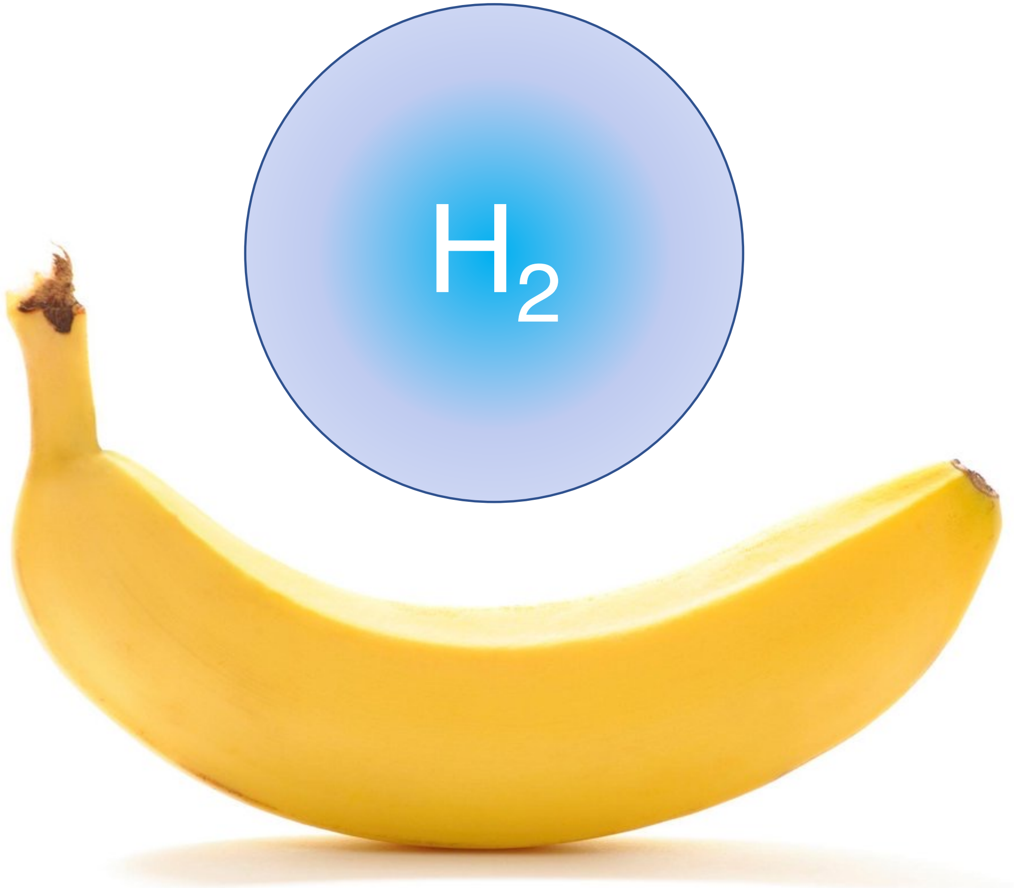
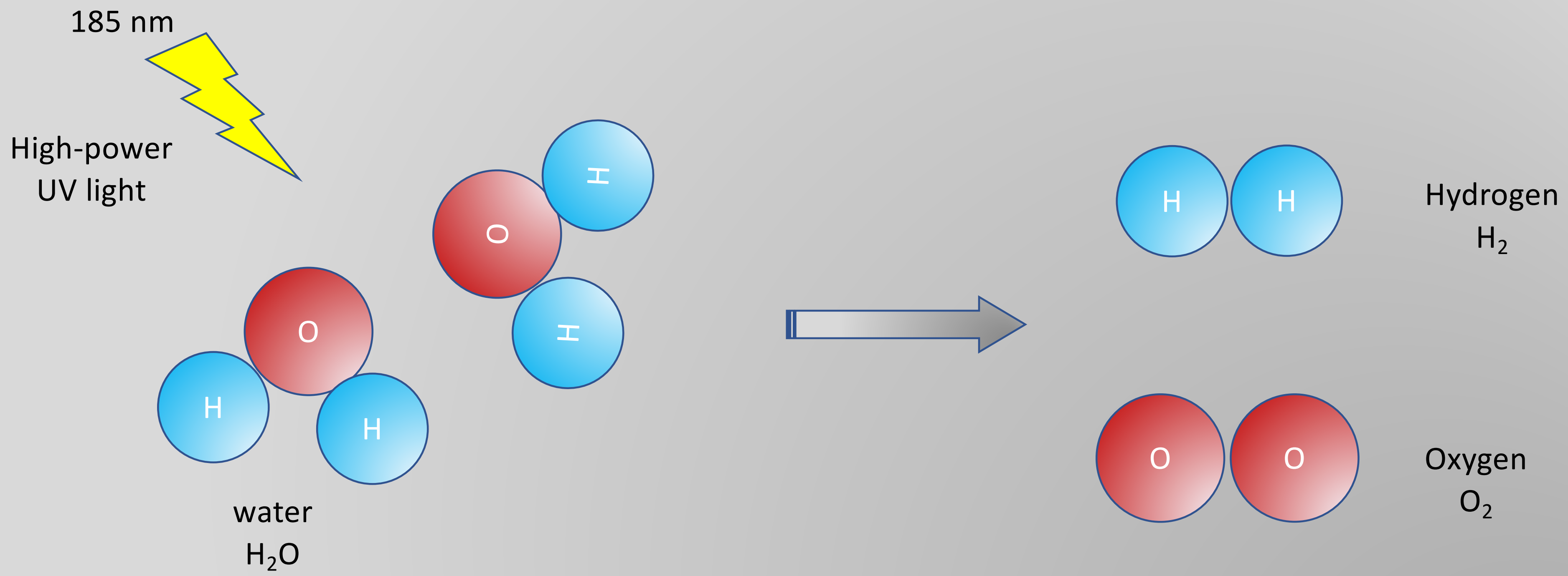

H_2

Photo-pyrolysis of biomass, polymers and hydrocarbon wastes

Photoproduction of hydrogen and solid carbon

Water splitting

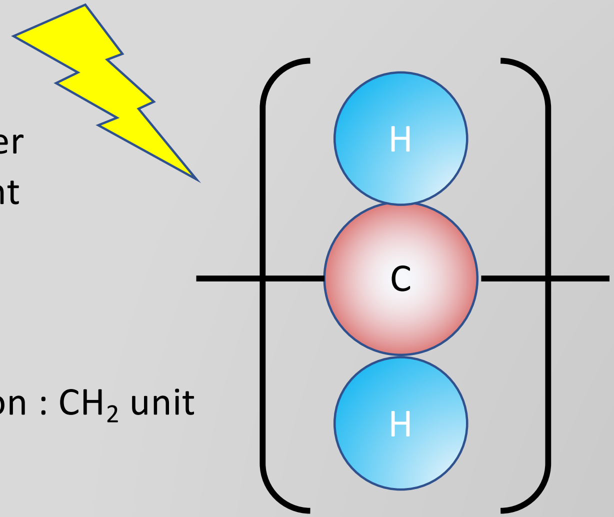


By electrolysis: 65 Wh/g H_2

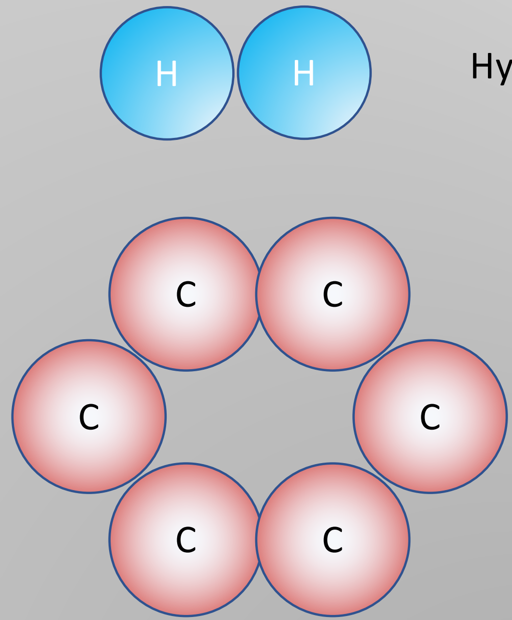
2g H_2 per 18 g water
11% in mass

Hydrocarbon splitting

High-power
visible light



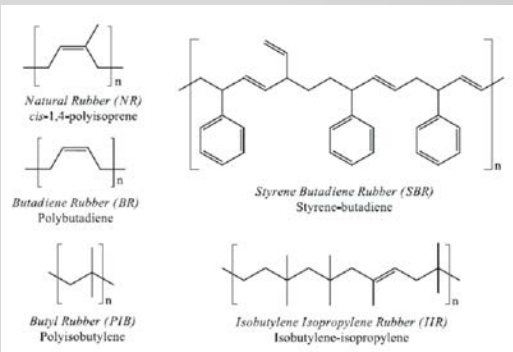
Hydrocarbon : CH_2 unit



Hydrogen
H_2

Carbon

Rubber : Butadiene and styrene butadiene



2 g H_2 per 14 g hydrocarbon
14 % in mass

Hydrogen content in mass

Compound	Formula	Hydrogen mass %
Methane	CH_4	25.0
Petrol RON 95	C_7H_{16}	16.0
Octane	C_8H_{18}	15.9
Diesel	$C_{7.25}H_{13}$	13.0
Rubber	$(C_5H_8)_n$	11.8
Water	H_2O	11.1
Cellulose	$(C_6H_{10}O_5)_n$	5.8

Same amount of hydrogen in water as in hydrocarbons $(CH_{1.5})_n$

Bond energy and dissociation energy

Bond energy (E) is defined as the amount of energy required to break apart a mole of molecules into its component atoms. It is a measure of the strength of a chemical bond. Bond energy is also known as bond enthalpy (H) or simply as bond strength.

Bond energy is based on an average of bond dissociation values for species in the gas phase, typically at a temperature of 298 Kelvin. It may be found by measuring or calculating the enthalpy change of breaking a molecule into its component atoms and ions and dividing the value by the number of chemical bonds. For example, the enthalpy change of breaking methane (CH_4) into a carbon atom and four hydrogen ions, divided by four (the number of C-H) bonds, yields the bond energy.

Bond energy is not the same thing as bond-dissociation energy. Bond energy values are an average of the bond-dissociation energies within a molecule. Breaking subsequent bonds requires a different amount of energy.

www.thoughtco.com/

Bond dissociation energies

Bond	Bond	Bond dissociation energy		Light wavelength
		kJ/mol	eV	nm
C–H	carbon-hydrogen bond	410	4,25	292
C–F	carbon-fluorine bond	490	5,08	244
C–Cl	carbon-chlorine bond	331	3,43	361
C–Br	carbon-bromine bond	285	2,95	420
C–C	carbon-carbon bond	347–356	3,60–3,69	340
Cl–Cl	chlorine	242	2,51	494
Br–Br	bromine	192	1,99	623
I–I	iodine	151	1,57	790
H–H	hydrogen	436	4,52	274
O–H	hydroxyl	460	4,77	260
O=O	oxygen	497	5,15	240
N≡N	nitrogen	945	9,79	127

Wikipedia

Bond dissociation energies in hydrocarbons

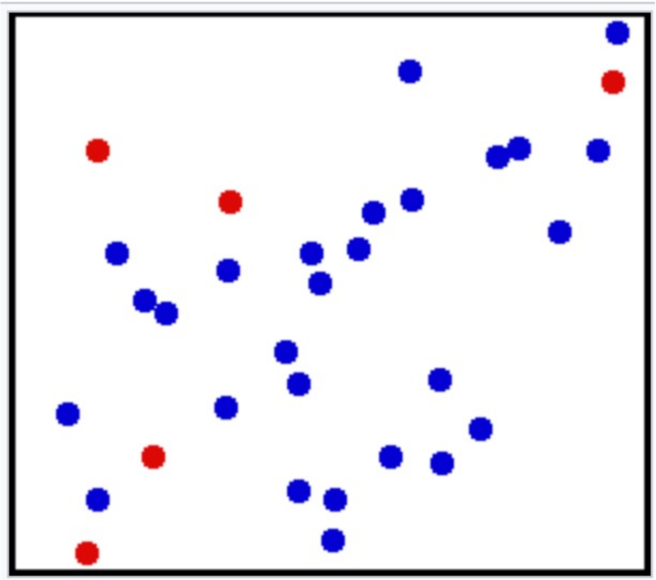
Bond	Bond	Bond dissociation energy	Light wavelength
		kJ/mol	nm
H_3C–H	C-H bond in methyl	439	272
C_2H_5-H	C–H bond in ethyl	423	283
$(CH_3)_3C$–H	Tertiary C–H bond	404	296
CH_2=CH–H	C–H bond in vinyl	464	258
HC≡C-H	C–H bond in acetyl	556	215
C_6H_5-H	C–H in phenyl	473	253
CH_2=$CHCH_2$-H	C–H bond in allyl	372	321
$C_6H_5CH_2$-H	C–H bond in benzyl	377	317
H_3C–CH_3	C–C bond in alkanes	347–356	342
H_2C=CH_2	C=C bond in alkene	611–632	193
HC≡CH	C≡C bond in alkyne	837	143

Wikipedia

Kinetic theory of gases

The temperature of a gas is a function of the kinetic energies of the molecules

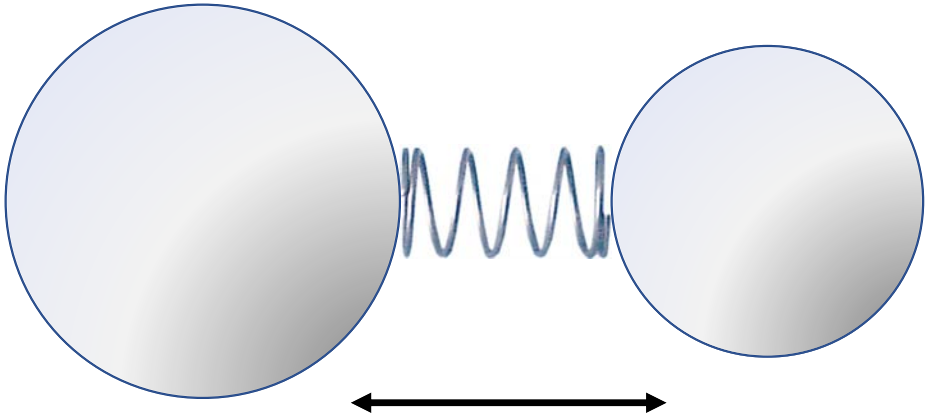
$$T = \frac{M < v^2 >}{3R}$$



M = molar mass, *e.g.* 2 for H_2, 18 for H_2O

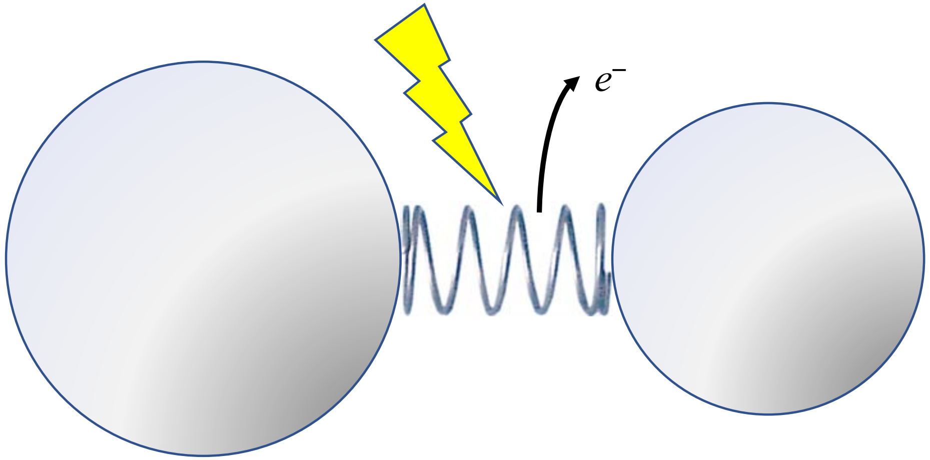
During the collisions, the kinetic energy can be used to break chemical bonds.

Pyrolysis



Chemical bonds between atoms can be considered as vibrating springs.
During collisions, the springs can absorb or give energy to other molecules.
Infrared light is absorbed by the springs that store this energy.
If the energy absorbed by infrared light or by collisions is too large, the springs can break, *i.e.* the bonds dissociate.
The higher the temperature, the more violent the collisions.

Photolysis



Chemical bonds between atoms are made of electrons, with different energy levels.
UV or visible light can eject electrons away from their energy level, which can result in chemical dissociations.

Pyrolysis

Pyrolysis is a process where molecules are heated to be dissociated into smaller ones being either gaseous, liquid or solid.

The heat in a pyrolysis reactor can be produced internally, e.g. by combustion, or externally.

Biomass pyrolysis is a process (100 to 500°C) to decompose biomass in the absence of oxygen.

The products obtained include :
- Syngaz (synthetic gas): H_2, CO, CH_4, etc.
- Bio-oil
- Biochar, a solid carbon with applications in industry and agriculture

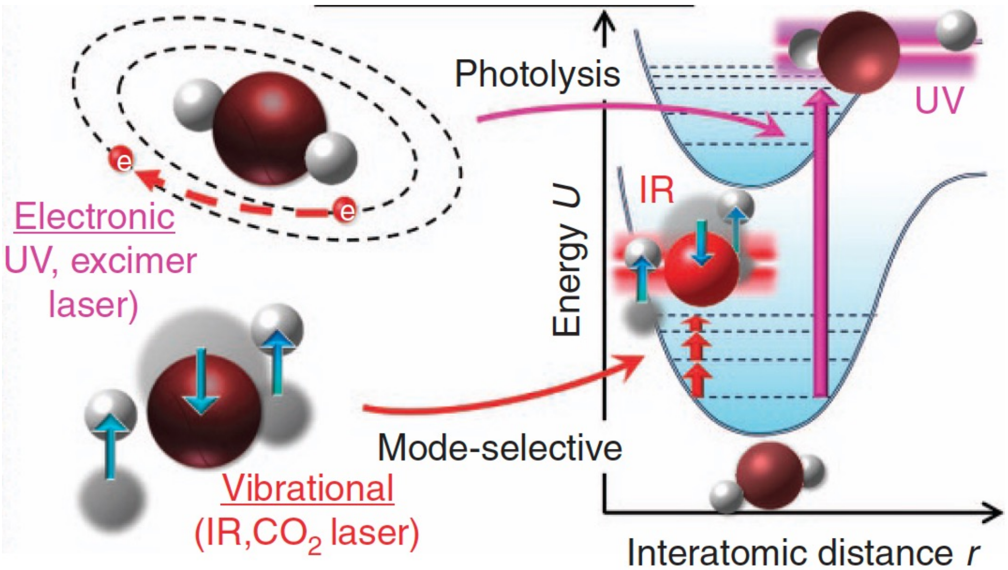
Photo-pyrolysis

Photo-pyrolysis is a process where molecules are heated under intense light to dissociate molecules to smaller gaseous ones and to solids.

The light is partially absorbed by the molecules or by the walls of the reactor.

By using intense flashes of white light, the temperature inside the reactor reaches values over 1000°C for few milliseconds. Collisions between photo-excited molecules lead to their dissociation to form only gaseous or solid molecules, all the liquid ones being vaporised and pyrolyzed.

Light absorption by molecules



Light: Science & Applications (2018) 7, 17177

The absorption of UV and visible light produces photo-excited molecules.

The absorption of infra-red light leads to vibrational excitation of the molecules.

Electronic and vibrational energies can be coupled

Another way to break molecules is to use light to increase their internal energy leading to their dissociation.

Molecular dissociation

Dissociation is one of the simplest chemical reactions, where a molecule breaks apart into two or more fragments, i.e., other molecules, atoms, ions, or radicals. Understanding the mechanisms of dissociation of reactions is essential as this knowledge can be the guide to the complex world of biomolecular processes.

Yet dissociation pathways may remain elusive in larger systems, constituted of more than three atoms. Until recently only two dissociation mechanisms were known:

(1) **stretching a bond until it breaks**;

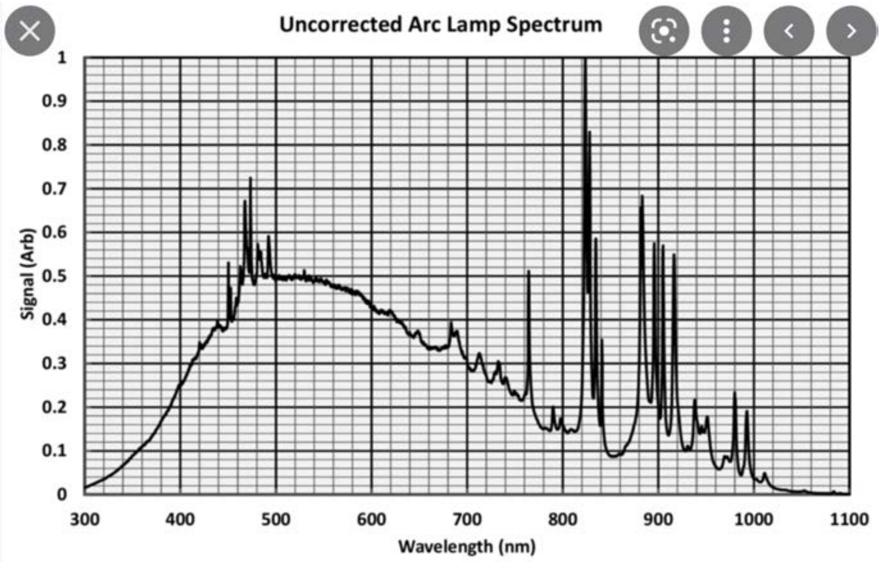
(2) **dissociation over a potential energy barrier through a so-called transition state, where electrons are rearranged** so that the old bonds are broken and new ones are formed. Recently a third dissociation modality was discovered

(3) **'roaming' reactions**, which don't follow the conventional mechanics of transition state theory. In this last type of chemical reactions, one atom wanders, or "roams", around the molecular fragment until it finds another atomic partner to make a bond with, and leaves the molecule.

https://www.synchrotron-soleil.fr/en/news/forth-way-dissociate

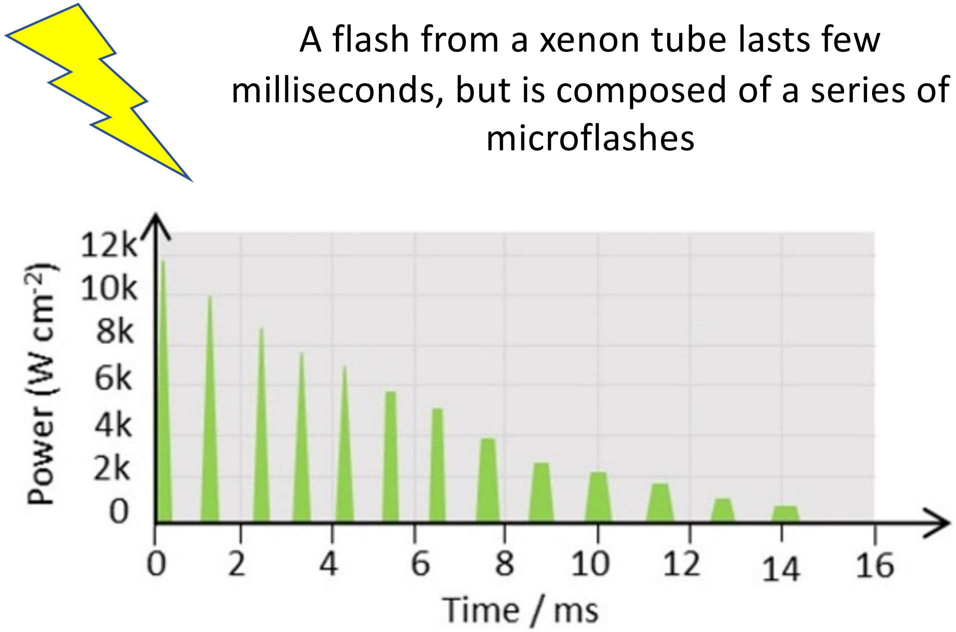
Xenon flash lamp

A xenon arc lamp is a gas discharge lamp, where light is produced by passing electricity through an ionized xenon gas at high pressure. It results in a bright white light that closely mimics natural sunlight.



https://doi.org/10.1117/12. 2232299

A flash from a xenon tube lasts few milliseconds, but is composed of a series of microflashes

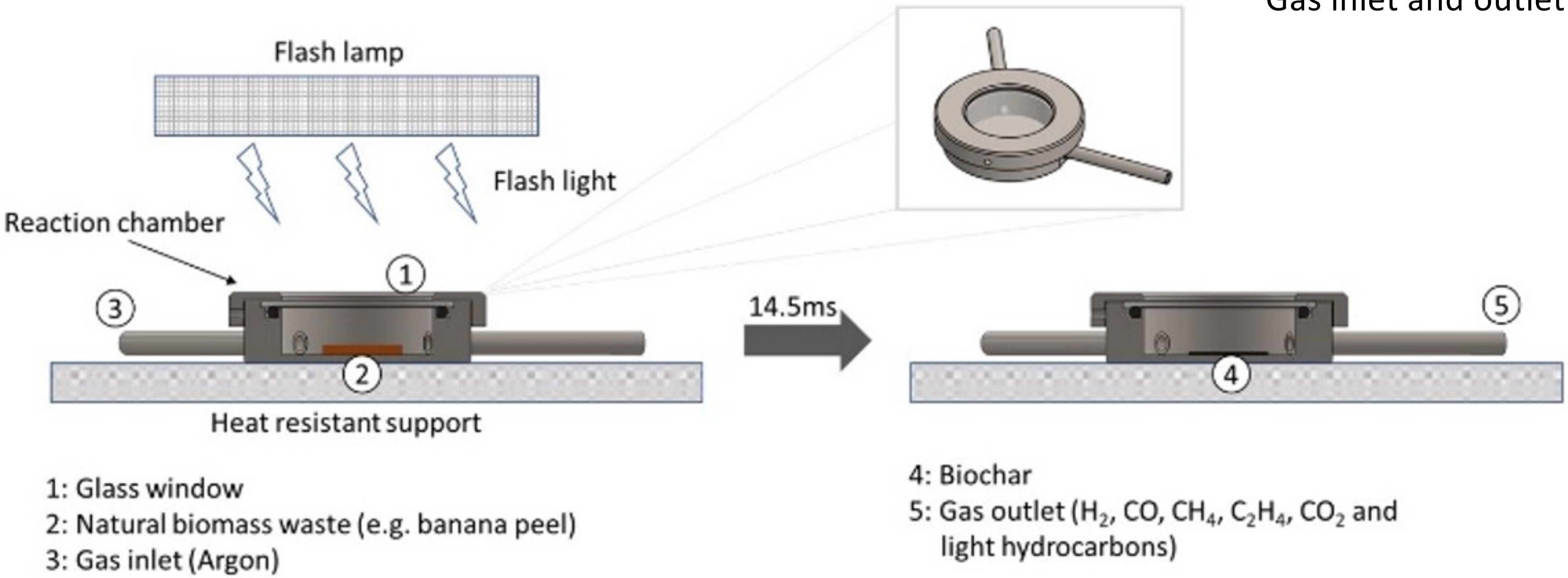


Flash from a xenon tube made of a series of microflashes
Voltage between electrodes: 575 V

Benchtop photo-pyrolysis reactor with a xenon flash lamp

Yield
Electric energy- light energy: 25-40%

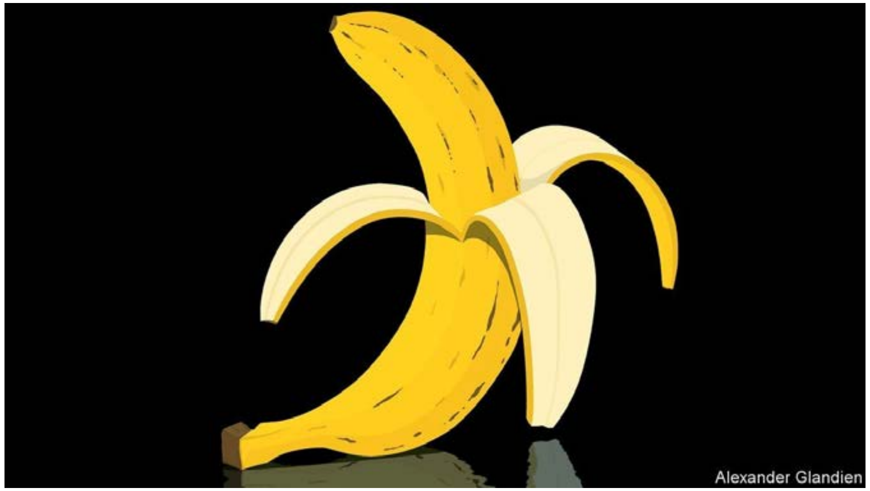
Gas inlet and outlet



The structure and size of the test reactor used is a like a watch with a stainless steel body and a glass cover

Dried biomass powder is placed at the bottom of the reactor. After closing the top window, air is replaced by an inert gas (argon). Only few flashes are necessary to photo-pyrolyze the sample.

Banana hydrogen recipe



1. Buy a fair trade banana
2. Eat the banana
3. Dry and grind the peel
4. Expose the powder to few flashes from a xenon flash lamp in the absence of oxygen
5. Recover the hydrogen rich gas and the solid carbon

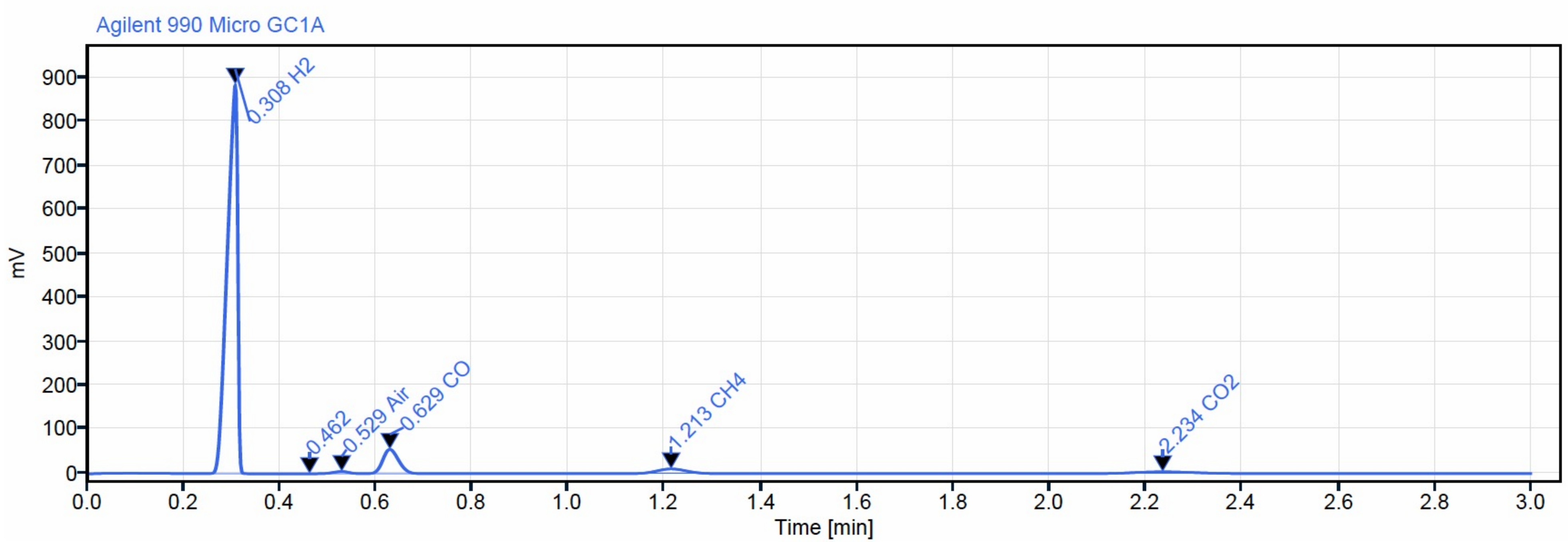
Banana peels contain about 60% of carbohydrates, 30% of water and some proteins

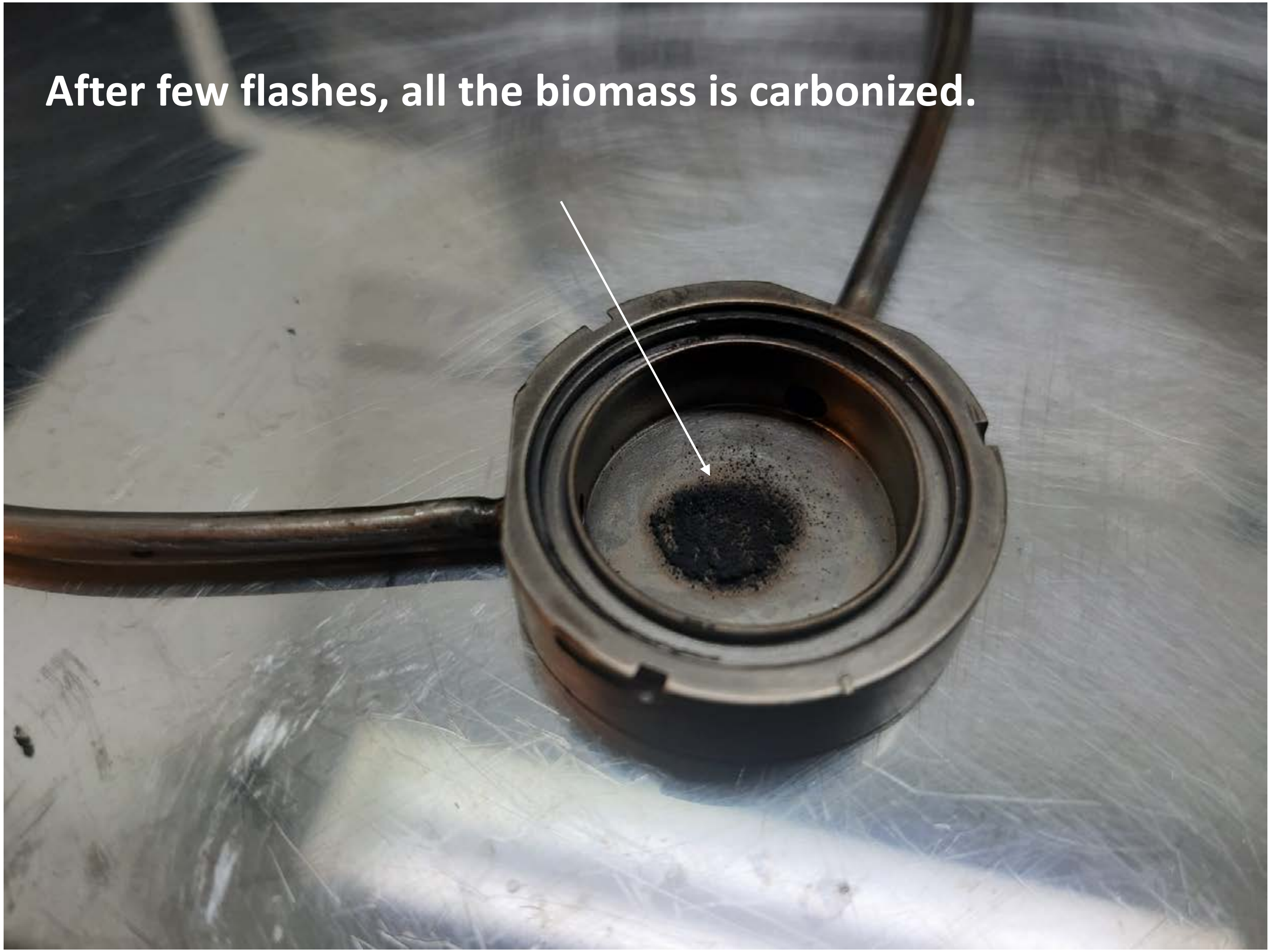
The annual production of bananas is about 115 millions tonnes. The annual production of peel (35 to 40% of the total mass) is about 40 millions tonnes. With 10% of dry matter, this represents about 4 millions tonnes per year.

One kilo of dried banana powder produces 100 litres of hydrogen = 0.1 Nm^3 = 10 grammes H_2, *i.e.* about 1% in mass.

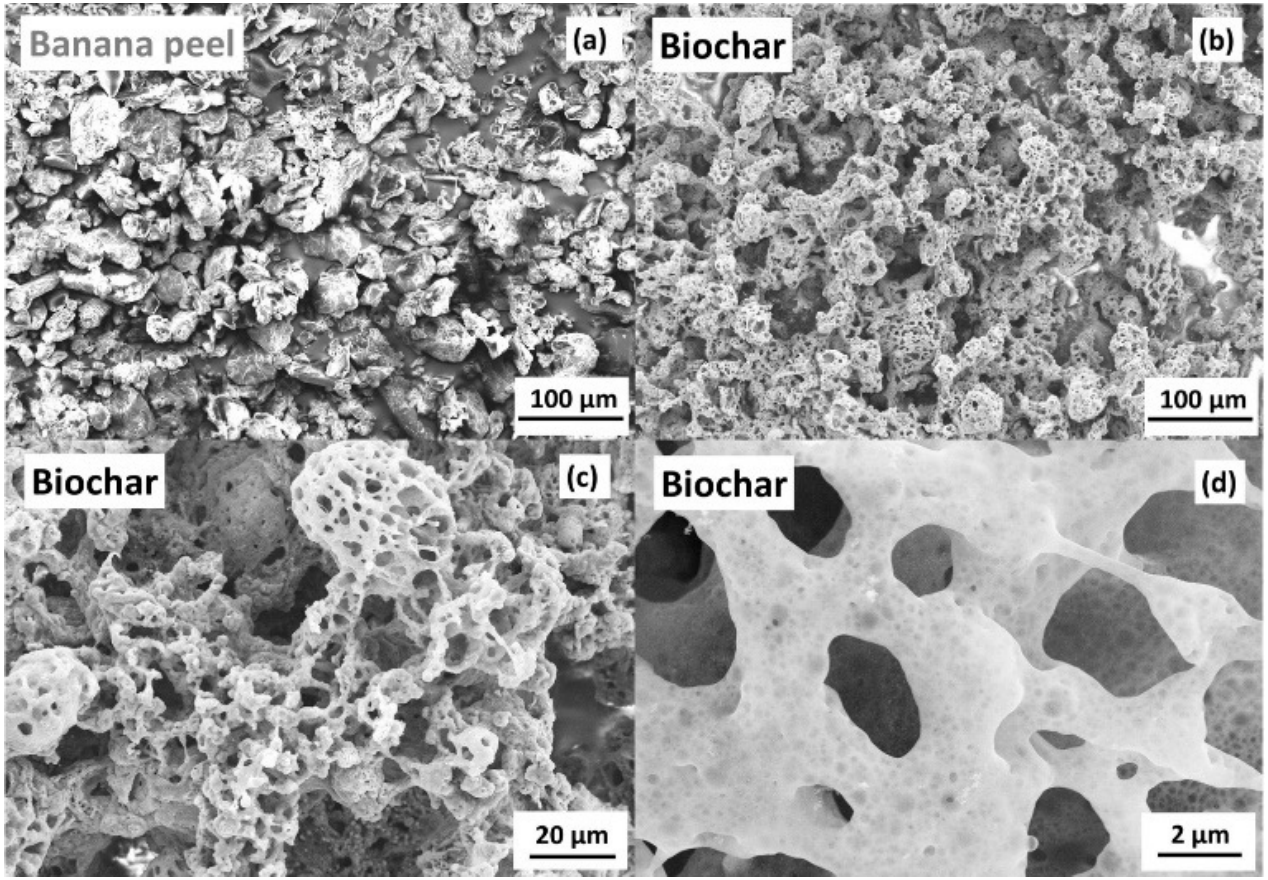
If all the banana peels of the world were used to produce hydrogen by photo-pyrolysis,
the annual production would be 40’000 tonnes, *i.e.* the annual production of a 300 MW electrolyser.

Gaz analysis after photo-pyrolysis
Banana Peels




After few flashes, all the biomass is carbonized.

Biochar from banana peels



Biochar :
Porous Carbon

Electronic microscopy of dried banana peels (a) and of biochar at different magnifications (b-d).
5 flashes with a voltage of 575V.

Hydrogen from coffee grounds

1. Buy fair trade coffee
2. Enjoy a good cup of coffee
3. Dry the coffee ground
4. Expose the dried coffee grounds to few flashes of a xenon flash lamp.
5. Recover the hydrogen rich gas and the solid carbon.

The world production of coffee is about 10 millions de tonnes.

Coffee grounds contain mainly lignocellulosic compounds.

1 kg of coffee ground produces about 10g of hydrogen, *i.e.* about 1% in mass.

If all the coffee grounds of the world were photo-pyrolyzed , the annual production of hydrogen would be 100’000 tonnes, i.e. the production of a 800 MW electrolyser.

Table 1 Chemical composition of spent coffee grounds and coffee silverskin

From: Chemical, Functional, and Structural Properties of Spent Coffee Grounds and Coffee Silverskin

Chemical components	Composition (g/100 g dry material)	
	Spent coffee grounds	Coffee silverskin
Cellulose (Glucose)	12.40 ± 0.79	23.77 ± 0.09
Hemicellulose	39.10 ± 1.94	16.68 ± 1.30
Arabinose	3.60 ± 0.52	3.54 ± 0.29
Mannose	19.07 ± 0.85	1.77 ± 0.06
Galactose	16.43 ± 1.66	3.76 ± 1.27
Xylose	nd	7.61 ± 0.02
Lignin	23.90 ± 1.70	28.58 ± 0.46
Insoluble	17.59 ± 1.56	20.97 ± 0.43
Soluble	6.31 ± 0.37	7.61 ± 0.16
Fat	2.29 ± 0.30	3.78 ± 0.40
Ashes	1.30 ± 0.10	5.36 ± 0.20
Protein	17.44 ± 0.10	18.69 ± 0.10
Nitrogen	2.79 ± 0.10	2.99 ± 0.10
Carbon/nitrogen (C/N ratio)	16.91 ± 0.10	14.41 ± 0.10
Total dietary fiber	60.46 ± 2.19	54.11 ± 0.10
Insoluble	50.78 ± 1.58	45.98 ± 0.18
Soluble	9.68 ± 2.70	8.16 ± 0.90

Results are expressed as mean ± standard deviation; $n = 3$. *nd* not detected

Food and Bioprocess Technology **volume 7**, pages 3493–3503 (2014)

Gaz analysis after photo-pyrolysis
Coffee grounds

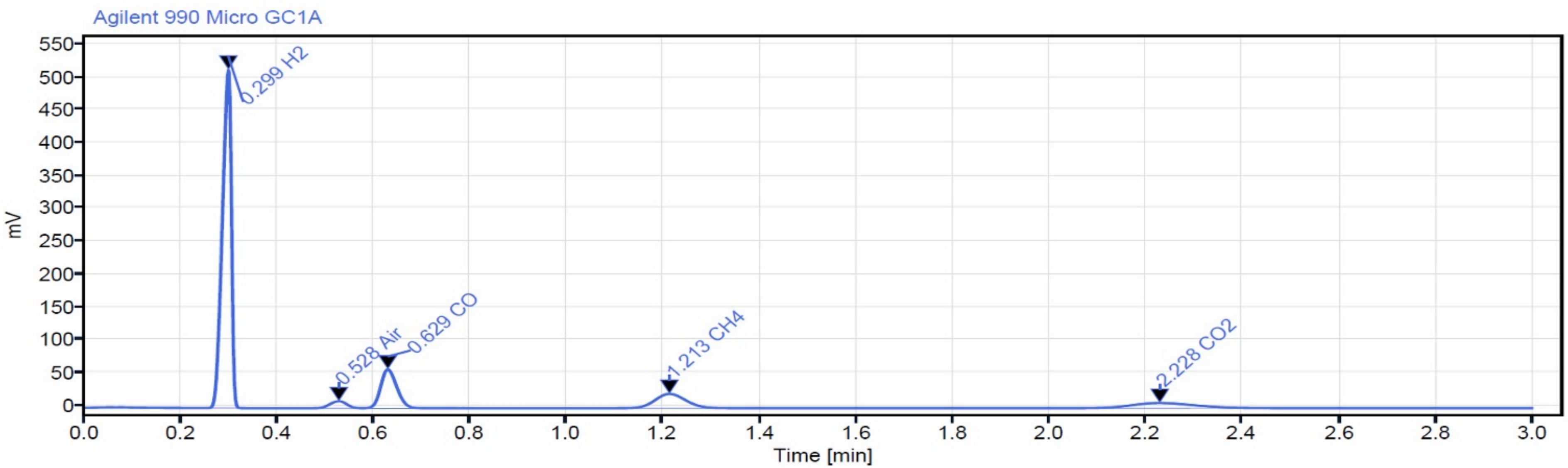


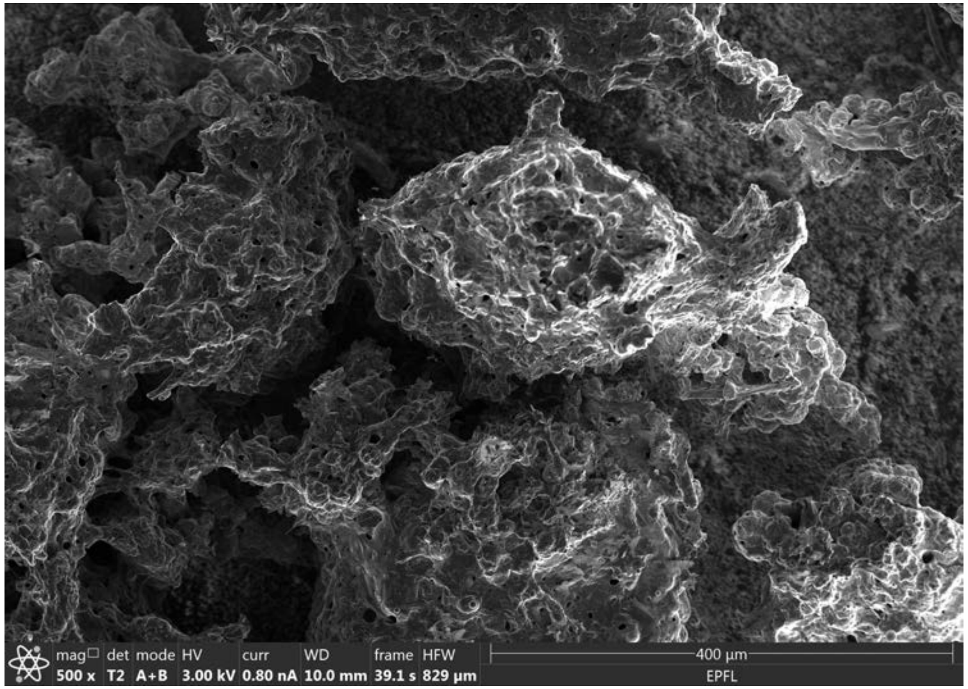
Photo-pyrolysis of coffee grounds

Dark brown used coffee beans ground
to a particle size of 200-400 nm

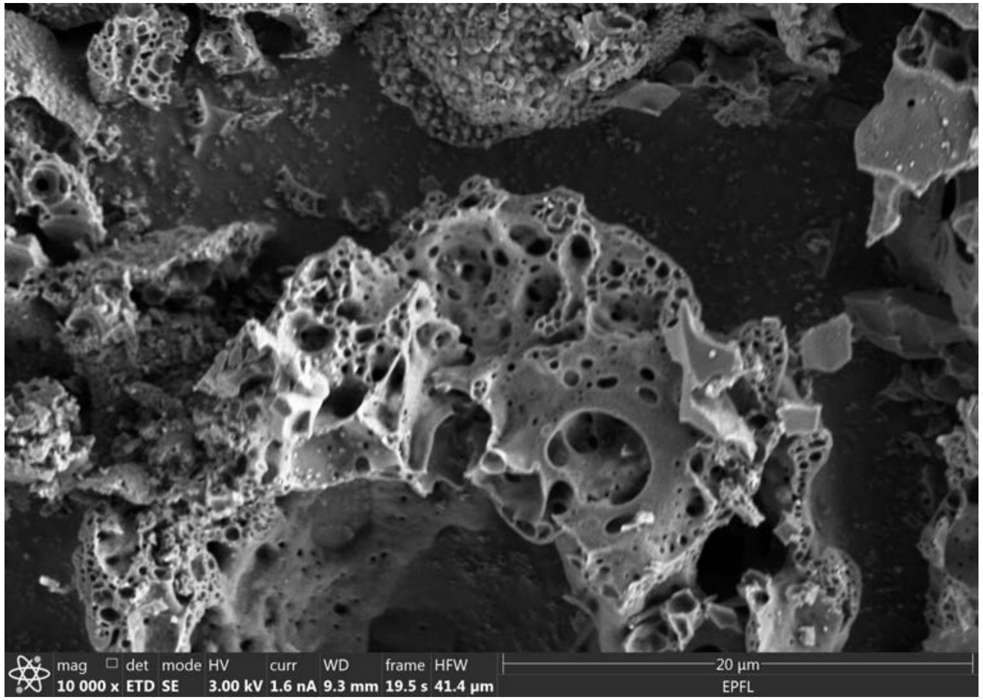
Flashing for 12 s

Completely converted black carbon
powder obtained after flashing

Biochar from coffee grounds



Coffee grounds



Biochar from coffee grounds

Hydrogen from used tyres

1. Collect old tyres
2. Separate the rubber(41%)
3. Grind the rubber into a fine powder
4. Expose the rubber powder to few flashes of a xenon flash lamp
5. Recover hydrogen and the solid carbon.

The world production of tyres is about 20 million tonnes, *i.e.* about 8 million tonnes of rubber

Rubber contains only hydrogen and carbon.

1 kg of rubber powder produces about 50 g of hydrogen, *i.e.* about 5% in mass

If all the rubber of used tyres were to be photo-pyrolyzed , the annual production of hydrogen would be 500’000 tonnes, *i.e.* the production of a 4 GW electrolyser.

Gaz analysis after photo-pyrolysis
Rubber

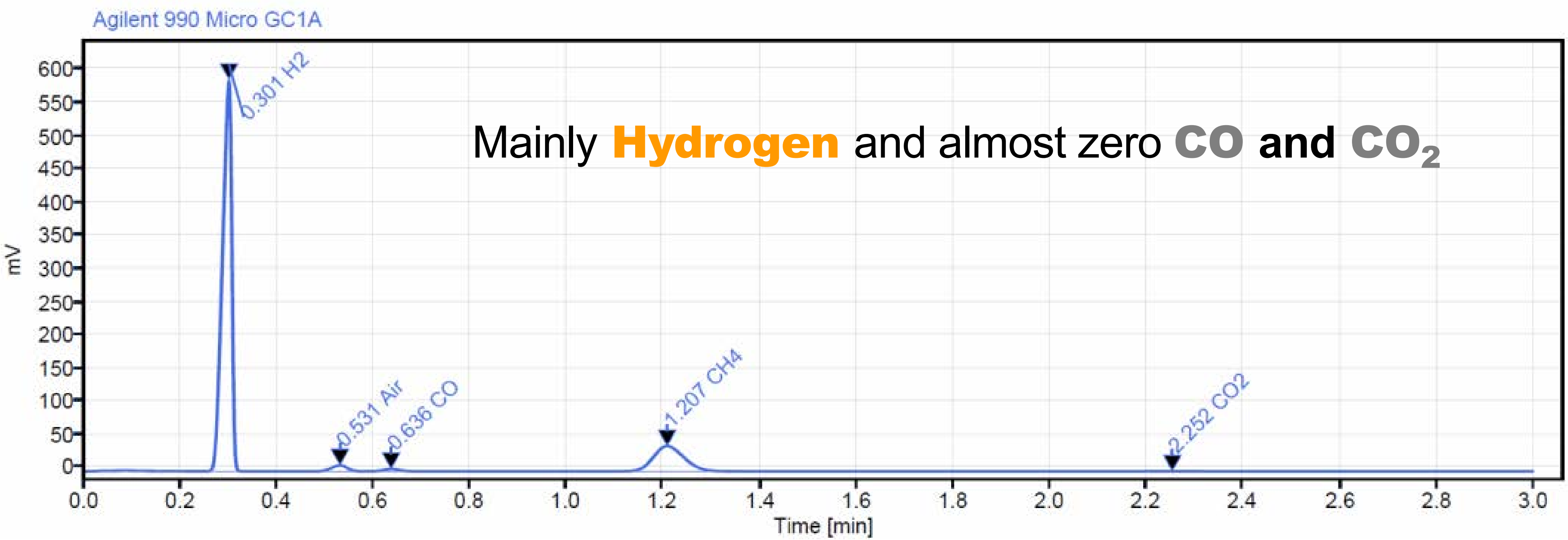
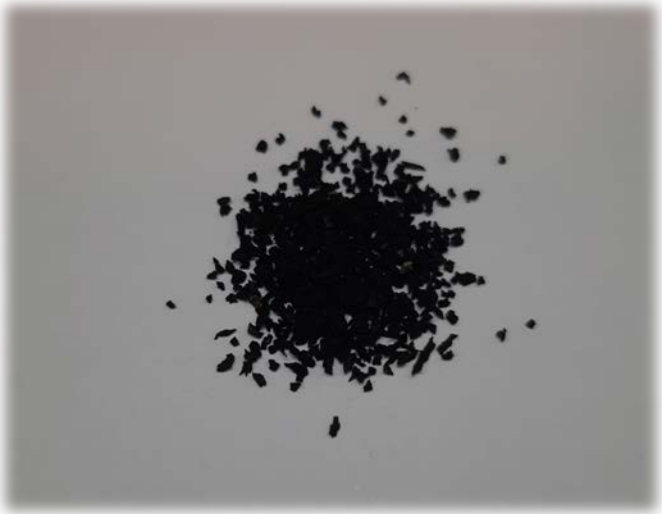


Photo-pyrolysis of rubber

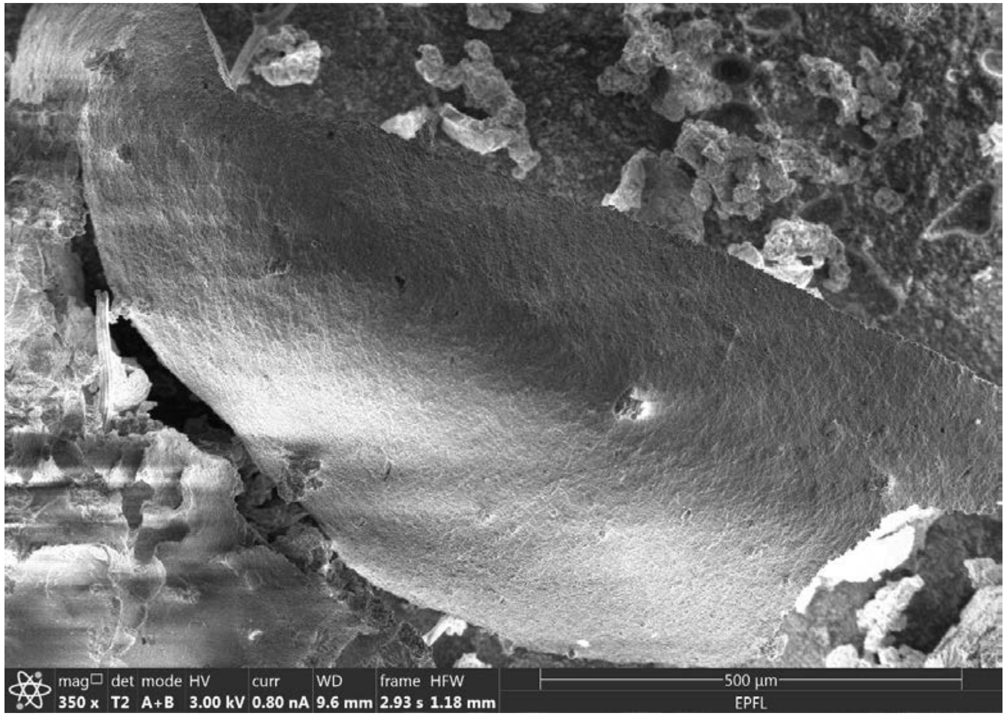


Particles of used tyres (1000 μm)

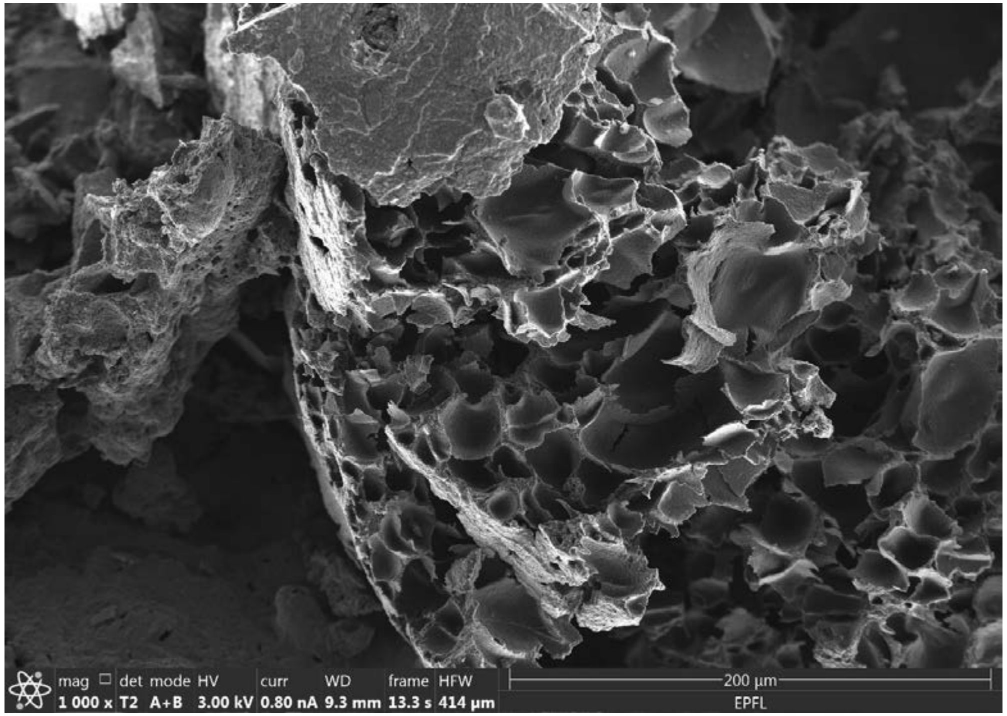
Flash Light Irradiation for 24s

Completely converted to **Carbon** and Hydrogen after flashing (20 μm)

Biochar from rubber



Flash Light
24s



Rubber powder

Biochar from rubber

Solar photo-pyrolysis

Solar photo-pyrolysis would consist in concentrating with reflectors sunlight on quartz tubes , and on passing very fast powders of the wastes to be treated to produce hydrogen and biochar.