Supplementary information

Hydrogen production by waste tires recycling by photo-pyrolysis

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List of abbreviations

American Society for Testing and Materials - ASTM

Brunauer-Emmett-Teller - BET

Carbon black - CB

Direct current – DC

Dynamic light scattering - DLS

Gas chromatography - GC

High heating value – HHV

Inductively Coupled Plasma Optical Emission spectroscopy - ICP-OES

International Union of Pure and Applied Chemistry - IUPAC

Mass spectrometry - MS

N-Methyl-2-pyrrolidone – NMP

Scanning Electron Microscopy – SEM

Thermal gravimetric analysis - TGA

Tire pyrolysis oil – TPO

Tire photo-pyrolysis oil (TPPO)

Transmission electron microscopy – TEM

Waste tire - WT

X-ray diffraction analysis - XRD

X-ray photoelectron spectroscopy - XPS

Figure S1 - Reactor design employed during the photo-pyrolysis of scrap tires: (1) quartz window, (2) reaction environment, (3) silicon O-ring, (4) screws, (5) and (6) inlet and outlet of gases.

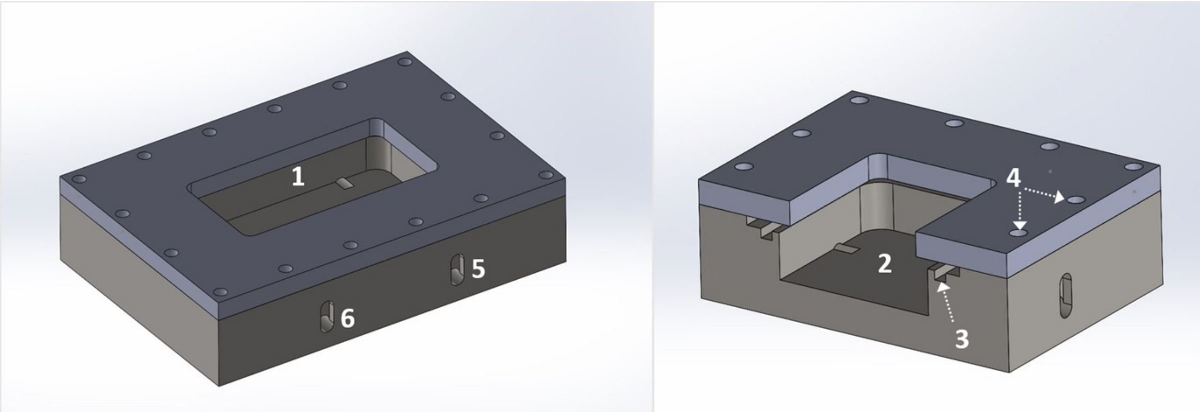

Figure S2 shows the typical system energy consumption of the Heraeus noble flash light system. For the detailed energy analysis, a pulse train of only 2.4 s, consisting of 100 individual pulses was used, which can be scaled without problems to longer pulse trains. The sample rate is at 100 Hz, but as already described previously, the power value is only updated five times a second. During standby, the energy stays constant at *ca.* 2.5 kW with little energy peaks each 4.3 s. To calculate precisely the mean standby energy, the period between t_1 and t_2 was taken into account, where t_1 and t_2 have 1 s distance to the rising flank of the previous energy peak. As result, the system has a mean standby power of P_{stb} = 2551.4 W. During the flash process, the consumption increases to more than 15 kW. To calculate the system energy for the flash process itself W_{flash} - corresponding to the blue area in **Figure S3** - the difference between the overall energy and the mean standby energy for the period between t_1 and t_3 was calculated using the measured active power P_{act} as

$$W_{flash} = \int_{t^1}^{t^3} P_{act} \partial t - \frac{t_3 - t_1}{t_2 - t_1} \cdot \int_{t^1}^{t^2} P_{act} \partial t = 31.71\ kJ$$

To determine the lamp energy W_{lamp} the voltage and the current at the lamp were measured with a sample rate of 100 kHz as already described. This energy also implies the losses due to the cable connection between the flash system and the lamp, as the voltage is measured inside the system. **Figure S3** shows voltage (**inset a**), current (**inset b**) and the resulting power (**inset c**) at the lamp during the flashing process. As the output energy outside the flashing process is negligible, the lamp energy W_{lamp} was simply calculated by integrating the power for the complete train of 100 pulses (222.222 samples) with 29.62 kJ as result.

Without taking into account the standby power, the flash system shows an efficiency of 93.4%. Including the standby power of 2551.4 W into the analysis, the efficiency drops to:

$$\eta = \frac{W_{lamp}}{W_{flash} + P_{stb} \cdot t_{flash}} = \frac{29.62\ kJ}{31.71\ kJ + 2551.4\ W \cdot \frac{100}{45\ Hz}} = 79.2\%$$

Figure S2 - Typical energy consumption profile of the flash light irradiation system performed at 325 V and frequency of 45 Hz.

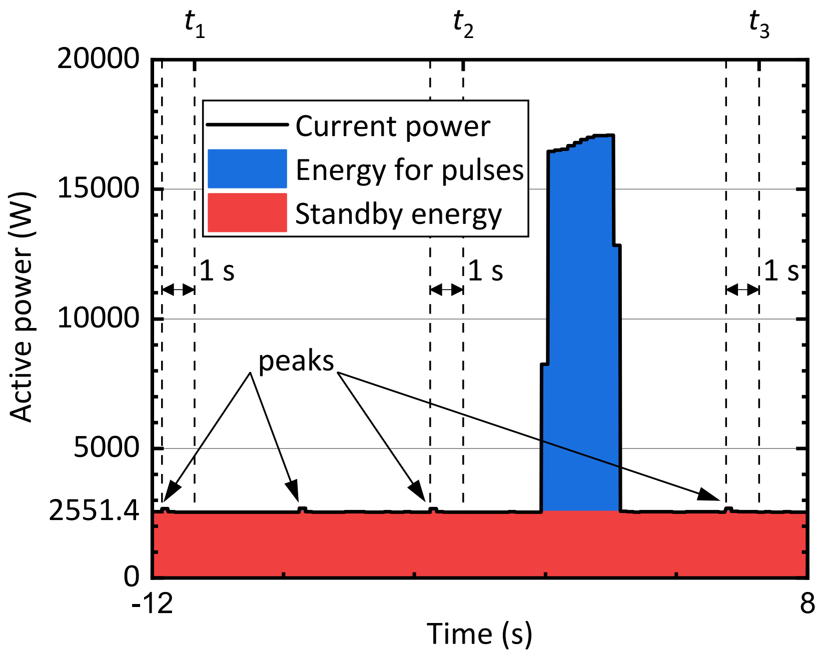

Figure S3 - Voltage (a), current (b) and power (c) provided by the Xe lamp during the flash light irradiation process performed at 325 V and frequency of 45 Hz.

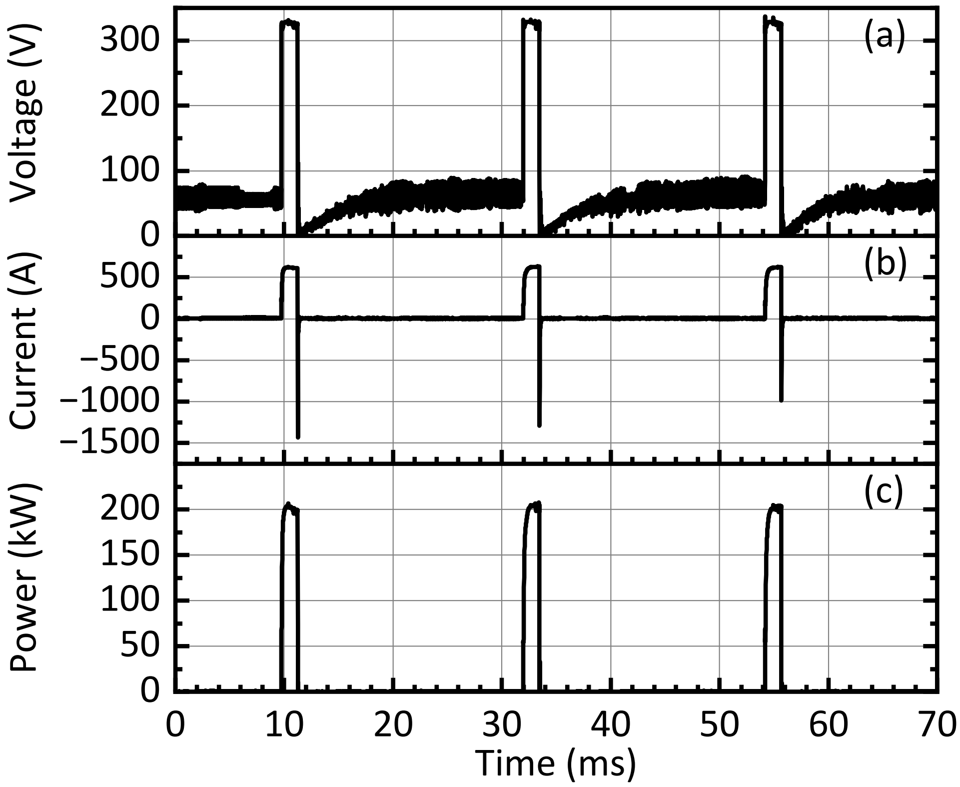

Table S1 – Elemental composition (wt%) and high heating value – HHV (MJ kg^{-1}) of the waste tire.

C (wt%)	H (wt. %)	N (wt. %)	S (wt. %)	O (wt. %)	Metals+ Inorganic fillers (wt. %)*	HHV (MJ kg^{-1})
76.4	7.1	0.4	1.5	2.9	11.7	32.3

*Metal+inorganic fillers calculated by difference.

Table S2 – ICP-OES analysis of the waste tire and char.

Element	Waste tire (µg/mg)	Char (µg/mg)
Na	1.47	3.60
Ca	12.08	-
Cr	0.02	-
Fe	1.05	1.82
Co	0.17	0.41
Ni	0.01	0.03
Cu	0.04	0.09
Zn	16.02	37.16
Sn	0.04	0.09
Pb	0.01	0.02

Figure S4 - (a) DLS analysis of the solid char obtained from the photo-pyrolysis of the waste tire powder.

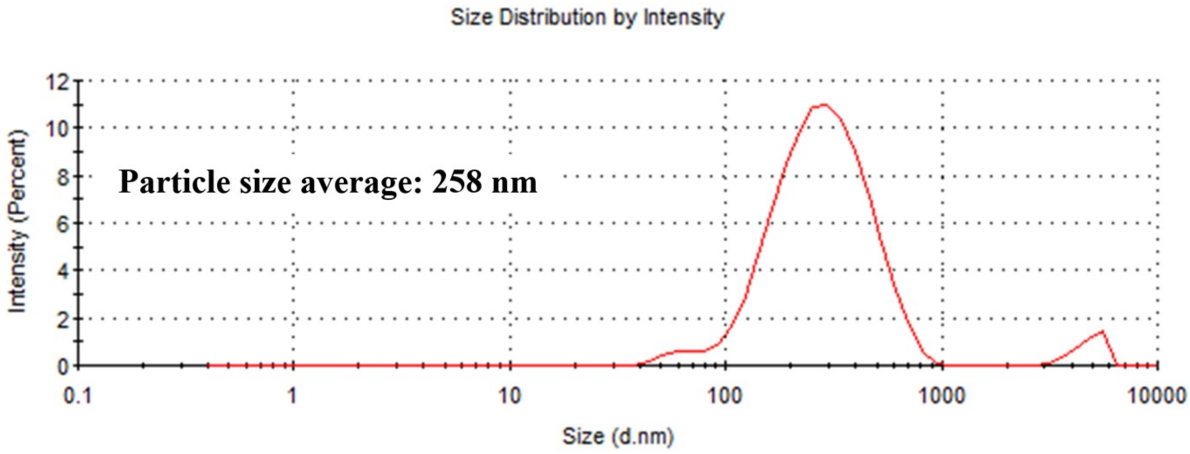

Figure S5 – Measured nitrogen adsorption-desorption isotherms at 77 K of the conductive carbon-rich solid powder synthesized from scrap tire powder by photo-pyrolysis during 20 s at 325 V-pulse.

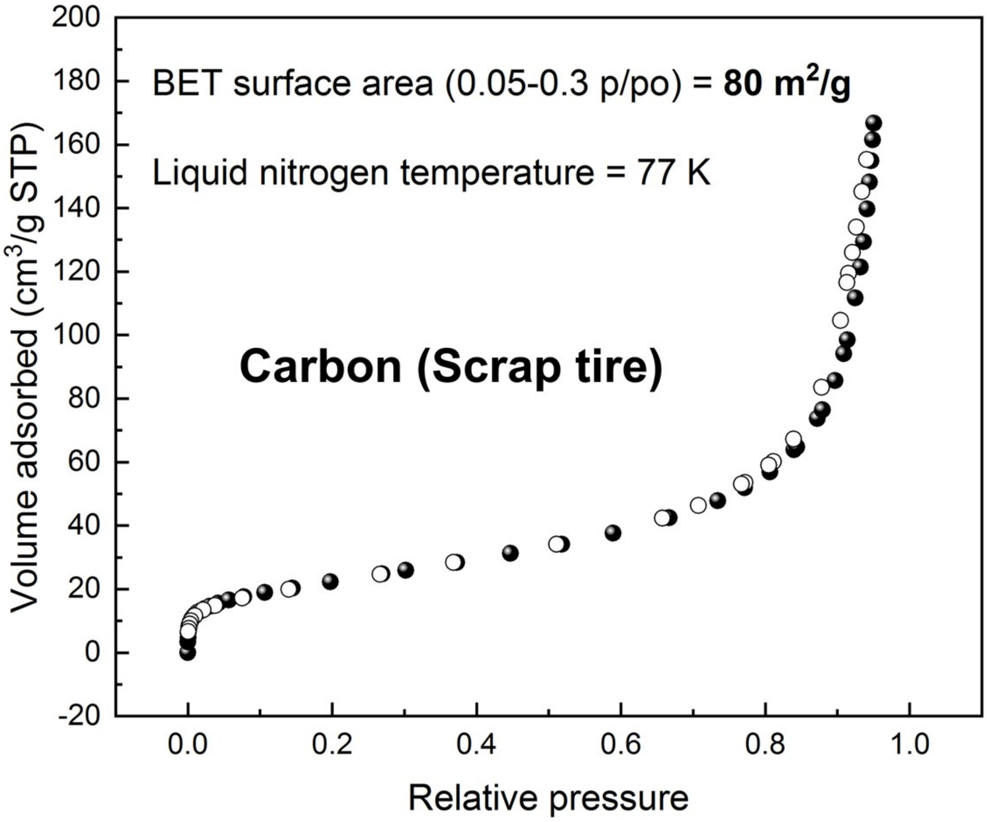

Figure S6 – Temperature provided by the waste tire powder and/or char during the flash light irradiation process.

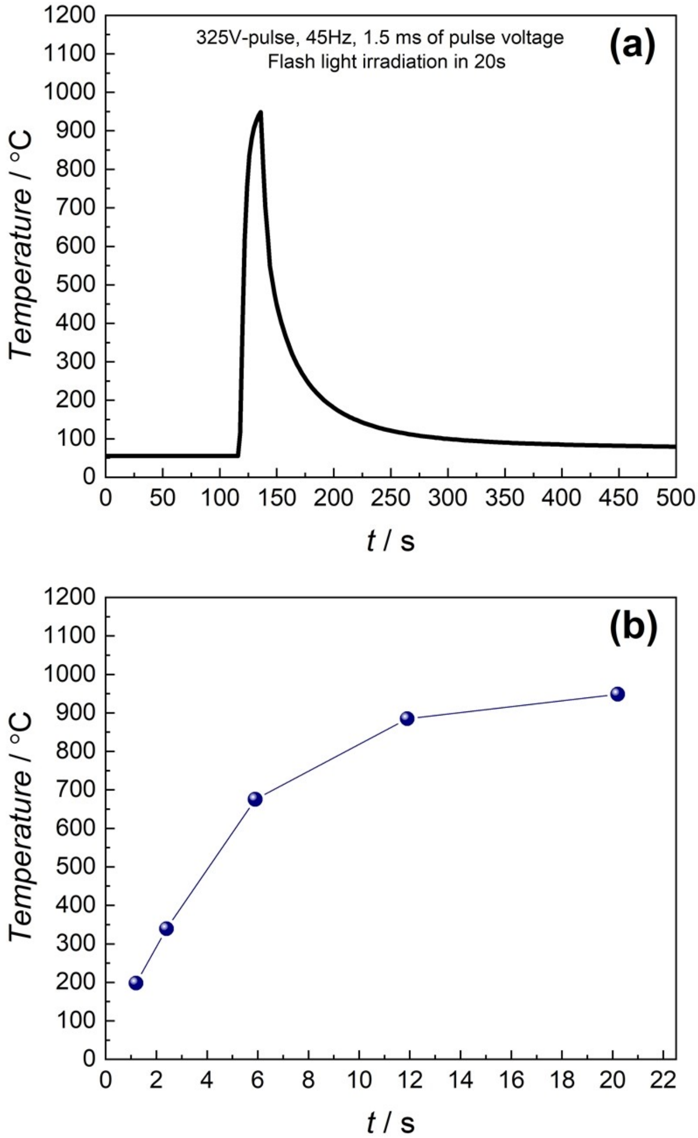

Figure S7 – Typical behavior of the product yields obtained from tire pyrolysis versus temperature: L = liquid phase, S = solid phase, G = gas phase. Ref. [1].

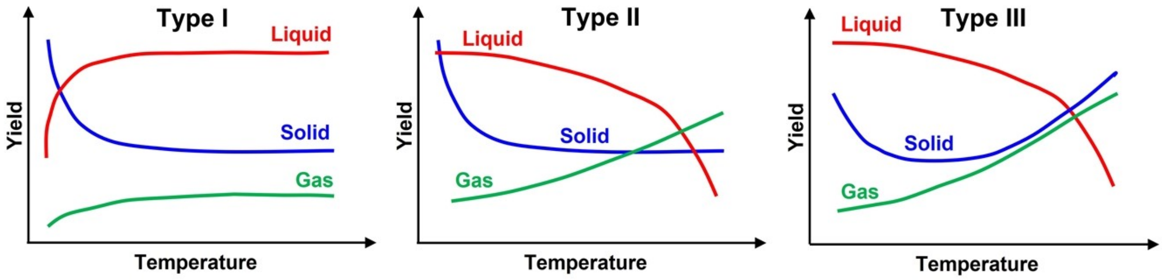

Figure S8 – (a) High resolution high mass accuracy mass spectrum of the tire photo-pyrolysis oil and plots of: (b) DBE vs. *m/z*, (c) DBE vs. number of carbon atoms, (d) DBE vs. number of hydrogen atoms, (e) DBE vs. number of sulfur atoms, (f) DBE vs. number of nitrogen atoms, (g) DBE vs. number of oxygen atoms and (h) H/C ratio vs. S/C ratio.

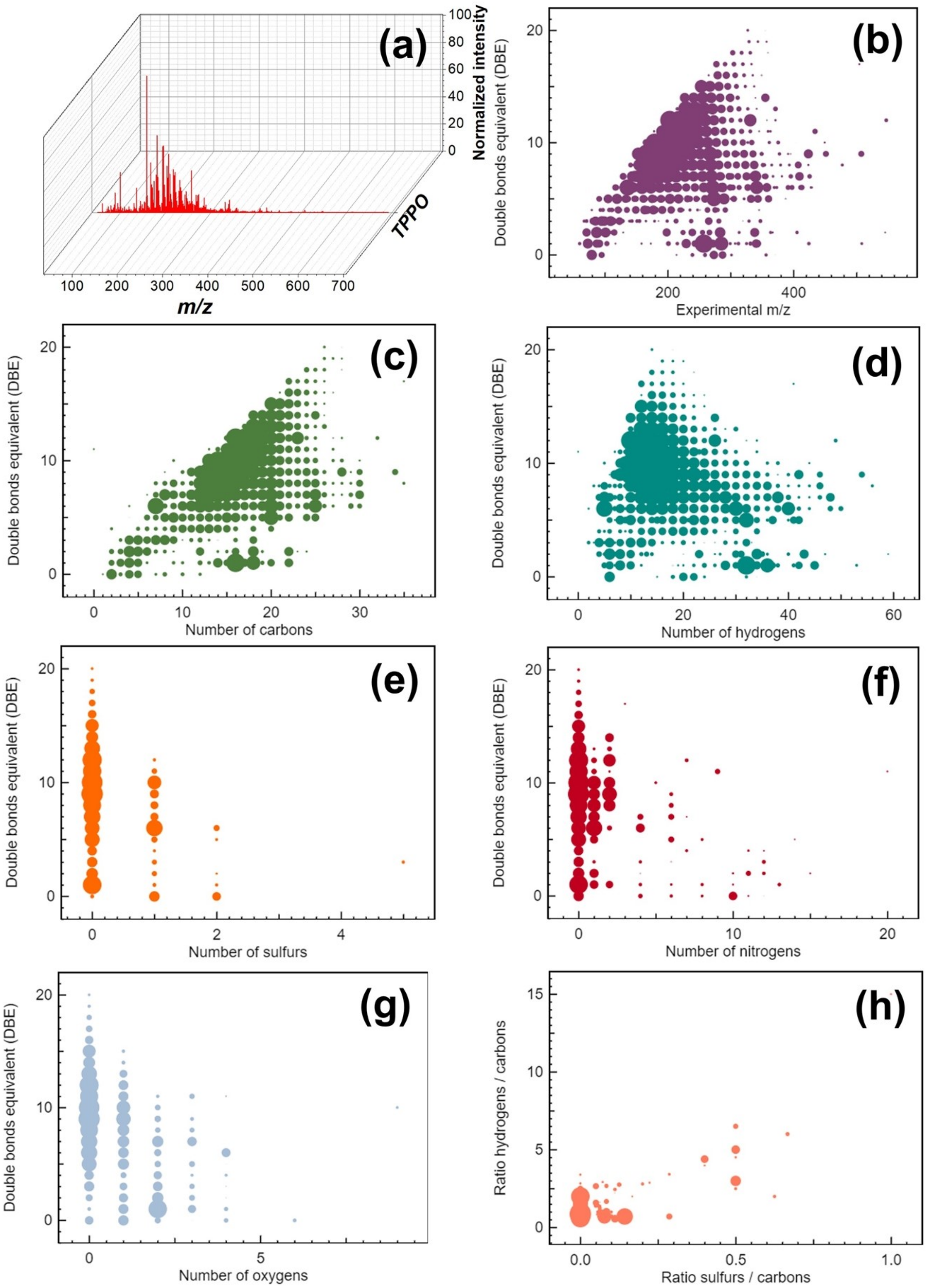

Figure S9 – (a) Number of carbon atoms vs number of hydrogen atoms and (b) experimental mass/charge vs relative intensity obtained from MS analysis of the tire photo-pyrolysis oil.

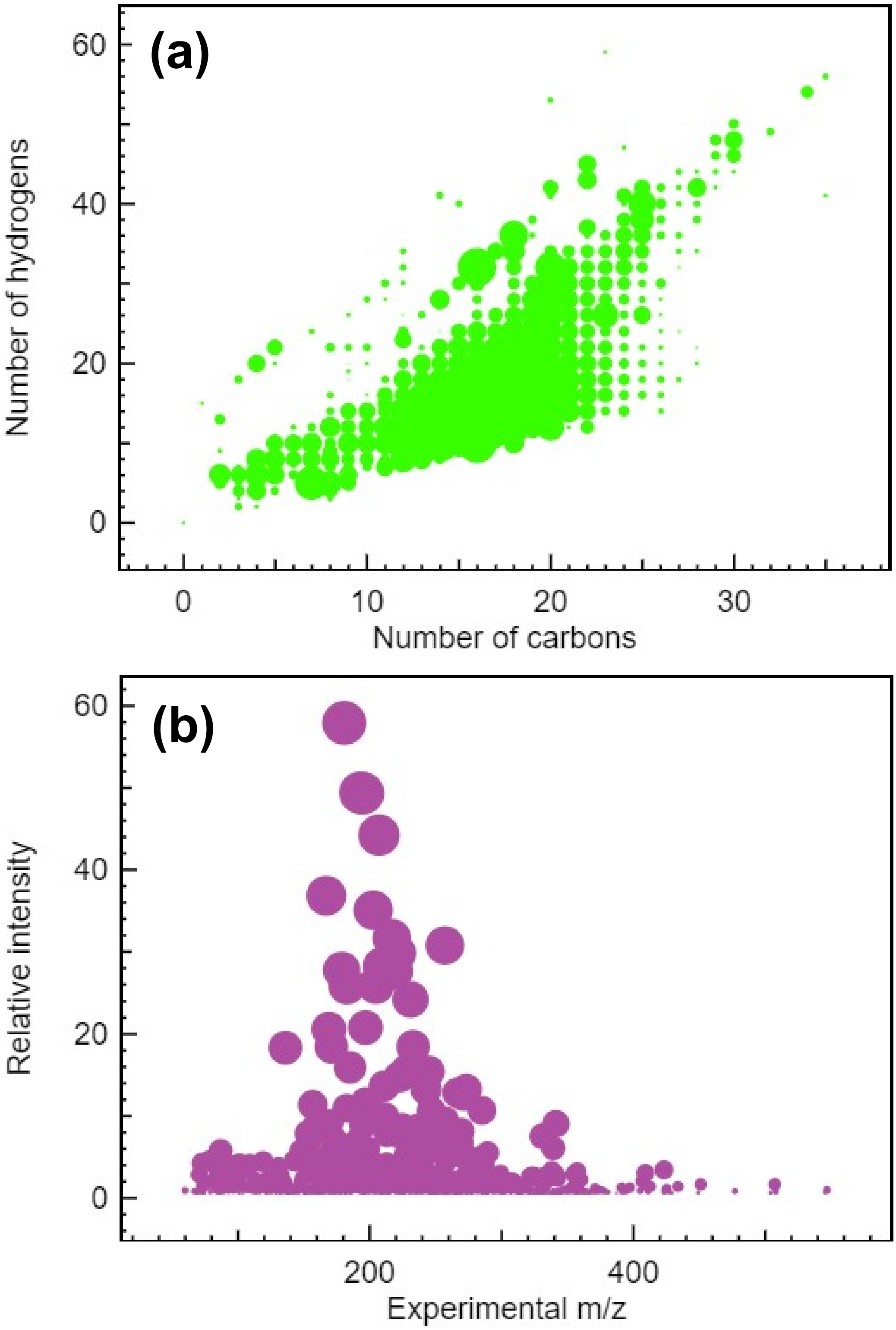

Figure S10 – Typical mechanism proposed for the pyrolysis of waste tire.[62]

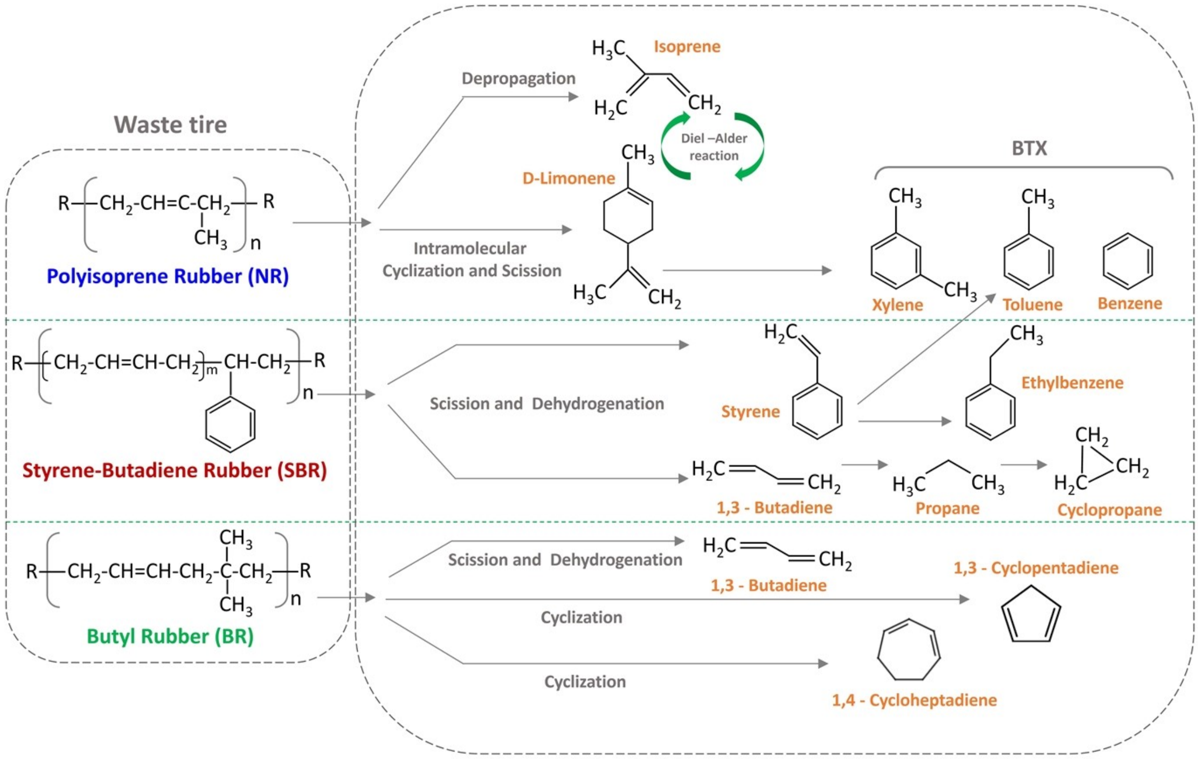

Figure S11 – Photo-pyrolysis of scrap tire shreds performed by photo-pyrolysis during 60 s at 325 V and frequency of 45 Hz.