Green Chemistry Innovations

Partners’ Content-90 min

If content not delivered, then Green Chemistry Innovations

Prof. Bruce Lipschultz

Towards Ending Our Dependence on Organic Solvents

- Development of surfactants that allow for chemical reactions in ‘nanomicelles’ in water
- Organic molecules are typically insoluble or unreactive in water, hence the need for toxic, flammable, petroleum-derived organic solvents
- Micelles have hydrophilic exteriors and hydrophobic interiors, allowing for encapsulation (and reaction) of organic molecules in aqueous environment
- Using safe, nontoxic, and inexpensive chemicals, 50-100nm micelles can be formed in water that, by increasing effective concentration, also dramatically increase reaction rates without energy input
- Applied to several important C-C bond forming reactions
- Recycling of surfactant is very efficient and purity of water is not very important

BioAmber, Inc.

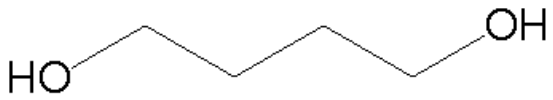
Integrated Production and Downstream Applications of Biobased Succinic Acid

- Development of a biobased route to succinic acid, an important ‘platform’ molecule used to produce many other chemicals and polymers
- Traditionally derived from petroleum
- BioAmber’s process uses an *E. coli* biocatalyst and a water-based purification to produce succinic acid from glucose on a commercially viable scale
- Fermentation in water, neutral pH, with no significant byproducts
- This method for producing succinic acid costs 40% less than the traditional petroleum-based route and consumes 60% less energy

Genomatica

Production of Basic Chemicals from Renewable Feedstocks at Lower Cost

- Development of a microbe-based synthesis of 1,4-butanediol (BDO, right)
- BDO is a precursor for many important chemicals and polymers, such as spandex



- Biobased BDO manufacture uses renewable natural sugars as feedstock, consumes 60% less energy and has a 70% smaller carbon footprint than petroleum-based means of manufacture
- Fermentation process is entirely in water, requires no organic solvents, and is nearly at ambient temperature and pressure
- Cost is projected to be 15-30% less than petroleum-based manufacture

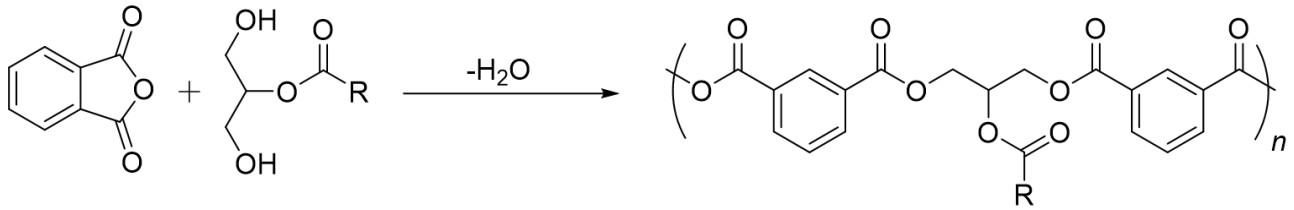
Kraton Performance Polymers, Inc.

for NEXAR™ Polymer Membrane Technology

- Development of novel polymers for use in membrane applications
- Membranes have a variety of applications, such as desalination by reverse-osmosis, water purification, and salt and acid waste recovery
- Effectiveness limited by the pressure that can be applied to the ‘dirty’ side of the membrane: higher pressure means higher flux across membrane
- Thus membrane strength is important for efficient high-pressure applications
- NEXAR™ polymer is strong enough to withstand up to 400 times more water flux than conventional membranes in reverse-osmosis applications, reducing membrane costs by 70% and energy costs by 50%
- Manufacture uses 50% less hydrocarbon solvent and does not require halogenated solvents or auxiliaries

The Sherwin-Williams Company

for Water-based Acrylic Alkyd Technology



alkyd polymer

- Development of water-based acrylic paints with the benefits of conventional oil-based ‘alkyd’ paints but low levels of volatile organic compounds (VOCs)
- Acrylic latex coatings, low-VOC alternatives to solventborne coatings, cannot match them in all aspects of performance
- Sherwin-Williams’ low-VOC, alkyd-acrylic dispersion (LAAD) technology combines beneficial aspects of both acrylic and alkyd paints
- Low-VOC content, low odor, non-yellowing, moisture resistance, high rigidity, hardness, and hydrolytic stability
- Manufactured from PET (plastic bottles) and soybean oil
- Removed 800,000 pounds of VOC solvents in 2010

Dr. James C. Liao

(Easel Biotech., LLC; UCLA)

for Recycling Carbon Dioxide to Biosynthesize Higher Alcohols

- Genetic engineering of microorganisms to produce higher alcohols from renewable feedstocks
- Ethanol is a naturally biosynthesized 2-carbon alcohol used as a fuel additive, but itself has low energy content
- Higher alcohols (3-8 C atoms) are more useful as fuel sources as well as chemical building blocks, but are not produced naturally in the biosphere
- Dr. Lao's group at UCLA has successfully engineered an amino acid metabolic pathway in microorganisms to produce alcohols with 3-8 C atoms from glucose
- They have also successfully transferred this pathway to a photosynthetic microorganism that produces isobutyraldehyde and isobutanol directly from CO_2
- Easel Biotechnologies, LLC is commercializing the process
- Successful commercialization could lead to an 8.3% reduction in total U.S. CO_2 emissions, or 500 million tons of CO_2

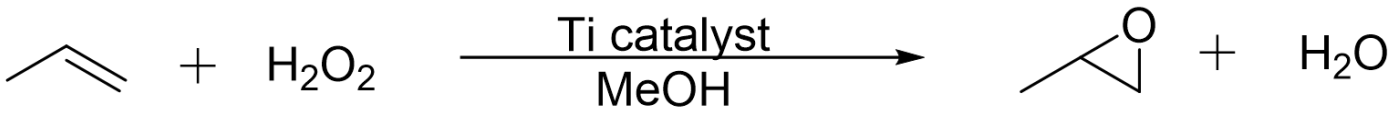
LS9, Inc.

for Microbial Production of Renewable Petroleum™ Fuels and Chemicals

- Development of a platform technology that allows microorganisms to produce final chemical products
- Biobased chemical production typically entails extraction from the microorganisms and purification of intermediates that require further processing
- LS9, Inc. has engineered a process by which the conversion of renewable biomolecules to long hydrocarbons is coupled to a process that converts them to their final product, eliminating the need for purification or further processing steps
- Has been applied to many different chemicals
- Has been tested, at pilot-plant scale, to make a biodiesel that is free from common fuel pollutants such as benzene, sulfur, and heavy metals, and reduces greenhouse gas emissions by 85%

The Dow Chemical Company & BASF

for Innovative, Environmentally Benign Production of Propylene Oxide via Hydrogen Peroxide

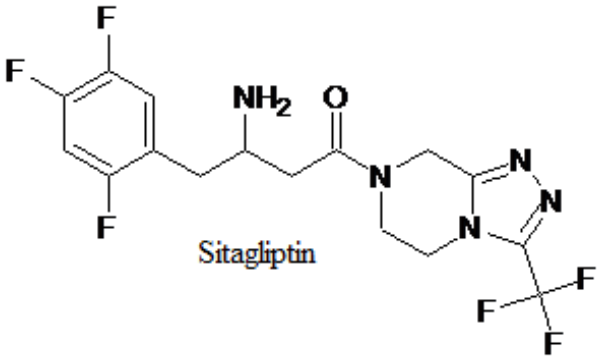


- Development of a hydrogen peroxide mediated process for the production of propylene oxide (PO)
- PO is one of the 30 highest-volume chemicals produced worldwide, production estimated at over 14 billion pounds
- Conventionally production methods entail hazardous starting materials such as organic peroxides or chlorohydrin and form large amounts of byproducts
- Dow and BASF have co-developed a process that uses hydrogen peroxide and a titanium-based catalyst and gives of water as its sole byproduct, with methanol as solvent
- Process uses less peroxide and does not require recycling, collection, or purification equipment, making plants cheaper
- Reduces amount of wastewater 75-80% and energy consumption by 35%

Merck & Co., Inc. and Codexis, Inc.

For Greener Manufacturing of Sitagliptin Enabled by an Evolved Transaminase

- Development of a biocatalytic approach to Sitagliptin
- Sitagliptin is the active ingredient in Januvia™, a type II diabetes treatment
- Previous synthesis was problematic, requiring a recrystallization, specialized mechanical equipment, a high-pressure hydrogenation, and an expensive rhodium catalyst
- Codexis and Merck collaborated to engineer a transaminase enzyme that could be used in an alternative route to circumvent the hydrogenation step
- New process affords 56% greater productivity, 10-13% increase in yield, elimination of all metals and chiral purification, and 19% reduction in waste
- Process (as of 2010) is moving to pilot-scale
- Transaminases are probably a highly versatile and general approach to similar problems in drug manufacture



Sitagliptin

Clarke

for Natular™ Larvicide: Adapting Spinosad for Next-Generation Mosquito Control

- Development of a method to encapsulate spinosad for use in mosquito abatement
- Spinosad is an environmentally safe pesticide but is not stable in water
- Clarke has developed a plaster matrix that can encapsulate the pesticide and release it slowly into water so as to effectively kill mosquito larvae
- This method eliminates the need for organophosphate and other traditional, toxic insecticides, and has been approved for use in organic-certified farming
- 2-10 fold reduction in application rate and 15-fold less toxic than organophosphates

Eco-Leather Corp.

Eco-Leather:

- Made out of natural fibers such as flax or cotton mixed with palm, corn, soybean, and other plant oils that are laminated together in layers to create something that looks and feels as if it came from an animal.

Leather Tanning:

- Uses Chromium (III) Sulfate
- Chromium gets oxidized to Chromium (VI) during the processes
  - Large water pollution, extremely toxic!

http://gizmodo.com/how-leather-is-slowly-killing-the-people-and-places-tha-1572678618

http://www.ecouterre.com/renewable-eco-leather-made-from-plant-oils-is-a-fashion-game-changer/richard-wool-plant-eco-leather-1/

Andalyze

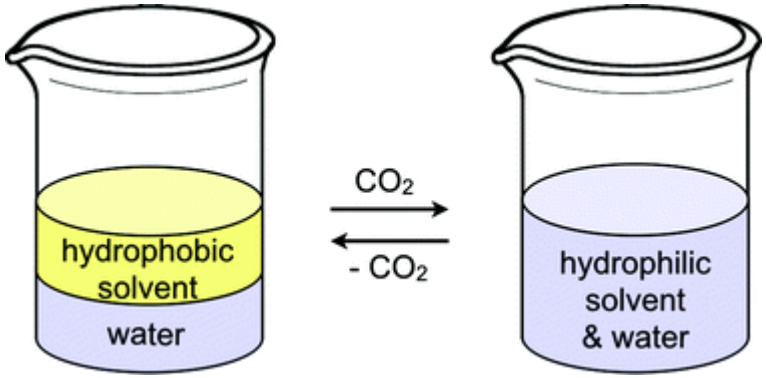
Real time heavy metal detection device

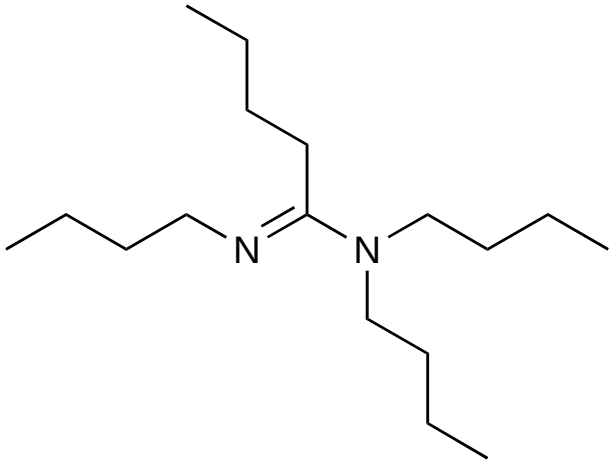
- Developed technology which accurately detects and measures heavy metal concentrations in water in less than 2 minutes
- This greatly reduces cost and complexity of testing water sources for trace metal contamination which had to be done in laboratory setting.

Switchable Solutions Inc.

Solubility characteristics of solvents can be tailored with the addition or removal of CO_2

- Without CO_2, behaves like a low-polarity regular organic solvent
- With CO_2, it turns into a very high polarity compound that is miscible with water!
- Use for:
  - Waste water treatment
  - Asphalt recovery and reuse
  - Polystyrene recycling
  - Purification of solids





N,N,N'-tributylpentanamidine

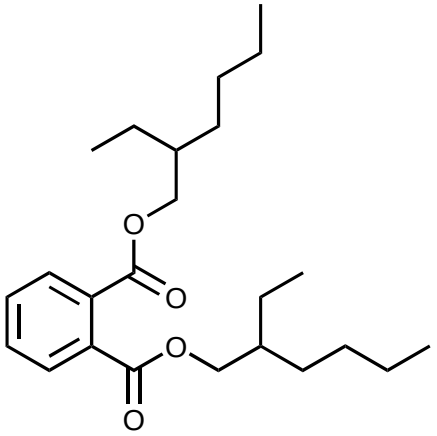
Alternative Plasticizers

The Case for DEHP/DINP

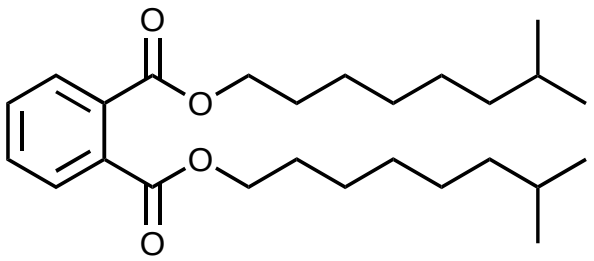
PVC requires plasticizers for its many applications (softer products)

Most widely used plasticizer: phthalates, particularly DiNP (previously DEHP was utilized)

- EU/US – banned DEHP/DINP & 5 others in products intended for children's use (under 3 years old)
- Phthalate exposure linked to liver toxicity, endocrine disruption, and carcinogenicity.



DEHP



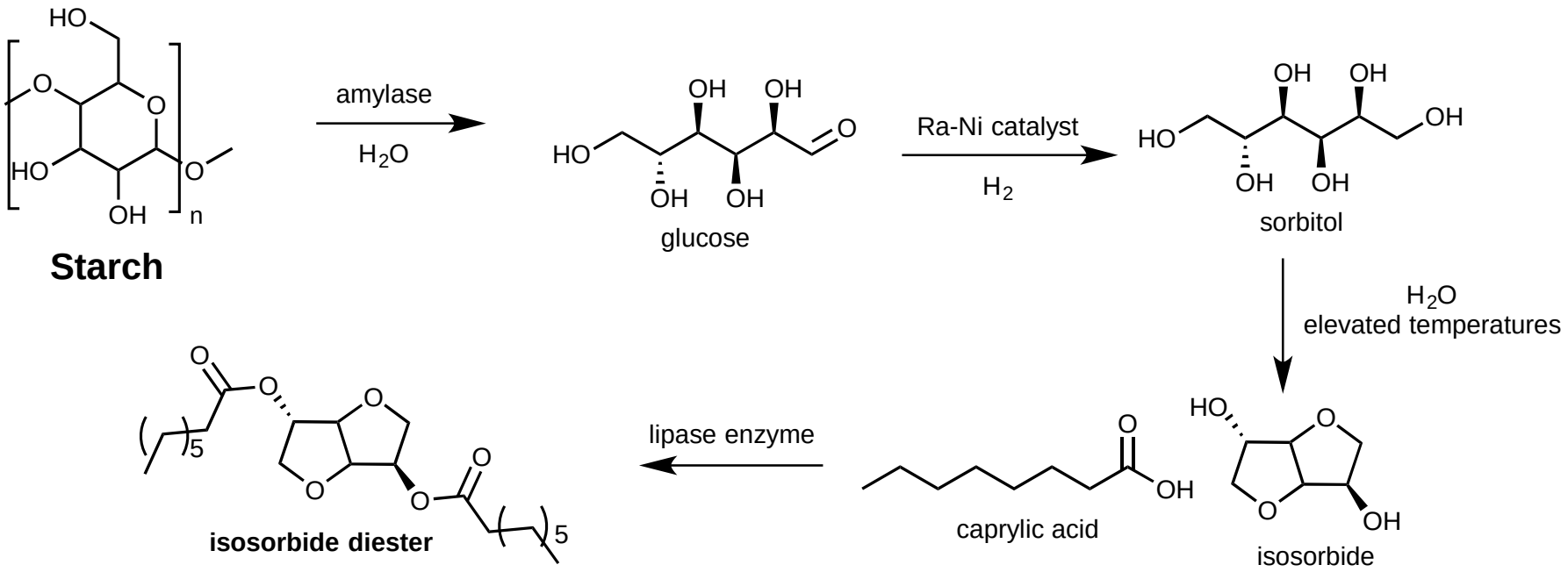
Diisononyl phthalate, DiNP

Alternative Plasticizers

Green Chemistry alternative in PVCs

Isosorbide Diester

- One to one substitution of phthalate additive in PVC
- Thermally stable, biodegradable, biosafe



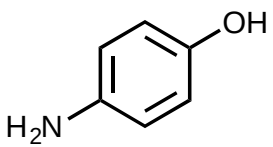
HairPrint – John Warner @ WBI

Usually, hair dying involves bleaching (oxidizing & decomposing natural pigments eumelanin and pheomelanin)

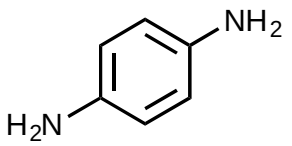
- hydrogen peroxide and ammonia or milder ethanolamine

PPD and para-aminophenol react with the oxidant at high pH to produce the dyes.

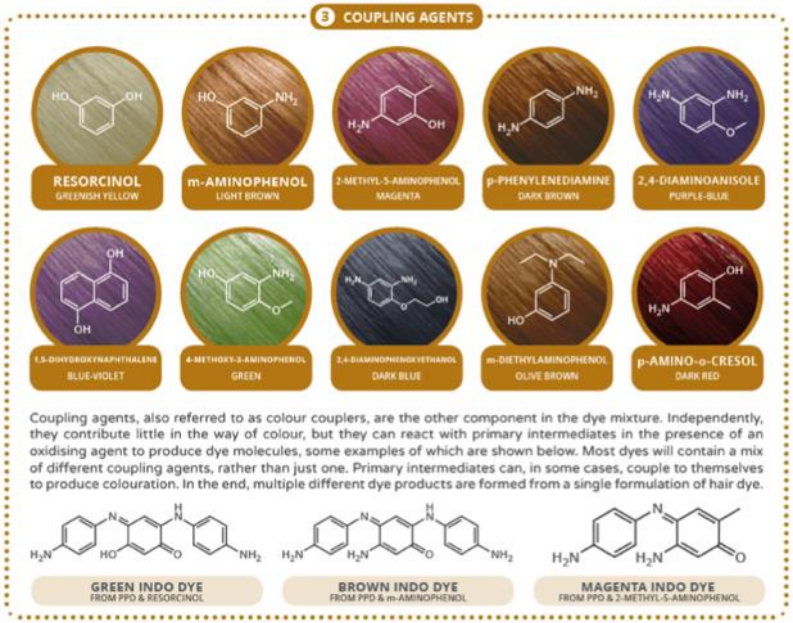
- Alkaline pH also swells the hair cuticle, and makes dye penetration easier.
- Toxins, endocrine disruptors, carcinogens… And not renewable.



paraaminophenol

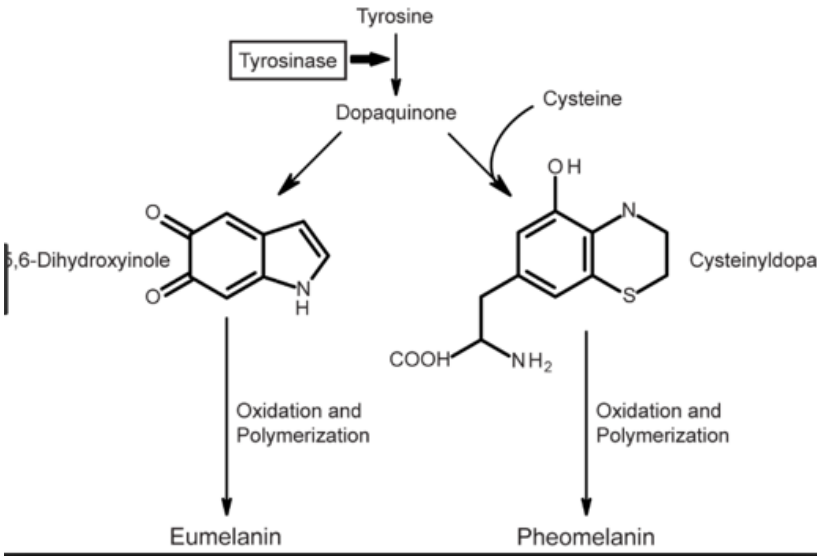


paraphenylenediamine (PPD)



HairPrint – John Warner @ WBI

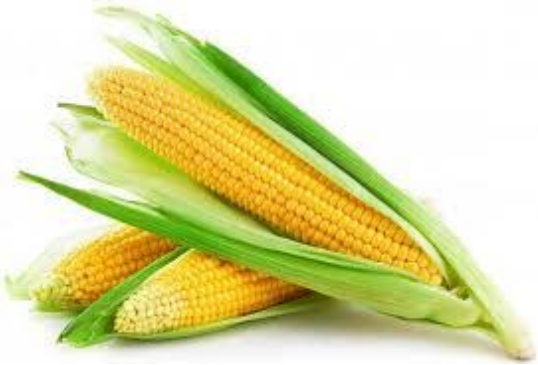
- Color **restoration** (not coloring)
- Mimics how hair gets its color naturally
  - Eumelanin synthesis (for brown and black hair) is the pigment our body synthesized (also responsible for skin tanning and eye iris color).



DOW Agrosciences LLC

for *Instinct® Technology* which makes nitrogen fertilizers work more effectively

- Crop genetics and precision application methods have improved the efficiency of applied nitrogen fertilizers, but losses to the environment are still significant after soil bacteria quickly convert nitrogen from the applied urea or ammoniacal form to nitrate
- In the nitrate form, nitrogen fertilizer is susceptible to losses through leaching or as emissions in the form of nitrous oxide
- This technology reduces fertilizer nitrate leaching to ground and surface waters and atmospheric nitrous oxide emissions
  - Nutrient pollution is one of America's most widespread, costly and challenging environmental problems.
- Retains applied nitrogen longer in the plants' root zone, optimizing crop utilization and yield, and reducing nutrient run-off.



Verdezyne

for *renewable nylon through commercialization of BIOLON™ DDDA*

- The current global demand for dodecanedioic acid (DDDA) is estimated to be 100 million pounds per year. All DDDA currently on the market is produced from fossil-based sources.
- This technology focuses on the production dodecanedioic acid (DDDA) which is used to make nylon.
- It is done by an aerobic fermentation process with genetically engineered *Candida sp.* Yeast and integrated with downstream product isolation and crystallization.

Professor Paul J. Chirik

Princeton University

for *catalysis with earth abundant transition metals*

- Catalyst technology has relied on some of the least abundant elements in the Earth's crust – palladium, platinum, rhodium, and iridium. In addition to their high cost, price volatility, and toxicity, extraction of these elements has significant environmental consequences.
- Alkene hydrosilylation is an example of a metal-catalyzed chemical reaction that is used on an industrial scale in the manufacture of silicones from alkenes and silanes.
- Silicones are found in a range of consumer products including adhesives, household utensils, medical devices, health care products, and low rolling resistance tires.
- Churik's group discovered a new class of hydrosilylation catalysts based on earth-abundant transition metals such as iron and cobalt that have superior performance to existing platinum catalysts.
- This base metal catalyst technology offers the opportunity to enable new chemical processes that provide the desired product exclusively, eliminate distillation steps, and avoid generation of byproducts and unnecessary waste.

Thank you!