Detailed evaluation of technologies for the pilot scale pyrolysis of plastic wastes

Jean-Bernard Michel*, Drew Gamage, Roger Gumy**, Christophe Pot**,**
Jullen Ropp*, Jacques Richard***, Philippe Gaemperle******
jbm@humana.ch
* Humana Consulting, Switzerland
** Spontis SA, Switzerland
*** University of Applied Sciences and Arts Western Switzerland
**** Sales Challenge Consulting Sàrl

Abstract

In Switzerland, as in some other industrialized countries, plastic wastes are eliminated together with municipal wastes by incineration with thermal energy recovery (“ITER”) for power production and district heating. However, although this is thought as one of the best methods to dispose of the wastes, the trend is for increased sorting, separate collection, and material recycling as it is already the case for PET bottles. In this context, an ambitious project is carried out by a group of industrial and R&D partners to find an innovative and complementary alternative with a strong ecological, economic, and societal impact.

The first phase, now completed, aimed at the comparison of best available pyrolysis technologies for distributed energy conversion plants which should be 10 times smaller or less than ITER plants.

The objective is to implement on a pilot scale a pyrolysis unit which should allow better energy recovery and thus contribute to the energy transition.

Several typical wastes already collected separately were considered for a 1500 t/year pilot plant:

The considered alternatives were technologies that produce liquid and/or gaseous fuels such as pyrolysis or gasification. The objective of the feasibility study was to evaluate the different options in terms of ecological, economic, and social impact for the recovery of plastic waste by comparing them to the existing solution, namely incineration with thermal energy recovery (“ITER”).

Only high-temperature pyrolysis or pyrogasification technologies were found to meet the technical requirements, types of waste and quantities to be treated and the environmental criteria of this project with half the GHG emissions and fossil fuel utilization compared to incinerators.

This project can serve as a model for the valorization of plastics in the future. It is important to stress that the deployment of these new technologies is complementary (and not in competition) to ITER, with a view to a transition of the latter towards a circular economy in the coming decades.

Theoretical basis of chemical recycling and pyrolysis

Definition of chemical recycling

The term "chemical recycling" refers to a diverse set of technologies. These subject plastic waste to a combination of heat, pressure and/or other chemicals inside one or more reactors.

An overview of the different methods is shown in Figure 1.

Chemical recycling technologies can be grouped into two categories:

- Thermolysis and
- Solvent-based processes or solvolysis, see Figure 2.

Thermolysis literally means "decomposition by heat," and although it encompasses combustion and a wide range of other chemical processes, only pyrolysis and gasification are thermolysis methods for chemical recycling. High temperature pyrolysis is also referred to as pyrogasification.

Pyrolysis and pyrogasification are presented as an essential step in the chemical recycling of plastics, producing the basic molecules used in their production.

These processes heat the plastic inside an oxygen-free (pyrolysis) or oxygen-depleted (gasification) reactor with the aim of breaking the polymers into smaller, lighter chemical components, which is why they are also called depolymerization technologies. As several plastic wastes contain oxygen, pyrolysis of mixed plastic is often associated with partial gasification.

Pyrolysis and gasification products could be used to produce new plastic after an additional upgrade but are usually burned to produce electricity and heat.

Solvent-based technologies use a variety of media to process plastics, often in stages; some depolymerize the plastic while others strip the impurities, leaving the polymer chains relatively intact. Many solvolysis technologies also involve high temperatures but are not considered thermolysis.

These solvolysis techniques are still at the development stage and will hardly be applicable to a mixture of plastics. A very efficient prior selective sorting would be necessary, or the use of constant industrial waste as feedstock.

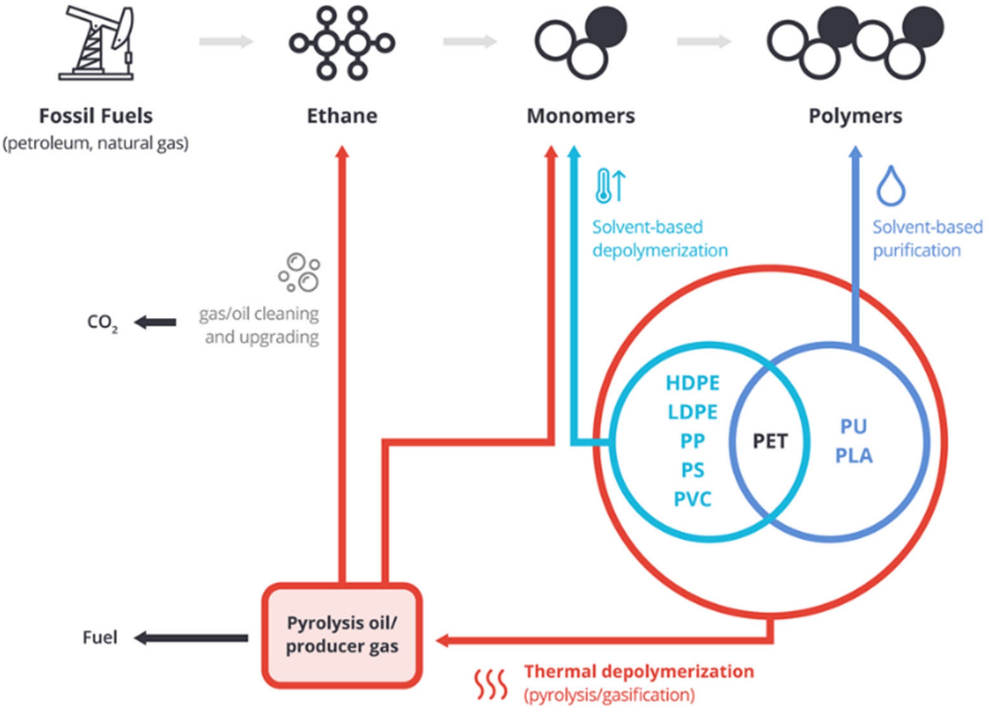

Figure 1. General schematic of chemical recycling processes [1]

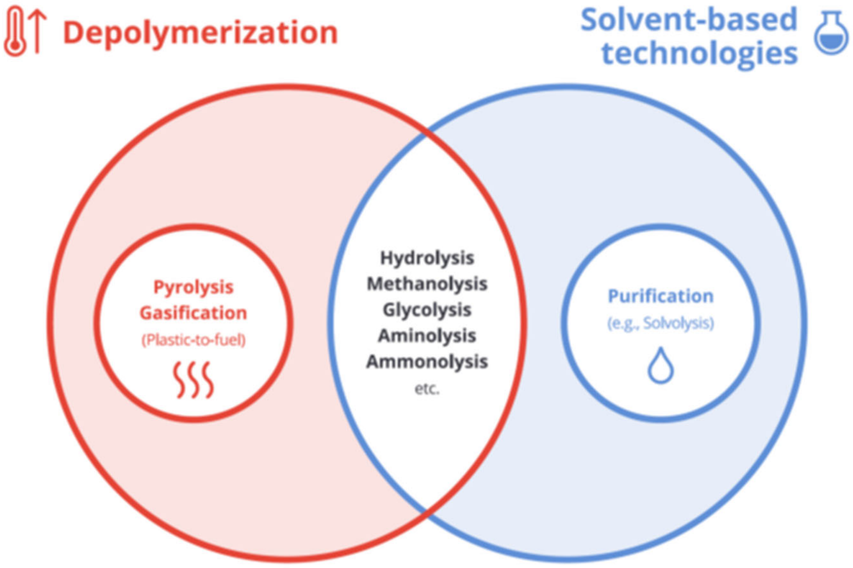

Figure 2. Terminology of chemical recycling [1]

Thermochemical processing

The thermochemical routes to convert polymers and biomass to valuable products is schematized on Figure 3. Gasification and pyrolysis are classified as controlled cracking techniques. Gasification or partial oxidation involves heating the material to very high temperatures (>800°C) in presence of oxygen or steam at high pressures (0.1–2 MPa) to produce syngas or producer gas, which is a mixture of carbon monoxide, hydrogen, and light hydrocarbons. Owing to high volatile matter content in synthetic polymers (>90%), hydrogen production efficiency of 60–70% is possible with minimal or negligible formation of toxic organics such as dioxins and polyaromatics. The syngas can be used to either run a gas engine to produce power or it can be subjected to the classic catalytic Fischer–Tropsch process to produce higher alkanes that are valuable as hydrocarbon fuels. The latter process, however, requires an additional step to convert the solid polymer to liquid fuels, while pyrolysis yields liquid products in a single step.

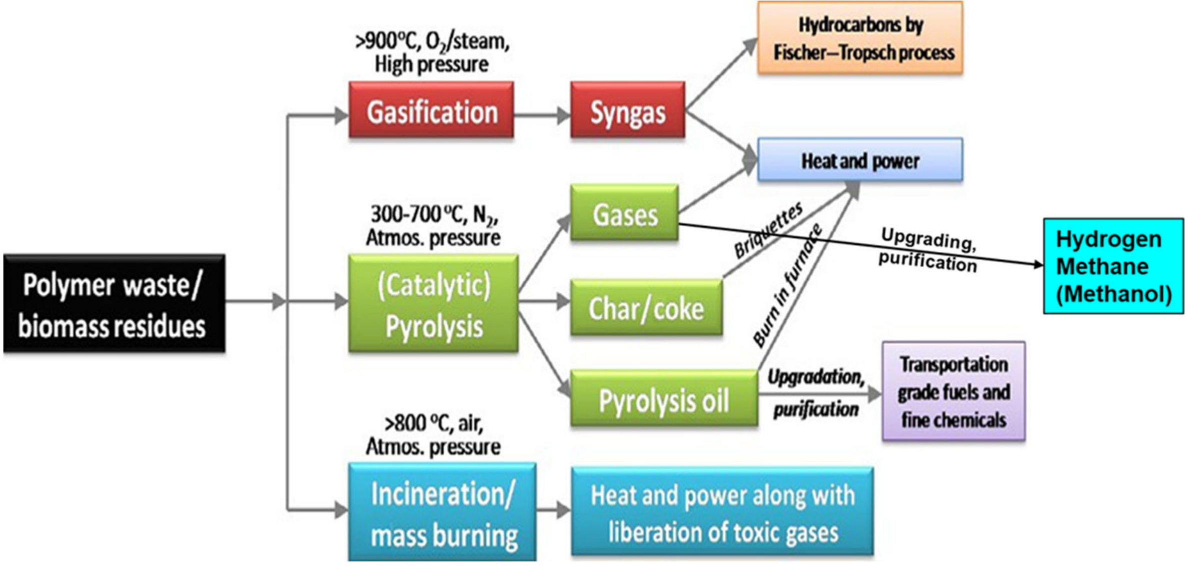

Figure 3. Various thermochemical techniques to convert wastes to useful products [2]

The gasification of plastics has been the subject of several experimental studies but, unlike that of solid biomass, has not led to significant commercial developments. One of the probable reasons is the low calorific value of the gas obtained (by air gasification), and the greater interest in the production of oil that can be transformed into fuel. On the other hand, the pyrolysis of biomass is more difficult to implement than its gasification, because of the very large number of decomposition products and the complexity of their post-processing.

Pyrolysis techniques can be classified according to different criteria:

- Process type: discontinuous, batch (batch or semi-batch) or continuous
- Temperature: medium (MT 350-450°C) or high (HT 750-1000°C)
- Heating: by flame (indirect) or electric (thermal resistance, induction., microwave)
- With or without catalyst

Numerous pyrolysis tests of plastics have been carried out on a laboratory scale with small batch reactors. Table 1 summarizes the results achieved.

MT pyrolysis produces liquids (condensable vapors or oil), solids (char) and non-condensable gases, the relative yields of which are determined by the process conditions. In general, MT pyrolysis gives a high yield of pyrolysis oil that can be upgraded by subsequent refining into fuels and other fine chemicals. HT pyrolysis produces a large gaseous fraction with a variable share of liquids and a minimal part of char (a few%).

However, most plastic will decompose into gaseous compounds at 400-450°C. Some of these gases will condense into liquid fuels at different temperatures (light fractions and heavier fractions), other will stay in the gaseous form at ambient conditions and will be qualified as “incondensable” (mostly C1 to C4 hydrocarbons).

It will be seen in the next section that most commercial technologies are operated at medium temperature and very few at temperatures above 800°C.

Table 1. Summary of several experimental results, laboratory reactors [3]

	Liquid % mass	**Gas % mass**	**Solid % mass**	**Temp. of fusion (°C)**
Polyethylene terephthalate (PET). 500°C, 10°C/minute	23–40	52–77	0-9	260
High Density Polyethylene (HDPE) 400-550°C, 5-10°C/minute 650°C 800°C	79-84 68.5 5.5	16-25 31.5 94.5	0 0 0	130.8

Low Density Polyethylene (LDPE) 500°C, 10°C/minute	95	5	0	115-135
Polypropylene (PP) 300°C 380-400°C	69.82 85-90	28.84 6-13	1.34 2-4	160
Polystyrene (PS) 425-581°C	97-89.5	2.5-9.9	0.5-0.6	240-270 or none

General information about plastics

Types and composition of common plastics

Most plastics used today are in the thermoplastic family, defined as polymers that can be melted and remelted almost indefinitely. They melt when heated and harden when cooled. Once frozen, however, a thermoplastic becomes like glass and prone to fracture. These characteristics, which give the material its name, are reversible, so the material can be reheated, remodeled and frozen repeatedly. As a result, thermoplastics are, in theory, mechanically recyclable (material recycling).

Some of the most common types of thermoplastics are listed below:

- Polypropylene (PP)
- Polyethylene (PE HD, PE LD)
- Polyvinyl chloride (PVC)
- Polystyrene (PS, EPS)
- Polyethylene terephthalate (PET)
- Polycarbonate (PC)
- Fluoropolymers (PFTE, Teflon).
- Thermoplastic polyurethane
- Polyamides (example: nylon)
- Thermoplastic polyimides

Within this family is the polyolefin group, which includes polyethylenes (PE) and polypropylenes (PP). They are produced mainly from oil and natural gas by a polymerization process of ethylene and propylene respectively. Their versatility has made them one of the most used plastics today with 50% of the total.

Other plastics, such as thermosets or epoxy resins, are not recyclable by melting, such as:

- Fiberglass
- Polyester resin
- Thermosetting polyurethane
- Silicone resin
- Bakelite
- Epoxy resin

The case of PVC is particular because of its high chlorine content and the risks induced by hydrochloric acid fumes during its combustion. It is present in electrical cables in varying quantities. Therefore, thermal processing plants must include a dechlorination step.

Figure 4 shows the typical thermal degradation behavior of four polymers when heated to 10K/min. For PE, PP and PE the degradation occurs in a single step without the formation of char. On the other hand, PVC shows a two steps mechanism, where the first step corresponds to the dehydrochlorination reactions with the formation of unsaturated poly-acetylene chains and with a significant formation of a char residue [2].Therefore two-steps pyrolysis of PVC could be used to remove the chorine during the process.

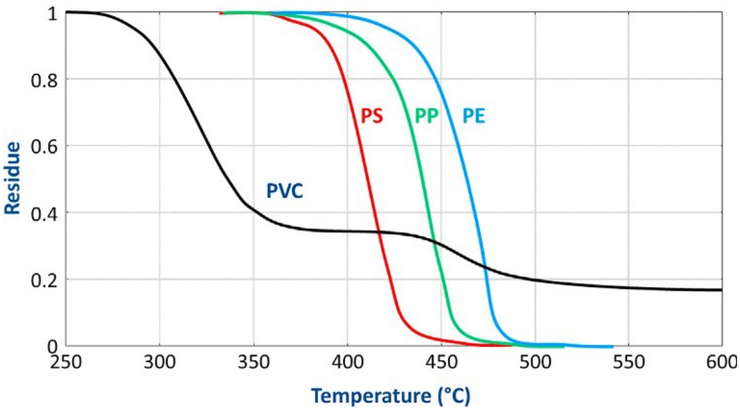

Figure 4. Thermogravimetric analysis of PS, PP, PE, and PVC degradation (10K/min) [2]

Although material recovery is preferable to any other method, only a very small portion of plastics are recycled in this way. The main reason is the difficulty or even impossibility of sorting due to the wide variety of compositions of plastic objects, with the use of specific additives to give them special properties. Many of these additives are toxic and pose a great threat to the environment, biodiversity, and human health [4].

The size of the global plastics market was valued at USD 579.7 billion in 2020 and is expected to grow at a compound annual growth rate (CAGR) of 3.4% from 2021 to 2028. Compared to the world population, this represents $74.38/capita [5]

Production consumed about 17.4 million barrels of oil per day in 2016, or nearly 20% of global oil consumption. With the anticipated reduction of fossil fuel consumption, major oil companies are expected to accelerate the production of plastics in future years [6].

Chemical composition of plastics

The results of immediate analysis of some plastics, has been reported in the literature by several authors [3],[7],[8]. It was found that all types of plastic have high volatile matter contents, which means that they have the potential to produce a high liquid and gaseous yield through the pyrolysis process. In a few cases, a content greater than 99.50% was observed for HDPE, LDPE, PS, and polyamide. In a 2004 study [7], three types of plastic waste (PS, PE, and PP) were pyrolyzed and the results showed that PS produced higher liquid level (89.5% by weight) than PE and PP. The same trend was also observed in another study, where the oil yield obtained was about 88.8% by mass at a temperature of 600 °C and a heating rate of 5 °C/min.

Amongst all current plastic types, PET was found to contain the highest amount of fixed carbon in the range of about 8-13% followed by PVC (5-6%) and LDPE (0-5%) [7]

It is also noted that the ash contents differ according to the types. If they were simple polymers of ethylene, propylene or styrene, the ash content should be zero, but this is not the case because they also contain additives, some of which are not combustible such as mineral or metallic compounds.

The theoretical elementary composition of common plastics can be deduced from that of the monomers from which they are derived, and the molar masses of their elements. The result of this calculation is given in **Table 2** with the calorific value determined experimentally (taken from the NIST database).

There are slight differences in compositions and calorific value compared to values reported in [7] and [8]. As mentioned above, commercial polymers include various additives or adjuvants, some of which produce ash in small to medium quantities. PVC is reported in [8] with an ash content of almost 8% which is relatively high for plastics. This results probably from impurities in the measured samples from other municipal waste.

Table 2. Theoretical elementary compositions of common plastics

		Monomer molar mass	C (%)	H (%)	O (%)	Cl (%)	CO_2 Production (kg/kg)	LCV (MJ/kg)
PET	$(C_{10}H_8O_4)_n$	192	62.5	4.2	33.3	0	2.29	21.85
PE	$(CH2=CH2)_n$	28	85.7	14.3	0	0	3.14	44.16
PP	$(-CH_2-CH(CH_3)-)_n$	42	85.7	14.3	0	0	3.14	44.16
PS	$(C8H8)_n$	104	92.3	7.7	0	0	3.38	40.72
PVC	$(C2H3Cl)_n$	62.5	38.4	4.8	0	56.8	1.41	16.75

Characterization of thermally recoverable waste

The first important task in a waste treatment project is that of waste inventory and characterization in view of the foreseen treatment processes. As stated before, the available yearly quantities have been defined to be about 1500 t/year for polyolefins and up to 2'500 t/y for cable residues (possibly much more for the whole of Switzerland).

To reduce the number of experiments, three plastic waste mixtures have been defined:

- Agricultural source + food packaging (abbreviated A&F);
- Electricity meters (abbreviated EM);
- Plastic electrical cable insulation (abbreviated CAB).

The analysis focused on the following elements of pre-dried waste.

Table 3. Quantities analyzed

Designation	symbol	standard used	unit
Mass loss	WL		% on dry
Ash content	Ash	ISO 1171	% on dry
Higher calorific value on dry and constant volume	$q_{v,gr,d}$	ISO 18125	$kJ \cdot kg^{-1}$
Lower calorific value on dry and constant pressure	$q_{p,net,d}$	ISO 18125	$kJ \cdot kg^{-1}$
Carbon content	C	ISO 16948	% on dry
Hydrogen content	H	ISO 16948	% on dry
Nitrogen content	N	ISO 16948	% on dry
Oxygen content	O	ISO 16948	% on dry

Representative samples were analyzed by EDXRF (X-ray spectrometry), the values are semi-quantitative.[1]

Many secondary elements were detected (35, from silver to zirconium); only a few have been retained as tracers, those found in all mixtures, and which are the most representative. They allow to follow the influence of the different parameters on their evolution during pyrolysis.

These include Aluminum, Calcium, Chlorine, Copper, Iron, Potassium, Silicon, Titanium, Zinc.

Characteristics and composition

The main physicochemical characteristics are given in **Table 4**. They show large disparities in calorific value. The mixture of agricultural plastics /food packaging (50/50 by mass) offers the best potential (38 MJ/kg) with a relatively low ash content (5.6%). On the opposite, cable insulation plastics have a much lower calorific value (16 MJ/kg) and a very high ash content (> 40%). However, in the latter case, the mixture has the advantage of being rich in secondary elements such as Aluminum and Copper, which could be recovered in the char. Also, the calorific value of the pyrolysis products is much higher, since all the inert material (cable insulation and fillers) are retained in the char.

Table 4. Analysis of the mixtures before pyrolysis

Characteristics	A&F	CAB	CPT
Ash material A [% dry]	5.6 ± 0.7	41.1 ± 5.0	11.6 ± 0.3
Higher calorific value $q_{v,gr,d}$ [$kJ \cdot kg^{-1}$]	38'154 ± 863	16'000 ± 606	23'977 ± 774
Lower calorific value $q_{p,net,d}$ [$kJ \cdot kg^{-1}$]	35'697 ± 863	15'284 ± 606	22'921 ± 774
C [% dry]	72.3 ± 2.0	24.1 ± 1.2	60.0 ± 1.5
H [% dry]	11.5 ± 0.3	3.3 ± 0.1	4.9 ± 0.2
N [% dry]	1.2 ± 0.1	0.1 ± 0.1	2.2 ± 0.2
O [% dry]	12.9 ± 1.4	19.6 ± 0.5	22.6 ± 0.6

The secondary elements contents, also exhibit large variations, especially in the CAB mixture from the CableBox® installation as shown on **Figure 5**.

---

[1] In theory, all elements of the periodic table, except for H and He, emit, when properly excited, a unique set of characteristic X-rays or X-ray photons. The energy level (keV) of X-rays (i.e., photons) corresponds to the element of the periodic table and the relative number of photons that emit fluorescence corresponds to the concentration of this element present in the sample. The EDXRF used is a NEX DE from Rigaku, measuring components from Na to U.

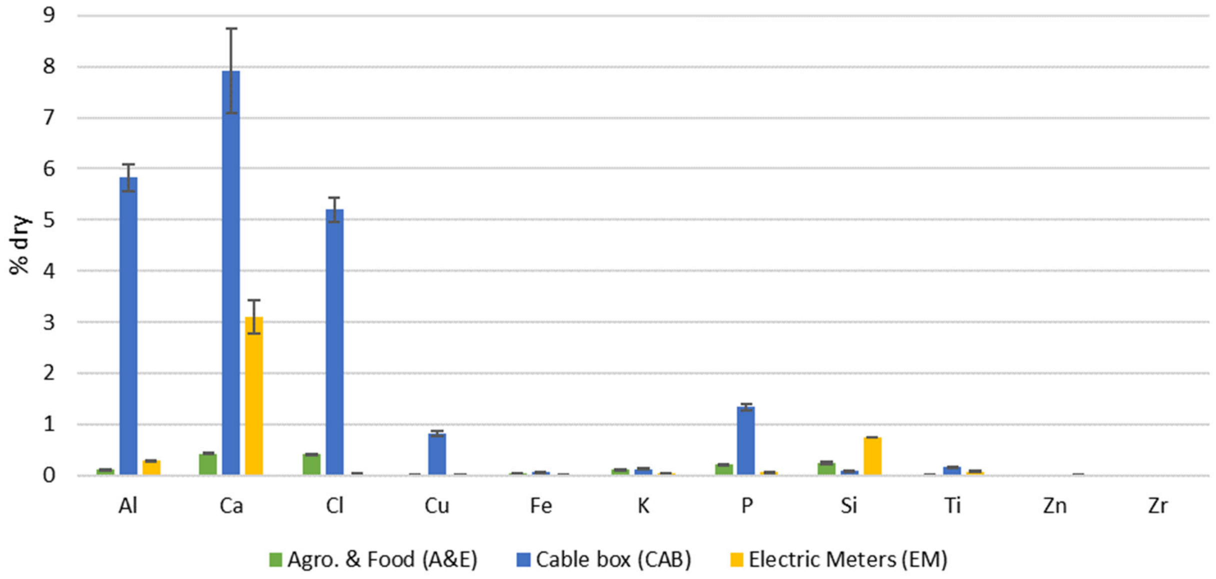

Figure 5. Secondary elements contained in the raw materials before pyrolysis

Laboratory characterization of the behavior of waste in pyrolysis

Organization of tests

Given the large number of parameters influencing the thermochemical decomposition of a plastic during pyrolysis, it was agreed to carry out tests according to a fractional plan of experiments of type L9 according to the Taguchi design of experiment method. The chosen factors were the processing temperature, time, the inertizing atmosphere, and the plastic type. The matrix of the nine test conditions and the validation test is given in Table 5.

The nine configurations were repeated three times to be able to estimate the reproducibility of the configurations. Pyrolysis of the samples was carried out in a calcination furnace, described schematically on **Figure 6**.

The factor T[°C] determines the temperature at which the mixture will be carried during pyrolysis. That of "Time", is the duration of exposure. The sample is introduced into the furnace at the desired temperature and removed after the allotted time has elapsed.

Table 5. Taguchi plan of experiments

Test N°	T [°C]	time [min]	Inertizing gas	Waste type
1	400	10	N_2	EM
2	400	15	CO_2	A&F
3	400	20	without	CAB
4	600	10	CO_2	CAB
5	600	15	without	EM
6	600	20	N_2	A&F
7	800	10	without	A&F
8	800	15	N_2	CAB
9	800	20	CO_2	EM
Validation test				
10	600	10	without	A&F

Inertizing consists of creating a controlled atmosphere of the oven enclosure. "Without" means that the reactor is closed, and that the pyrolysis gas will itself neutralize any presence of oxygen that may beforehand. N_2 or CO_2, are the gases used for other environments.

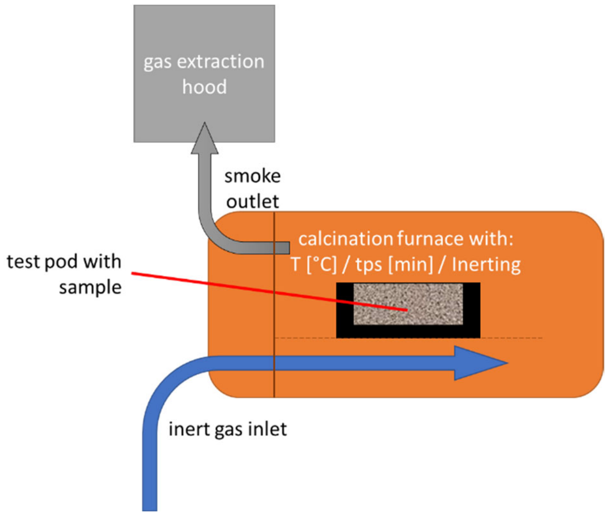

Figure 6. schematic diagram of the pyrolysis test furnace

Quantities evaluated

The quantities recorded or calculated for each of the configurations are the same as before (Table 3). The specificity of the Taguchi design of experiments method, is the evaluation of the results regarding a signal/noise criterion (S/N), in dB, representing the stability of the system and which should thus be maximized in our case.

It is also desirable to maximize:

- The upper and lower calorific value of pyrolysis effluents (liquid + gases combined)
- The mass loss, to minimize residual solids (char).

On the other hand, one seeks to minimize:

- The calorific value of solid residues
- The proportion of char (note that the mineral/inert matter remain mostly unchanged by pyrolysis)

Results

The main measured parameters for the residual solids are given in **Table 6**, **Table 7** and **Table 8**. The first column is for the raw feedstock. Since the combination of temperatures and exposure times are different for each test, it is not directly possible to draw conclusions directly. One can however observe that the increase of temperatures (with increasing test number) leads to an increase of mass loss and a decrease of calorific value.

Table 6. Results obtained with A&F plastic wastes

Parameter	Test N° 2 400°C, 15’	Test N° 6 600°C, 20’	Test N° 7 800°C, 10’	Test N° 10 600°C, 10’
Mass loss (%)	16.0 ± 3.6	90.6 ± 0.6	91.6 ± 1.0	89.4 ± 1.7
Ash content (815°C) A (% dry) As per ISO 1171	6.1 ± 0.2	43.5 ± 6.5	49.3 ± 10.2	49.1 ± 4.5
Higher calorific value, dry HCV ($kJ\cdot kg^{-1}$) $q_{v,gr,d}$ As per ISO 18125	41'556 ± 424	13'555 ± 1281	13'704 ± 1985	15'835 ± 292
Lower calorific value, dry LCV ($kJ\cdot kg^{-1}$) $q_{p,net,d}$ As per ISO 18125	38'938 ± 424	13'350 ± 1281	13'506 ± 1985	15'591 ± 292

Table 7. Results obtained with Cable plastic wastes

Parameter	Test N° 3, 400°C, 20'	Test N° 4 800°C, 10'	Test N° 8 600°C, 15'
Mass loss (%)	33.3 ± 6.5	57.0 ± 2.7	59.0 ± 0.9
Ash content (815°C) A (% dry) As per ISO 1171	46.1 ± 2.7	68.1 ± 0.1	75.6 ± 2.0
Higher calorific value, dry HCV (kJ·kg⁻¹) $q_{v,gr,d}$ As per ISO 18125	17'764 ± 1'618	4'304 ± 379	3'994 ± 1'076
Lower calorific value, dry LCV (kJ·kg⁻¹) $q_{p,net,d}$ As per ISO 18125	16'700 ± 1'618	4'056 ± 379	3'842 ± 1'076

Table 8. Results obtained with Electric Meters plastic wastes

Parameter	Test N° 1 400°C, 10'	Test N° 5 600°C, 15'	Test N° 9 800°C, 20'
Mass loss (%)	14.8 ± 1.9	70.0 ± 1.6	72.5 ± 1.7
Ash content (815°C) A (% dry) As per ISO 1171	8.3 ± 0.3	20.8 ± 0.0	22.9 ± 0.3
Higher calorific value, dry HCV (kJ·kg⁻¹) $q_{v,gr,d}$ As per ISO 18125	27'813 ± 391	23'613 ± 213	22'561 ± 11
Lower calorific value, dry LCV (kJ·kg⁻¹) $q_{p,net,d}$ As per ISO 18125	26'714 ± 391	23'266 ± 213	22'499 ± 11

Figure 7 illustrates the variation of the calorific value of the residual solids with the mass loss following pyrolysis. The temperatures, exposure time and inertizing atmosphere are displayed on each point. The label "wo" is for without inertizing. As explained previously, since the sample was surrounded by its own pyrolysis gas, in the calcination furnace, one estimate that no oxidation reaction with air has taken place. On can observe that for all plastic types, and irrespective of the surrounding gas and exposure time, the sample calorific value tends to increase with mass loss at first (tests at 400°C) and then decrease with higher temperature and, therefore, greater mass loss. This is quite surprising but can be attributed with the release of molecules having a lower energetic content. A similar phenomenon has been observed during the torrefaction of woody biomass at about 250°C (of course very different in structure and composition), due in that case to the release of hemicellulose components.

Also, one can see that the mass loss and calorific values obtained at 600°C and 800°C are very close to each other irrespective of the surrounding gas nature and exposure time. This indicates that the volatile mater of the samples was nearly fully liberated at 600°C and the remaining solid fraction did not evolve significantly between 600°C and 800°C. However, the exhaust gas contains heavy molecules that condense to produce oil. The proportion of condensable could not be determined with the type of apparatus that was used; it is known from previous literature studies that this proportion decreases with higher temperatures as additional cracking occurs in the gas phase.

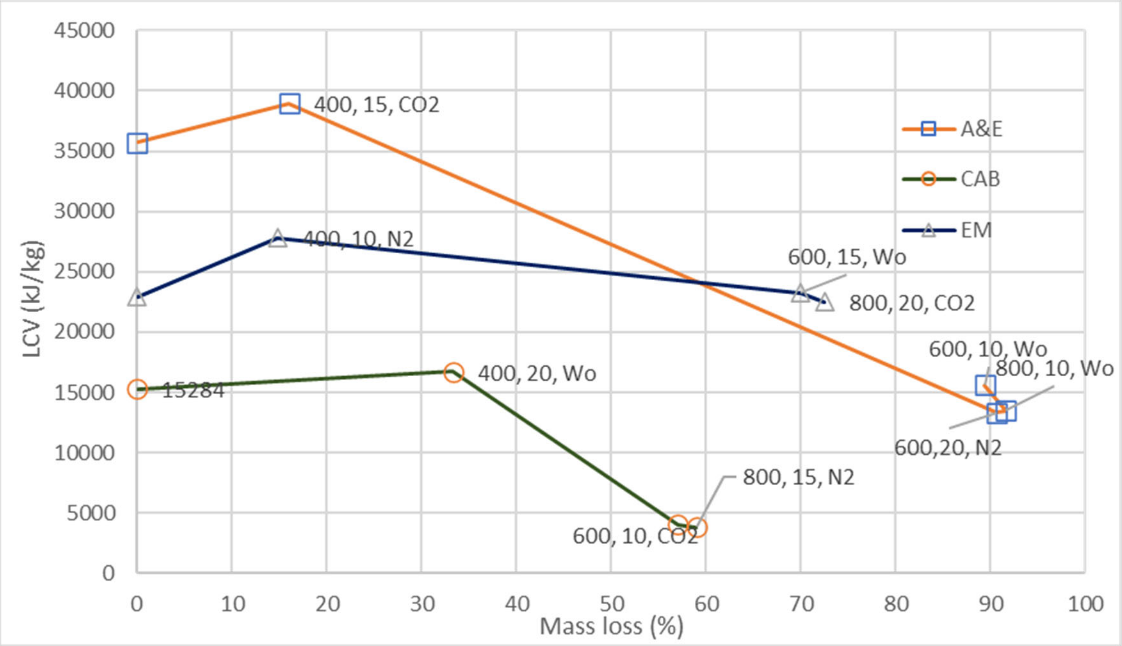

Figure 7. Variation of solids calorific value with the mass loss during pyrolysis

Using the Taguchi method, one could estimate the separate effect of the four parameters considered on the values of all measured data: calorific value and composition of the residual solids, mass loss (condensable and incondensable gas) as well as on the signal/noise ratio.

This was done for 3^4 combinations of the parameters.

The calorific value of the effluents was calculated from the calorific value of the raw samples, the mass loss due to pyrolysis and the caloric value of the residue obtained according to the formula:

$$q_{v,gr,d-effluents} = \frac{q_{v,gr,d-init} - (1-WL)\cdot q_{v,gr,d-resid}}{WL} \qquad [1]$$

The lower calorific value is obtained as follows:

$$q_{v,net,d-effluents} = q_{v,gr,d-effluents} - 212\cdot w_H - 0,8\cdot(w_N + w_O) \qquad [2]$$

With w_H, ,w_N and w_O are the contents of hydrogen, nitrogen and oxygen respectively.

The plan of experiments was validated by a tenth test, chosen empirically, and the results obtained are very close to those that had been estimated theoretically from the first nine tests (the variations on the signal/noise are less than 3%, mostly around 0.1%.)

The modelled value of the gas LCV as plotted on **Figure 8** as a function of exposure time and temperature for the three plastic wastes considered. Again, one can observe that there is little difference in LCV for the 600°C and 800°C cases, except for the cable coating wastes.

A greater exposure time always leads to a slight increase of the effluent calorific value as expected. Existing industrial pyrolysis reactors in plug flow mode typically use a 20-minute residence time.

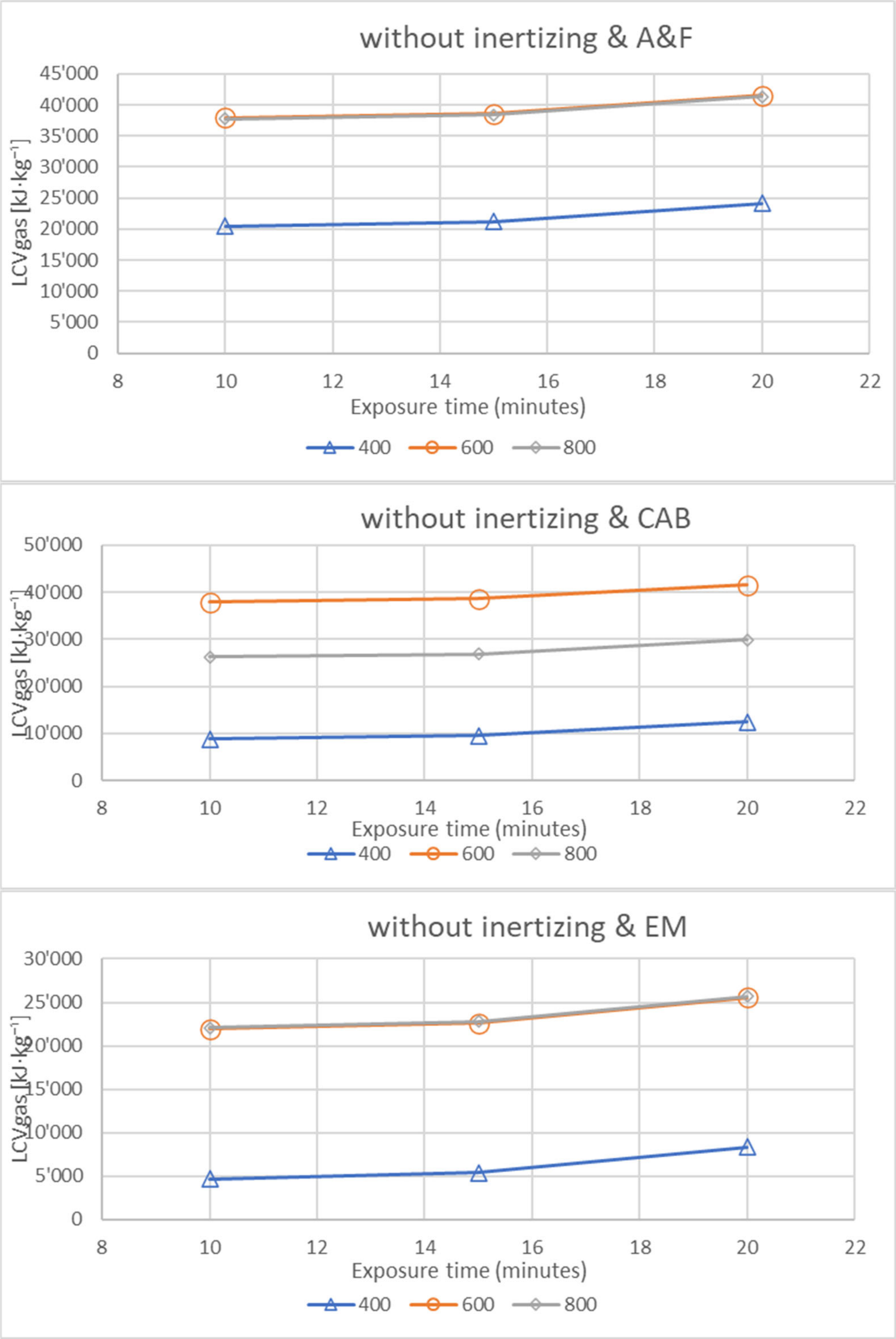

Figure 8. Modelled influence of exposure time and temperature on the effluents LCV
(Top: agricultural plastic and food containers, middle: cable coatings, bottom: electric meters)

One can observe that the LCV of the effluents is quite high for the two first types of wastes with values approaching those of natural gas, which was also expected.
The LCV of EM effluents is lower, but this would not be a problem for the intended application, because the expected quantities are much lower (about 30 t/y) and would not make a difference in the mixed wastes.

Small-scale pyrolysis results

The company Greenlina S.A. located in Avenches (CH) who develops plastic pyrolysis reactors, contributed to the study with pyrolysis tests on a small scale 5-liter prototype with high power induction heating. According to Greenlina, this small electromagnetic induction pyrolysis system has better energy efficiency than hot gas heating systems, especially when operating in batch mode. The reactor temperature rises rapidly, and it can reach the thermal cracking temperature and produce crude oil in a very short time (about 15 minutes).

A larger reactor of 300 tons/year was under construction at the time of the tests (May 2021)

Figure 9. Greenlina electromagnetic induction pyrolysis system

Pyrolysis products of waste packages unsold food consisted of liquid crude oil, paraffin wax and water, as shown in **Figure 10**. Cable residues were also tested but are not reported here.

(a) Pyrolysis oil (b) Paraffin wax (c) Solid residues

Figure 10. Pyrolysis products from food packages

The oil, wax and water yield altogether were about 53% of the mass of the sample. The raw food packages contain a lot of water with a moisture content of about 50%. Therefore, condensed water enters the pyrolysis oil, which decreases its viscosity compared to other pyrolysis oils.

The ratio of solid residues,11.36%, was rather low since most of the sample is composed of organic elements that evaporate during pyrolysis. Solid residues consist of carbon black and inorganic ash/dust. The ratio of non-condensable gases and water vapor was calculated by difference based on the mass balance. We have noticed that this ratio is relatively large, reaching 36%. This is because during the pyrolysis process, before the oil is produced, part of the moisture in the samples will be released into the air via the exhaust gas system. As the current experimental device is a demonstration device, the non-condensable gases and water are simply passed through a buffer tank, sealed with water, and then evacuated after adsorption with activated carbon.

One can conclude from the two types of pyrolysis tests, laboratory, and small prototype that:

- The experiment plan made it possible to explore the influence of all the main parameters in a 4-dimensional space (types of plastics, temperature, reaction time and inertizing). The results are consistent, and the additional test carried out validated the resulting model. The model was used to predict what would be the results obtained for all the points of the space considered (3^4 combinations)

- The results obtained in the laboratory at 600 ° C and 20 minutes are close to those of Greenlina with a temperature of 370 ° C.
- The mass loss, i.e., the transformation into gases and liquids, increases with the pyrolysis temperature, but it varies little between 600°C and 800°C. As it was not possible with the test equipment to separate the gaseous and liquid parts of the effluents, one cannot define the influence of temperature on the respective proportions. It is likely that the proportion of light gases increases with temperature by thermal cracking.
- In the laboratory, the degree of conversion into liquid and gas is the highest for A&F mixtures (nearly 92%) followed by electric meters (72.5%) and cables (59%). This is very consistent with Greenlina's results.
- The lower calorific value of the oils obtained is high: 36.9 MJ/kg for cables and 22.8 MJ/kg for food packaging.
- Cable granules contain a significant fraction of PVC and require specific treatment. The results of the analysis show that chlorine is found partly in oil (4% by mass) and in solid residues (16% by mass).
- Heavy metals accumulate in solid residues, which paves the way to a possible recovery of these elements that remain in cable granules (in concentrations of 4% for Al and 2% for Cu).

Inventory and preliminary evaluation of identified technologies

Many different technologies are commercialized or entering the market. The trend was accentuated in recent years due to the ban of Asian countries on plastic waste imports. A total of 25 technologies were identified and briefly reviewed., 8 in more detail. The main categories of processes identified are presented on **Table 9** according to their modus operandi. Large oil or chemical companies already have or are considering "chemical recycling" facilities: production of liquid plastic derivatives by MT pyrolysis: naphtha, pyrolysis oil, etc. These products are then processed by existing refineries.

For example, Shell, Total, ÖMV, BP, Chevron, Exxon Sabic, BASF, offer or advertise units up to 50 tons per day or more. Some like RES Polyflow / Brightmark advertise 100,000 t/year.

Many other companies offer MT pyrolysis reactors from 2 t/d to 50 t/d. Very few companies offer high-temperature reactors to produce syngas.

Table 9. Main Technologies identified (partial list)

Temperature ranges	**Batch process**	**Continuous process**
Average temperature 400°C – 450°C Plastic to Fuel	1 to 5 t/day Greenlina (Switzerland) R-ONE (Taiwan) Cycle of 4 to 6 hours Normally 2 batch/day Plans for semi-batch or continuous	1-30 t/d • Biofabrik (Gernany) • TCC-Energy (Switzerland) • APchemi (India) 30 – 50 t/d • Valoren (BR) • Recycling Technology (UK) • Nexus Fuel (USA) 15t/d at > 50 t/d : • Plastic Energy • Quantafuel
High temperature 750°C – 1000°C Plastic to gas	Not commercially applicable	25 t/d: Powerhouse (UK) 12 t/d: Metal Expert (Poland) Up to 5 t/d: ETIA/VOW (France)

Life cycle assessment and impact of selected technologies in comparison with UVTD

Life cycle assessment and impact was carried out with the SIMAPRO software completed by the IMPACT 2002+ method to aggregate the impacts on the greenhouse gas emissions (CO_2 equivalent) and on the use of fossil fuel resources. Three scenarios were compared:

- Incineration of plastic waste with standard energy recovery (ITER) electrical efficiency of 15 %, thermal efficiency of 35% to feed a district heating network
- Transformation of plastic waste by pyrolysis into diesel. Energy efficiency of 70% to 50% depending on the type of plastic.
- Transformation by high-temperature pyrolysis into synthesis gas for energy recovery in CHP units. Electrical efficiency 30%, thermal efficiency of 50%

For one ton of treated waste, it was found that the third scenario was best of all three, with half the GHG emissions and half the use of fossil fuel resources compared to ITER plants.

Financial simulations based on different waste recovery scenarios

Financial simulations were carried out using Retscreen Expert [11] clean energy management software platform. It enables the planning, implementation, monitoring and reporting of low-carbon projects in a cost-effective manner. Its interest in our case was limited to the calculation of financial profitability and risk analysis.

A HT pyrolysis plant of 200kg/h operating 7500 h/year was considered. The electricity selling price was 110 CHF/MWh and the heat selling price was 98 CHF/MWh. Two persons are needed to operate the plant on a 24h basis.

Another scenario, where the gate fee is zero but where the electricity is valued at 270 CHF/MWh (own use) is envisaged on an existing waste handling plant.

The quoted investment cost is about 3 MCHF and the resulting operations and maintenance cost are 0.66 MCHF. The fuel cost, i.e., the net revenue for taking the waste at the plant was taken at minus 136 CHF/ton. These three parameters were varied by +/-20% and the effect was evaluated with the Monte-Carlo method (5000 instances). It was found that the operating costs have the biggest influence on the financial results. The return-on-investment period was found to vary between 7.6 years and 13.9 years with a confidence interval of 95% (nominal 10 years). The Internal Rate of Return varied between 0.91% and 9.34% with the same confidence interval (nominal 5%)

Conclusions and further work

Only high-temperature pyrolysis or pyrogasification technologies were found to meet the technical requirements, types of waste and quantities to be treated and the environmental criteria of this project. The annual quantities are sufficient for a pyrolysis solution, but the economics are largely dependent on the operating costs, especially the gate fee revenue and the salaries, number of operators, and energy revenues.

Waste cable plastic is a good candidate for a larger size demonstration unit (possibly more than 20 t/day) to produce locally recoverable gas. Two ways of valorization are then envisaged: either the production of electrical and thermal energy (CHP) with the need to valorize the heat locally, or the production of hydrogen and, in part, heat.

The environmental impact of the different options was assessed for greenhouse gas emissions and fossil resource economy. That of HT pyrolysis with CHP is always better than that of the existing solution (ITER). The impact of hydrogen production has not been assessed and should be subject to a specific analysis.

The next steps will be to gain credibility on the potential solutions with visit to planned pyrogasification plants (expected in 2022)

References

[1] Rollinson, A., Oladejo, J. (2020). Chemical Recycling: Status, Sustainability, and Environmental Impacts. Global Alliance for Incinerator Alternatives. doi:10.46556/ONLS4535, Available online at: www.no-burn.org/cr-technical-assessment

[2] Thermochemical Process Engineering, Advances in Chemical Engineering, Volume 49, 1st Edition (2016), Editor: Kevin Van Geem, ISBN: 9780128097779, Chapters 1 & 2

[3] S. D. A. Sharuddin, a review on pyrolysis of plastic wastes, Energy Conversion and Management, Volume 115, 1 May 2016, Pages 308-326

[4] J.N. Hahladakisa et al. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling, Journal of Hazardous Materials Volume 344, 15 February 2018, Pages 179-199

[5] https://www.grandviewresearch.com/industry-analysis/global-plastics-market accessed 15.11.21

[6] The Story of Plastics. On-line video https://www.youtube.com/watch?v=PCNanJNJ8JA accessed 15.11.21

[7] F. Abnisa et al. A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil, Energy Conversion and Management, Volume 87, November 2014, Pages 71-85

[8] B. Kunwar et al., Plastics to fuel: a review, Renewable and Sustainable Energy Reviews 54 (2016) 421–428

[9] B. Kunwar et al., Plastics to fuel: a review, Renewable and Sustainable Energy Reviews 54 (2016) 421–428

[10] https://www.greenlina.com/en/home-en/ accessed 15.11.21

[11] www.retscreen.net accessed 15.11.21