline when burnt releases sulfur oxides and aromatic particulate in the atmosphere. Aromatics being very stable are hard to treat and they are highly toxic. When sulfur oxides are released in the atmosphere they can cause acid rains which lead to corrosion, damages to monuments and are toxic if inhaled. Sulfur can be removed by either using fuels that don't contain it, such as biofuels (sugar plants don't contain sulfur), or by flue gas desulfurization. The method is based on putting SO<sub>2</sub> in contact with an aqueous solution containing limestone Ca(OH)<sub>2</sub> which generates Calcium Sulfite CaSO<sub>3</sub> which is not dangerous and water. The method only needs some water and has a low need of chemicals. All of the products of the reaction can be reused. Also natural oxidation removes S: natural oxygen is injected into the waste gas generating CaSO<sub>3</sub>. The process can also be obtained without water (dry fgd process) through a spray dryer, where lime is sprayed in the waste gas flow generating CaSO<sub>3</sub>. Sulfur can also be removed by Pre-Combustion using H<sub>2</sub> which converts sulfur into H<sub>2</sub>S. SO<sub>x</sub> can be transformed in other non-toxic molecules by using basic additives during combustion. For example



### 4 - Discuss the advantages and drawbacks of hydrogen technologies to produce energy, related to the production, storage, and use.

To separate hydrogen gas from its companion substances takes a lot of effort, but it produces a powerful, nearly clean source of energy. As a gas, it can be used in fuel cells to power engines. Hydrogen gas is extracted from water by a technique known as electrolysis, which involves running a high electric current through water to separate hydrogen and oxygen atoms. The electrolysis process is expensive since it involves high energy expenditure. The energy used to generate electricity in the electrolysis process is harnessed from fossil fuels like oil, natural gas or coal. It can also be tapped from renewable energy sources like solar, wind and hydropower to ensure there are no greenhouse gas emissions.

The advantages of hydrogen energy are:

- It's a renewable energy source and in high supply
- There are numerous sources to produce hydrogen locally
- It's practically a clean energy source
- Hydrogen energy is non-toxic
- The use of hydrogen greatly reduces pollution
- It's far more efficient than other sources of energy
- Used for powering spaceships
- It's a sustainable production system

Disadvantages of hydrogen energy are:

- Hydrogen energy is expensive
- Storage complications
- It's not the safest source of energy
- It's tricky to move around
- It's dependent on fossil fuels
- Hydrogen energy cannot sustain the whole population

**5 - Discuss the advantages of using supercritical fluids toward the typical liquid solvents and why, in your opinion, supercritical water is not a good choice in the extraction of natural organic products.**

A supercritical fluid is a substance at a temperature and pressure above its critical values. Critical temperature is the temperature above which a pure gas cannot be liquefied regardless pressure values. They have properties intermediate between gasses and liquids, which can be controlled by both temperature and pressure.

Supercritical fluids are very useful as they have the following advantages:

- Increased mass transport
- Gases are totally miscible
- No surface tension
- Excellent for infusion
- Inert and non-toxic
- They come from inexpensive fluids
- They are environmentally compatible
- Solvent is tuneable with pressure

Water becomes super critical at higher temperatures and pressures than CO<sub>2</sub>, thus making it harder to reach the right conditions to obtain supercritical water.

When using supercritical fluids for the extraction of products it's key that the SCF and the product have the same polarity. Thus, supercritical water is not a good choice in removing natural organic products because while water is a polar molecule, organic products are usually apolar. A better choice would be supercritical CO<sub>2</sub> which is apolar like organic products and it's also easier to achieve as it becomes supercritical at lower temperatures and pressures compared to water.

**6 - Why does enzymatic catalysis is typically used in the synthesis of molecules with pharmacological activity? Give an example.**

The enzymatic catalysis is used in the synthesis of molecules with pharmacological activity because drugs must be prepared in a living organism. Enzymes are the catalysts used and produced in living systems (not just in humans), they are very specific for the biotransformation that is needed to perform.

Enzymes are used a lot in biotechnology, for example for the biosynthesis of penicillin. Penicillin molecule must be modified often because viruses become resistant to it, for this reason the use of an enzymatic process is fundamental to produce synthetic penicillin. Thanks to enzymes the production of drugs has become greener and we could use it for many reactions like: selective acylation and diacylation, selective hydrolysis, deracemization, kinetic resolution of racemic mixtures, esterification, transesterification, etc.

Enzymes are also used for therapeutic purposes, for example in the treatment of various metabolic disorders and genetic diseases such as DCID, Parkinson, etc. They can also be used in the cure of cancer and infectious diseases.

**7 – What is a bioplastic? Give an example of bioplastic, discussing its production and uses. [Se ti Avanza tempo ho altro negli appunti]**

A plastic material is defines as a bioplastic if it is either biobased, biodegradable, or features both properties. Biobased means that the material or product is (partly) derived from biomass (plants).

Biodegradable means that material or product can be converted into natural substances like CO<sub>2</sub>, H<sub>2</sub>O and others through microorganisms in the environment without the use of artificial additives.

Bioplastics are divided based on their origin:

- Chemically synthesized polymers: PGA, PLA, polyvinyl alcohol, polyethylene oxide, polycaprolactone (although they do not match all of the properties of plastics)
- Starch-based biodegradable plastics: blends of starch and plastic
- Polyhydroxyalkanoates: Similar properties and completely biodegradable (but very expensive)

### 8 - Discuss the use of starch in the production of bioplastics

Bioplastics can be produced by starch. The bioplastic which derives from starch are usually used as single use items such as garbage bags, mulch film, fast food table ware etc. The main advantage of starch-based bags is of course the fact that it's biodegradable, compostable, and degradation leads to CO<sub>2</sub> and water. The issues with the use of starch are the poor adhesion, thus adhesion promoters are required; poor mechanical stability and polyester is more expensive than polyolefin.

Starch and plastic mix bags also exist. These bags are made from the mixture of starch and other polymers (polyethylene-co-acrylic acid, polyethylene-co-vinyl alcohol) to give the bags different characteristics. These mixtures are partially biodegradable, making them better than polyolefin bags which are not decomposable.

### 9- Discuss how polyethylene (PE) can be used in the production of bioplastics?

Polyethylene comes from the hydration of ethanol, thus if it comes from biomass Bio-PE is obtained. If bio-PE is used in combination with starch it can create a bioplastic which is still not completely biodegradable. It is still defined as a bioplastic because it comes from a biological resource as a bioplastic is a plastic which is either biodegradable or it comes from biological resources. The PE and starch blend is used as it gives me the benefits of starch (biodegradable) but also it gives me the mechanical properties of PE. When these mixtures are disposed, we obtain a powder of PE (all of the starch will be decomposed) which is easier to burn.

### 10 - Suggest possible routes to obtain butanol and acetic acid from renewable resources.

Butanol can be created by various bio-feedstocks to generate bio-butanol.

From oil plants and waste oil we obtain triglyceride which through biodiesel synthesis generates glycerol which is then fermented into butanol.

From municipal industrial wastes, agricultural residues, forestry residue we obtain lignocellulose which is transformed to butanol through a process of hydrolysis and fermentation.

From starch and sugary biomass through hydrolysis and then fermentation or a catalytic converter we obtain butanol.

At last, through biomass and renewable electricity, biogas, industrial offgases and atmospheric CO<sub>2</sub> we obtain syngas which is then transformed into butanol through a process of catalytic conversion and syngas fermentation.

**11 - Discuss how lignocellulosic materials can be used as source of renewable energy.**

Biofuel is a mixture of organic compounds derived from biological carbon fixation and whose energy content can be recovered by combustion. Biofuels include fuels derived from biomass conversion, as well as solid biomass, and various biogases. Biofuels include fuels derived from biomass conversion, as well as solid biomass, and various biogases.

Lignocellulosic materials including wood, agricultural, or forestry wastes are a mixture of natural polymers based on lignin, cellulose, and hemicellulose, and tannins. These fall under the group of the so called "Second Generation Biofuels" as they generate fuel from low-value biomass with high levels of cellulose, which humans don't eat leading to lower competition with the food industry, major problem of first-generation biofuels. Fuels obtained from lignocellulosic material have a higher yield compared to first generation fuels, thus generating less waste. Also, since the yield in first generation biofuels is a lot lower, second-generation fuels don't need as much biomass, thus not as much land is needed (less deforestation and lower impacts on biodiversity).

**12 - Discuss the advantages of heterogeneous catalysis vs the homogeneous one, in particular by the green chemistry point of view.**

Catalysis can accelerate a reaction to make a new route viable or an existing process more efficient, as well as promote one reaction over another to reduce waste. Catalysis will play a major role in tackling major issues such as energy consumption and environmental degradation. They can be divided in:

- Heterogeneous: The catalysts are usually solid while the reagents are gases or liquid. An example of heterogeneous catalysts are enzymes. It's key that catalysts must have good affinity to the reagents to promote the reaction, but they shouldn't have affinity to the products, in this way the separation of the catalyst from the final product is possible. The higher the absorption, the more efficient the catalyst. In order to have optimal reactivity it's important that reagents and the catalyst have sufficient contact, to make this possible there must be a uniform distribution of reagent molecules on the surface of the catalyst. This kind of catalysis makes the separation of the catalyst easier, facilitating the reuse of the catalyst. These catalysts produce less waste as it's a continuous process that can be done in several steps.
- Homogeneous: It happens in the same phase as the reagent, the collision between it and the reagent is better than the one which occurs with heterogeneous catalysis. Since reagents and the catalyst are in the same phase, the transfer of heat is more efficient, at the end of the reaction we are going to have to separate the waste produced caused by non-reacting reagents with the catalyst.

Since heterogeneous catalysts produce less waste compared to homogeneous catalysts, they are considered more green.

→ Vedi il confronto nello schema delle slides

*In fase omogenea riesco a massimizzare la reazione. Se sono nella stessa fase posso avere un miglior contatto garantendo anche un miglior trasferimento di calore.*

**13 - Based on the definitions of the 12 principles of green chemistry and the 12 principles of green engineering, answer briefly to the following questions (include examples):**

- Are renewable natural molecules necessarily green?
- How can we be sure to have a green chemical/product?

The 12 principles of green chemistry are:

- Waste Prevention
- High atom economy
- Less hazardous chemical synthesis
- Designing safer chemicals
- Safer solvents and auxiliaries
- Design for energy efficiency
- Use of renewable feedstocks
- Reduce derivatives
- Catalysis
- Design for degradation
- Real time pollution prevention
- Safer chemistry for accident prevention

From this it is clear that a natural molecule isn't necessarily green as the origin of the reagents to create energy or another product doesn't determine the efficiency of the reaction, thus the production of waste. Also, oil and coal are both natural products meaning that they come from ancient organisms that were transformed by natural processes, but still they cannot be considered green sources of energy as the combustion of oil and carbon release in the atmosphere CO<sub>2</sub> that was fixed million of years ago, their reintroduction in the atmosphere means that we are raising the amount of total CO<sub>2</sub> and that the CO<sub>2</sub> emitted in the atmosphere is more than the amount of CO<sub>2</sub> that plants are able to fix through photosynthesis.

Also, nuclear power can't be considered renewable (fission at least). Although it generates a lot of power the nuclear waste it produces is extremely dangerous and toxic for the environment.

So, the most important aspect on which green chemistry focalizes is the efficiency of the reaction, trying to minimize the amount of waste produced. It has no regards towards industrial and economic aspects but focalizes only on the fundamental aspects of chemistry. This means that we should prefer addition reactions to substitution reactions, we should avoid the use of solvents, or we should use environmentally friendly solvents: water or supercritical solvents (in conditions where the liquid has some characteristics of a liquid and some of gases: they provide faster separating speeds); using catalysts; using non toxic reagents; renewable resources; recycled products; improve atom efficiency and e-factor.

For example, we can use Acetic Acid CH<sub>3</sub>COOH as green solvent, obtained through the aerobic fermentation of ethanol (in this case a sustainable process) OR through the oxidation of ethene, depending on the source of ethene this can either be a sustainable or not sustainable method. The overall impact of chemical industry can be reduced by implementing the 12 principles of Green Chemistry.

#### **14 - Discuss the advantages of using biodiesel with respect to traditional petroleum diesel. Why is the combustion of biodiesel much cleaner than that of petroleum one?**

Biodiesel is obtained from fatty acids sourced by vegetable oils or animal fat. The most used liquid fuel is fame obtained from catalyzed trans-esterification of oils with methanol. Biodiesel problem is that to form it we use a hydrolysis process thus all functional groups must be transformed. The partial converted groups are not good as they are undesired components in biodiesel.

The combustion on biodiesel generates lower quantities of particulate compared to fossil fuels. Also the levels of sulfur emitted in the atmosphere are a lot lower thus avoiding all of the problems involved with

NOx emissions. Also, the combustion of bioethanol is a lot cleaner and more efficient, making it greener compared to fossil fuels. Last but certainly not least, biodiesel can be reused, becoming useful for the generation of new biodiesel, thus it can be considered a sustainable resource.

One of the greatest concerns over using biodiesel fuel has been regarding its quality and long-term effects on diesel vehicles. The other major concern is how fueling stations treat biodiesel compared to other fuels. Because it's made using vegetable-based products, it must be stored at the correct temperature. If it's left for too long in a warm storage tank, it can grow mold. Conversely, if it is stored at temperatures that are too cold, it could thicken and become difficult to dispense.

### **15 - What does the genetical manipulation consist of?**

A GMO, or genetically modified organism, is a plant, animal, microorganism, or other organism whose genetic makeup has been modified in a laboratory using genetic engineering or transgenic technology. This creates combinations of plant, animal, bacterial and virus genes that do not occur in nature or through traditional crossbreeding methods. This is a technology that involves inserting DNA into the genome of an organism. To produce a GMO plant, new DNA is transferred into plant cells. Usually, the cells are then grown in tissue culture where they develop into plants. The seeds produced by these plants will inherit the new DNA. The characteristics of all living organisms are determined by their genetic makeup and its interaction with the environment. The genetic makeup of an organism is its genome, which in all plants and animals is made of DNA. The genome contains genes, regions of DNA that usually carry the instructions for making proteins. It is these proteins that give the plant its characteristics. For example, the color of flowers is determined by genes that carry the instructions for making proteins involved in producing the pigments that color petals. The DNA contains the genes, while the RNA transcribes the genes into messages that dictate proteins, which in turn determine specific traits in a plant or animal

### **16 - Discuss why microwave chemistry is an advantageous technology from the green point of view**

Microwave technology is based on the production of microwaves 2,45 GHz that cause the rotation of molecules inside the oven, this movement causes energy and heat. It could be used for enhancing reactions that need higher temperatures starting to heat the mass in a more homogeneous way than the other heating technologies. This technology has the peculiarity of performing reactions with less solvents (or none) and faster, also the use of space is reduced and the energy costs.

Microwaves technology is particularly useful in food processing, drying industry, polymer chemistry, ceramics/materials, plasma, waste remediation, analytical chemistry, biochemistry/pathology, medical.

**[Vedi risposta numero 21]**

### **17 - Discuss what is a biorefinery and how the processing waste can be used to reduce the energy request of the facilities.**

Biorefinery is the use of biomass to produce materials, fuels etc. To do so seed and lignocellulose are used. It is very useful as it valorizes liquid and solid waste. The residues of biomass which are not used to produce chemicals or other products are used to generate energy, typically heat. The most important industry in terms of volume transformed is the paper industry.

The energy produced by biorefinery is always higher than the energy required by the plant, the remaining quantity is sold to the users.

Lignocellulose resources are generally second generation resources, for example sawdust, green waste, grain shells etc.. They are mainly composed by lignin, cellulose and hemicellulose. Cellulose and hemicellulose are particularly important as they are the most abundant polysaccharides. The amount of single constituent depends on the crop from which the lignocellulosic material comes from.

### **18 - Why is starch edible for us, whereas cellulose don't? Draw a simple sketch just to better justify it.**

Both starch and cellulose are polysaccharides made of sugar monomers (glucose) with glycosidic bonds. Their chemical characteristics depend on the position of OH groups. The position of the hydroxyl group respect the plain of the sugar is crucial for determining the capacity of the human body to digest that particular kind of sugar.

If we have an alpha sugar (OH pointing down) the molecule is edible, beta configuration (OH pointing up) it's not edible (at least for humans, certain animals like herbivores can still digest it).

Starch contains amylose and amylopectin, both have alpha configurations bonds making it edible for us; cellulose on the other hand contains only beta bonds that humans enzymes aren't able to transform into energy during digestion.

[Vedi disegno sugli appunti]

### **19 - Discuss the advantages of using zeolites as catalysts by the green chemistry point of view.**

Zeolites are mainly used as catalysts in many reactions. One of their applications is air depuration because they are solid and air could easily pass through them due to their honeycomb structure. They are also used for water treatments for the same reasons. The aspect that makes it really green is that they are completely recyclable once the pollutants have detached from them. Zeolites are heterogenous catalysts which makes them easily separable from the mixture to purify or react.

They are very high efficiency catalysts because of their high surface of reaction (pores) and very stable at high temperature.

They are also used for reactions to produce useful molecules like cyclo-hexanol and cyclohexanone oxime (higher atom efficiency and lower e-factor compared to the traditional method).

In the air pollution field they could be used to transform N<sub>2</sub>O (a greenhouse gas produced in adipic acid production) into N<sub>2</sub>.

### **20 - Discuss the advantages of using supercritical CO<sub>2</sub> in the extraction of natural fragrances**

Supercritical gases are usually used for extracting substances. The most important feature they must have to extract a certain substance is that they both have to be polar or non polar. To extract fragrances it's important to use supercritical fluids that is apolar like CO<sub>2</sub> and thus H<sub>2</sub>O can't be used as it is polar.

A better solution is to use liquid CO<sub>2</sub> at low temperature because it maintains the fragrances from degradation.

Supercritical water at high temperatures and high acidity levels can't be used in the field of extraction.

### 21 - Consider a reaction performed in batch, why are microwaves so efficient in heat transfer if compared to the traditional use of heating coils?

Microwaves are much more efficient because they transfer energy through direct interaction with the molecules, exciting the molecules generating heat directly inside of it. Heating coils on the other hand need direct contact between the hot and cold body to transfer heat (the hot body dissipates heat to warm the cold body). This leads to more efficient heat transfers in microwave technologies.

Since heat is generated directly inside the body we have less dispersion of energy in the environment, specifically microwaves interact with the electromagnetic field generated by the dipole of a molecule (so they are able to interact only with polar molecule). If we use the right frequency we can promote a continuous inversion of the dipole, increasing the vibration of all the molecule. Another benefit of microwaves is that they don't need matter to transfer energy, they can also travel in the void.

A big advantage of microwaves is also the fact that they don't need solvents to perform reactions, this is very useful if we need to transfer heat to the reagents. In this case a solid support is usually utilized, like a zeolite. Not using a solvent and using a catalyst is one of the main principles of green chemistry as it doesn't generate waste.

We can also promote a reaction without the use of a catalyst but only if the heat transferred is enough to overcome the activation energy.

### 22 - In your opinion, although their similar structure, why toluene is considered just as a "problematic" solvent whereas benzene is targeted as "very hazardous"? [Boh non sono sicuro]

Benzene and toluene are used as solvents. Both have similar structures, but benzene was replaced by toluene as it has similar properties but has lower toxicity. When we decide to replace a solvent it is key that the new solvent has at least the same effects on the reaction, for example yield.

A solvent can affect the rate of a reaction, chemo-, regio- and stereoselectivity, the outcome of a reaction, workup of reaction mixtures. When substituting a solvent we must decrease the use of the solvent (the new one must be more efficient!), decrease the toxicity of solvent, move to more sustainable solvent, move to less volatile solvents and move to a biodegradable solvent or at least one that is cheaper to dispose.

Benzene is formed by a ring structure of 6 carbons. All atoms are  $sp^2$  so all of the sigma bonds are on the same plane, thus the electrons are delocalized around the circle. This particular delocalization of electrons make the benzene very stable and a great solvent for apolar compounds thus organic ones too (since they are apolar).

Both molecules are aromatic and have a benzene ring. The main difference between the two molecules is that one of the hydrogens connected to the benzene ring is replaced by a methyl group in toluene. This causes differences in reactivity and use. In fact, the presence of the methyl group makes toluene less reactive than benzene. Toluene is oxidized on the external chain due to the high selectivity towards the methyl group by our blood enzymes. For this reason, compared to benzene, the oxidation produces less problems and is less carcinogenic.

**23 - Discuss building blocks C-6 and their sources.**

A building block is a molecule from which we can obtain more complex and important molecule or precursors of other products. The most used building blocks come from oil refinery but society is trying to move to building blocks that derive from natural resources. The C building blocks come from sugars contained in starch, hemicellulose and cellulose (biomass). These three could be extracted from used residues, agricultural residues and crops. The sugars must be extracted in a biorefinery.

C-6 building blocks are named like this because of the C6 sugars used to produce them (hexose). They come from glucaric acid, furandicarboxylic acid, sorbitol. Glucaric acid, for example, is obtained with one step: nitric acid oxidation of starch or catalytic oxidation of starch with bleach. Its derivatives are lactose solvents and polyglucaric esters-

Most common building blocks:

- C-2 building blocks: ethanol
- C-3 building blocks: glycerol, 3-hydroxypropionic acid
- C-4 building blocks: succinic acid, aspartic acid, 3-hydroxybutyrolactone
- C-5 building blocks: Itaconic acid, Levulinic acid, Glutamic acid, Xylonic acid, Xylitol & Arabinitol, Furfural
- C-6 building blocks: Glucaric acid, FDCA (Furandicarboxylic acid), Sorbitol (potentially useful for polymer industry)

**24 - Discuss the use of CO<sub>2</sub> in the production of biofuel. [Non sono sicuro di aver risposto alla domanda principale]**

A biofuel is a mixture of organic compounds derived from biological carbon fixation and whose energy content can be recovered by combustion. Biofuels include liquid fuels derived from biomass conversion, as well as solid biomass, and various biogases. Biofuels are gaining increased public and scientific attention, driven by factors such as oil price hikes, the need for increased energy security, and concern over greenhouse gas emissions from fossil fuels.

Biofuel burning technically doesn't increase the whole level of CO<sub>2</sub> in the world, the CO<sub>2</sub> absorbed by the crop compensates for the greenhouse gas emissions related to the burning (no increasing greenhouse effect due to the use of biofuel). Such a material is said to be "carbon neutral". In practice the industrial production of agricultural biofuels can result in additional emissions of greenhouse gases (example the production of fertilizers, growing corn process to generate bioethanol consumes fossil fuels in farming equipment, corn transportation, ethanol distillation). Thus the production of biofuels isn't completely green, yes the actual use of biofuels is carbon neutral but the production of these fuels is linked to other processes that require (or at least for now) the use of carbon fossil fuels. Biofuels are still considered a renewable resource as biomass can be replenished readily.

Why we need to use biofuels:

- To face the increase in price of fossil fuels and their reserves decreasing
- To have a wider resource delocalization
- No sulfur content which leads to no problem related to sulfur (and thus the various desulfurization processes)
- Burning them doesn't increase the CO<sub>2</sub> quantity in the atmosphere
- The price of biofuels are stable, price of oil depends on politics, wars etc

The origin of biomass differentiates the biofuel in:

- First generation Biofuels: Related to biomass that can be eaten, thus It can compete with the food industry. Also the yield of the reactions used for the transformation into fuel is very low meaning that there will be a lot of waste which isn't green. Also we need a lot of crop to generate fuel causing deforestation, not a sustainable use of land.
- Secondo generation: From low-value biomass with high levels of cellulose (that we don't eat meaning no competition with the food industry). It has higher yield, making it greener. They also don't have sulfur and all of its problems related to it.

Also third and fourth generation biofuels are being currently tested.

*Parla anche degli energy crops*

**25 - Discuss why, in the recent years, the production of adipic acid has become a "hot topic" by the green and environmental point of view.**

Adipic acid is produced from cyclohexanol. The first step to produce cyclohexanol is the use of typical catalyst (Co or Mn naphthenate). In this step the catalyst is not recovered, generating waste. The second step is carried out with boric acid which again, produces acid wastes.

Adipic acid can also be produced starting from benzene, transformed to cyclohexane, then to cyclohexanone + cyclohexanol. Through HNO<sub>3</sub> oxidation it generates adipic acid

Adipic acid is mainly produced with two methods: [slide 462 per strutture]

- Industrial Nitric Acid Process: Starting from cyclohexane, through the use of O<sub>2</sub> at 8-15 atm and Co and Mn salts at temperatures higher than 125C, KA-oil is obtained with a 4-11% of conversion and 85% selectivity. This first step already shows low sustainability due to the low conversion. The next step is the generation of adipic acid through NH<sub>4</sub>VO<sub>3</sub> and the use of HNO<sub>3</sub> oxidation. The conversion is at 100% while selectivity is at 93-95%. The major concern is the presence of N<sub>2</sub>O as co products. NO<sub>x</sub> are considered one of the major pollutants and are a concern for human health.
- O<sub>3</sub> – UV method : Starting from cyclohexane, through the use of O<sub>3</sub> UV light at 1 atm and room temperature we obtain two isolated intermediates which are then converted to adipic acid. Although the yield is still not at 100% (50-70%) this process doesn't generate co products, resulting in a greener method.

**26 - Why biotransformations are so important in the synthesis of molecules with biological activity?**

**27 - Discuss how the International Community is moving toward the reduction of waste's production.**

Green chemistry is based on trying to maximize efficiency and minimize the amount of waste and energy consumption. The production of waste can be reduced in various ways. In the energetic sector studies are trying to move towards nuclear fusion. It's main advantage is the fact that no waste is produced (or at least in very small quantities) making it more green compared to nuclear fission (the technology currently used). The main problem is that this technology is very hard to perform, the energy required for the use and maintenance of this technology is very high thus the energy produced must be higher. Generally, the main way to not produce waste in the energetic industry is the use of renewable resources. These include:

- Solar Power
- Hydropower
- Geothermal
- Wind Energy
- Bioenergy

All of these resources produce zero waste, if not only when the structures must be disposed. This is the main disadvantage for solar panels for example. The main disadvantage of renewable resources is that they are generally less reliable than non renewable energy, with seasonal or even daily changes in the amount of energy produced. The most used renewable resource is currently hydropower but solar, wind, geothermal and bioenergy are rapidly becoming more used. Bioenergy is a very important solution. Biofuels are produced from biomass waste. Biomass wastes, which include solid waste of agricultural residues (rice straw, wet birch pulp), agroindustrial wastes (mushroom waste, cotton cellulose) and industrial wastewater are abundant feedstock for renewable biohydrogen, biomethane and biochemicals productions etc. This technology of waste to energy and biochemicals includes the pretreatment of biomass, subsequently converted to sugars (hydrolyzate). Sugars are then transformed into biofuels such as hydrogen, methane, ethanol, and the biomaterial building blocks such as volatile fatty acids: Lactic acid, Acetic acid, Propionic acid, and Butyric acid etc. Thus, biofuels don't reduce the amount of waste but they reuse the organic waste already produced making waste an opportunity, as we are able to transform it into higher value products. Biofuel is considered to be a source of renewable energy as biomass can be easily replenished. Another major positive in the use of biofuel is that it doesn't contain sulfur, thus it doesn't need to be treated afterwards.

The EU defines waste as "any substance of object which holders discards or intends or is required to discard". Potentially represents an enormous loss of resources in the form of both materials and energy. Waste can also have environmental impacts. Waste causes the pollution of air, water and soil. The EU directive 2008/98/Ce aims to prevent waste but also to re-use, consequently recovering, and finally disposing. This can be done by reducing or eliminating waste at the source by modifying production processes, promoting the use of nontoxic or less toxic substances, implementing conservation techniques and reusing materials. Pollution prevention approaches include:

- Increasing efficiency in energy use
- Use of environmentally benign fuel resources

In the agricultural sector, pollution prevention approaches include :

- Reduction of water and chemical inputs
- Adoption of less environmentally harmful pesticides
- Protection of sensitive areas.

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## **28 - Discuss the main technologies used to produce paper in modern biorefinery and how the processing waste can be used to reduce the energy request of the facilities.**

Paper is obtained through biorefinery. Biorefinery is the use of biomass to produce materials, fuels etc. To do so seed and lignocellulose are used. It is very useful as it valorizes liquid and solid waste. The residues of

biomass which are not used to produce chemicals or other products are used to generate energy, typically heat. The most important industry in terms of volume transformed is the paper industry.

Considering the energy required, paper manufacturing is the 4<sup>th</sup> industry in the world for energy demand. The problem of paper manufacturing is the need of huge amount of energy and particularly a very huge amount of water, this is why paper plants are usually near lakes or rivers.

The first step in paper manufacturing is preparation of the raw materials. The raw materials is wood that has been received at a pulp mill in different forms as it depends on the pulping process and the origin of the raw materials. It may be received as short logs of round-wood with the bark still attached, as chips about the size of half a dollar that may be produced from sawmill.

The next step is pulping which aims on removing lignin without losing fiber strength, thereby freeing the fibers and removing impurities that cause discoloration and possible future disintegration of the paper. Some pretreatments to separate this component can be done by using:

- Acids
- Bases
- Hydrothermal processes

Pulping can be done in the mechanical way (cheaper) or chemically (expensive). The chemical way is more used. Chemical pulp is done with either sulfate or sulfite. The difference is that the sulfate method needs more energy and it uses strong bases (so basic pH) while the other method works in more mild conditions.

The mechanical properties vary depending on the method used during the pulping phase. If we use the mechanical method we will obtain shorter fibers, meaning higher strength.

After pulping we need to bleach using chlorine or ozone to give the paper the white color.

After bleaching we have some low weight molecules we need to remove with evaporation methods. We obtain a final residue we can also use to burn and produce energy.

### **29 - Considering the actual technologies, can hydrogen be considered a “real” green and sustainable source of energy?**

To separate hydrogen gas from its companion substances takes a lot of effort, but it produces a powerful, nearly clean source of energy. As a gas, it can be used in fuel cells to power engines. Hydrogen gas is extracted from water by a technique known as electrolysis, which involves running a high electric current through water to separate hydrogen and oxygen atoms. The electrolysis process is expensive since it involves high energy expenditure. The energy used to generate electricity in the electrolysis process is harnessed from fossil fuels like oil, natural gas or coal. It can also be tapped from renewable energy sources like solar, wind and hydropower to ensure there are no greenhouse gas emissions.

The advantages of hydrogen energy are:

- It's a renewable energy source and in high supply
- There are numerous sources to produce hydrogen locally
- It's practically a clean energy source
- Hydrogen energy is non-toxic
- The use of hydrogen greatly reduces pollution
- It's far more efficient than other sources of energy

- Used for powering spaceships
- It's a sustainable production system

Disadvantageous of hydrogen energy are:

- Hydrogen energy is expensive
- Storage complications
- It's not the safest source of energy
- It's tricky to move around
- It's dependent on fossil fuels
- Hydrogen energy cannot sustain the whole population

Because of the difficulties in obtaining energy from hydrogen we still can't consider it as a sustainable source of energy, mainly regarding the storage complications and the regards due to safety, stockage and transport. Still it represents a great opportunity for the future as it can be obtained from renewable energy sources (solar, wind, hydro)