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# Techno-economic assessment of pyrolysis of rubber and plastic wastes

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# Introduction

Globally plastic waste production accounts to 380 million tons of plastic each year *(Plastic Oceans)*. Plastic pollution is a problem globally, plastics have entered the food chain and are therefore ubiquitous contaminants. Their good mechanical properties made them became an everyday item, present in all aspects of day-by-day life. Moreover, plastic ability to last in time makes them more subjected to improper discarding and their light weight makes it possible to travel for long distances.

The situation is similar for end-of-life tires (ELTs); each year 290 million tires are disposed of in the USA and about 3.1 million tires in Europe (European Tyre and Rubber Manufacturers' Association*)*. The dispersion ability of tire is negligible, but their wrong disposal is something that everyone of us has experienced on many occasions. This is due to ELTs mismanagement, in fact most people do not know how to correctly dispose of tires.

To comply with more restrictive regulations and laws being introduced each year and to evolve towards a circular economy system there is an urgent need for new recycling technologies. One of the most promoting is thermochemical recycling, where under the influence of high temperature materials decompose, or else chemical bonds are broken to form lighter compounds.

The first step of this work consisted in the assessment of the feasibility of the pyrolytic conversion of plastic waste and rubber into value-added products by conducting a detailed literature review to understand how the process works and how equipment and process parameters affect the final products.

After an in-depth knowledge has been acquired experimental activities have been carried out. All the experimental activities have been carried out at the Institute for Chemical and Fuels from Alternative Resources (ICFAR) of Western University (Ontario, Canada). Virgin HDPE and LDPE have been processed in a single stage and double stage pyrolysis configuration. The reactor utilized for this work is a vertically mechanically fluidized reactor, operated at temperatures between 450 °C and 550 °C. Some additional experiments have been performed by further cracking the products of the first stage utilizing a secondary furnace heated to 800°C ~ 900 °C. Rubber chunks have also been pyrolyzed my means of a horizontal mechanically fluidized unit at different temperatures

The final goal of this work was to perform a techno-economic evaluation of the pyrolysis of plastic and rubber wastes and to critically compare the results, with the aim to assess the economic sustainability of the scale-up of the considered processes. Both routes have been scaled up to 2500 kg $h^{-1}$ of treated material and the economic sustainability of different technical scenarios has been evaluated.

# 2 Wastes

## 2.1 Plastic waste

The term plastic is used to define a family of polymers which present some peculiar characteristics, such as: lightweight, strong, flexible, resistant to corrosivity and electrical insulator.

Plastics are classified as thermosets or thermoplastics depending on their ability to melt when heated. Thermosets have linked bonds that do not allow them to melt, they present a permanent solid state and if hated they undergo to a charring like process. The types of plastic which enter this category are polyurethane (PUR), silicon, epoxy resins and other. Thermoplastics have the ability to melt if hated and harden if cooled. They can be subjected to this loop many times and their physical properties are not going to change. The types of plastic included in this group are polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl-chloride (PVC) and others.

The previously listed types of plastic are the most used and therefor the most common resins found in plastic waste. A report on plastic released by PlasticEurope, states the main employments of the most common types of plastic:

- Polyurethane is used to produce insulating foams, pillows, and matrasses.
- Polyethylene has different uses based on his density. Linear low-density PE (LLDPE) and low-density PE (LDPE) is employed in food packaging films, agricultural films, bags, and others. Medium and high-density PE is crafted into pipes, shampoo bottles, cleaning products bottles, toys, and others.
- Polypropylene is used to produce pipes, automotive parts, microwave containers, candy wrap, food packaging and others.
- Polyethylene terephthalate is employed to produce water, soft drinks, juice cleaner bottles.
- Polystyrene is used as insulation material, in electrical and electronic equipment, food packaging and others.
- Polyvinyl chloride is the main component of window frames, floor and wall covering, profiles, pipes, cable insulation and others.

Furthermore, in *Figure 1* are shown the main plastic resins used by different industrial sectors. For each segment is reported the percentage of used resin related to a total plastics request of 51.2 Mt in Europe.

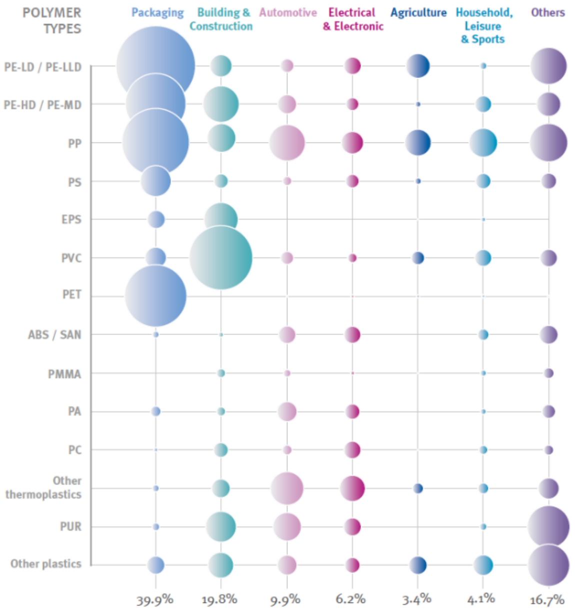


*Figure 1 - Main resin employment for each sector (PlasticEurope Report, 2018)*

The resin demand is then converted into products which have a lifetime ranging from less than 1 year up to 50 years based on the application field. After their service life these products became waste. In Europe each year are produced around 25.8 Mt of plastic waste *(Plastic Strategy EU Commission,2018),* each industrial sector contributes with a different waste share since the product life varies according to its purpose (*Figure 2*).

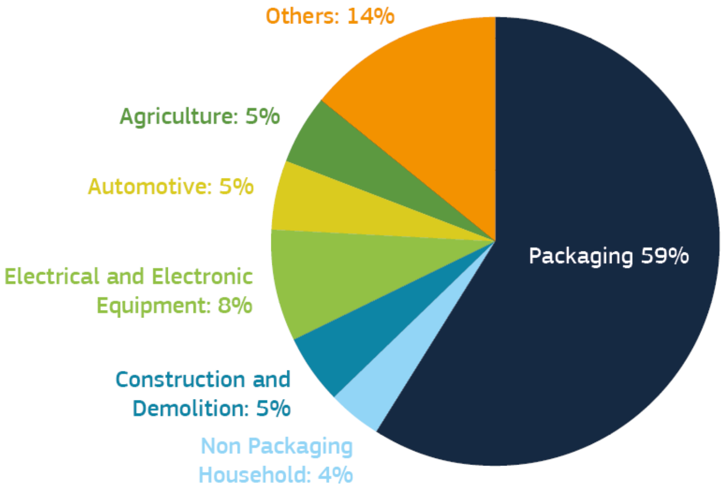


*Figure 2 – EU plastic waste production by each sector (Eunomia, 2017)*

The waste production leading sector is packaging because the end product has a life of 1 year on average. For this field is present an EU regulation 'Packaging and Packaging Waste Directive 94/62/EC' which sets targets on recovery and recycling. The 2018 revision sets the recycling target up to 75%.

Considering the total amount of plastic waste was estimated by PlasticEurope in 2019 that 32.5% is sent to recycling, 42.6% is used in energy recovery and 24.9% is sent to landfill. More action is taken by the European Union to lead plastic economy towards a circular system. To achieve this goal zero plastic should be sent to landfill so the recycling collection system needs to be improved and new recycling technologies need to be developed and be affordable for industries. At this time energy recovery is the most used option but plastic incineration leads to a money loss because its value is not exploited *(Plastic Strategy EU Commission,2018)*.

## 2.2 Waste tires

Tires are complex composition of rubber, steel, textile, filler, and additives *(Figure 3)*. The percentage of each component is dependent on tire application (car or truck) and producers. They keep the composition and mixture secret, so the reported quantities are derived from tires analysis. Rubbers are the main component of tires, and they are dived into natural and synthetic. Natural rubber is retrieved from *Hevea brasilienis* tree and it cannot be replaced by petroleum derived ones because it shows good natural fatigue and tear resistance. The main synthetic rubbers used in tire manufacturing are butyl and styrene-butadiene rubber. Their physical and chemical properties affect tires performance. Moreover, important components of tires are filler, especially carbon black and amorphous silica. Their addition to rubber improves its quality resulting in higher tear, abrasion resistance and tensile strength. So, the overall tire performance is increased. Sulphur and zinc are also found in tires compositions because they are used as vulcanization agents. During vulcanization, sulfur addition helps rubber transformation to a solid and durable material by cross-linking enhancement in the matrix; ZnO acts as activator reducing vulcanization time. Steel wires are used to reinforce the tire case and to reduce wear. Other additives such as antioxidants and antiozonants are added during the manufacturing process to improve temperature, oxygen, and ozone exposure *(U.S Tire Manufacturing Association Czajczynska et al.,2017 Martínez et al.,2013, Nanda et al.,2021)*.

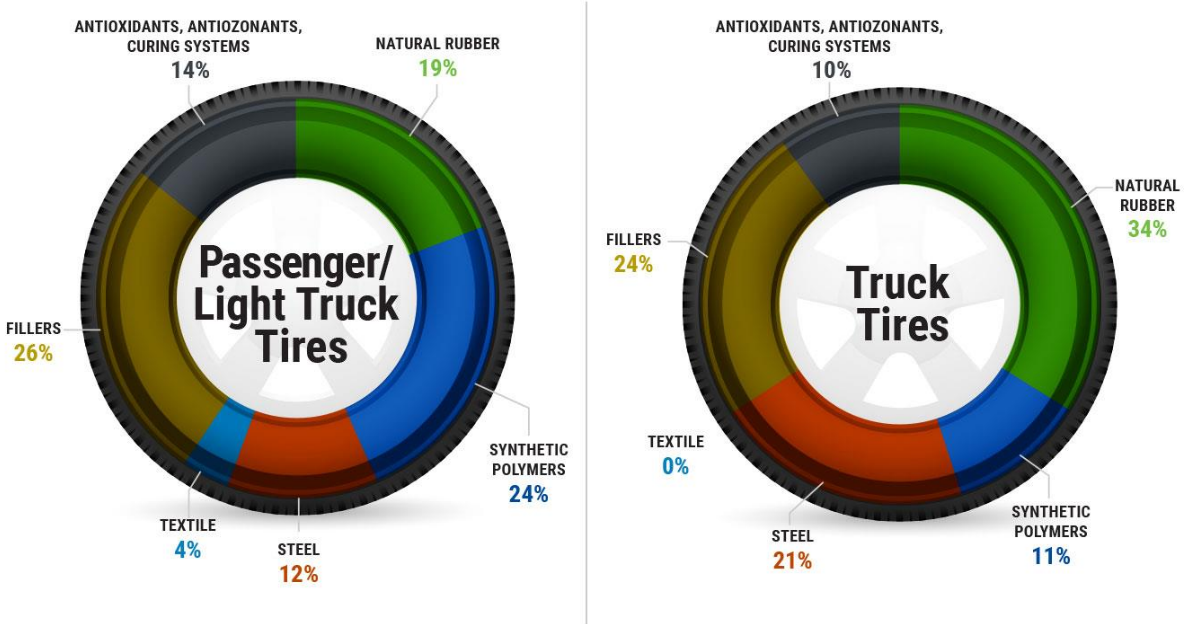


*Figure 3 - Tire composition depending on type (U.S Tire Manufacturing Association)*

Tire's structure is also complex and composed by different layers *(Figure 4)*. Tire's bread is formed by a steel cord consisting of a steel wire bundle. Its function is to secure the tire on the wheel. Starting from the inside the other components are *(U.S Tire Manufacturing Association Czajczynska et al.,2017)*:

- Inner liner is composed of a rubber mixture which gives it air impermeable properties, so it can retain pressure inside the tire.
- Plies are formed by fiber cords included in a rubber matrix. Their function is to give structure to the tire and to help increase strength to contain tire pressure. Body plies are the carcass of the tire, they help sustain the weight of the car and absorb shocks.
- Steel cords framed in a rubber matrix compose belts. They are placed between the carcass and the tread to avoid their contact. Belts are wrapped around the carcass to stabilize it which improves wear and traction.
- Tread is composed by a thick layer of rubber, and it comes into direct contact with the road. Its composition is resistant to abrasion, fracture, and shock.
- Sidewall is a rubber layer at the sides of the tread which covers carcass and bread.

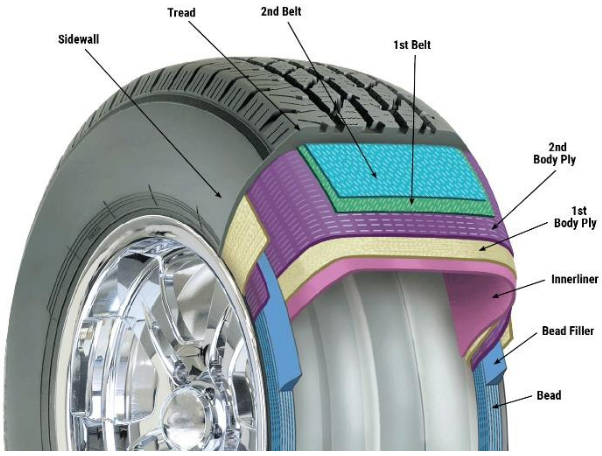


*Figure 4 - Tire structure*

The European Tyre and Rubber Manufacturers' Association (ETRMA) estimated 4.5 billion of tires sold in Europe during 2018 *(ETRMA,2019)*. In the same year 3.1 million tons of end-of-life tires were disposed or sent to recovery in the EU28, this number showed an increase of the 4% with respect to 2017 *(ETRMA,2018)*. Tire properties make them resistant to heat, electricity, chemicals, and bacterial, resulting in difficult disposal. *Czajczynska et al. (2017)* in their review reported that microorganisms need more than 100 years to degrade tires. Moreover, waste tire is a bulky material adding another challenge to their disposal. 75% of their matrix is composed by air which can gather toxic components and increase fire hazard. In fact, fires concerning waste tire are difficult to extinguish and can last for several days, in addition they release harmful compounds for human health, such as dioxins, and they pollute air, soil, and water. Waste tire management follow the waste hierarchy: minimization, reuse, recycling, energy recovery and landfilling. The EU Directive 1999/31 (Landfill Directive) prohibits waste tire disposal in landfills. As showed in *Figure 5*, in the years following the directive emission a substantial decrease is reported. Furthermore, the landfill directive increased recovery and promoted research for alternative technologies. In 2015, reuse and retreading accounted for 12 and 6% respectively. Retreading is a recycling methodology consisting of warn-out tread replacement, it is mostly applied with truck tires which can undergo up to two retreading *(ETRMA,2017)*. It has been reported that the retreading process could not be economic advantageous with respect to new tire production, and it also poses concerns towards safety and stability at high velocities *(Arabiourrutia et al.,2020)*. Other available reuse options are crumb rubber for playground paving, sport pitches, rubber asphalt, and concrete manufacturing *(ETRMA,2017)*.

Waste tires present high calorific value of 30-40 MJ/kg *(Isalm et al.,2008)* which make it appalling for energy recovery; 28% of waste tire are used for energy recovery *(Figure 5)*. The main application of end-of-life tire (75wt%) is in cement kiln. Here, they are mixed with coal and used as fuel. The high temperature of 1200°C ensures complete combustion of all tire components. Environmental safety concerning emission is observe because addition of waste tire result in emission reduction when compared to coal (*Czajczynska et al.,2017)*. Recycling is the biggest treatment route (46%), and it consists mainly of granulation and application in steel mill and foundries. It is understandable that recycling cannot tackle the disposal problem alone. Energy recovery poses environmental problems because of SOx, NOx, VOC, PAHs, dixions and other harmful compounds emission.

Thermochemical process like gasification and pyrolysis seems to be an environmental safety route to follow. They allow waste tire valorization by generation of added value products and avoid hazardous emissions.

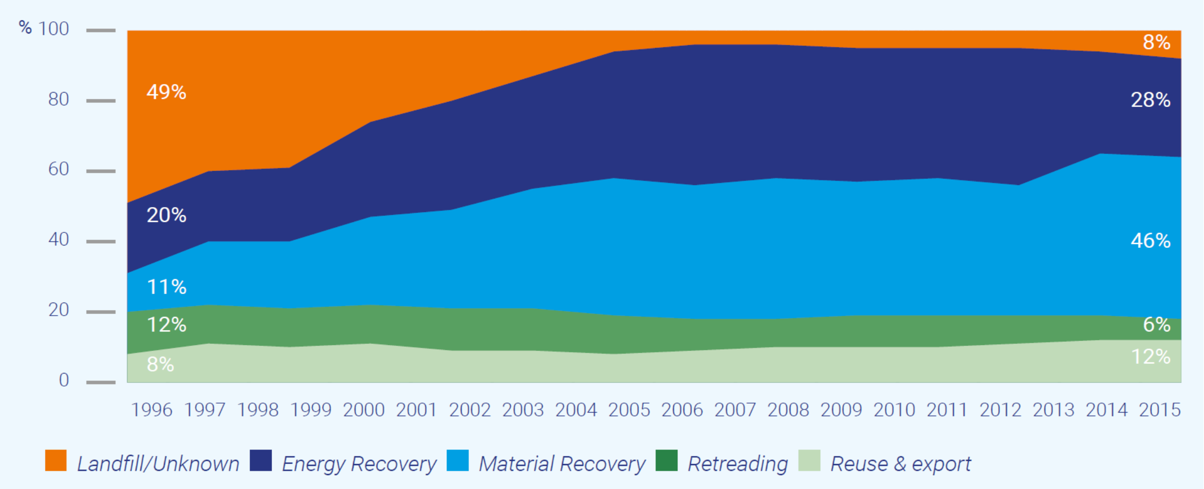


*Figure 5 - Waste tire management evolution between 1996-2015 (ETRMA,2017)*

# 3. Thermal treatments

Aiming at a zero-waste economy, the viable alternative to plastic waste disposal are the recycling processes. These are classified in: primary, secondary, tertiary, and quaternary.

Primary recycling is re-extrusion which is applied mainly to plastic waste from industrial processes. Re-extrusion can also be used for post consumers plastic wastes, but it is not cost effective since it requires a complex collection system for small quantities.

Mechanical recycling is the secondary recycling method. This is a complex process since it can only be applied to polymer homogeneous classes what can be performed by a separation system based on optical properties or resin. Furthermore, each product needs to be de-labeled, crushed, washed, and dried. The recycled product obtained at the end of this process can be re-used in many manufacturing processes. The main problems of this industrial treatment are heterogeneity, contamination, and degradation of plastic. Also, it is a high energy-consuming process.

Tertiary treatment is chemical recycling; it is called chemical because during the process occurs a bound change into the polymer which leads to the formation of monomers or useful petrochemicals. The main advantage of this treatment method is the low need of pre-treatments. Chemical recycling processes are gasification, hydrogenation, and pyrolysis *(Nanda et al., 2021)*.

Energy recovery is the last recycling option, and it consists in plastic waste incineration. Nowadays, is the second used treatment method but it does not allow to value the plastic again. Moreover, this process generates exhaust gasses in need of further treatments before release into the atmosphere *(Nanda et al., 2021)*.

This study will focus on plastic waste chemical recycling treatments, because the final products can be reused in virgin plastic production processes, as fuels and petrochemicals.

## 3.2 Plastic waste pyrolysis

Pyrolysis is a thermochemical process for feedstock conversion to valuable added products, like fuel oil substitute or petroleum refinery raw material. The thermal degradation occurs in a wide range of temperatures and in presence of an inert atmosphere. During the last decades pyrolysis has been widely studied as waste chemical recycling technology to achieve a zero-waste economy.

Depending on ceiling temperature, heating rate and residence time pyrolysis can be classified as slow or fast. In slow pyrolysis lower temperature is achieved, the feedstock is subjected to small temperature rises and longer residence time (minutes, hours) are required to achieve degradation completion. These parameters affect the final product, leading to higher char formation. Fast pyrolysis operates at higher temperature and low residence time (order of seconds). The almost instantaneous rise in temperature allows the feedstock transformation into volatile matter with almost no solid residue left *(Table 1)*.

*Table 1 - Pyrolysis processes (Jung et al., 2006)*

| **Pyrolysis process** | **Heating rate** | **Residence time** | **Temperature (°C)** | **Products** |
|---|---|---|---|---|
| Carbonization | Very low | Days | 450-600 | Charcoal |
| Slow Pyrolysis | 10-100 K/min | 10-60 min | 450-600 | Gas, oil, char |
| Fast pyrolysis | Up to 1000 K/s | 0.5-5 sec | 550-650 | Gas, oil |
| Flash pyrolysis | Up to 10000 K/s | < 1 sec | 450-900 | Gas, oil |

The main products of the pyrolysis process are gas, liquid and solid. From the main reactor a gas mixture is extracted, this is composed by a condensable fraction called liquid oil and a non-condensable fraction. The latter can be used to power the process. By its combustion heat can be retrieved and used as source to maintain or rise the reactor temperature. The most interesting part is the liquid oil, it is composed by heavy molecular weight compounds that can be used as feedstock in the refinery industry.

Plastic waste pyrolysis has interested many researchers because plastic is composed by petrochemical products (hydrocarbons) and its decomposition produces compounds like those hydrocarbons.

Plastic waste is a suitable feedstock for pyrolysis since they can be thermally decomposed. It is of common understanding that when exposed to heat polymeric materials brake. The degradation can happen rather randomly or from the end. Random chain scission occurs when the polymer breaks in an arbitrary point creating polymers with lower molecular weight. End-chain scission is given by monomer formation. In other words, the monomer present at the end of the chain is liberated.

Other main chain reaction can happen during decomposition like chain stripping where two adjacent polymers link together after side group removal. This is an important reaction for tar formation. Moreover, elimination and cyclization reaction happen to either break side groups or to link them together. Cyclization is fundamental in char formation because cyclic compounds have more carbon than the original polymer.

Generally, the main reaction in plastic degradation is random chain scission. It can be distinguished by end chain reaction by monitoring monomer evolution and mass weight loss. When random break occurs, a consistent mass is lost in the process. Both are based on free radical process and can be described by three steps *(Witkowski et al., 2016)*:

- Initiation - the process starts with the rupture of the first bond and the creation of two radicals. It is likely to break the weakest link generally the second single bond from a double bond (β-scission). If end-chain occurs the small free radical formed is highly unstable and readily attaches to another chain.
- Propagation – the free radical reactivity propagates within the chain and rapidly other reactions take place.

- Termination – at a certain time the reaction is going to stop. It can occur when two radicals are oriented in a favorable way which promotes their combination or when the chain ends.

The following section provides a brief description of decomposition behaviors of the main plastic waste components.

### 3.2.1 Polyethylene

Plastic waste is composed by two type of polyethylene high density and low density. HDPE has a packed structure where linear chains of polymer with low branching degree are linked together, hence high density is achieved. LDPE present a higher degree of branching; thus, lower crystallinity makes it suitable for filming. Both types of PE follow the same decomposition mechanism: random chain scission. Many studies found that the initiation occurs at a branching point, so LDPE presents a lower decomposition temperature than HDPE. When exposed to high temperature PE back bone breaks creating great quantities of smaller molecules and radicals. These active radicals further decompose and react yielding different products like alkanes, alkenes, and dienes *(Witkowski et al., 2016)*.

Many studies have investigated the applicability of high-density polyethylene in pyrolysis process. As a result, its usability was proven, first the high volatile content makes HDPE and all plastic suitable for oil production by pyrolysis. In fact, it has been proven a direct correlation between volatile content and liquid yield; higher the content in the feedstock higher the oil product *(Sharuddin et al., 2016)*. *Ahmad et al.* (2015) reported that non conversion of HDPE to liquid or gas was found at a temperature of 250°C. Meaning that higher temperatures must be applied during pyrolysis of high-density PE in a micro steel reactor. Also, they measured a maximum liquid yield of 80.88% at a temperature of 350°C. With further increase of temperature lower liquid were recovered and higher gas was yielded, the cracking temperature is above 550°C. Other studies reported a liquid yield of 79.08wt% at a temperature of 550°C during thermal pyrolysis in semi-batch reactor *(Kumar et al.,2011)*.

LDPE is another common plastic type found in PSW, its branched structure favors pyrolysis at lower temperature. *Marcilla et al.* (2008) performed thermal and catalytic pyrolysis of low-density PE in batch reactor at a temperature of 550°C, a liquid yield of 93.1 mg/100mg of LDPE and 61.6 mg/100mg of LDPE were measured, respectively. In this case catalyst addition enhanced conversion to gaseous products. Moreover, other researchers reported liquid yields of 89.2wt% at 500°C in fluidized bed reactors.

### 3.2.2 Polypropylene

Polypropylene is synthesized in three different forms but only the isotactic one is employed commercially. PP present a highly crystalline structure with a melting temperature around 170°. Its decomposition, as for PE, follows random chain scission producing mainly propane compounds and other fragments. *Ahmad at al.* (2015) reported a higher overall conversion for PP with respect to PE. This is due to a greater decomposability of polypropylene thanks to its branched structure. Also, the higher amount of tertiary carbon in the backbone sponsors thermal cleavage. By TGA application they were also able to identify the maximum degradation temperature range (400-500°C) but appreciable decomposition was detected already at temperatures lower than 400°C. They also identify the maximum liquid production in micro steel reactor at 300°C to be 69.82%. Other studies have reported higher liquid yields of 80.1wt% for PP pyrolysis at 380°C in batch reactor *(Sakata et al.,1999)*. It is a common result that higher temperatures (>500°C) increase the solid formation by promoting secondary reaction like recombination or condensation.

### 3.2.3 Polyethylene terephthalate

PET is the most known and used polyester. Its decomposition starts with the formation of a ring structure in the backbone chain, then it brakes leading to the formation of smaller polymers. Other reactions happening lead to the formation of vinyl end chain and consequently polyene structures. The proximate analysis showed that polyethylene terephthalate has the lowest volatile content, thus oil production is not much favored. This has been observed in many studies; the gas production is greater 52-77wt% while oil production ranges between 23-40wt% *(Sharuddin et al.,2016)*. Moreover, studies showed that the oil fraction collected is composed by high quantities of benzoic acid which gives to the liquid corrosivity properties that makes it unsuitable for application.

### 3.2.4 Polystyrene

PS is a polymer consisting of a backbone hydrocarbon chain with phenyl groups attached to every carbon. Depending on its method of synthesis polystyrene structure changes showing a different degree of irregularities, hence the decomposition rate. The decomposition yields mainly styrene, benzene, and toluene; dimer, trimers, tetramers and pentamers are present in significant quantities. Studies have observed a high oil production during pyrolysis of PS. Yields greater than 96% have been measured for different type of reactors at temperatures ranging between 400-600°C *(Sharuddin et al.,2016)*.

### 3.2.5 Polyvinylchloride

PVC differs from the other thermoplastic because it is not derived only from oil. At the name suggests it is a mixture of chlorine (57%) and carbon (43%) deriving from hydrocarbons. The decomposition of polyvinylchloride take place by dichlorination, chlorine is liberated by β-elimination from the polymer chain to react with hydrogen and form hydrogen chloride. This reaction is catalyzed by acid like HCl itself, so it happens at very high rate. Literature on PVC pyrolysis is not so common, this is due to the formation of corrosive and toxic compound during processing. Furthermore, low oil yields were measured, and char formation was higher than gas and liquid. To be successfully converted by pyrolysis PVC should be subjected to a dichlorination process which can be achieved by stepwise or catalytic pyrolysis, and with adsorbent addition in the feedstock. Ultimately, feedstock processing is an additional step in the process leading to a higher cost *(Sharuddin et al., 2016)*.

The following *Table 2* contains the main characteristics, applications, challenges, and products of the above describe plastic types.

*Table 2 - Plastic type, characteristics, application, and role in pyrolysis (Miandad et al., 2017)*

| **Plastic type** | **Characteristics** | **Applications** | **As pyrolysis feedstock** | **Pyrolysis oil composition** |
|---|---|---|---|---|
| Polyethylene (PE) | HDPE<br>• Long polymer chain<br>• Highly crystalline<br>• High strength properties polymer<br>LDPE<br>• Less tensile strength<br>• Less hardness<br>• Excellent water resistant | • Toys<br>• Oil containers<br>• Detergents bottles<br>• Milk bottles<br>• Trash bags<br>• Wrapping foil for packaging<br>• Plastic bags | • Requires high temperature >500°C due to its long chain structure<br>• It converts into wax instead of liquid fuel in thermal pyrolysis<br>• Wax formation occurs in external site of catalyst while further cracking of wax into gasses and liquid in internal catalyst site | • 1- and 3- methylcyclopentene<br>• 1-hexene<br>• Cyclohexene<br>• 1- octene<br>• 1-nonene<br>• 1-decene<br>• Benzene<br>• Toluene<br>• Xylene<br>• Di and tri methylbenzene indane<br>• Indene<br>• Aphthalene<br>• Fluorene<br>• Acenapthene |
| Polypropylene (PP) | • Good heat and chemical resistance<br>• Low density<br>• High rigidity<br>• High hardness | • Pail<br>• Carpets<br>• Furniture<br>• Storage box<br>• Office folder<br>• Flowerpot<br>• Car bumpers | • Requires high temperature<br>• Difficult to degrade under thermal pyrolysis<br>• Produces liquid yield with high aromatic compounds under catalytic pyrolysis | • Benzene<br>• Toluene<br>• Xylene<br>• Ethylbenzene<br>• Indene<br>• Biphenyl<br>• 1-heptene<br>• 1-octene<br>• 2-methyl 1-1-pentene |
| Polyethylene terephthalate (PET) | • Lightweight<br>• Pressure resistance<br>• Larger capacity<br>• Versatile polymer | • Food packaging<br>• Electrical insulation<br>• Magnetic tapes<br>• X-ray<br>• Printing sheet<br>• Photographic film | • It contains heteroatoms | • 1-propanone<br>• Benzoic acid<br>• Biphenyl<br>• Fluorene<br>• Diphenylmethane<br>• Anthracene<br>• Benzophenone<br>• 1-butanone |
| Polystyrene (PS) | • Heat resilience<br>• Lightness<br>• High strength<br>• Reasonable durability | • Toys<br>• Medical stuff<br>• Electronics<br>• Food packaging<br>• Construction stuff | • Requires low temperature in comparison to PP and PE plastic types<br>• Produces less viscous oil in comparison to PP and PE plastic types | • Styrene<br>• Toluene<br>• Ethylbenzene<br>• Benzene<br>• Xylene<br>• Cumene<br>• Naphthalene<br>• Anthracene<br>• Di and tri methylbenzene |
| Polyvinylchloride (PVC) | • Resist to fire<br>• Versatile plastic | • Automotive interior<br>• Credit cards<br>• Medical devices<br>• Packaging<br>• Electrical insulation<br>• Food foil<br>• Boots<br>• Window frame | • Produce hazardous chlorine gas<br>• Dichlorination at low temperature (250-320°C) or physical or chemical adsorption<br>• Presence of chlorine and deposition of coke affect the catalyst activity | • Azulene<br>• Biphenyl<br>• Phenanthrene<br>• 9H-fluorene<br>• Naphthalene and its monomers |

### 3.2.6 Reactor type

Many reactors have been studied and used for plastic waste pyrolysis, each of them present advantages and disadvantages. A brief description of those and their influence on the desired product is reported in this section.

#### *3.2.6.1 Batch reactor*

Batch reactors are closed systems requiring to be charge at one time, then it is necessary to wait until reaction completion to be able to feed it again. For this reason, its main drawback is high labor cost, also product composition can differ from batch to batch making it not suitable for large scale implementation. Although, batch reactors have easy designs and operational parameters can be controlled efficiently. Therefore, they are wildly used at laboratory scale for plastic waste pyrolysis both thermal and catalytic. If catalysis is employed another problem has been highlighted; catalyst is easily deactivated by char formation on its surface. Thus, stirrers can be implemented to improve mixing and contact between plastic and catalyst. An improvement to lower labor costs and to enhance process selectivity is given by semi-batch reactors. These systems allow simultaneous addition of catalyst and removal of products. Generally, batch reactors work in a temperature range of 300-800°C *(Sharuddin et al., 2016)*.

Results from different studies on plastic waste pyrolysis using batch and semi-batch rectors are reported in *Table 3*.

*Table 3 - Batch reactor set up and products*

| **Type of reactor** | **Type of plastic** | **Operational parameters** | | | **Yields** | | | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| | | **Inert gas** | **Temp (°C)** | **Catalyst** | **Gas (wt%)** | **Liquid (wt%)** | **Solid (wt%)** | |
| Batch | PE | $N_2$ | 430 | Thermal | 9.6 | 69.3 | 21.1 | Sakata et al., 1999 |
| | | | | SA-2 | 13.4 | 74.3 | 12.3 | |
| | | | | FSM | 9.3 | 81.9 | 8.8 | |
| Batch | PP | $N_2$ | 380 | Thermal | 6.6 | 80.1 | 13.3 | |
| | | | | Silica-gel | 8.6 | 80.6 | 10.8 | |
| | | | | FSM | 6.6 | 86.4 | 6.9 | |
| Stirred batch | HDPE | $N_2$ | 450 | Thermal | 13 | 84 | 3 | Seo et al., 2002 |
| | | | | Zeolite-Y | 17.5 | 81 | 1.5 | |
| | | | | Alumina | 15.9 | 82 | 2.1 | |
| Stirred batch | PP | $N_2$ | 420 | Spent FCC | 8.3 | 88.6 | 3.1 | Abbas-Abadi et al., 2014 |
| | | | 450 | | 4.1 | 92.3 | 3.6 | |
| | | | 480 | | 12.5 | 82.4 | 5.1 | |

### *3.2.6.2 Fixed bed reactor*

Fixed bed reactors are vessels containing a packed bed of material. This asset has been used extensively for plastic waste pyrolysis because they are easy to design and maintain. Problems highlighted by those studies involve the feeding operation; shape and size of plastic waste can generate complication. Moreover, when catalytic pyrolysis is performed the catalyst is mixed with the bed material and the available surface area exposed to the reacting material is limited. Another implementation of fixed bed reactor is in two step pyrolysis. Here they are employed as second reactors, the feeding is mainly liquid or gaseous so no problem with the supply system rises. Two step pyrolysis is not so common because operational cost is high, and results are comparable with single step processes.

*Table 4* reports outcomes from different studies on plastic waste pyrolysis using fixed bed reactors.

*Table 4 - Fixed bed reactor set up and products*

| **Type of reactor** | **Type of plastic** | **Operational parameters** | | | **Yields** | | | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| | | **Inert gas** | **Temp (°C)** | **Catalyst** | **Gas (wt%)** | **Liquid (wt%)** | **Solid (wt%)** | |
| Fixed bed | Mixture (PE, PP) | $N_2$ | 500 | Thermal | 67.91 | 30.66 | 1.43 | Papuga et al., 2016 |
| Fixed bed | PE | $N_2$ | 500 | Thermal | 5 | 95 | - | Bagri et al., 2002 |
| | | | 400 | Y-Zeolite | 5 | 85 | 10 | |
| | | | 600 | | 20 | 70 | 10 | |
| | | | 400 | ZSM-5 | 2 | 88 | 10 | |
| | | | 600 | | 30 | 68 | 2 | |

### *3.2.6.3 Fluidized bed reactor*

Fluidized bed reactors (FBR) are the most used vessels for plastic waste pyrolysis at pilot scale. Here, bed material is allocated on a distribution plate. The injection of fluidizing gas (typically $N_2$) allows the solid to be suspended and act as a fluid *(Milne et al.,1999)*. The behavior of the solid bed as fluid helps overcome the problem of poor contact between catalyst and feed material. Also, it promotes heat transfer allowing a constant temperature in the reactor. Furthermore, FBR is a continuous system so frequent charging is avoided and the operational costs decrease if compared to batch reactors. The main problem found when using fluidized bed reactors is bed defluidization. It occurs when melted plastic adheres on the bed particle surface creating an agglomerate. Plastic waste pyrolysis in FBR is carried out in a temperature range of 290-850°C for both thermal and catalytic. Studies results are shown in *Table 5*.

*Table 5 - Fluidized bed reactor set up and products*

| **Type of reactor** | **Type of plastic** | **Operational parameters** | | | **Yields** | | | **Ref.** |
|---|---|---|---|---|---|---|---|---|
| | | **Inert gas** | **Temp (°C)** | **Catalyst** | **Gas (wt%)** | **Liquid (wt%)** | **Wax (wt%)** | |
| FBR | HDPE | $N_2$ | 645 | Thermal | 17.5 | 79.7 | | Mastral et al., 2001 |
| | | | 700 | | 64.2 | 32.1 | | |
| | | | 800 | | 83.1 | 13.7 | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| FBR | LDPE | $N_2$ | 500 | Thermal | 10.8 | 43.9 | 45.3 | Williams et al., 1998 |
| | | | 600 | | 24.2 | 51.0 | 24.8 | |
| | | | 700 | | 71.4 | 24.6 | 4.0 | |
| FBR | PP | $N_2$ | 668 | Thermal | 54.4 | 43.1 | - | Jung et al., 2009 |
| | | | 703 | | 57 | 35.9 | - | |
| | | | 746 | | 65.9 | 29.6 | - | |

### *3.2.6.4 Conical sprouted bed reactor*

Conical sprouted bed reactors have been used in plastic waste pyrolysis since they showed good ability to handle large particle with different density and no segregation occurs based on the design of the vessel. So, it can work with viscous materials and avoid defuidization. On the other hand, CSBR requires a complex set up with many pumps, so its implementation is not favorable at large scale due to high operating costs.

### *3.2.6.2 Microwave-assisted reactor*

Microwaved-assisted pyrolysis is a reasonably recent technology. Plastic waste is mixed with microwave absorbent material such as carbon and placed into the reactor. Then an external magnetic field is applied generating an altering electric field inside the vessel which stimulates adsorbent material dipolar molecules to rotate in phase with this field. Friction generates from the resistance to the rotation and consequently heat generates *(Lam et al.,2012)*. This method is considered advantageous with respect to 'traditional' heating approach because energy is not wasted heating the surrounding area; heat is produced within the material and brought to process temperature. Plastic waste can be employed in microwaved-assisted technology since it is transparent to electromagnetic wave, but it requires mixing with microwave absorbent material because it has low dielectric constant. As of now, microwave technology still needs to be further studied to determine the dielectric properties of the treated material. When data are collected and analyzed, industrial scale can be explored.

### 3.2.7 Process parameters

To achieve the desired final product process parameters must be controlled. Pyrolysis literature defined those parameters as temperature, pressure, residence time and catalyst. Catalytic pyrolysis is discussed in next section. A detailed analysis of the other is reported in the following sections.

### *3.2.7.1 Temperature*

Temperature is the parameter regulating cracking of polymers. Polymer chain scission is achieved when molecules vibration energy induced by increasing temperature is higher than bonds (Van der Waals and carbon bonds) strength. Then, during pyrolysis temperature must be carefully monitored to produce desired products generally liquid or gaseous. For this reason, thermogravimetric analysis has been conducted on all plastic types to define thermal degradation intervals *(Table 6)*.

*Table 6 - Degradation temperature of different plastic types*

| **Plastic type** | **Degradation temperature (°C)** | **Reference** |
|---|---|---|
| PE | 360-550 | López et al. 2011 |
| PET | 350-520 | |
| PP | 400-500 | |
| PS | 350-460 | |
| PVC | First range 260-385<br>Second range 385-520 | |

In literature many studies are reported with different operating temperatures *(Papari et al., 2021)*. The common behavior is:

- If lower decomposition temperature is not achieved than most of the final product is solid.
- After the lower decomposition temperature waxy compound are formed.
- With increasing temperature greater liquid amounts are produced until a maximum temperature where the highest oil yield is reached.
- Form this temperature on, secondary reactions take place leading to lager gas yields.

So, depending on the desired product pyrolysis temperature changes. When the temperature is set another parameter influence product yield: residence time.

### *3.2.7.2 Residence time*

Residence time can be defined as the average amount of time that a particle takes to travel through the reactor. It can influence product distribution into different phases and their composition. The production of lower molecular weight fractions, hence non-condensable gases has been linked with longer residence times because they allow primary products to further react and degrade. Moreover, *Mastral et al.* (2001) reported a temperature dependence of residence time influence. They highlighted how residence time has a greater influence on product distribution until 685°C. At temperatures higher than this little change was observed *(Table 7)*.

*Table 7 - Residence time influence on product distribution in HDPE fast pyrolysis (Mastral et al., 2001)*

| **Temperature (°C)** | 650 | 650 | 685 | 685 | 730 | 730 | 850 | 850 |
|---|---|---|---|---|---|---|---|---|
| **Residence time (s)** | 1.46 | 2.57 | 0.79 | 2.12 | 0.78 | 2.27 | 0.64 | 1.71 |
| **Wax + oil (wt%)** | 68.5 | 72.3 | 33.4 | 40.7 | 19.6 | 13.5 | 11.4 | 12.2 |
| **Gas (wt%)** | 31.5 | 22.1 | 60.1 | 55.9 | 79 | 76.1 | 75.1 | 64.5 |
| **Total yield** | 100 | 94.4 | 93.5 | 96.6 | 98.6 | 89.6 | 86.5 | 76.7 |

*Papuga et al. (2016)* studied the influence of residence time at fixed temperature of 500°C in plastic waste pyrolysis. They recorded an increase in gas and liquid yield until a residence time of 60 minutes, after a slight change was measure which did not compensate energetic and operational costs *(Table 8)*. Also, a time of 45 minutes were enough for the total conversion of the mass (solids 1.46 wt%) and the maximum liquid yield (32.8 wt%).

*Table 8 - Residence time influence on product distribution in mixed plastic waste pyrolysis (Papuga et al., 2016)*

| **Residence time (min)** | 30 | 45 | 60 | 90 |
|---|---|---|---|---|
| **Gas (wt%)** | 5.08 | 1.46 | 1.43 | 1.47 |
| **Pyrolysis oil (wt%)** | 28.80 | 32.80 | 30.66 | 30.37 |
| **Solid residue (wt%)** | 66.13 | 65.75 | 67.91 | 68.17 |

By the previous data, the dependence of residence time on temperature can be deducted. Residence time must be carefully considered when pyrolysis at temperatures lower than 450°C are performed.

### *3.2.7.3 Pressure*

Plastic waste pyrolysis process is generally conducted at atmospheric pressure, mainly because operational costs will increase consistently when high pressure is required. So, pressure effects on product yield and distribution have not been fully researched. A study carried out by *Murata et al* (2004) investigates the effect of pressure on HDPE pyrolysis products. They brought to light that an increase in pressure (from 0.1 to 0.8 MPa) in a continuous stirred allowed a rise in gas production from 6 to 13wt% at a temperature of 410°C. With rising temperature, the effect of pressure decreased; at 440°C the increment in gas product was from 4 to 6wt%. So, it can be concluded that pressure is a temperature dependent parameter, and it must be carefully considered when low temperatures are employed.

### 3.2.8 Catalytic pyrolysis

Catalytic pyrolysis has been developed to overcame thermal pyrolysis problems, such as energy request, oil products contamination due to presence of nitrogen, sulfur and chlorine in the feedstock and products upgrading. Catalysts are applied in pyrolysis processes because they lower the operating temperature decreasing the energy cost of the process which is the main concern for industrial scale applications. Moreover, they increase the gaseous yield while enhancing the quality of the oil products leading to less upgrading operations *(Papari et al., 2021)*.

Hydrocarbon molecules react on the surface of the catalyst, hence high weight loss happens here. Lower molecules then penetrate the channel of the porous material where further degradation takes place. Therefore, wax is generated at the catalyst surface while gaseous products are achieved on the inside *(Miandad et al., 2016)*.

Catalysts can be homogeneous or heterogeneous. Homogeneous catalyst involves only one phase, and it is typically a liquid solution. Heterogeneous catalysts are the most applied because they can be easily separate from the gaseous output and then they can be regenerated and reused; hence they are economically feasible. The main characteristics influencing heterogeneous catalysts performances are reported by *Miandad et al. (2016)* as:

- BET surface area, higher BET values and higher cracking is achieved leading to higher amounts of gaseous products.
- Pore size, two different types of catalysts are defined based on pore size: microporous and macro-porous. The first one presents a high internal crystalline structure leading to high gas yields and lower oil quantities but showing better quality. Macro porous catalysts do not influence the liquid yield and it generates products with higher weight.
- Crystalline structure, higher internal crystalline structure enhances degradation producing greater amounts of gaseous products.
- Acidity, catalyst with acid bases increase thermal degradation if compared to base catalyst. Higher thermal degradation means higher gas yields.

The most common catalysts used in plastic waste pyrolysis are zeolite, fluid catalytic cracking (FCC) and silica-alumina.

#### *3.2.8.1 Zeolite catalyst*

Zeolites are natural sieves with a crystalline tridimensional structure given by the silico aluminate disposition. They present a different level of acidity depending on the silicate/alumina ($SiO_2/Al_2O_3$) ratio. The most common types applied in plastic waste pyrolysis are HZSM-5 and Y-zeolite (HUSY). *Table 9* reports different results for plastic pyrolysis with zeolites catalyst. It shows how zeolites improve lighter fraction formation; hence higher gas yields are achieved. Moreover, HZSM-5 is commonly used since it shows a low deactivation factor meaning longer employment time and easier regeneration.

*Table 9 - Effect of zeolite catalyst on pyrolysis products*

| Catalyst type | Plastic type | Reactor type | Temp. (°C) | Catalyst quantity | Product yields | | | Catalyst effect | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | **Gas (wt%)** | **Liquid (wt%)** | **Char (wt%)** | | |
| HZSM-5 | HDPE | FBR | 500 | 20 wt% | 86.10 | 4.40 | 9.50 | • At lower temperatures, the gas yield is enhanced when compared to thermal pyrolysis.<br>• At higher temperatures, coke deposition contributes to catalyst deactivation hence lower yields are obtained.<br>• Overall increase in volatile compounds and process yield. | Hernàndez et al. 2007 |
| | | | 700 | | 78.40 | 7.30 | 14.30 | | |
| HZSM-5 | HDPE | Batch | 450 | - | 63.50 | 35.00 | 1.50 | • Excellent catalytic efficiency on cracking, isomerization and aromatization due to strong acidic sites and micropore crystalline structure.<br>• Compared to other zeolites yields lower char amounts due to its uniform pore size distribution and acidic properties. | Seo et al. 2003 |
| HZSM-5 | HDPE | FBR | 500 | 0.93 | 83.13 | 19.87 | 0.00 | • Increasing the polymer/catalyst ratio reduces liquid formation and increases gas yields.<br>• Slight yield difference is measured when the ratio is around one.<br>• It is economically favorable to use lower catalyst amounts to achieve comparable results. | Mastral et al. 2006 |
| | | | | 1.41 | 78.48 | 21.52 | 0.00 | | |
| | | | | 9.2 | 46.86 | 53.14 | 0.00 | | |
| HZSM-5 | HDPE | Batch | Dynamic conditions | 10 wt% | 72.60 | 17.30 | 0.7 | • The results obtained for the two PE types are comparable meaning that the catalyst presents the same behavior.<br>• HZSM-5 present not strong and weak acid site leading to higher catalytic degradation and cracking than HUSY. | Marcilla et al. 2009 |
| | LDPE | | | | 70.70 | 18.30 | 0.5 | | |
| HUSY | HDPE | Batch | Dynamic conditions | 10 wt% | 39.50 | 41.00 | 1.90 | • HUSY presents mainly weak acid sites which do not promote catalytic cracking.<br>• HUSY has larger surface area and pores which should promote degradation, but large pores also promote coke precursor formation meaning faster deactivation of the catalyst.<br>• Accordingly, the results reported present higher liquid and coke yields. | Marcilla et al. 2009 |
| | LDPE | | | | 34.50 | 61.60 | 1.90 | | |
| Y-zeolite (pellet) | HDPE | Batch | 450 | - | 17.50 | 81.00 | 1.50 | • Powder Y-zeolite has larger surface area, so catalytic cracking of polymers is enhanced; lighter and gaseous fraction are produced. For this reason, pellet Y-zeolite yielded more liquid fraction. | Seo et al. 2003 |
| Y-zeolite (powder) | | | | | 27.00 | 71.50 | 1.50 | | |

### *3.2.8.2 FCC catalyst*

FCC catalyst is composed mainly by zeolite, silica-alumina and other additives. It is primarily used in fluidized catalytic cracking, which is a process carried out in refinery industries, where heavy hydrocarbons are cracked into lighter fractions such as gasoline and liquid petroleum gas (LPG) *(Sharuddin et al., 2016)*. In the pyrolysis process spent FCC catalyst is re-used; lower catalyst cost makes it interesting for industrial scale applications. Moreover, re-use of material increases the environmental sustainability of pyrolysis leading towards circular economy. The main problem with spent FCC employment is its contamination level; it could affect the quality of the products obtained. Studies results and FCC catalyst characteristics are reported in *Table 10*. Looking at these results it can be concluded that spent FCC catalyst is employed in plastic waste pyrolysis when high liquid oil yield is desired.

*Table 10 - Effect of FCC catalyst on pyrolysis products*

| Catalyst type | Plastic type | Reactor type | Temp. (°C) | Catalyst quantity | Product yields | | | Catalyst effect | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Gas (wt%) | Liquid (wt%) | Char (wt%) | | |
| FCC | HDPE | Semi-batch | 400 | 10 wt% | 17.00 | 82.00 | 1.00 | • The goal of the study was to obtain liquid oil from the pyrolysis process, so the FCC catalyst performance was good.<br>• PS produced the higher yield of liquid products because it is composed by benzene rings which are difficult to degrade. This is also the reason why high solid residues are produced and low gases.<br>• PP and PE produced higher gas yield due to easier degradation. Also, low char residues were produced with overall high conversion efficiency. | Lee et al. 2002 |
| | LDPE | | | | 19.50 | 80.00 | 0.50 | | |
| | PP | | | | 13.50 | 86.00 | 0.50 | | |
| | PS | | | | 5.00 | 90.00 | 5.00 | | |
| FCC | HDPE | Semi-batch | 450 | 10 wt% | 6.30 | 90.30 | 3.40 | • An increase in catalyst quantity leads to a higher conversion into products.<br>• Catalyst/HDPE ratio of 20 wt% produces the higher liquid conversion, hence it is the optimum value for this configuration.<br>• An increase in catalyst to polymer ratio leads to char formation due to secondary reactions like aromatization. | Abbas-Abadi et al. 2013 |
| | | | | 20 wt% | 4.10 | 91.20 | 4.70 | | |
| | | | | 40 wt% | 7.40 | 87.20 | 5.40 | | |
| | | | | 60 wt% | 8.80 | 85.00 | 6.20 | | |

### *3.2.8.3 Silica-alumina catalyst*

Silica-alumina catalyst are amorphous acid catalyst. Their acidity is determined by the $SiO_2/Al_2O_3$ ratio; high values mean high acidity and vice versa. The acidity directly affects the products distribution; higher acidity lowers liquid oil production and enhances gaseous products *(Miandad et al., 2016)*. The main type of silica-alumina catalyst are SA-1, SA-2 and ZSM-5. They present different acidity so their effect on the product distribution is different. SA-1 is the most acidic, followed by ZSM-5 and SA-2 *(Sharuddin et al., 2016)*. Silica-alumina catalyst are used to improve liquid oil production, some results are reported in *Table 11* along with the catalyst effect on the process.

*Table 11 - Effect of silica-alumina catalyst on pyrolysis products*

| Catalyst type | Plastic type | Reactor type | Temp. (°C) | Catalyst quantity | Product yields | | | Catalyst effect | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Gas (wt%) | Liquid (wt%) | Char (wt%) | | |
| ZSM-5 | HDPE | Batch | 450 | - | 63.50 | 35.00 | 3.00 | • ZSM-5 presents a combination of large intracrystalline pore structure which favors internal cracking and moderately high acidity. These characteristics make possible to achieve good gas yields.<br>• Silica-alumina with strong acidity showed a good behavior for liquid production and slightly increased gas yield. | Seo et al. 2003 |
| Silica-alumina | | | | | 21.00 | 78.00 | 1.00 | | |
| SA-1 | PE | Batch | 430 | 10 wt% | 23.70 | 67.80 | 8.50 | • ZSM-5 generates more gaseous product since it presents both strong and weak acid sites, whereas silicate-alumina presents only weak sites.<br>• The highest liquid yield is produced by SA-2, the lowest acid catalyst. | Sakata et al. 1999 |
| SA-2 | | | | | 13.40 | 74.30 | 12.30 | | |
| ZSM-5 | | | | | 44.30 | 49.80 | 5.80 | | |
| SA-1 | PP | Batch | 380 | 10 wt% | 11.30 | 78.30 | 10.40 | • Silicate and silica-gel are non-acidic porous materials and produced good results, comparable with SA-1. | |
| ZSM-5 | | | | | 50.00 | 47.00 | 3.00 | | |
| Silicate | | | | | 12.10 | 75.40 | 12.50 | | |
| Silica-gel | | | | | 8.60 | 80.60 | 10.80 | | |
| ZSM-5 | HDPE | Horizontal tube | 520 | 5 wt% | 12.50 | 84.38 | - | • Higher gas yields for PP can be explained by the lower initial cracking energy required with respect to HDPE.<br>• No char formation was reported probably because the small amount formed was separated with the catalyst. | Miskolczi et al. 2009 |
| | PP | | | | 14.84 | 82.04 | - | | |

### 3.2.8 Pyrolysis products

Plastic waste pyrolysis process yields three different products gas, liquid oil, and solid residue. The quantity produced depends on temperature, heating rate, residence time and catalyst. In thermal pyrolysis an increase in temperature leads to higher amounts of gas product. This is also valid for catalytic pyrolysis but here the main reason for yields variations it is the catalyst itself. Moreover, in catalytic pyrolysis solid reside yields are higher due to inorganic fractions of the catalyst and its impurities. Gas and liquid product exit the reactor in gaseous form, after condensation two streams are obtained liquid oil and non-condensable gases.

#### *3.2.8.1 Gas*

Gases are the result of the compete degradation of the solid feedstock. Depending on the plastic type different propensity to form gaseous products has been found. It is mainly due to polymer ramification and bond strength. *Williams et al. (1999)* pointed out that PET and PVC are the highest gas forming plastics. As already mentioned, the main problem with polyvinylchloride is the formation of HCl which is a harmful ad corrosive gas. Moreover, they found out that polyolefins (PE and PP) yield similar quantities of gas and polystyrene produces the lowest amount. Gas chromatography of the non-condensable flow identified hydrogen, methane, ethene, ethane, propene, propane, butene and butane as the main compounds present in gaseous fraction of all plastic. Generally, in all research an increase of temperature generated an increase in gas products yields, methane, hydrogen, and ethylene production increases with temperature.

When catalytic pyrolysis is carried out the gas product presents different composition with respect to thermal pyrolysis products. HZSM-5 catalyst improves olefinic gases production like butene, ethene and propylene. Low catalyst/polymer ratios, at 500°C, increase butene production ($C_4$ compounds) and reduce $C_5$-$C_7$ fraction and no hydrogen or methane are produced *(Mastral et al., 2006)*. *Manos et al. (2000)* reported that all catalysts used did not produced measurable amounts of methane, ethane or ethene. Furthermore, they reported that Y-zeolite enhances alkanes production like isobutane and isopentane, and ZSM-5 produces more alkenes gases like butene, propene and pentene.

*Jung et al. (2010)* measured the higher heating value ranging between 42 and 50 MJ/kg of gas product yielded by thermal pyrolysis of PE and PP in a fluidized bed reactor. These values make pyrolysis gas suitable for boiler heating or as combustible fraction in gas turbines. Moreover, after separation ethene and propene can be used as feedstock in petrochemical processes such as polyolefins production *(Sharuddin et al., 2016)*.

#### *3.2.8.2 Liquid*

The quantity of liquid oil produced depends on plastic type, reaction temperature and time and catalyst employment. Generally, plastic pyrolysis is carried out at the optimum degradation temperature which can be defined by TGA. For the main plastic types (PE, PP, PS), *Miandad et al. (2017)* defined this temperature as 450°C to obtain more than 50% degradation. They reported that at this temperature PS showed the highest liquid production while PE only produced wax. This difference is due their structure, polystyrene has simpler structure than other plastic types. *Ahmad et al. (2015)* studied PE and PP pyrolysis and define the best temperature for liquid oil formation as 300°C for PP (70wt%) and 350°C for PE (80wt%). The difference in quantity achieved is due to polyethylene better disposition to crack into liquid oil than polypropylene which tends to form gaseous products. Moreover, residence time influences liquid yield; slow pyrolysis produces more oil and char while fast pyrolysis generates gases. Also, as discussed in the previous chapter if catalysts are applied higher gas yields are achieved.

Generally, liquid oil is analyzed with GC-MS for compounds identification. As reported in *Table 4* each plastic type produces many compounds present in the liquid fraction. Depending on the process parameters the number of the compounds varies, furthermore using catalyst can narrow the product range because of this selectivity towards some compounds. The main components of the pyrolytic oil are (*Miandad et al., 2017 Sharuddin et al., 2016 Jung et al., 2010, Milne et al.,1999, Lovett at al.,1997, Sodero et al.,1996)*:

- Polystyrene yields styrene for around 48%wt. The main constituents are aromatic hydrocarbon, this is due to their high stability to cracking and hydrogenation which convert them into paraffins and olefins.
- Polyethylene terephthalate liquid oil is formed by benzoic acid for almost 50%wt. The presence of this acid, specifically its corrosiveness, make it unsuitable for engine application.
- Polyvinylchloride yields low liquid oil quantities mainly because during degradation dehydrochlorination takes place leading to gas formation such as hydrochloric acid and chlorine. The presence of this compounds makes the liquid fraction not adequate to be used as fuel.
- Polyethylene produces mainly aliphatic compounds, followed by monoaromatic and polyaromatic. Moreover, when temperature increases a decrease in aliphatic content was reported with higher yields of aromatics. Nonetheless, in PE pyrolysis the aliphatic amount is still quite high meaning difficult degradation. The analysis of the BTX-aromatic fraction showed that the main component is benzene. Also, a temperature increase leads to higher quantity of benzene and toluene while xylene decreases. *Miskolczi et al. (2009)* reported the liquid oil composition for ZSM-5 catalytic pyrolysis to be mainly paraffin (n- and i- types), followed by vinylene, vinyl and vinylidene olefin and almost no aromatic. Meaning that catalyst can change the liquid composition with respect to thermal pyrolytic oil.
- Polypropylene as PE produces aliphatic, monoaromatic and polyaromatic compounds but it shows higher yields form the aromatic fraction if compared with polyethylene. As for PE, aliphatic production decreases with temperature increase and benzene and toluene increase while xylene reduces. Also, PP produces benzene as main BTX-aromatic. *Miskolczi et al. (2009)* reported a liquid fraction composition like PE, but pyrolysis of PP with ZMS-5 yielded more i-paraffin and vinylidene olefin.

When the pyrolytic oil wants to be used as fuel its physical properties must be assess and comparted with gasoline and diesel ones. All these characteristics are determined following ASTM organization tests.

First, calorific value of the pyrolysis liquid oil must be measured. PP, HDPE, LDPE have calorific values higher than 40 MJ/kg *(Sharuddin et al., 2016)* which makes them suitable for fuel application since they are comparable with gasoline and diesel values. PS, PET and PVC show lower heating values due to the presence of aromatic rings, benzoic acid, and chlorine compounds, respectively. Aromatic rings in the structure present lower combustion energy than aliphatic fractions. Benzoic acid and chlorine compounds deteriorate fuel quality.

The density of the oil is measure by API (American Petroleum Institute) gravity methodology. API results for HDPE, PP, PS, PET and PVC liquid oils are comparable with diesel values, LDPE showed values near gasoline. The densities of all pyrolytic oils are comparable with both gasoline and diesel standard values *(Sharuddin et al., 2016).*

Viscosity is an important parameter since it affects the injection process. All liquids presented values comparable with diesel ones, with exception of PS that was near to gasoline. Also, the ash content is important since it is correlated with metal contamination. *Ahmad et al. (2015)* reported negligible values of ash content in HDPE and PP pyrolytic oil meaning that no metal or soot contamination occurred.

Research octane number (RON) and motor octane number (MON) express that anti-knock ability of the oil; higher the value better the ability to avoid knock. *Ahmad et al. (2015)* measured these number for PP and HDPE and found them in the rage of gasoline products (60 to 120). Furthermore, they reported that PP has higher RON and MON meaning better anti-knock behavior.

Other important parameters to be measure are pour point and flash point. Pour point is defined as the temperature below which the fluid loses its ability to flow. *Sharuddin et al. (2016)* reported values of -5 °C, -9 °C and -67°C for HPDE, PP and PS, respectively. These values are lower than diesel pour point 6°C. So, pyrolysis oil for these plastics can be used in tropical regions to avoid freezing. Flash point is the lowest temperature at which the liquid passes to vapor phase in quantity high enough for the mixture to ignite when heat is applied. PP and PS present values lower than gasoline and diesel standards, so they need to be handled carefully. The other plastic oils showed valued comparable with gasoline standard *(Sharuddin et al., 2016).*

Since HDPE and PP were the only two plastic reporting all the values (*Ahmad et al., 2015)* and they were comparable to gasoline and diesel standards, is possible to affirm that they can be used as fuel or can be blended with transportation fuels.

#### *3.2.8.3 Solid*

The pyrolysis process has been widely studied mainly focusing on pyrolysis oil and gas since they are the most valuable products from an economic point of view, but most pyrolysis processes produce some solid residue. Slow heating rate and high residence time tend to produce more char if compared to fast pyrolysis. When using plastic waste as feedstock both processes produce low char quantities, this is due to plastic waste high volatile matter content (80-100%) and low moisture (0.1-1%) and ash (0.02-4%) *(Sharuddin et al., 2016)*. The feedstock initial composition influences the solid residue content. Jamradloedluka et al. (2014)

reported char composition derived from fast pyrolysis of HDPE of 51.40wt% volatile matter, 46.03wt% fixed carbon, 2.4wt% moisture and 0.16wt% ash. Moreover, they performed elemental analysis on the residue and found out that the main elements are hydrogen and carbon with lower amounts of nitrogen and sulfur. Also, they measured the calorific value of the char of 18.84 MJ/kg and for its low sulfur content they found it suitable for combustion.

## 3.3 Waste tire pyrolysis

Waste tire are suitable feedstocks for pyrolysis leading to gas, liquid, and solid production. As previously reported tire composition is complex; in addition to natural rubber (NR), butyl rubber (BR), styrene-butadiene rubber (SBR), carbon black (CB) and various additives such as accelerators and fillers are present. Different quantities and mixture are used depending on tire type and producer. For this reason, it is not possible to describe tire thermal cracking as single rubber type degradation mechanism. As of now the mechanism of tire thermal decomposition is still not fully understood; it is achieved by numerous reactions that cannot be identified one by one. As general rule, thermal decomposition is carried out by free radicals' formation which undergo scission, rearrangement, hydrogenation, and cyclization. To understand the mechanism of thermal degradation of tires thermogravimetric analysis has been conducted by many researchers, TG curves highlighted a single stage degradation between 200 and 500 °C. Below 200°C the weight loss measured is minimal and could be linked to moisture evaporation. The higher slope which is directly correlated with significant weight loss can be further divided into three stages *(Cheng et al., 2021)*:

- 200-300°C vaporization of additives and oils
- 300-420°C natural rubber degradation
- 420-500°C styrene-butadiene rubber and butyl rubber degradation.

These results were also confirmed by the derivative thermogravimetric curve where different peaks could be identified corresponding to the different degradation stages. *Lee et al. (2020)* tried to fit the DTG curve as a sum of different gaussian functions representing the decomposition of NR, SBR, and BR, respectively. The fitting showed good results with higher coefficient of determination ($R^2$=0.99980) for 20°C/min as heating rate. Anyway, in all cases the $R^2$ value was higher than 0.999.

Waste tire pyrolysis yields mainly solid residue and oil, with low quantities of gas. The high char yield is due to the presence of carbon black (CB) in the tire matrix; generally, a mass of around 40wt% is collected as solid residue and it does not degrade even at high temperatures (~1000°C) *(Kwon et al.,2009)*. As in plastic waste pyrolysis, the most interesting fraction is the liquid one which can be further process to obtained added value products. The low amount of gas produced make them suitable for in situ application as additional fuel for heat production in the process. It must be carefully considered the presence on nitrogen, sulfur and chlorine in the feedstock because it could lead to the formation of acid gas which could lead to equipment corrosion or formation of $SO_x$, $NO_x$, and dioxins when combusted *(Cheng et al., 2021)*. Moreover, the presence of N, S, Cl compounds in the liquid fraction can lower the quality of the liquid products.

The following chapters present an in-depth review of different process set ups, how process parameters affect them, and product yields.

### 3.3.1 Reactor types

As common understating waste tire must be treated prior application in pyrolysis. The fundamental step is size reduction which can be performed by shredders. Depending on the rector type different sizes are required; lower the dimension and higher the energy required in the process. The energy consumption addressed in this pretreatment must be considered thoughtfully since it can change the economic feasibility of the process. Moreover, the feedstock can be dried to reduce the moisture content. Another possibility is wires and filters removals from the tire to have a feedstock much more alike to a rubber mixture. This can be feasible in lab scale but could not be economically advantageous at industrial scale.

The reaction process, as for the previously analyzed case, can be slow or fast. Fast pyrolysis requires small particle size (<1mm) due to short permeance in the reactor (tens or hundreds of seconds) and it yields higher liquid amounts. Slow pyrolysis can be feed with coarser material (5-50mm) and greater char quantities are produced.

Waste tire pyrolysis reactors can be classified based on how the material is moved inside the vessel in *(Lewandowski et al., 2019)*:

- Pneumatic reactors such as, fixed and fluidized beds
- Mechanical reactors like auger, stirred and rotary reactors
- Gravity reactor with column vessel.

The following section analyzes the main characteristic of the most used reactors in waste tire pyrolysis.

#### *3.3.1.1 Fixed bed reactor*

Fixed bed reactors are quartz or stainless-steel vessels in which a mixture of feedstock material and bed material or only raw material lies. It is characterized by the slow gas flow which renders the bed stationary, and it has no particle size limitation. Fixed bed reactors are generally employed in slow pyrolysis process where the inert gas removes the volatile fraction. They are employed at laboratory or pilot scale in batch conditions because of their easy design and operation. Fixed bed reactors main disadvantage is poor heat transfer which renders difficult to control the temperature inside the vessel. This problem and the difficult modifications needed to use them in continuous makes them non suitable for large scale application. Different configuration can be found in the literature but the most common is a vertical fixed bed reactor as showed in *Figure 6*.

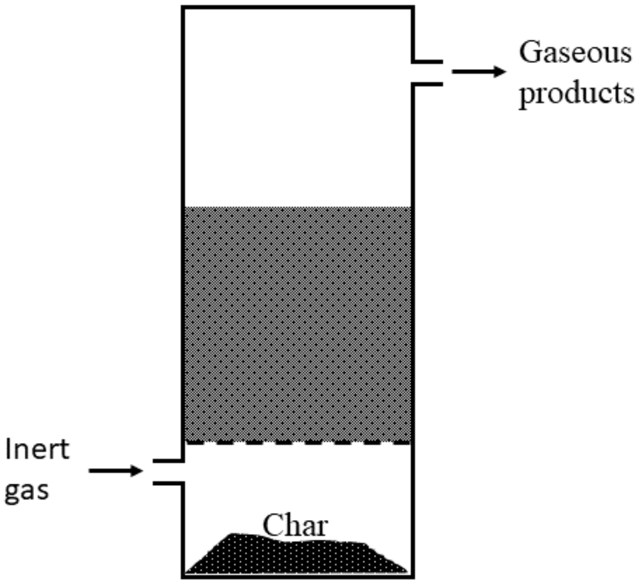


*Figure 6 - Fixed bed reactor scheme for WT pyrolysis*

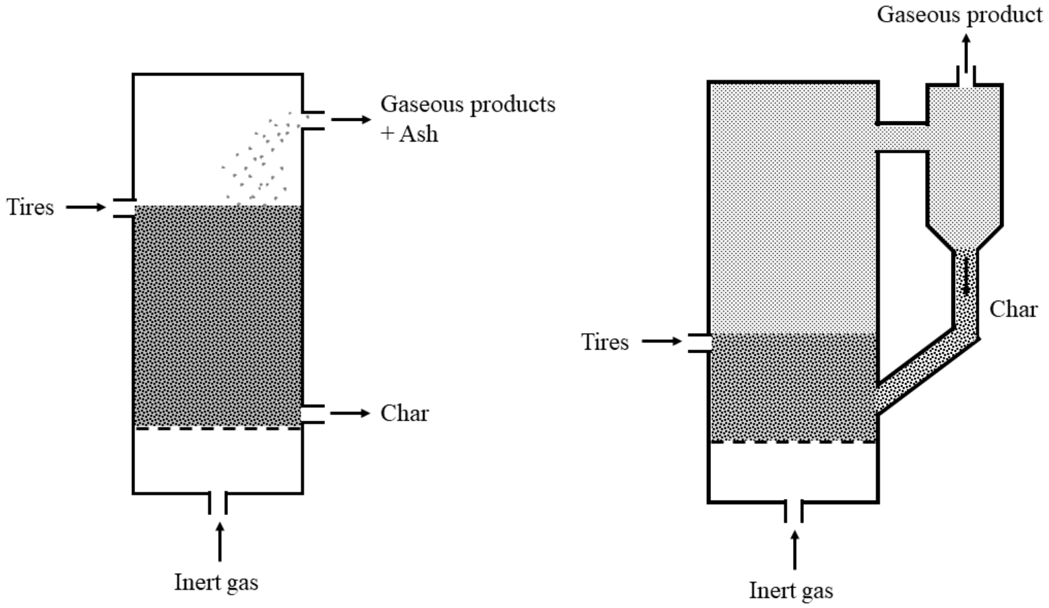
The literature review performed by *Lewandowski et al. (2019)* depicted that fixed bed reactors are generally used between 300-600°C, higher temprature have been research but the influence on the distriìbution of the final product is not so stong to make it attainable. The products dirtibution changes mainly between liquid and char depending on operational parameters; liquid yield range is 32-66wt% while char production is 33-49wt%. The gas yield at pyrolysis temparutres of 400-550°C ranges between 7-18wt%; temperatures higher than 700°C and catalyst employment can rise the gaseous fraction up to 30-40wt%.

### *3.3.1.2 Fluidized bed reactor*

Fluidized bed reactors solve some of the fixed bed reactors problems. The higher contact between the inert bed material and the feedstock achieves higher heat transfer and uniform temperature inside the bed. This leads to lower residence time of the volatile fraction, so fast pyrolysis conditions are achieved, and tire pyrolysis oil production is enhanced. Moreover, they can be operated in continuous; for this they are already widely applied at the commercial scale. On the other hand, they present more complex design and operation, and they require smaller particle size (0.3-4mm) *(Arabiourrutia et al., 2020)*. The most used fluidized bed reactors are bubbling fluidized bed and circulating fluidized bed *(Figure 7)*.

In a *bubbling fluidized bed reactor (BFBR)*, the carrier gas has a velocity high enough to keep the particle in suspension but non so great to carry them out of the reactor. Generally, inert gas velocities range between 0.5-3m/s. If the carrier gas is also used as heat source, then the system is directly heated; a pre-heater must be installed right before the gas inlet in the reactor to warm it up at the desired temperature. Otherwise, an indirect heat source is used like external electrical heating. Also, the feeder is positioned right above or in the fluidized bed so clogging problems must rightly address and a cooling system may be implemented. A review of the current literature *(Lewandowski et al., 2019)* showed that BFBR can operate in a large temperature range 300-750°C, with liquid yields of 30-65wt% depending on the operational parameters. In addition, char and gas yields range between 27.5-46wt% and 5-45.5wt% respectively.

*Circulating fluidized bed reactors (CFBR)* are characterized by a close loop system consisting of reactor, cyclone, and cyclone-reactor connection pipe. The implementation of the cyclone is fundamental since the inert gas velocity is high enough to embed char, sand, and ash in its flow. After separation, the solids are recirculated into the reaction vessel while the gaseous fraction undergoes condensation to separate liquids from gas products. The carrier gas high velocity leads to grater mixing so better heat transfer. Moreover, a uniform temperature along all the height of the reactor is achieved. CFBR operates at slightly higher temperature if compared with BFBR. Also, here the gas residence time and the particles residence time must be distinguished; usually, 0.5-1s and 1s or more for gas and solids, respectively. The recirculation of the solid fraction leads to further cracking so higher gas and liquid yields can be observed *(Lewandowski et al., 2019)*. As of now, circulating fluidized bed are still on the early-stage application in waste tire pyrolysis but researches are advancing. *Lewandowski et al. (2019)* reprted a summary of the main parameters; temperature of 500°C , paricle size 0.32-0.8 mm, liquid, char, and gas yileds of 41.3-50.5wt%, 14.5-45.4wt%, 10-31.5wt%, respectively.



a) Bubbling fluidized bed reactor

b) Circulating fluidized bed reactor

*Figure 7 - Fluidized bed reactors configuration for WT pyrolysis*

### *3.3.1.3 Conical sprouted bed reactor*

Conical sprouted bed reactors (CSBR) have characteristics like FBR. The main difference lays in the injection mode of the inert gas. In FBR the carrier gas passes through a distribution plate equipped with many tiny holes which results in a gas-solid mixture like a boiling fluid. In CSBR the inert gas is injected in the conical part of the reactor via a single inlet opening, this creates a circular motion that can be divided into two parts. The first one in located near the opening until the conical section ends and it is characterized by moving particles and strong mixing; the second one is places above the bed surface and its main feature is a fountain like movement of the particles while falling *(Figure 8)*. This type of movement presents some advantages like *(Lewandowski et al., 2019) (Arabiourrutia et al., 2020)*:

- Ability to handle sticky material, coarse, and irregular particles; so, particles size can be higher leading to lower pre-treatment costs
- No bed defluidisation due to particle agglomeration
- Constant reactor temperature along the height
- Elevated heat transfer reduces volatiles compounds residence time so, it can operate under fast pyrolysis conditions where secondary reactions are discouraged resulting in higher tire pyrolysis oil
- High mixing rates lead to elevated contact between particles so, catalyst addition in the reactor shows excellent results.

Moreover, CSBR can be heated by direct or indirect methods, they are used in a temperature range of 400-600°C, and residence times of 30-500 seconds. With different combinations of these parameters *Lewandowski et al. (2019)* reported yields of 54.0-65.3wt% of liquid, 34.0-36.92wt% char, and 0.7-5.91wt % gas.

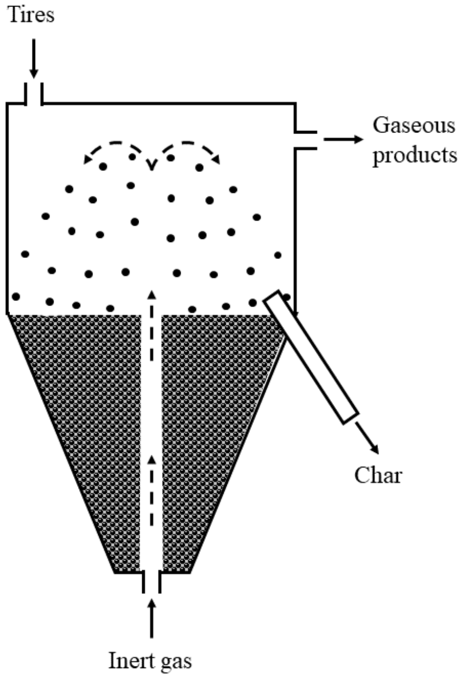


*Figure 8 - Conical sprouted bed reactor for WT pyrolysis*

### *3.3.1.4 Rotary kiln*

Rotary kilns are rotating cylindrical vessels, this mechanical movement is responsible for particle mixing and heat transfer. The feedstock can be processed alone or in presence of inert bed material like sand, catalyst can be used in situ with good results thanks to the mixing movement. Rotary kilns are mainly horizontals vessels, and they can present an inclination to help residue evacuation; this can be helpful if sticky materials are pyrolyzed. They main characteristics are *(Lewandowski et al., 2019) (Arabiourrutia et al., 2020)*:

- They present a better temperature control when the reactor is indirectly heated because the waste material in contact with the wall which is where the coil is placed
- Heat transfer is higher at lower rotation velocities leading to uniform distribution of the products. So, they can operate under slow or intermediate pyrolysis condition.
- They can be operated in continuous with a hopper as feeding system, char extraction located at the lower opposite hand of the WT inlet, and gas extraction system in the higher part *(Figure 9)*
- They can handle different particle size and shape making the economical prospect more favorable
- The solids residence time can be easily controlled and generally is around 30 seconds
- They present an easy design.

The most common operating temperature ranges between 400-600°C but experiments at higher values have been performed which produced higher gas products (~30wt%). The literature review reported by *Lewandowski et al. (2019)* presents particle size dimention between 2-15mm and, 43.0-57.5wt% of liquid production, 30.3-41.3wt% char and, 7.31-18.3wt% gas for common temprature ranges.

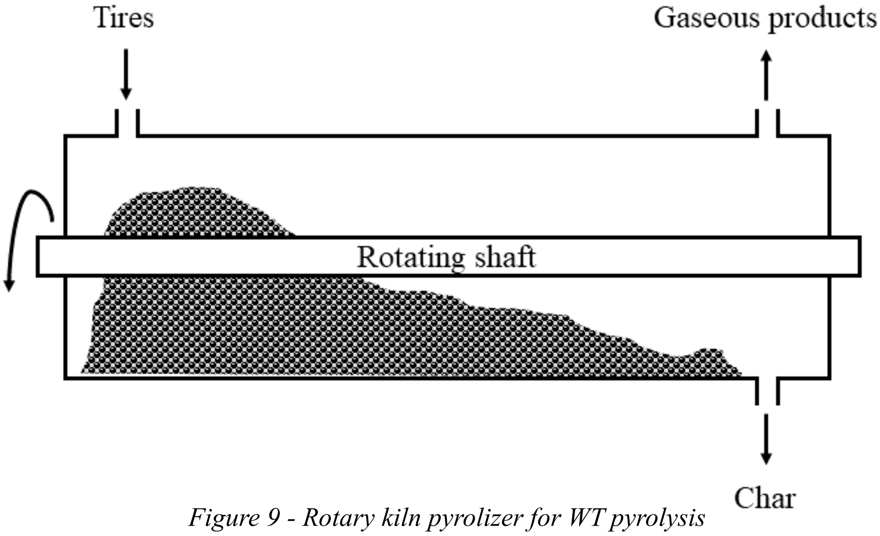


*Figure 9 - Rotary kiln pyrolizer for WT pyrolysis*

*3.3.1.5 Auger reactor*

Auger reactors are also called screw reactors since the mechanical movement of the material is generated by a rotating screw *(Figure 10)*. They are suitable for continuous processing and present simple design; these conditions lead to broad research and implementation. Moreover, the rotating movement of the screw provides good mixing, easy control on process parameters and, possible waste tire processing without heat carrier such as sand. Also, they can be heated by direct or indirect methods in intermediate pyrolysis conditions. Normal thermal conditions are of 400-600°C and solid residence time of 5-30 seconds. Different research work tested liquid production at 30.31-54wt%, char at 36.0-53.0wt% and, gas at 6.0-18.8wt%.

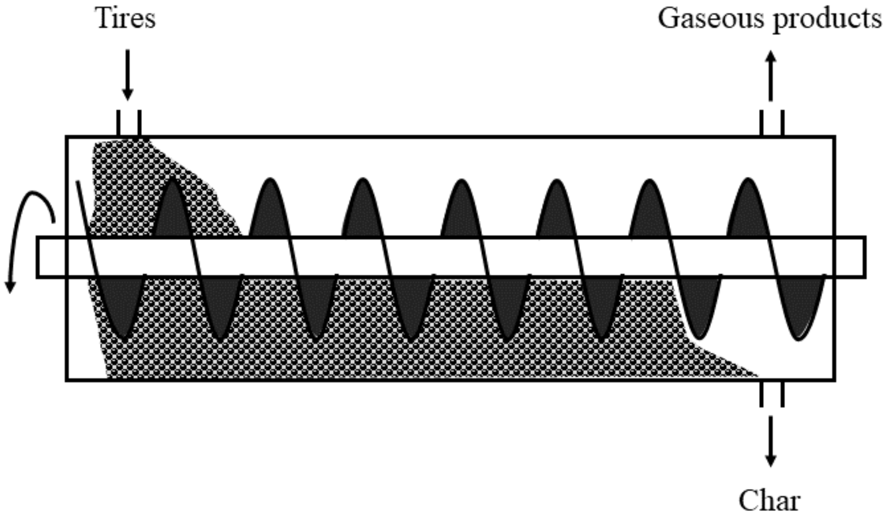


*Figure 10 - Auger reactor for WT pyrolysis*

### 3.3.2 Process parameters

The operating condition in which waste tire pyrolysis is performed have significant effect on product distribution and their composition. The parameters controlling the process have been identify as temperature, heating rate, solid and volatile residence time, and pressure.

#### *3.3.2.1 Temperature*

The literature on waste tire pyrolysis has identified temperature as the main parameter affecting the yield of gas, liquid, and char. Below 450°C high concentration of char products can be found due to non-complete devolatilization of tires main components such NR, SBR, and BR. They remain in the solid fraction resulting in a sticky and gummy heterogeneous mixture *(Martínez et al., 2013 Taleb et al., 2020)*. The complete conversion of the feedstock is achieved at 500°C and the optimum temperature to obtain high tire pyrolysis oil (TPO) yields under thermal condition is 450-550°C. The full conversion of the initial mass can be identified by constant solid yields which value is generally around the sum of fixed carbon and ash content. Temperatures higher than 500-550°C promote gas formation by secondary reaction; liquid compounds react to form permanent gas components. So, it can be concluded that gas yields can be increased by operating at higher temperature. On the other hand, when reaction temperatures are elevated (>800°C) or when high gas-solid contact reactors (FBR and CSBR) are used secondary reactions concerning the carbonaceous fraction of the solid and the hydrocarbon gases may occur leading to an increase in char formation. These secondary reactions involve the absorption of volatiles on the carbon surface creating new carbon-based material *(Martínez et al., 2013 Taleb et al., 2020 Arabiourrutia et al., 2020)*. Moreover, the effect of temperature on products yields cannot be considered alone but it must be coupled with other parameters, especially residence time of the fraction since it controls the number of reacting species available for secondary reactions.

*Table 12 - Temperature effect on products yields for different types of reactors*

| Reactor | Temperature (°C) | Products yields | | | Process conditions | | Reference |
|---|---|---|---|---|---|---|---|
| | | Liquid (wt%) | Gas (wt%) | Soild (wt%) | | | |
| Batch | 400 | 42.0 | 16.8 | 41.2 | Particle size 10 mm<br>Nitrogen gas flow 0.35 m$^3$/h<br>Lab scale | | Barbooti et al., 2004 |
| | 430 | 50.8 | 16.6 | 32.6 | | | |
| | 460 | 53.0 | 12.9 | 34.1 | | | |
| Batch | 400 | 28.0 | 26.0 | 46.0 | Particle size of 0.18, 0.42, 1 mm<br>Helium flow 1 mL/min<br>Lab scale | | Taleb et al., 2020 |
| | 500 | 32.0 | 27.0 | 41.0 | | | |
| | 600 | 22.0 | 38.0 | 40.0 | | | |
| FBR | 475 | 41.0 | 32.2 | 26.8 | Nitrogen gas<br>Retention time <1s<br>Lab scale | Particle size of 0.71 mm | Raj et al., 2013 |
| | 550 | 35.2 | 34.0 | 30.8 | | Particle size of 1 mm | |
| | 600 | 25.3 | 46.0 | 28.7 | | Particle size of 0.71 mm | |
| CSBR | 425 | 65.2 | 1.81 | 34.5 | Particle size 0.63-1 mm<br>Nitrogen gas 9.5 Nl/min<br>Lab scale | | Lopez et al., 2011 |
| | 500 | 62.6 | 4.5 | 34.6 | | | |
| | 600 | 56.9 | 8.6 | 36.5 | | | |

### *3.3.2.2 Heating rate*

Heating rate is a fundamental control parameter in pyrolysis processes not only because it affects products distribution but also due to its correlation with energy consumption. Low heating rates are linked to slow pyrolysis which requires less energy but longer process time. High heating rates demand higher energy but lower times to achieve complete degradation *(Cheng et al.,2021)*. Moreover, the increase in heating rate is associated with increasing degradation rates which results in higher start and end temperatures of devolatilization; the decomposition is delayed due to lower heat transfer and changes in process kinetics *(Martínez et al.,2013)*. Heating rate mainly influences heat and mass transfer occurring inside the waste tire particle. Slow heating rates enhance heat transfer and coupled with longer pyrolysis times results in deep particle heating with vapors release and diffusion. This behavior favors secondary reactions in both particle and volatiles. High heating rates enable heat transfer leading to grater liquid oil and less char production such as in fast pyrolysis. *Table 13* reports literature results on the heating rate influence on products yield.

*Table 13 - Heating rate effect on products distribution in WT pyrolysis*

| Reactor | Temp. (°C) | Heating rate (°C/min) | Products yields | | | Process conditions | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | Liquid (wt%) | Gas (wt%) | Soild (wt%) | | | |
| Flow tube | 600 | 5 | 50.75 | 10.67 | 38.58 | Particle size <0.42 mm<br>Argon flow rate 300 mL/min<br>Pyrolysis time 1 h<br>Lab scale | | Cheng et al., 2021 |
| | | 10 | 48.28 | 13.66 | 38.06 | | | |
| | | 20 | 46.04 | 15.84 | 38.12 | | | |
| | | 30 | 44.75 | 17.42 | 37.83 | | | |
| | | 40 | 45.51 | 16.27 | 38.22 | | | |
| Fixed bed | 350 | 5 | 27.20 | 11.54 | 61.26 | Particle size 2.8-3.4 mm<br>Nitrogen gas flow 1 L/min<br>Lab scale | Pyrolysis time 120 min | Mkhize et al., 2016 |
| | | 25 | 22.59 | 17.15 | 60.62 | | | |
| | 550 | 5 | 43.50 | 19.86 | 36.64 | | Pyrolysis time 30 min | |
| | | 25 | 43.43 | 20.37 | 36.20 | | | |

### *3.3.2.3 Residence time*

Residence time can be referred to the volatile fraction or the solid particles. The volatile residence time is linked to carrier gas flow rate by an inversely proportional relationship. An increase in flow rate results in lower volatile permanence inside the reactor resulting in minimum secondary reaction occurrence. These secondary reactions such as thermal cracking, recondensation, repolymerization, and char formation, increase gas and char yields. So, it can be concluded that higher flow rates reduce the permanence of the vapors inside the reactor leading to greater amounts of liquid oils. As the volatile residence time increases secondary reactions take place yielding higher gas quantities *(Islam et al.,2008)*.

How long tire particles remain inside the reactor defines the pyrolysis time also called reaction time. It is mainly dependent on particle size and reactor type. Increasing particle size results in higher reaction times; it can be lowered by a processing temperature increase or higher heating rates, but secondary reactions may occur changing the products distribution. Moreover, each reactor has peculiar characteristics which affect the pyrolysis time such as particle size limitation, applicable heating rates, and volatile residence time. In conclusion, both residence time must be carefully chosen based on implemented technology and its scale, and final desired products.

### *3.3.2.4 Pressure*

Vacuum pyrolysis of waste tires is of interest because it results in fewer secondary reactions, mainly due to lower residence time of the volatile fraction. This is achieved with a positive pressure gradient generated by the vacuum pressure which promotes diffusion of the vapors formed inside the particle *(Lopez et al.,2010)*. Moreover, vacuum pressure positively affects the volatilization of primary products resulting in lower process temperatures and faster reaction if compared to atmospheric pressure pyrolysis. The effect of vacuum pyrolysis on product distribution is to yield higher liquid oil and to avoid cyclization and condensation reactions on char surface resulting in greater surface area and active sites *(Martínez et al.,2013)*.

### 3.3.3 Catalytic pyrolysis

Catalytic pyrolysis is used to increase liquid oil and gas fraction quality by higher aromatics and light olefins contents and reduction of contaminants such as nitrogen, sulfur, and chlorine. Catalysts are divided into acid and basic; both are characterized by Bronsted and Lewis sites where the first exchanges protons (donates if acid and accepts if basic) and the latter accepts electrons if in acid form and donates electrons when in base form. The main acid catalyst used in pyrolysis are zeolites both micro- and meso-pours. Concerning basic catalyst, alkali metal earth oxides are the most employed. Characteristics and effects of catalyst on pyrolysis process and products are described in the following sections.

The contact between the volatile fraction and the catalyst can be in situ or ex situ. In situ contact happens in the same reactor where the pyrolysis is carried out; here the catalyst is mixed with the feedstock material. This is the main exploited technology since it presents simple design and operation, but the main drawback is catalyst deactivation by char deposition on the surface. For this reason, ex situ contact has been largely research. It consists of two stages (*Arabiourrutia et al., 2020)*:

- Tire waste pyrolysis at its optimized temperature
- Volatiles contact with catalysts which can be performed at a different temperature more suitable for catalyst operation. Moreover, it avoids contact between impurities (N, S, Cl) and catalyst because they remain in the pyrolysis reactor.

Even if ex situ contact has many advantages it requires an additional reactor which rises both capital and operational costs. To overcome this problem in line pyrolysis is currently under research. This configuration is applicable with fixed bed reactors in batch conditions. In line installations consist of a fist fixed bed in which pyrolysis is carried out and a second fixed bed (in upper position) where catalyst-volatile contact is performed *(Figure 11)*.

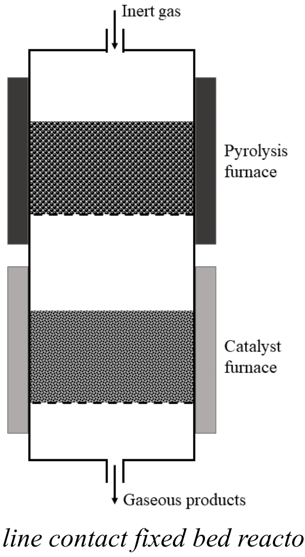


*Figure 11 - Example of in line contact fixed bed reactor for tire pyrolysis*

#### *3.3.3.1 Zeolites*

Zeolites are acid material presenting microporous structure characterized by uniform pore size with dimension comparable to molecules. This feature makes them selective in regard of molecules within range size; these can enter the particle and react but, the products leaving must present, again, the right dimension resulting in product selectivity. Reactive acid sites are responsible for cracking initiation and further reaction. Depending on their characteristics the carbon single bond cleavage can occur by addition of a hydrate ion to an olefin (Bronsted acid stie) or by extraction of a hydrate ion to a paraffin (Lewis acid site) (*Arabiourrutia et al., 2020)*. The acidity of the zeolite is controlled by Si/Al ratio, low values correspond to higher acidity. Other reactions happening inside or at the catalyst surface are hydrogen transfer, isomerization, cyclization, aromatization, and condensation. Depending on pore size and acidity the most used zeolites can in waste tire pyrolysis are: HZSM-5, HY, Hβ, HZSM-22, and SAPO-11.

HZSM-5, HY, and Hβ are three dimensional zeolites with different pore size. The largest pores are showed by HY, followed by Hβ and HZSM-5. HY allows $C_{12}$ compounds diffusion and presents higher acid density which leads to greater aromatization ability resulting in BTX and PAH formation. A problem linked with PAH formation is the possibility of condensation to form coke which deposits on the catalyst and leads to its deactivation. On the other hand, HZMS-5 hinders hydrogen transfer and aromatization reactions. Hβ presents halfway behavior between HY and HZSM-5 (*Arabiourrutia et al., 2020)*. HZSM-22 and SAPO-11 are one dimensional zeolite so, they do not present interconnected pores. SAPO-11 shows larger pores of elliptical shape and higher acidity with respect to HZSM-22 which enhances primary and secondary catalytic reactions resulting in higher aromatic yields *(Li et al.,2016)*.

*Li et al. (2016)* reported little influence of the catalyst on the liquid fraction yield, in comparison grater gas yields and lower char production were measured. This can be explained by catalyst influence on tire material conversion to light hydrocarbons. The higher gas yield was reached with SAPO-11 which possess high acidity resulting in grater feedstock transformation, hence the lowest char production, and higher low molecular weight compounds. The highest liquid yield was produced by HZSM-5 addition. *Arabiourrutia et al. (2008)* compared HZSM-5 and HY zeolites at different temperatures. Gas yields are higher when catalyst is used at both temperatures; HZSM-5 produced higher quantities of gas if compared to HY. This behavior is enhanced with increasing temperature since it increases HZSM-5 cracking ability and HY aromatization reactions. Moreover, catalyst application affects liquid products distribution; nonaromatic compounds production decreases and aromatic compounds yield increases. Between the two catalysts HZSM-5 generates higher nonaromatic compounds while HY enhances aromatic production due to its aromatization ability. Also, tar was measure by the research group; higher temperature results in lower tar production, HY yields the highest tar amount to condensation reactions forming carbonaceous coke.

*Table 14* reports the previously discussed results.

*Table 14 - Zeolite catalyst influence on products yields in waste tire pyrolysis*

| Reactor | Temp. (°C) | Catalyst | | Products yield | | | Reference |
|---|---|---|---|---|---|---|---|
| | | | | Liquid (wt%) | Gas (wt%) | Char (wt%) | |
| Stirred batch | 500 | Thermal | - | 55.50 | 4.50 | 40.00 | Li et al.,2016 |
| | | HZSM-5 | 1wt% | 55.65 | 6.49 | 37.89 | |
| | | USY | | 53.49 | 9.97 | 36.54 | |
| | | Hβ | | 54.00 | 8.24 | 37.76 | |
| | | SAPO-11 | | 55.12 | 6.17 | 38.71 | |
| | | HZSM-22 | | 55.12 | 6.17 | 38.71 | |
| CSBR | 425 | Thermal | - | 64.68 | 0.10 | 35.22 | Arabiourrutia et al.,2008 |
| | | HZSM-5 | 30g in 15g of bed sand | 58.34 | 7.56 | 34.09 | |
| | | HY | | 62.16 | 3.34 | 34.50 | |
| | 500 | Thermal | - | 63.21 | 3.48 | 33.31 | |
| | | HZSM-5 | 30g in 15g of bed sand | 45.48 | 19.32 | 35.20 | |
| | | HY | | 61.81 | 2.49 | 35.70 | |

### *3.3.3.2 Alkali metal earth oxides*

Alkali metal earth oxides are base catalysts are less reactive if compared to acid catalysts. The catalytic pyrolysis starts with $H^+$ extraction form the reacting molecule with consequent formation of an anionic specie and an electron donating site on the catalyst. Other possible reaction occurring when base catalyst is employed are isomerization, addition, decomposition, alkylation, and esterification *(Shah et al.,2008)*. Alkali metal earth oxides such as MgO and CaO are the most used in waste tire pyrolysis since they showed high catalytic activity and liquid oil quality improvement (*Arabiourrutia et al., 2020)*.

*Miandad et al. (2018)* used in their research activated $Al_2O_3$ and $Ca(OH)_2$. When compared to thermal pyrolysis these two catalysts did not enhanced liquid production. $Al_2O_3$ showed the highest gas production which can be explained by its mild acidity. On the other hand, $Ca(OH)_2$ produced the highest char yields which can be linked to its low surface area, low acidity, and meso-pours structure which favors char deposition. *Shah et al. (2008)* investigate the effect of temperature on MgO and $CaCO_3$ catalytic pyrolysis. The optimum temperature achieving complete degradation and highest liquid yields is 350°C. Moreover, $CaCO_3$ yields higher gas quantities and lower char formation. MgO produces high liquid yield and high char leading to the assumption of grater deposition of carbonaceous coke on the catalyst. Generally, increasing temperature results in lower char and higher gas and liquid formation, however at values higher than 350°C grater gas production is achieved at the expenses of liquid oils.

*Table 15 - Base catalyst influence on products yields in waste tire pyrolysis*

| Reactor | Temp. (°C) | Catalyst | | Products yield | | | Reference |
|---|---|---|---|---|---|---|---|
| | | | | Liquid (wt%) | Gas (wt%) | Char (wt%) | |
| Batch | 450 | Thermal | - | 40.0 | 20.0 | 40.0 | Miandad et al.,2018 |
| | | $Al_2O_3$ | 10wt% | 32.0 | 34.1 | 33.9 | |
| | | $Ca(OH)_2$ | | 26.0 | 18.4 | 55.6 | |
| Batch | 300 | MgO | - | 4.83 | 6.4 | 88.7 | Shah et al.,2008 |
| | | $CaCO_3$ | | 1.76 | 19.30 | 65.93 | |
| | 350 | MgO | - | 34.06 | 13.70 | 52.20 | |
| | | $CaCO_3$ | | 30.20 | 27.46 | 42.33 | |
| | 400 | MgO | - | 27.00 | 19.33 | 53.50 | |
| | | $CaCO_3$ | | 29.20 | 31.90 | 39.06 | |

### 3.3.4 Products

The main waste tire pyrolysis products are liquid oils and char. From the pyrolysis reactor two fractions are retrieved volatile and solid. The vapor phase exiting the vessel must be cooled, this is achieved by implementation of heat exchangers in the process setup. In the cooling step the condensable fractions of the volatile stream are collected; these are the most valuable and abundant products of pyrolysis of waste tires. Moreover, the remaining gas fraction is now at lower temperatures and can be further treated in cyclones or filters to produce a clean gas stream. When fast pyrolysis is performed the condensation step is fundamental to avoid secondary reactions progress in the stream, so it must be carried out close to the reaction output. On the other hand, in continuous setup the char fraction is retrieved from the reactor in a continuous way, generally by gravity aid. Waste tire pyrolysis products characteristic and main applications are detailed in the following sections.

#### *3.3.4.1 Gas*

Gases are not the main products of tire waste pyrolysis, nevertheless they require some consideration since they can be fundamental in the economy of the process. In fact, product gases can be used directly in the process to heat waste tire particle up to the reaction temperature. The main components of the gas fraction are hydrogen ($H_2$), carbon dioxide ($CO_2$), carbon monoxide (CO), methane ($CH_4$), light hydrocarbons $C_2$-$C_4$ such as ethane ($C_2H_6$), ethene ($C_2H_4$), propane ($C_3H_8$), propene ($C_3H_6$), butane ($C_4H_{10}$), butene ($C_4H_8$), and butadiene ($C_4H_6$). Moreover, some sulfur, nitrogen and chlorine compounds can be found, due to agent addition during tire manufacturing, and contribute to secondary pollution. Alkenes, dienes, and butadiene are the products of primary thermal degradation. Light hydrocarbons derive from secondary reaction of volatile primary products in the hot zone *(Williams, 2013)*. $C_4$ fractions are direct products of SBR, and BR rubber degradation, $CO_2$ and CO are imputable to oxygenated additives *(Martínez et al.,2013 Arabiourrutia et al., 2020)*. The quantity of each component depends on the initial waste tire composition and process parameters. As already discussed, a temperature increase result in higher gas yields since secondary reactions and thermal degradation are enhanced. The gas composition is also dependent on temperature *(Table 16)* and an increase of this parameter leads to greater concentration of all compounds. Methane, ethene, propene, and butadiene formation is favored with respect to the others. Butadiene is the main component at all temperatures. Another parameter that has major influence on the gas composition distribution is the catalyst. As previously discussed, catalytic pyrolysis leads to higher gas yields and consequently the concentration of all components increases. From *Table 17* is possible to see the difference influence of HZSM-5 and HY zeolite catalysts. HZSM-5 shows great selectivity towards propene and butadiene due to its ability to favor monomolecular cracking. On the other hand, HY enhances butane and methane production and present high activity for butadiene. The low yield of butadiene, lower than the thermal value, is due to HY elevated hydrogen transfer which promotes condensation reactions.

*Table 16 - Temperature effect on gas composition in WT pyrolysis*

| **Reactor** | **Temp. (°C)** | **Gas yield (wt%)** | **Gas composition (wt%)** | | | | | | | | | | | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **$H_2$** | **$CO_2$** | **CO** | **$CH_4$** | **$C_2H_6$** | **$C_2H_4$** | **$C_3H_8$** | **$C_3H_6$** | **$C_4H_{10}$** | **$C_4H_8$** | **$C_4H_6$** | |
| CSBR | 425 | 0.10 | - | 0.01 | <0.01 | - | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 | 0.02 | Arabiourrutia et al.,2008 |
| | 500 | 3.48 | - | 0.26 | 0.38 | 0.06 | 0.30 | 0.18 | 0.12 | 0.18 | 0.18 | 0.29 | 1.12 | |
| FRB | 450 | 2.5 | 0.06 | - | - | 0.29 | 0.17 | 0.24 | 0.16 | 0.04 | <0.01 | 0.08 | 1.26 | Williams et al.,2003 |
| | 500 | 4.5 | 0.13 | - | - | 0.61 | 0.31 | 0.56 | 0.21 | 0.41 | <0.01 | 0.09 | 1.75 | |
| | 525 | 6.0 | 0.17 | - | - | 1.04 | 0.45 | 0.90 | 0.27 | 0.90 | <0.01 | 0.11 | 1.95 | |
| | 550 | 7.5 | 0.20 | - | - | 1.28 | 0.53 | 1.15 | 0.30 | 1.20 | <0.01 | 0.17 | 2.19 | |
| | 600 | 14.0 | 0.24 | - | - | 2.39 | 0.74 | 3.84 | 0.40 | 1.92 | <0.01 | 0.26 | 2.60 | |

*Table 17 - Catalyst effect on gas composition in WT pyrolysis*

| **Reactor** | **Catalyst** | **Temp. (°C)** | **Gas yield (wt%)** | **Gas composition (wt%)** | | | | | | | | | | | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **$H_2$** | **$CO_2$** | **CO** | **$CH_4$** | **$C_2H_6$** | **$C_2H_4$** | **$C_3H_8$** | **$C_3H_6$** | **$C_4H_{10}$** | **$C_4H_8$** | **$C_4H_6$** | |
| CSBR | HZSM-5 | 500 | 19.32 | - | 0.35 | 7.06 | 0.41 | 0.32 | 2.74 | 1.15 | 5.97 | 1.38 | 1.68 | 3.94 | Arabiourrutia et al.,2008 |
| | HY | | 2.49 | - | 0.09 | - | 0.09 | 0.06 | 0.18 | 0.18 | 0.59 | 0.24 | 0.47 | 0.68 | |
| FBR | HZSM-5 | 500 | 10.50 | 0.15 | 0.41 | 0.12 | 0.57 | 0.30 | 1.31 | 1.24 | 2.60 | 1.34 | <0.01 | 2.01 | Williams et al.,2003 |
| | | 600 | 15.0 | 0.31 | 0.52 | 0.28 | 1.70 | 0.55 | 2.75 | 1.44 | 3.80 | 0.80 | <0.01 | 2.48 | |
| | HY | 500 | 12.5 | 0.13 | 0.48 | 0.10 | 0.51 | 0.32 | 0.66 | 0.77 | 1.60 | 4.08 | 0.11 | 1.26 | |
| | | 600 | 17.5 | 0.32 | 0.42 | 0.16 | 2.51 | 1.00 | 2.14 | 1.14 | 2.50 | 3.64 | 0.35 | 1.73 | |

Pyrogas is a good fuel, and its main characteristics are heating value and contaminants concentration. *Martínez et al. (2013b)* measured the low heating value of mixed tire pyrolysis gas processed in a pilot scale auger reactor at 550°C with a nitrogen flow of 5 Nl/min, LHV ranged from 34.49 to 38.45 MJ/Nm$^3$. Other reviews set the heating value of pyrogas between 30-40 MJ/ m$^3$ for waste car tire and from 20 to 65 MJ/ m$^3$ for waste truck tire; these values are comparable with natural gas heating value 35-40 MJ/ m$^3$ *(Czajczynska et al.,2017 Williams 2013)*. Based on the calorific value pyrolytic gas can be used as a fuel, but another issue rises contaminants concentration. All waste tire contains nitrogen (0.37-0.76wt%) and sulfur (1.06-1.76wt%), some brand also shows chlorine content (0.19-0.23wt%) *(Cheng et al.,2021)*. These compounds can be found in the gas fraction of the pyrolysis process in form of $NH_3$, NO, HCN, $H_2S$, $CS_2$, COS, $CH_3SH$, $C_6H_5SH$, and HCl. Even if these compounds are mainly found in the char fraction their concentration in the gas cannot be disregarded. Sulfur compounds are the most abundant and rise concern for pyrogas application as fuel due to $SO_x$ formation, nitrogen leads to $NO_x$ formation when oxidized, and chlorine compounds in oxidizing atmosphere result in dioxins formation which are toxic compounds. In fact, if pyrolysis gas is combusted then incineration plant emission limits must be satisfied as prescript in the European Directive 200/76/EC, Annex V emission limits. As of now there is a lack of data on emission values from pyrogas combustion, so further research must be conducted since flue gas treatment can change the economy feasibility of the process.

#### *3.3.4.2 Liquid*

Waste tire pyrolysis oil (TPO) is the most valuable product generated by the process. It presents itself as a dark brown dense material with a strong sulfur odor. It is a complex mixture of more than a hundred compounds that can be divided into aliphatic, aromatic, heteroatoms, and polar fraction. There is no variation in terms of single compounds; they are always the same, but their concentration is dependent on tire composition, reactor type, and process parameters. The most valuable components found in TPO are benzene, toluene, xylene, styrene, and limonene. It has been reported *(Williams 2013 Islam et al.,2008 Martínez et al.,2013)* that process temperature changes the pyrolysis oil composition, specifically:

- Temperature increase results in higher aromatic fraction concentrations with consequently decrease in aliphatic quantities due to secondary reactions. Also, an increase in aromatic contents result in lower calorific value of the oil.
- Higher temperature (>500°C) leads to lower limonene content which decomposes to isoprene, benzene, toluene, xylene, and styrene.
- Increasing temperatures and longer residence time result in higher PAHs concentrations due to aromatization reactions such as Diels-Alder reactions which include cyclisation of alkenes and hydrogenation.
- Polycyclic aromatic hydrocarbons containing sulfur or nitrogen present higher formation with increasing temperature.

Catalytic pyrolysis can be used to change and narrow TPO composition. Many researches *(Li et al.,2016 Arabiourrutia et al.,2008 Williams et al.,2003 Arabiourrutia et al.,2020)* showed that catalyst can:

- Lower S and N in the oil fraction due to higher velocity in C-S, and C-N cleavage which lowers the resulting heteroatoms concentration.
- HZSM-5 and HY zeolites increase the aromatic fraction yield with higher concentrations of single ring hydrocarbon such as benzene, toluene, xylene. This is due to zeolites ability to enhance monoaromatic hydrocarbons formation. They operate by different mechanism, HZSM-5 favors tar cracking to from lighter aromatic compounds and HY promotes condensation and alkylation of limonene producing BTX, but also heavier compounds linked to tar formation.
- All catalysts do not have effect on limonene reduction with increasing temperatures.
- Base catalyst, especially CaO can promote desulfurization reactions forming calcium sulfide (CaS) which presents solid form.

Moreover, *Lopez et al (2010)* studied the effect of vacuum pyrolysis on TPO components distribution and reported lower limonene production because vacuum pressure inhibits isoprene dimerization to form limonene. Consequently, higher quantity of isoprene where measured. Styrene followed the same reduction of limonene. On the other hand, aromatic compounds such as ethylbenzene, toluene, and xylene were not affected by changing pressure.

Fuel properties of TPO are assessed to understand if it can be used as fuel-like or if it can be blend with other fuels. The measure properties are *(Williams 2013 Islam et al.,2008 Martínez et al.,2013 Campuzano et al.,2021)*:

- Density is an important parameter to be tested especially when TPO in used in internal combustion engines which work on volume basis. Raw TPO presents density values higher than commercial diesel, much closer to distillate marine fuels.
- Viscosity reflects the oil ability to flow in pipes and pumps. High values can lead to pipe occlusion due to oil sticking, lower pump performance and ware. Raw pyrolysis oil presents viscosity values between gasoline and diesel standard.
- Flash point defines the temperature at which the liquid forms an inflammable gas fraction which leads to fire hazard and is directly link with handling, storage, and transportation safety. TPO flash point is generally lower than commercial diesel values due to TPO wide range of compounds with diverse boiling points (70-551°C). Lower flash point requires higher safety in all operations.
- Carbon residue measures the tendency of TPO to form coke under poor combustion conditions. High values of this parameter can result in injection nozzles blockage after extensive time use. TPO values are higher than diesel ones; so, engine injection system can be ruined.
- pH is used as indicator of metal contamination. Depending on the initial composition and process conditions TPO pH can range from slightly acid (4.40) to neutral (~7). As conclusion no metal contamination is detected.
- Calorific value of pyrolysis oil shows good results 40-42.6 MJ/kg which is comparable with diesel standard.

In the past years many studies on TPO application as fuel were carried out, the most significant results reported in the reviews of *Williams et al. (2013) and Martínez et al. (2013)* are:

- Modified diesel engines are not able to run with 100% of TPO
- Bends of diesel and pyrolysis oil can be used in common combustion engines up to 70% TPO without substantial performance loss
- Hydrocarbons, NOx, and particulate emission are increased if compare with diesel ones. HC higher emission can be correlated to higher PAHs content in TPO. Ultimate analysis of pyrolysis oil shows higher nitrogen concentration. Moreover, higher CO and SOx emission were found due to poor atomization and higher concentration of TPO, respectively.
- Application in larger combustion unit or in boiler can improve the quality of the emissions.

*Campuzano et al., (2021)* studied TPO distillation into light, low middle, high middle, and heavy fractions based on the boiling point difference; 70-176°C, 176-240°C, 240-285°C, 285-551°C respectively. Then, they compared each fraction fuel properties with gasoline, diesel, and heavy fuel oils. As a result, light fraction shows comparable properties with gasoline, low middle with diesel, high middle with distillate marine fuels, and heavy fraction with bitumen. In this way, each fraction can be used in the same applications of the comparable fuel.

TPO can also be used to retrieve added value chemicals such as BTX and limonene. Benzene, toluene, and xylene are used as primary feedstocks for plastic, resin, surfactants, and others, production. Limonene is used in industrial solvent, resin, adhesives, cosmetics, and pigments production. Moreover, due to is orange sent is used in fragrances and flavorings (*Martínez et al.,2013).* As of now, pure limonene production for TPO is not economically feasible and too complex. Another application for raw tire pyrolysis oil is in carbon black production.

#### *3.3.4.4 Solid*

The solid fraction generated by waste tire pyrolysis is called char or pyrolytic carbon black (CBp). It is composed by:

- Carbon black which is used as filler during tire manufacturing to enhance strength and abrasion resistance.
- Hydrocarbons resulting from condensation and alkylation reactions on the char surface.
- Inorganic additives such as zinc and calcium which are present in the initial feedstock composition.

Char composition is mainly affected by pyrolysis parameters and initial waste tire composition. *Table 18* present proximate and ultimate analysis of CBp obtained by different pyrolysis processes. It is to be noted the high carbon content of the char which is attributed to the carbon black, also high sulfur and ash content are reported. These are due to sulfur and metal addiction during tire manufacturing, respectively. Moreover, ash content is increased by dust deposition in waste tires. These characteristics rend raw CBp direct application as carbon black impossible. Char shows calorific values comparable with coal, but its use as fuel is minimal because of its properties. In fact, CBp present low reactivity which leads to longer reaction time, also low particle size and bulk density result in high unburned material concentrations, the low volatile matter content creates conditions for heterogeneous gas-solid reactions which result in combustion without flame. In the following table the temperature effect on the char composition is also highlighted. Increasing temperature result in a volatile matter decrease meaning that the volatile components are released by secondary reactions. Moreover, at 400°C the highest analyzed VM content was found leading to the conclusion that this condition did not result in complete degradation. The higher ash amount reported by *Czajczyńska et al. (2020)* is due to complete tire shredding without steel and beads recovery.

*Table 18 - Proximate and ultimate analysis of pyrolytic carbon black*

| **Reactor** | **Temp. (°C)** | **Char yield (wt%)** | **Ultimate analysis (wt%)** | | | | **Proximate analysis (wt%)** | | | | **CV (MJ/kg)** | **Reference** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **C** | **H** | **N** | **S** | **Moisture** | **Ash** | **Volatile Matter** | **Fixed carbon** | | |
| Auger | 550 | 40.50 | 84.40 | 1.30 | 0.50 | 2.30 | 3.60 | 12.40 | 4.70 | 79.30 | 30.30 | Martínez et al., 2013b |
| Rotary kiln | 500 | 41.30 | 82.17 | 2.28 | 0.61 | 2.32 | 2.35 | 12.32 | 16.14 | 69.19 | 31.50 | Li et al., 2004 |
| | 600 | 39.30 | 81.00 | 1.38 | 0.51 | 2.53 | 1.98 | 14.30 | 5.86 | 77.93 | 30.40 | |
| Batch | 400 | 41.60 | 84.10 | 1.30 | 0.33 | 2.50 | 0.70 | 16.40 | 42.8 | 40.10 | 35.50 | Czajczyńska, et al., 2020 |
| | 500 | 37.20 | 84.50 | 0.67 | 0.41 | 2.80 | 1.10 | 17.70 | 6.10 | 75.10 | 28.70 | |
| | 600 | 37.40 | 86.60 | 0.45 | 0.44 | 2.90 | 1.10 | 18.10 | 4.90 | 75.90 | 27.40 | |

The possible applications of pyrolytic carbon black are crucial for the economic feasibility of the process since char is the second product of WT pyrolysis. The most common use is as activated carbon. Other possible applications are pure carbon black substitute in rubber manufacturing and to obtain electrode materials for energy storage.

Pyrolytic carbon back presents a mixture of different pore size ranging from macro-pore (>50nm), meso-pores (2-50nm), to micro-pores (<2nm). *Li et al. (2004)* reported a comparison between CBp and commercial activated carbon pore size, as result char pore size present higher quantities of meso-pores and it shows a pore volume of at least one order of magnitude lower with respect to commercial activated carbon in the micro-pore interval. Meaning that raw char can be used to absorb bulky organic molecules. Another, important parameter to determine the absorption capacity of pyrolytic char is the BET surface area. BCp presents values of BET surface area raining 63.0-89.1 $m^2/g$ as reported in literature. These values are around 1/10 of commercial activated carbon BET meaning that for application as adsorbent material pyrolytic char need further treatment. Pyrolytic char activation can be carried out by physical or chemical means. Physical activation consists of CBp oxidation at 800-900°C with $CO_2$ or steam. The high temperature is used to maintain a high reaction rate to decrease the reaction time. *Mui et al. (2004)* in their review reported that steam activation results in higher surface area (>1000 $m^2/g$) with respect to $CO_2$ (270-980 $m^2/g$). They explain this result base on the molecular nature of the activation agents; water present lower dimension which result in faster diffusion which also involves micro-pores. Moreover, steam increases char micro porosity and consequently its ability to absorb gas molecules. Chemical activation allows to obtain CBp with good properties in a single process. Chemical activators such as KOH, $H_2SO_4$, and $H_3PO_4$ can be mixed with waste tire and pyrolyzed resulting in a pyrolytic char with high BET surface and low contaminant concentrations. Active chars can be used as organic and inorganic compounds adsorbents in industrial effluents such as phenols, dyes, halogenated hydrocarbons and pesticides, metals, natural gas, and $SO_2$.

Application of pyrolytic carbon black as pure carbon black in rubber manufacturing can be achieved after demineralization. Commercial CB is categorized by ASTM; classes are identified by the letter ‘N’ which states that the CB has a normal vulcanization rate and three digits specifying the average particle dimension. N100 to N700 are the most used classes in rubber manufacturing, where their middle surface area ranges between 30-90 $m^2/g$. These values are comparable raw CBp. Since impurities and ash are the main barrier to pyrolytic carbon black application a demineralization process can be carried out to lower their content. *Martínez et al. (2013c)* reported a decrease in ash content of 80% (from 14.9 to 3.0wt%) and in increase of BET surface from 72.42 to 78.39 $m^2/g$ after demineralization. The increase in BET surface leads to better interaction between the CBp and the rubber. They also reported that pyrolytic carbon black present sphere-shaped particles such as commercial CB, but their dimension are higher so a milling step may be required.

# 4. Experimental activities

All the experimental activities were carried out at Western University’s Institute for Chemicals and Fuels from Alternative Resources located in London, Ontario, Canada.

## 4.1 Polyethylene pyrolysis

The experimental data reported in this work has been performed along different months. The plastic pyrolysis tests have been performed by Stephanos Horvers, Anastasia Lara Maslak and Maddalena Laghezza at ICFAR.

### 4.1.1 Feedstock Material

Nova Chemical Corp. (Calgary, Canada) is the supplier of virgin HDPE and LDPE. They are supplied in pellet of 5 mm and are used as is. *Table 19* lists the feeding material characteristics.

*Table 19 - Virgin HDPE and LDPE characteristics (Horvers, 2021)*

| Characteristic | HDPE | LDPE |
|---|---|---|
| Density (kg/m3) | 970 | 940 |
| Melt flow index (g/10 min) | 8.0 | 2.3 |
| Melting point (°C) | 130.8 | 105 |
| Crystallinity (%) | 60 | 55 |
| Hating value (MJ/kg) | 45 | 43 |

Also, an ultimate analysis of the material has been performed, the results are displayed in *Table 20*. Oxygen amount was calculated by difference.

*Table 20 - Virgin HDPE and LDPE ultimate analysis (%wt on dry basis)*

| | **C** | **H** | **N** | **S** | **O** |
|---|---|---|---|---|---|
| HDPE | 83.82 | 13.57 | 1.55 | 0.41 | 0.66 |
| LDPE | 83.52 | 12.96 | 0.03 | 0.40 | 3.08 |

Each tests used 300g of material. Different blends of HDPE and LDPE were also tested but for the further evaluations in this work only single material tests were considered.

### 4.1.2 Method

The experiments were performed using a vertical mechanically fluidized reactor (MFR). The tests are at laboratory scale, in fact the volume of the reactor is 1.4 L which allows to better control the parameters and maximize product conversion. Even if at low scale the set up comprises different components:

- Feed hopper, feeding arguer and motor with a feed rate of around 0.705 kg $h^{-1}$.
- Heat traces, one before the reactor and one immediately after. The first one serves to emulate an extruder and it keeps the feeding tube at 200°C. The latter keeps the exiting vapors from condensing before reaching the condensation section. It is also kept at 200°C.
- Reactor, SS316 stainless steel cylindrical vessel. External diameter 12 cm, internal diameter 11 cm, external and internal height 24 and 22 cm, respectively. The outlet port, the mixing paddle and the release vale are attached to the detachable top flange of the vessel.
- Char collector.
- Condensation system, it is composed by two condensers with different cooling medium. The first one uses oil which is kept worm to avoid waxes condensation which will result in equipment clogging. The second one employs an ice bath.

A nitrogen flow of 0.5 L $min^{-1}$ is injected with the plastic feed. It creates an inert atmosphere inside the reactor and favors vapors residence time control. A 12kV induction systems (Superior Induction Company, California, US) heats the reactor to the desired temperature.

The second step of the research was to evaluate product conversion and distribution with the addition of a furnace (Lindberg Blue M, Asheville, NC, US). Its characteristics are:

- Length 101 cm.
- Width 40 cm.
- Height 40 cm.
- Heating zone OD 7.6 cm, length 100 cm.
- Power 5.4 kW, intensity 23 A, frequency 50/60 Hz-
- Maximum temperature 1200°C.

The furnace operates at higher temperature than the reactor to favor secondary reaction and further cracking of the vapors.

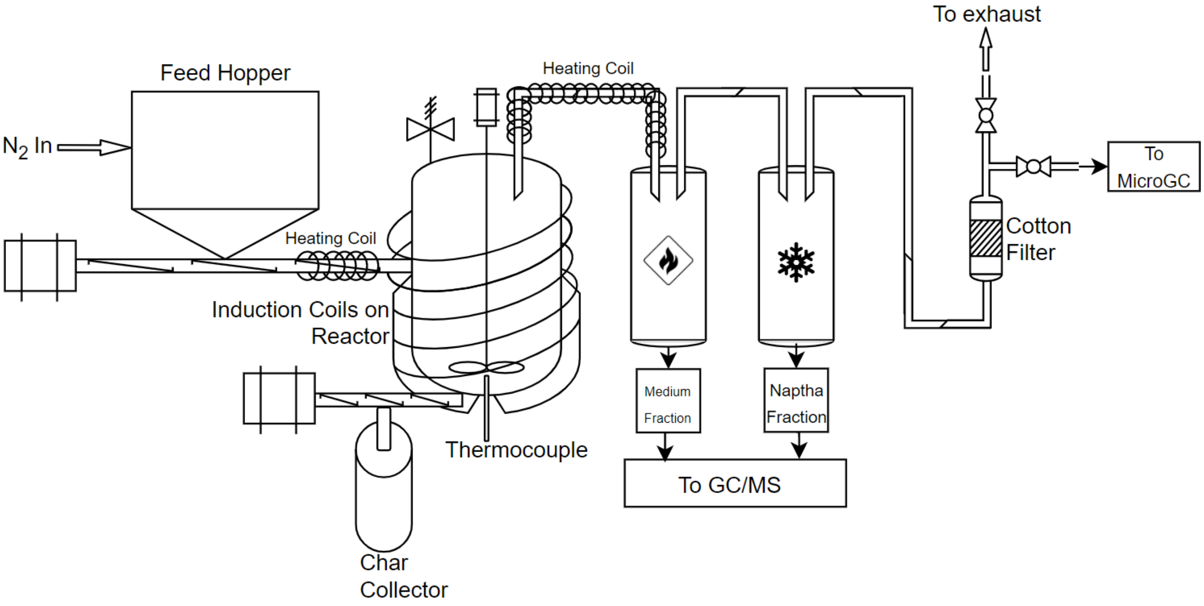


*Figure 12 - Single stage PE pyrolysis set up (Horvers, 2021)*

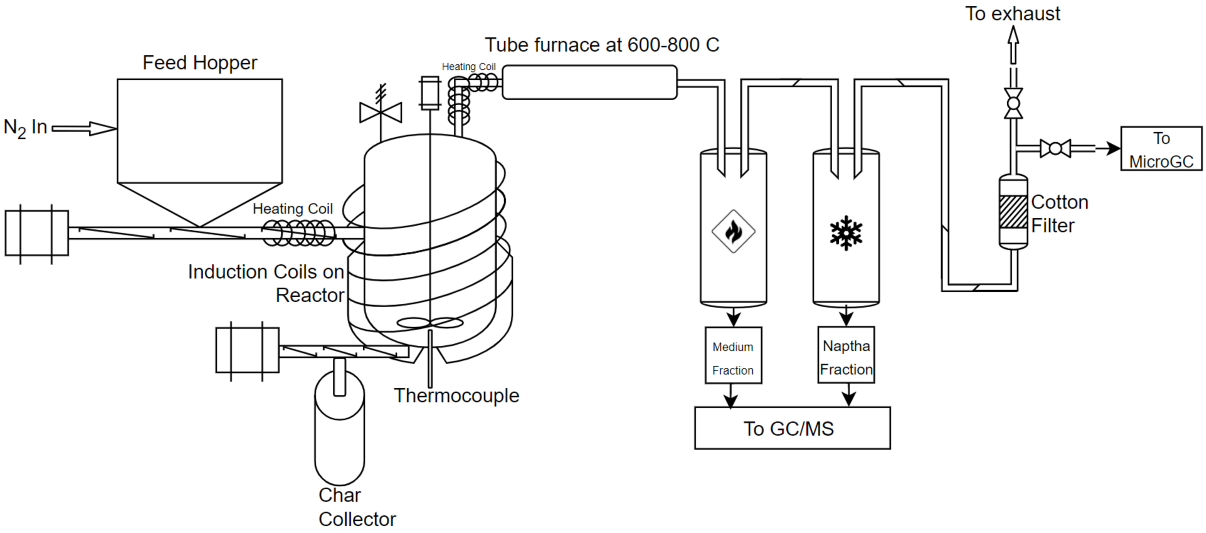


*Figure 13 - Double stage PE pyrolysis set up (Horvers, 2021)*

### 4.1.3 Results

To determine products composition and quality Gas-Chromatography Mass-Spectrometry (GC-MS), Micro Gas-Chromatography (Micro GC), Karl Fischer Titration (KF Titration) and Bomb Calorimetry were performed. GC-MS and Micro GC are used to define gas and liquid composition. KF Titration and Bomb calorimetry measure moisture content and higher heating value, respectively. Further information on tests set up and operating parameters are reported in *Horvers, 2021*.

In this work two different working conditions were considered for both HDPE and LDPE:

- One stage process with reactor temperature of 550°C.
- Two stage process with reactor and furnace temperatures of 550 and 800°C.

Moreover, HDPE has been processed in a double stage pyrolysis configuration where the reactor temperature was of 480°C, the furnace was at 850°C and the nitrogen flow was of 10 L $min^{-1}$. This set parameters have been decided after having a better control over temperature in the pyrolysis plant. The goals of this experiment were to:

- increase the liquid yield in the first stage by lowering the temperature and the residence time.
- Increase ethylene monomer production by secondary cracking at higher temperature, the residence time plays a fundamental role in this step because it regulates the vapors cracking degree.

*Figure 14* displays the results of the experiments carried out at ICFAR (*Horvers, 2021)*. Both, HDPE and LDPE present similar yields for the single stage process at 550°C. Oil and gas amount are about 65.7-65.1% and 34.5-34.9%, respectively. In the double stage process the gas yields is increased for both materials due to vapors exposure to higher temperature in the furnace which enhances cracking. Condensable fraction consists of 21.8% and 7%, non-condensable are 78.2 and 93% for HDPE and LDPE, respectively. Even if the rector temperature was lower in the last HDPE experiment the increase in the furnace led to a higher gas yield (90%) and a decrease in oil production (10%). Moreover, char was considered negligible due to concentration far lower than 1%. This is due to absence of contamination in the feedstock material.

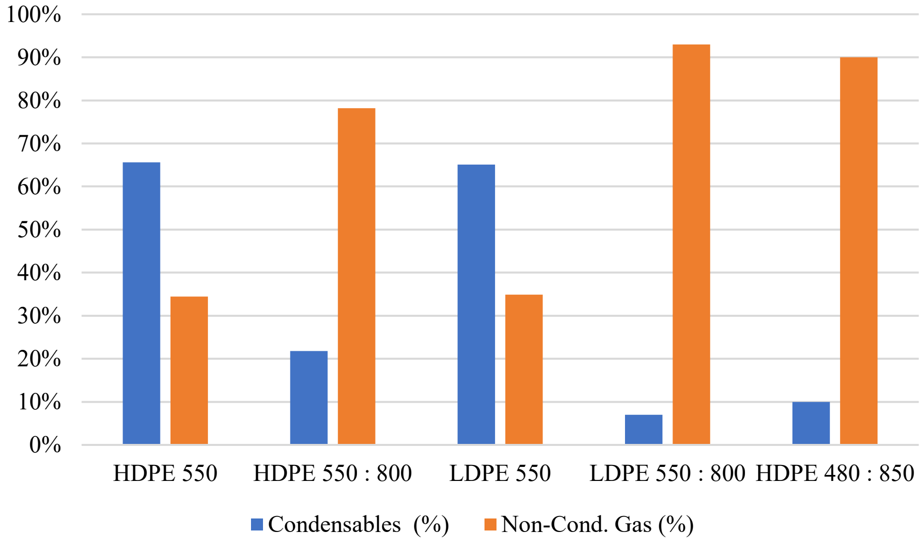


*Figure 14 - Single- vs. Double-Stage Pyrolysis of HDPE & LDPE*

Oil fractions were analyzed with GC-MS to identify the composition of the sample. From the results obtained 14 compounds were selected to describe the product. The selection has been made considering the compounds with higher pick area. Furthermore, oil has been divided into three fractions gasoline ($C_6$-$C_{11}$), diesel ($C_{12}$-$C_{18}$), and heavy ($C_{19+}$).

Micro GC has been used to identify gas composition and the results are reported in *Figure 15*. The main compounds present in the gas are methane, ethylene, and hydrogen. Both materials show similar propensity towards the formation of these compounds, LDPE produces higher ethylene amounts in all tests; this could be due to lower density, crystallinity, and melting point. When the secondary furnace is used the overall tendency is an increase in methane production meaning that further cracking is increased to the point that the final stable compound is achieved. The evidence of the cracking is also sustained by the decrease of high molecular weight compounds present in the gas. A significant increase in ethylene (30%) and hydrogen (28%) can be identified in the last experiment with HDPE, these results support the initial hypothesis of lower temperature in the reactor to increase liquid yields, lower residence time in high temperature furnace to stop the secondary cracking at the monomer stage.

Water content in oil must be low if for it to be used as a fuel, otherwise engine and injection problems arise. To test this vale KF Titration analysis is used. Both oil sample reported low water content (<1%) which allows them to be used as fuel substitutes. The main difference between the samples is their viscosity. One stage oil is in form of wax and very viscous, on the other hand two stage oil is pourable which makes it more attractive from a point of view of transportation and employment.

The bomb calorimetry result performed on the oil fraction showed consistent heating values of 45.8 and 45.5 MJ kg$^{-1}$ on average for HDPE and LDPE, respectively. This makes plastic pyrolysis oil calorific value comparable and higher than diesel, meaning that it can be successfully used as fuel substitute.

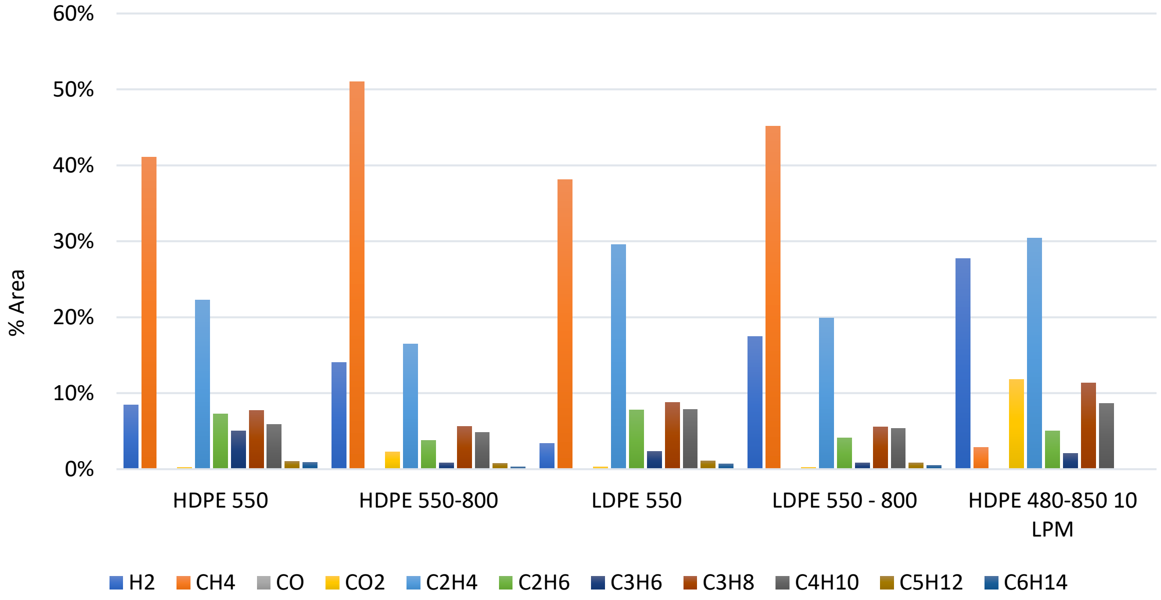


*Figure 15 - Gas composition of plastics pyrolysis with and without Secondary furnace on a $N_2$ & $O_2$ Free Basis*

## 4.2 Rubber pyrolysis

### 4.2.1 Material

The rubber used in these experiments is a common gardening rubber which can be found in many garden centers in Canada. It has been obtained from tires grounding, it comes in chunks of about 1-2 cm, presents high content of textiles and has a dark brown color.

Ultimate and proximate analysis have been conducted and the results are showed in *Table 21*. The elemental analysis of the sample was conducted using a Thermo Flash EA 1112 unit. Here samples are combusted at 900°C in a helium environment with controlled amount of oxygen. The gasses produced during the combustion ($N_2$, $CO_2$, $H_2O$ and $SO_2$) are then analyzed in a chromatography packed column. In the ultimate analysis, the oxygen content has been calculated by difference.

To perform the proximate analysis different steps must be followed:

1. Moisture evaporations form the crucibles in muffle at 750°C for 10 min.
2. After addition of about 1 g of the sample, place the crucibles in the oven at 105°C for two hours.
3. 7 minutes in muffle at 950°C with partial covering for volatile matter measurement.
4. Crucibles in muffle at 750°C for 6 hours without lid to define ash content.

After each step, the sample were weighted, and the proximate analysis parameter were computed as follows:

$$Moisture\ (\%) = \frac{mass_{sample} - mass_{sample,105°C}}{mass_{sample}} \cdot 100$$

$$Volatile\ matter\ (\%) = \frac{mass_{sample,105°C} - mass_{sample,950°C}}{mass_{sample,105°C}} \cdot 100$$

$$Ash\ (\%) = \frac{mass_{residue}}{mass_{sample,105°C}} \cdot 100$$

$$Fixed\ carbon\ (\%) = 100 - moisture\ (\%) - volatile\ matter\ (\%) - ash\ (\%)$$

*Table 21 - Ultimate and proximate analysis of the rubber feedstock*

| **Ultimate analysis (wt.% on dry basis)** | | | | | |
|---|---|---|---|---|---|
| **N** | **C** | **H** | **S** | **O** | **Ash** |
| 0.49 ± 0.02 | 66.75 ± 0.30 | 5.88 ± 0.09 | 1.12 ± 0.07 | 19.97 ± 0.18 | 5.79 ± 0.05 |
| **Proximate analysis (wt.% on dry basis)** | | | | | |
| **Moisture** | **Volatile matter** | **Ash** | | **Fixed carbon** | |
| 1.94 ± 0.20 | 64.32 ± 0.43 | 5.79 ± 0.05 | | 27.95 | |

Moreover, bomb calorimetry was performed on the rubber feedstock to measure its higher heating value which resulted to be 36.611 MJ/kg. All the values obtained are in accordance with the literature *(Martínez at al., 2013)*.

### 4.2.2 Method

The initial idea was to process the rubber with mechanically fluidized bed unit. This set up requires small particle size as feedstock and we were not able to further reduce the size of the rubber chunks. To grind the rubber feedstock liquid nitrogen was added to lower the material temperature and make it achieve the brittle point (about -70°C), then a blender was used to reduce its size. The output of this trial was not successful, in fact only a little part of the feedstock was comminuted and the blender broke due to nitrogen cooling which made the plastic break. So, the unit used to process the coarse rubber is a horizontal batch unit.

The horizontal batch mechanically fluidized reactor (MFR) is a slow pyrolysis system heated with a 12 kV induction furnace. The reactor is manually charged and emptied every time an experiment is performed. It is connected to an ice packed single stage condenser; the resulting gases are directed into the exhaust line. A scheme and picture of the set-up process are shown in *Figure 16 & 17*.

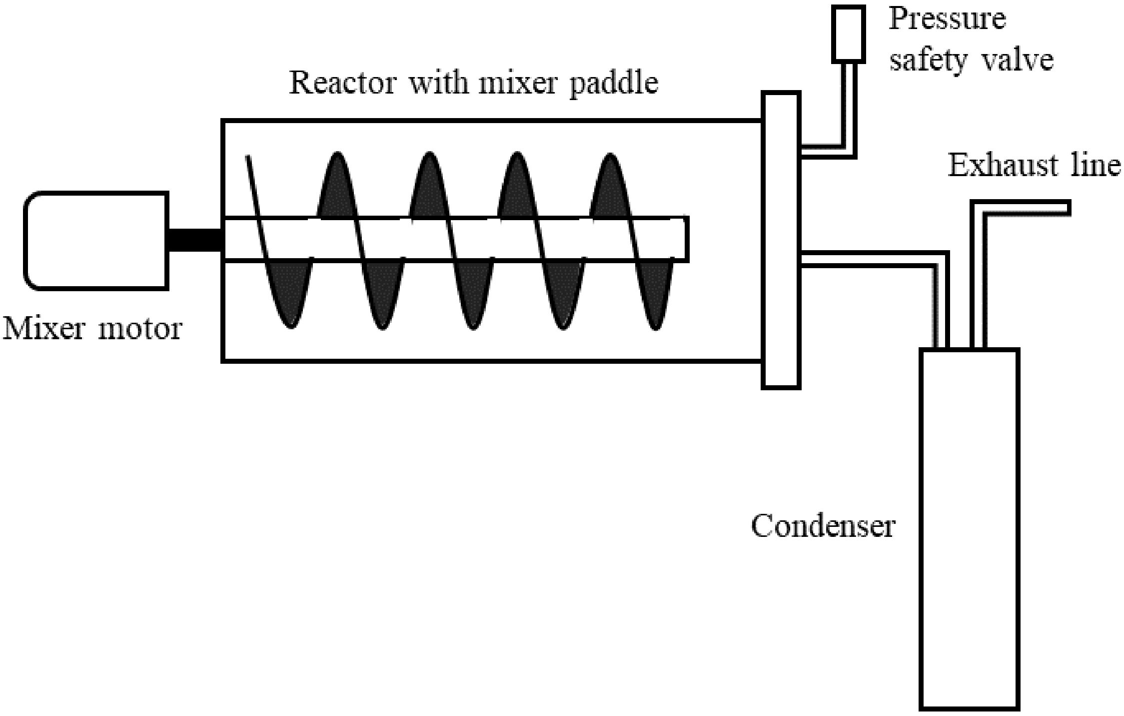


*Figure 16 - Horizontal MFR unit scheme*

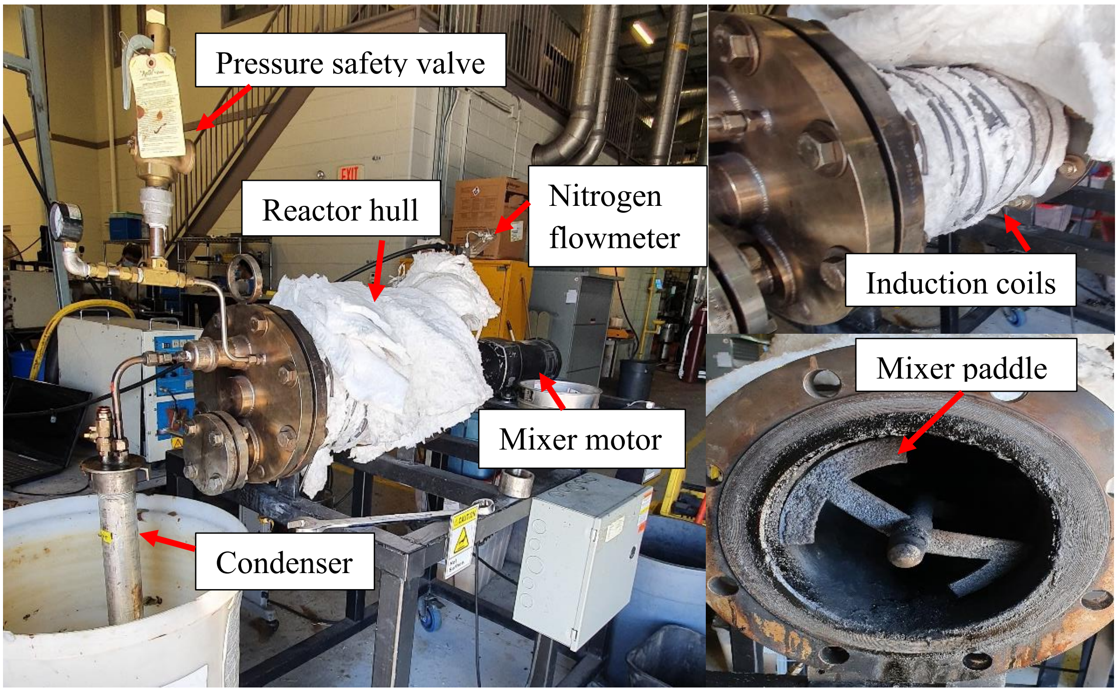


*Figure 17 - Horizontal MFR*

All the runs used 1 kg of rubber, 1 L min$^{-1}$ as nitrogen frow, a mixing rate of 30 rpm and ambient pressure. During the first run the reactor was brought to a temperature of 500°C with a heating rate of 25°C/min. When the temperature was achieved, after about 20 minutes, this was maintained for about 1 hour. After this time no more gas was produced. The second run used a heating rate of 10°C/min and was kept at 500°C for one hour. For the third and fourth run, plateaus experiments were conducted with a heating rate of 10°C min$^{-1}$ to reach them. The third run investigated gas and oil composition at 300,400, and 500°C. Each temperature was maintained until little or no gas was produced, which resulted in 45 minute for 300°C, 30 minutes at 400°C, and 50 minutes at 500°C. The last run aimed to investigate products composition at 200,300, and 400°C. During this experiment, the time periods required to have no gas production were 15, 30 and 60 minutes, respectively.

### 4.2.3 Results

#### *4.2.3.1 Yields*

The main products obtain by these experiments were gas, oil, and char, as expected. The gas fraction presents an intense odor, the oil shows very low viscosity and dark brown color. The char is brittle and black, some of it is still sticky which highlights the presence of cold spots in the reactor towards the end. Figure 18 shows oil and char fractions obtained by the pyrolysis of rubber.

*Figure 18 - Oil and char form rubber pyrolysis*

*Figure 19* shows the yields comparison between all the experiments. In accordance with the literature around 50% of the products are solids. Moreover, gas yields range between 24.5-31 % and oil between 17-22.5%.

For run 3 and 4 oil samples were collected at different temperatures to characterize them and to define their yields. The third run is the one showing the highest amount of liquid produced, the highest oil yields is reached at 400°C *(Figure 20)*. During the investigation of lower temperatures in run 4, almost no oil was produced at 200°C meaning that the pyrolysis process has not started yet. The maximum oil amount was obtained again at 400°C *(Figure 21)*.

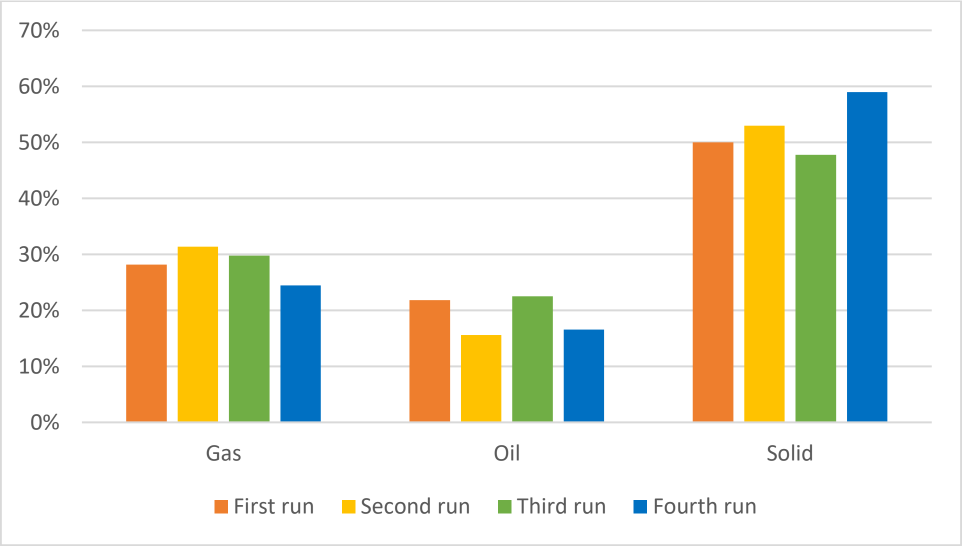


*Figure 19 - Rubber pyrolysis yield comparison*

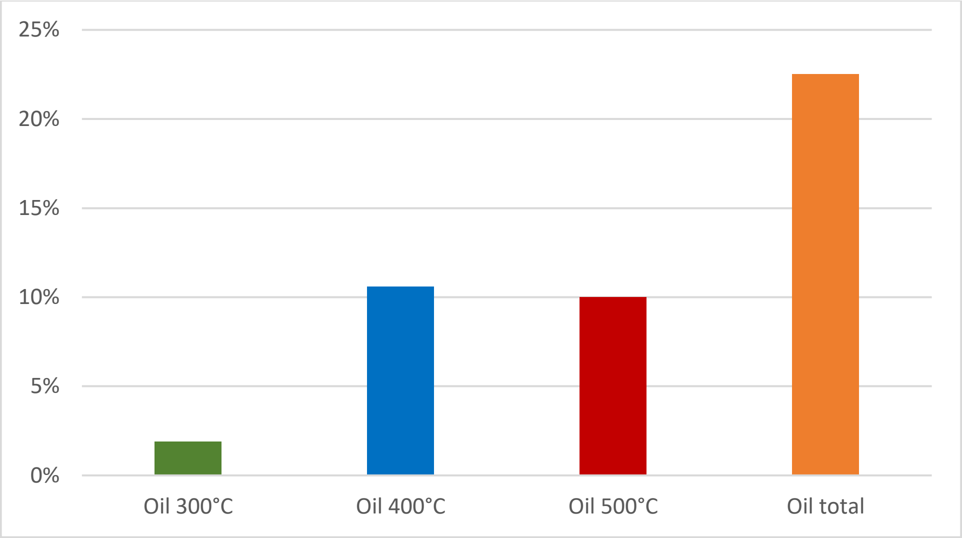


*Figure 20 - Third run oil yields at different temperatures*

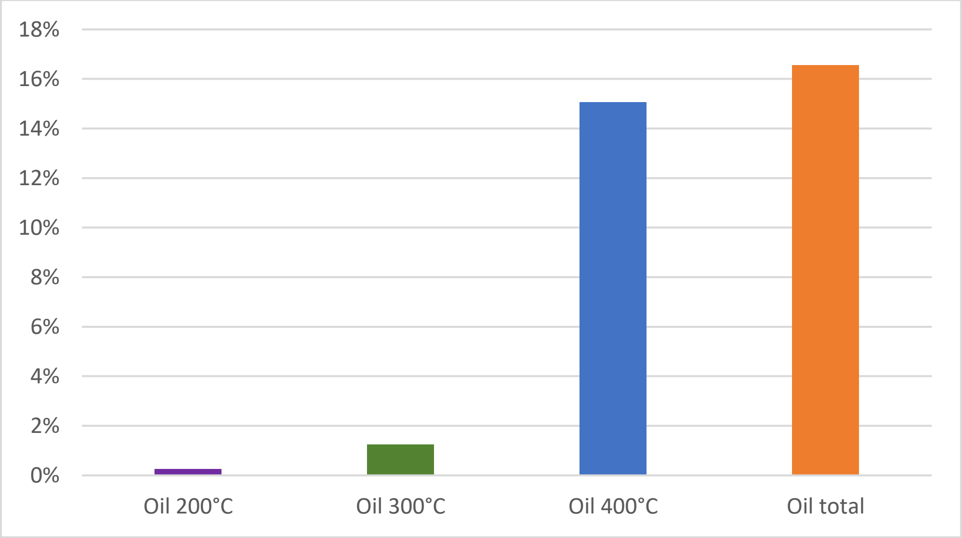


*Figure 21 - Fourth run oil yields at different temperatures*

#### *4.2.3.2 Solid analysis*

To assess the char characteristics, ultimate, proximate and bomb calorimetry were performed. *Table 22* reports the values obtained. Rubber char higher heating value is 30.829 MJ/kg, it also presents a carbon content of 84.42% which makes it interesting for carbon black production. The HHV of the char makes it promising for the fuel market since it is comparable with bituminous coke (30.2 MJ/kg).

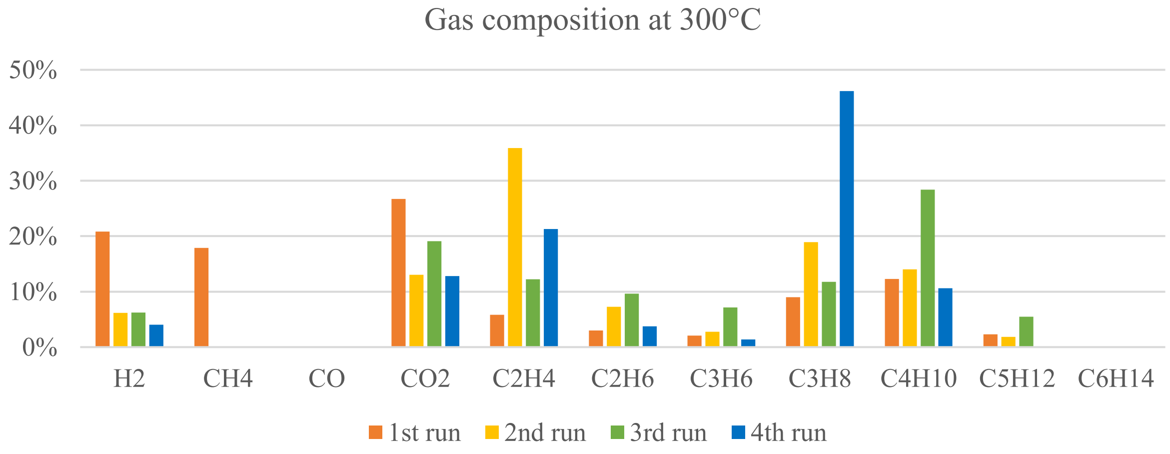
*Table 22 - Runner char ultimate and proximate analysis*

| **Ultimate analysis (wt.% on dry basis)** | | | | | |
|---|---|---|---|---|---|
| **N** | **C** | **H** | **S** | **O** | **Ash** |
| 0.54 ± 0.01 | 69.87 ± 0.82 | 0.72 ± 0.01 | 2.03 ± 0.03 | 15.95 ± 0.99 | 10.90 ± 0.23 |

| Proximate analysis (wt.% on dry basis) | | | |
|---|---|---|---|
| **Moisture** | **Volatile matter** | **Ash** | **Fixed carbon** |
| 1.32 ± 0.02 | 3.37 ± 0.33 | 10.90 ± 0.23 | 84.42 |

#### *4.2.3.3 Gas analysis*

To analyze the non-condensable fraction produced by the pyrolysis of rubber, sample of the gasses where collected. The collection is carried out at the desired temperature by connecting a sample bag to the exhaust gas line. A cotton filter is inserted into the line to avoid contamination of the sample by condensable compounds that can still be present. These sample were then analyzed by micro gas chromatographer (Varina mobile CP-4900). This unit is equipped with a column module containing a molecular sieve and a polar plot unit to identify $H_2$, $CH_4$, CO, $CO_2$, $C_2H_4$, $C_2H_6$, $H_2S$, $SO_2$, $C_3H_6$, $C_3H_8$, $C_4H_{10}$, $C_5H_{12}$, and $C_6H_{14}$. The thermal conductivity detector (TCD) uses helium and argon as carrier gasses at a pressure of 80 psi. each sample is analyzed three times and the average is calculated to estimate the concentration. *Figure 22* shows the gas composition for the different experiments at the different temperatures. It is possible to notice how the increasing temperature shifts the gas composition towards more stable compounds ($H_2$ & $CH_4$), which are the main compounds found at 500°C. There are some differences between the experiments results, but it is possible to identify the cracking evolution of the higher molecular weight compounds. To reinforce this thesis, at 300°C the main components are $C_2H_4$, $C_3H_8$, and $C_4H_{10}$. While at 400°C hydrogen and methane present concentration higher than 20% and at 500°C H2 ranges between 46 and 69% and methane is around 21-36%.



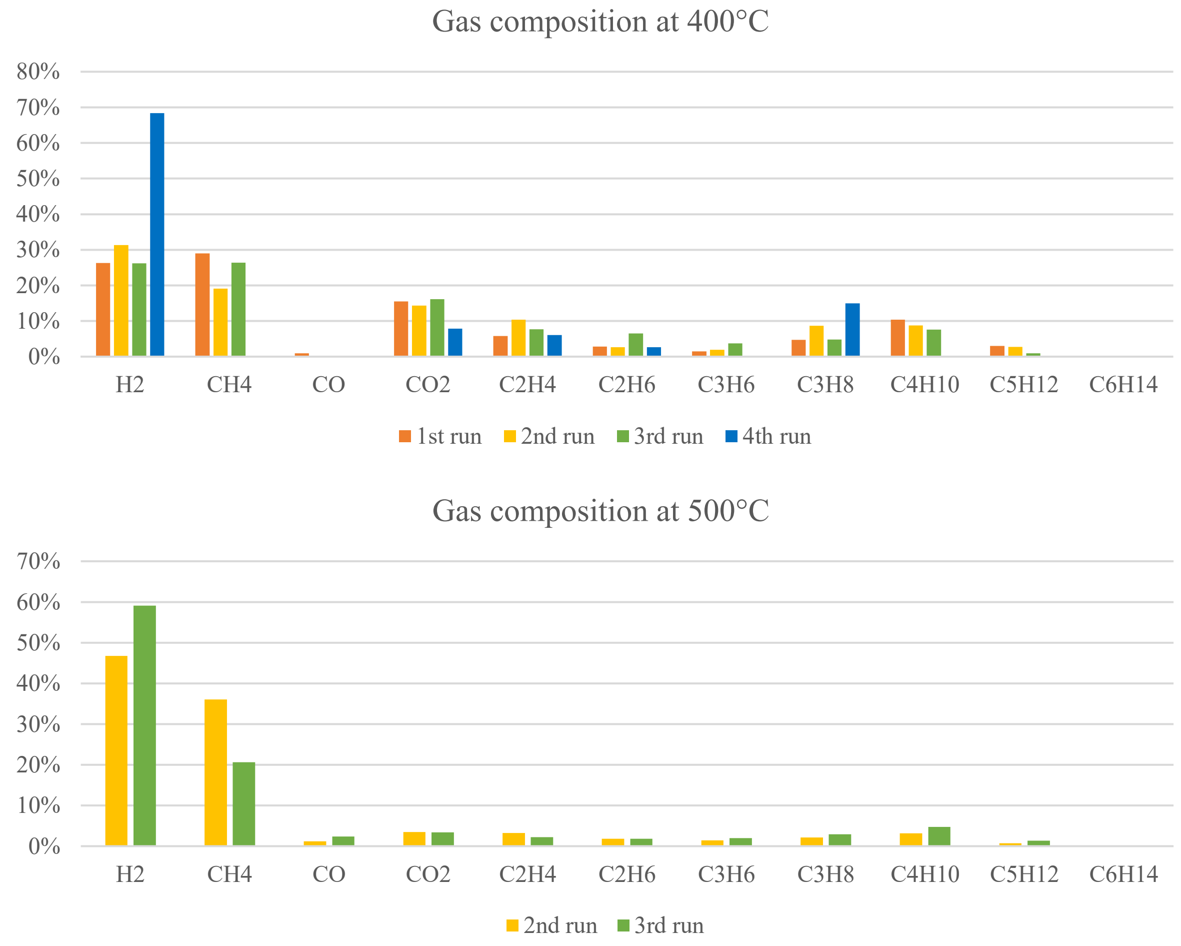


*Figure 23 - Rubber pyrolysis gas composition at different temperatures on a nitrogen and oxygen free basis*

### *4.2.3.4 Oil analysis*

The rubber oil was analyzed with gas chromatography mass spectrometry (GC-MS). To perform this analysis 1 ml of 2-propanol is added to 9 ml of oil, the 2-propanol is used to extract the chemical compounds from the sample. To achieve maximum contact between chemical the sample is shaken for 30 minutes. To avoid particulate contamination of the sample this must be filtered two time with 0.22 micrometers filters. The GC-MS system consists of a gas chromatograph coupled with a quadruple mass spectrometer and allows for the detection of chemical species composing the oil sample.

Rubber oil characterization returned more than 100 compounds, so to perform a comparison between the samples only compounds presenting a peak area higher than 1% are considered. Moreover, all the compounds highlighted by the GC-MS are aromatic compounds. Since most of the compounds present a carbon number lower than is possible to affirm that rubber oil is comparable to unrefined gasoline. As for the gas composition a temperature increase leads to lighter compounds meaning that cracking reaction are enhanced with higher temperatures. At 300°c the oil is mainly composed of $C_{10}$ compound like benzene, D-limonene, cyclo-hexadiene and cyclo-heptane. The composition at 400°C is a mix of $C_7$ to $C_{10}$ hydrocarbons and benzene compounds present the highest concentration. The oil components at 500°C are like the ones present at 400°C, what can be noticed is the concentration decrease of $C_{10}$ compounds and mutual increase of $C_7$. *Figure 24* shows the oil composition (%) at different temperatures.

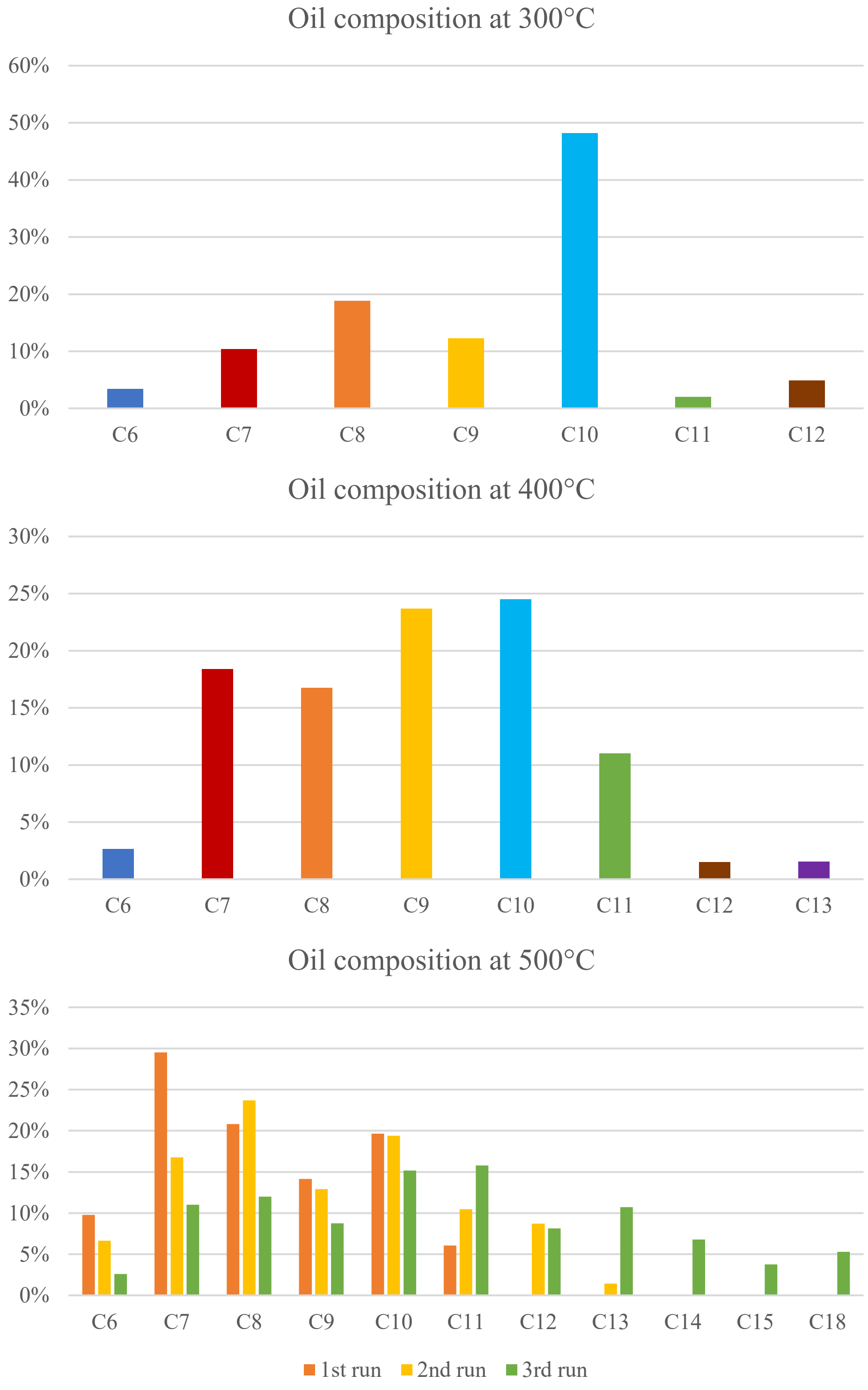


*Figure 24 - Rubber oil composition at different temperatures*

Bomb calorimetry to assess pyrolysis rubber oil higher heating value has been performed and it resulted in 40.933 MJ/kg. This is a good result because it is close to gasoline HHV (46.5 MJ/kg), diesel (43.15 MJ/kg) and heavy fuel oil (43.00 MJ/kg) *(Campuzano, 2021)*.

# 5. Techno-economic analysis

The economic assessment methodology applied in this thesis followed the outline reported in *Figure 25*.

*Figure 25 - Economic analysis methodology*

| | |
|---|---|
| Equipment cost | • For single stage pyrolysis: extrusion heater, pyrolizer, and condensers.<br>• For double stage pyrolysis: extrusion heater, pyrolizer, furnace, and condensers. |
| Total capital investment | • Direct costs, accounted as percentage of the equipment cost.<br>• Indirect costs, accounted as percentage of the equipment cost.<br>• Fixed capital is the sum of direct and indirect costs.<br>• Working capital, accounted as the 20% of the fixed capital |
| Annual income | • Annual gas production time its selling price. The selling price is calculated as the sum of hydrogen, methane and ethylene market price times their concentration.<br>• Annual oil production times its list price.<br>• Annual char production times its market value. |
| Total product cost | • Annual manufacturing cost: feedstock, utilities, labor, maintenance, etc.<br>• Annual general expenses: administrative, R&D, etc. |
| Operating income | • Difference between total product cost and annual income. |
| Depreciation | • Monetized using the straight method line with total equipment salvage value at the end of service life equal to 2000$ (single stage), 32000$ (double stage). |
| Income before tax | • Difference between the operating income and the depreciation. |
| Income after tax | • Difference between income before tax and taxes. |
| Annual net cash income | • Sum of income after tax and depreciation. |
| Annual present value | • Annual net cash income discounted at the reference year. Discount factor is 1% for the first year, and 5% for all the following. |
| Net present value | • Sum from the first to the last year of the annual present values minus the total capital investment. |

## 5.1 Polyethylene pyrolysis

The goal of the following chapter is to define the economic sustainability and profitability of a plastic pyrolysis plant. The analysis is based on results obtained by tests performed with virgin polyethylene using two different pyrolysis set ups. The first one is a single stage process performed at 550°C, the other one is a two stages process with rector at 550°C and secondary furnace at 800°C.

### 5.1.1 Mass and energy balance

The plant configuration analyzed are completely powered by electricity. The main reactor is heated by an induction system which consists of a coil wrapped around it. The furnace has a bult in induction system. The material loss is defined as the 2% and feeding rate is 0.72 kg/h. Low heating value on dry bases has been calculated with the following empirical formula:

$$HHV_{dry}\left(\frac{MJ}{kg}\right) = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0.015 \cdot N - 0.0211 \cdot A$$

$$LHV_{dry}\left(\frac{MJ}{kg}\right) = HHV_{dry} - 2.442 \cdot 8.936 \cdot \frac{H}{100}$$

Where C stands for carbon content, H is hydrogen content, S is sulfur content, O is oxygen, N is nitrogen content, and A is the ash content.

HDPE and LDPE low heating values are slightly different because their composition varies. The energy entering the system due to HDPE amounts to 8.45 kW and to 8.26 kW for LDPE.

A theoretical method has been used to analyze energy stream. From the first law of thermodynamics is known that:

$$E_{in} = E_{out} + E_{loss}$$

Where $E_{in}$ is the energy input, $E_{out}$ is the energy of the products and $E_{loss}$ is the energy lost in the process. Based on *Figure 12 and 13* is possible to rewrite the input and output energy as:

$$E_{in} = Q_{pw} + Q_s$$

$$E_{out} = Q_{gas} + Q_{liquid} + Q_{char}$$

Where $Q_{pw}$ is the energy content of the plastic, $Q_s$ is the energy required by the reactor to run at set conditions. The potentially recovered energy is the maximum energy recovred from the pyrolysis products. It is calculated as the sum of the energy content of each product fraction (gas, liquid, solid). Since in this work char production is negligible, the energy in the products can be written as:

$$E_{out} = Q_{gas} + Q_{liquid}$$

The energy content calculation is based on the higher heating values of the compounds *(López et al. 2011b, Mei et al. 2016)*:

$$Q_{pw} = HHV_{pw}$$

$$Q_i = X_i * HHV_i$$

Where $X_i$ is the mass yield of the products per kg of virgin plastic in input and $HHV_i$ is the corresponding heating value.

The total energy recovery ratio (ERR) is defined as:

$$ERR_{total}(\%) = \frac{Q_{recovery}}{Q_{pw}} \cdot 100$$

Where $Q_{pw}$ is the maximum energy potential of the plastic waste, and it is a measure of the available heat of combustion obtained by plastic combustion.

Finally, the theoretical energy efficiency of the pyrolysis process can be computed as follows:

$$\eta\ (\%) = \frac{Q_{recovery}}{Q_{pw} + Q_s} \cdot 100$$

### *5.1.1.1 Single stage*

*Figure 26* presents the mass and energy balances of the 0.72 kg $h^{-1}$ HDPE and LDPE plants. The HDPE plant produces 0.47 kg $h^{-1}$ of oil (6.04 $LHV_{dry}$) which corresponds to 65.7% mass yield. A similar oil amount is produced by the LDPE plant 0.469 kg $h^{-1}$ (5.96 $LHV_{dry}$), which corresponds to a mass yield of 65.1%. These values are consistent with the literature, as previously reported. Due to the endothermic nature of pyrolysis a continuous source of heating is required. The induction system used provides a power of 9 kW.

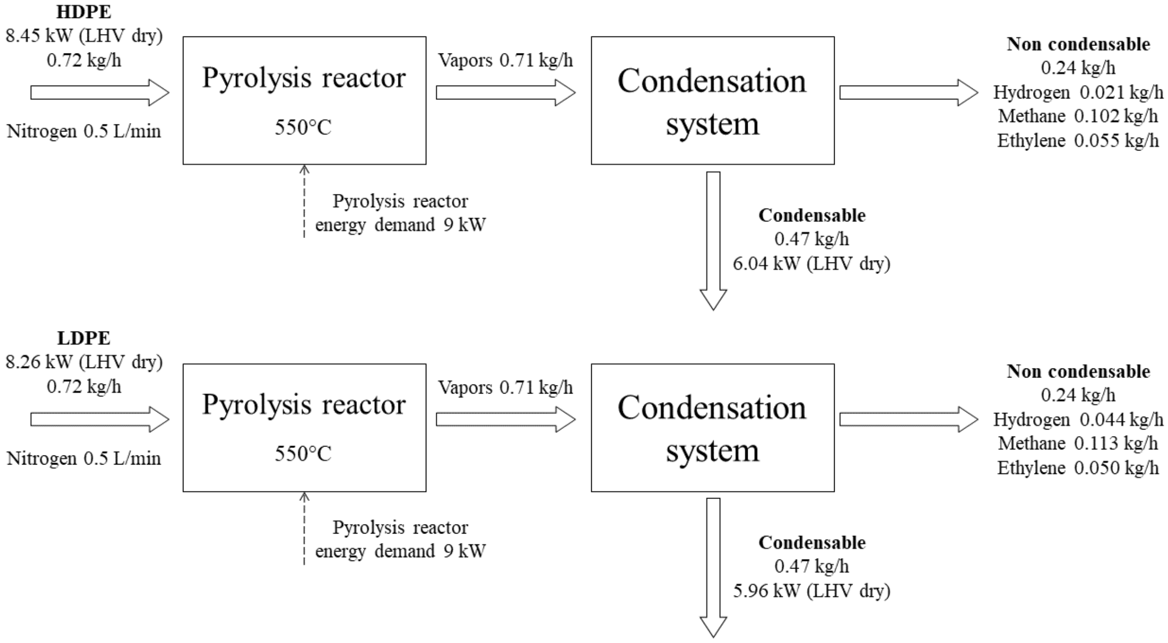


*Figure 26 - HDPE & LDPE single stage plant mass and energy balances*

*Table 22* reports the values of the energy analysis for the single stage process. As expected, the energy recovery ratio shows high values meaning that a valorization of the feedstock occurs. On the other hand, the total energy efficiency of the process is low. This could be due to not perfect isolation of the reactor which leads to high energy losses. In the future works an evaluation of the influence of the isolation set up on the overall energy balance should be performed.

*Table 22 - Single stage plant energy analysis*

| Plastic type | $Q_{pw}$ (MJ/kg) | $Q_{s}$ (MJ/kg) | $E_{in}$ (kW) | $Q_{liquid}$ (MJ/kg) | $Q_{gas}$ (MJ/kg) | $Q_{recovery}$ (MJ/kg) | $E_{out}$ (kW) | $E_{loss}$ (kW) | ERR (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| HDPE | 45.20 | 50.90 | 19.2 | 30.2 | 20.7 | 50.8 | 10.17 | 9.1 | 112.5 | 54.6 |
| LDPE | 44.15 | 50.90 | 19.0 | 29.8 | 23.9 | 53.7 | 10.74 | 8.3 | 121.6 | 58.2 |

### 5.1.1.2 Double stage

*Figure 27* reports mass and energy balances for HDPE and LDPE double stage plant set up. The feeding rate is 0.72 kg $h^{-1}$ and oil fraction produced is 0.15 kg $h^{-1}$ (1.92 kW $LHV_{dry}$) for HDPE and 0.05 kg $h^{-1}$ (0.59 kW $LHV_{dry}$) for LDPE. These account for 21.8% and 7.0% of mass yield, respectively. The furnace provides 5.4 kW power and enhances non condensable yields of 43.7% and 58.1% for both HDPE and LDPE.

*Table 23* reports the values of the energy analysis for the double stage process. As expected, the energy recovery ratio shows high values meaning that a valorization of the feedstock occurs. The double stage process shows energy efficiency values even lower than the single stage. This is due to the addiction of the furnace which increases the overall energy demand.

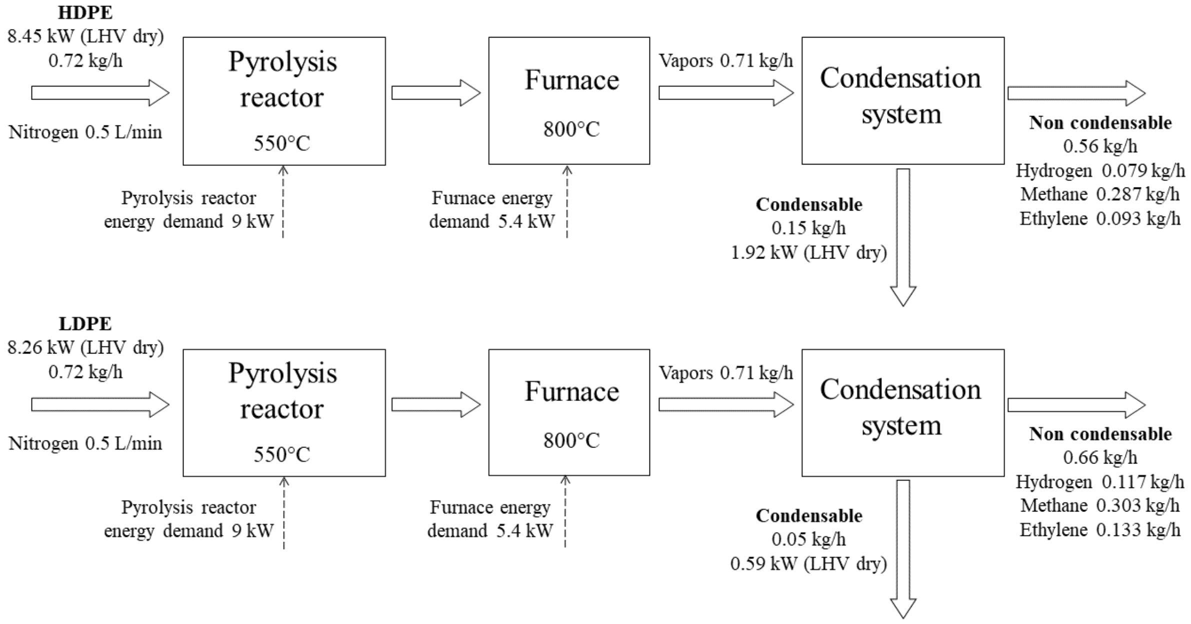


*Figure 27 - HDPE & LDPE double stage plant mass and energy balances*

*Table 23 - Double stage plant energy analysis*

| Plastic type | $Q_{pw}$ (MJ/kg) | $Q_s$ (MJ/kg) | $E_{in}$ (kW) | $Q_{liquid}$ (MJ/kg) | $Q_{gas}$ (MJ/kg) | $Q_{recovery}$ (MJ/kg) | $E_{out}$ (kW) | $E_{loss}$ (kW) | ERR (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| HDPE | 45.20 | 79.00 | 24.5 | 9.7 | 50.6 | 60.3 | 11.89 | 12.6 | 133.4 | 49.7 |
| LDPE | 44.15 | 79.00 | 24.3 | 3.0 | 63.7 | 66.7 | 13.15 | 11.1 | 151.0 | 55.4 |

### 5.1.2 Base scenario

The base scenario is the 0.72 kg $h^{-1}$ plant. *Table 24* reports all the costs considered in the analysis. The equipment cost was defines based on the experience and knowledge of its cost. The main difference between single and double stage process is the presence of the furnace, this additional equipment increases equipment costs and consequently the total capital investment. The total capital investment is composed by fixed and working capital. Fixed capital includes direct costs (installation, piping, buildings, instrumentation, control, etc) and indirect costs (engineering, construction, legal fees, etc). All these costs have been estimated following an order of magnitude approach based on percentages of equipment cost, as reported in *Peters et al, 1991*. The working capital is estimated as a percentage (20%) of the fixed costs.

Plastic pyrolysis oil price is defined based on crude oil price, 0.377 $/kg (60 $/barrel). On the other hand, the gas price is calculated based on the three most abundant compounds, hydrogen, methane, and ethylene. The gas price is then obtained as the product between the relative amount of each compound and their selling price. The list price of these products is 2 $/kg for hydrogen *(Hydrogen strategy for Canada, 2020) (Hydrogen Council, 2020)*, 1.01 $/kg for ethylene *(Statista, 2021)*, and 0.077 $/kg for methane *(EIA, 2021)*.

To evaluate production expenses annual manufacturing costs and general expenses are considered. More in detail, manufacturing costs consist of direct production costs (raw material, labor, maintenance, utilities), fixed charges (taxes, depreciation), plant overhead costs (hospital and medical services, safety services, payroll overhead, etc). General expenses include administrative costs (engineering and legal expenses, wages), distribution and marketing expenses (R&D, selling, etc). Raw material cost is assumed to be 0$ since wastes are considered. To assess labor costs the following assumptions where made:

- 8 hours shifts.
- 3 shifts a day.
- Average Canadian salary 44018 USD/year.

The total amount of 4.5 workers daily was set assuming that a small plant needs one person per shift to operate in normal conditions. The excess of 1.5 workers is considered to cover vacation, sick days and overlapping. The only utility considered in this work is electricity since all the equipment is powered by it. The electricity cost consider is of 0.093 $/kWh *(Statista, 2021b)*. The power consumption has been estimated by the energy balance of the plant. As reported by

*Peters et al. (1991)*, other voices accounted in the manufacturing cost have been computed as follows:

- Maintenance and repair: 7% of equipment cost.
- Operating supplies: 15% of maintenance and repair.
- Laboratory charges: 15% of operating labor.
- Taxes: 13% for Canadian standards.
- Plant overhead: 50% of total operating labor and maintenance.

As for general expenses:

- Administrative: 20% of operating labor.
- Distribution and selling: 5% of total product costs.
- Research and development: 3% of sales.

The operating income is then obtained as the difference between sales income and total annual operating costs.

The economic evaluation of the four cases assessed present its only difference in the annual income since the composition of the products and their yields where different as reported in the experimental activities chapter. Gas and oil annual production and relative percentages of hydrogen, methane and ethylene are also displayed in the table below. In terms of sales the LDPE double stage plant is the most convenient, highest income, because it presents the highest production of methane which has the best list price in today's market.

Depreciation has been evaluated based on a period equal the total life of the plant (20 years), assuming that the equipment is not going to be replaced during this time. Moreover, the final value of the equipment has be presumed to be 2000 $ for all cases.

At this point the annual net cash income can be calculated. It is the sum of the annual operating income after tax plus the depreciation. In all cases the net cash income resulted negative meaning that the scale of the plant is not sufficient to generate earnings at any time in the supposed operating time.

*Table 24 – 1 stage and double stage base scenario economic analysis for HDPE and LDPE*

| **Voice** | **Unit** | **HDPE 1 stage** | **HDPE 2 stages** | **LDPE 1 stage** | **LDPE 2 stages** | **HDPE 2 stages 480 - 850** |
|---|---|---|---|---|---|---|
| Extrusion heater | USD | 2300 | 2300 | 2300 | 2300 | 2300 |
| Pyrolizer | USD | 20700 | 20700 | 20700 | 20700 | 20700 |
| Furnace | USD | - | 9700 | - | 9700 | 9700 |
| Condenser 1 | USD | 4600 | 4600 | 4600 | 4600 | 4600 |
| Condenser 2 | USD | 4600 | 4600 | 4600 | 4600 | 4600 |
| **Total Equipment Cost** | USD | **32200** | **41900** | **32200** | **41900** | **41900** |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| Installation costs | USD | 9660 | 12570 | 9660 | 12570 | 12570 |
| Instrumentation and control | USD | 8050 | 10475 | 8050 | 10475 | 10475 |
| Piping | USD | 25760 | 33520 | 25760 | 33520 | 33520 |
| Power system | USD | 32200 | 41900 | 32200 | 41900 | 41900 |
| Buildings | USD | 12880 | 16760 | 12880 | 16760 | 16760 |
| Service equipment | USD | 3864 | 5028 | 3864 | 5028 | 5028 |
| **Total Direct Costs** | USD | **124614** | **162153** | **124614** | **162153** | **162153** |
| Engineering and supervision | USD | 9660 | 12570 | 9660 | 12570 | 12570 |
| Legal Fees | USD | 1246 | 1622 | 1246 | 1622 | 1622 |
| Construction and erection | USD | 9969 | 12972 | 9969 | 12972 | 12972 |
| Contingencies | USD | 9969 | 12972 | 9969 | 12972 | 12972 |
| **Total Indirect Costs** | USD | **30844** | **40136** | **30844** | **40136** | **40136** |
| **Fixed Capital Costs** | USD | **155458** | **202289** | **155458** | **202289** | **202289** |
| **Working Capital** | USD | **31092** | **40458** | **31092** | **40458** | **40458** |
| **Total Capital Investment** | USD | **186550** | **242746** | **186550** | **242746** | **242746** |
| Gas production | kg/y | 1382 | 3226 | 1382 | 3802 | 3681 |
| Hydrogen | % | 12 | 17 | 5 | 21 | 28 |
| Hydrogen sale price | USD/kg | 2 | 2 | 2 | 2 | 2 |
| Methane | % | 57 | 63 | 54 | 55 | 3 |
| Methane sale price | USD/kg | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| Ethylene | % | 31 | 20 | 42 | 24 | 30 |
| Ethylene sale price | USD/kg | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Gas sale price | USD/kg | 0.588 | 0.594 | 0.557 | 0.710 | 0.865 |
| Oil production | kg/y | 2707 | 864.0 | 2707 | 288.0 | 409.0 |
| Oil sale price | USD/kg | 0.377 | 0.377 | 0.428 | 0.428 | 0.377 |
| **Annual Income (sales)** | **USD/y** | **1834** | **2242** | **1929** | **2821** | **3339** |
| Raw material | USD/y | 0 | 0 | 0 | 0 | 0 |
| Workers | day | 4.5 | 4.5 | 4.5 | 4.5 | 4.5 |
| Salary | USD/y | 44018 | 44018 | 44018 | 44018 | 44018 |
| Operating labor | USD/y | 198081 | 198081 | 198081 | 198081 | 198081 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Utilities | USD/y | 49796 | 50021 | 49796 | 50021 | 50021 |
| Maintenance and repair | USD/y | 2254 | 2933 | 2254 | 2933 | 2933 |
| Operating supplies | USD/y | 338 | 440 | 338 | 440 | 440 |
| Laboratory charges | USD/y | 29712 | 29712 | 29712 | 29712 | 29712 |
| Taxes | USD/y | 238 | 292 | 251 | 367 | 434 |
| Plant overhead | USD/y | 100168 | 100507 | 100168 | 100507 | 100507 |
| **Annual Manufacturing Cost** | USD/y | **424610** | **426008** | **424622** | **426083** | **426151** |
| Administrative | USD/y | 39616 | 39616 | 39616 | 39616 | 39616 |
| Distribution and selling | USD/y | 2548 | 2556 | 2548 | 2556 | 2557 |
| Research and development | USD/y | 55 | 67 | 58 | 85 | 100 |
| **Annual General Expenses** | USD/y | **42219** | **42240** | **42222** | **42257** | **42273** |
| **Total Annual Product Cost** | USD/y | **466829** | **468248** | **466844** | **468341** | **468424** |
| **Annual Operating Income** | USD/y | **-464995** | **-466005** | **-464915** | **-465520** | **-465085** |
| Annual depreciation | USD/y | 1510 | 1995 | 1510 | 1995 | 1995 |
| Income before tax | USD/y | -466505 | -468000 | -466425 | -467515 | -467080 |
| Income after tax | USD/y | -466743 | -468292 | -466675 | -467882 | -467514 |
| **Annual Net Cash Income** | USD/y | **-465233** | **-466297** | **-465165** | **-465887** | **-465519** |

To assess the economic profitability of the plant the Net Present Value (NPV) and Payback time have been calculated. A discount factor of the future cash flow of 5% has been used to calculate the annual present value, as follows:

$$A_{PV} = \frac{A_{CF}}{(1+d)^n}$$

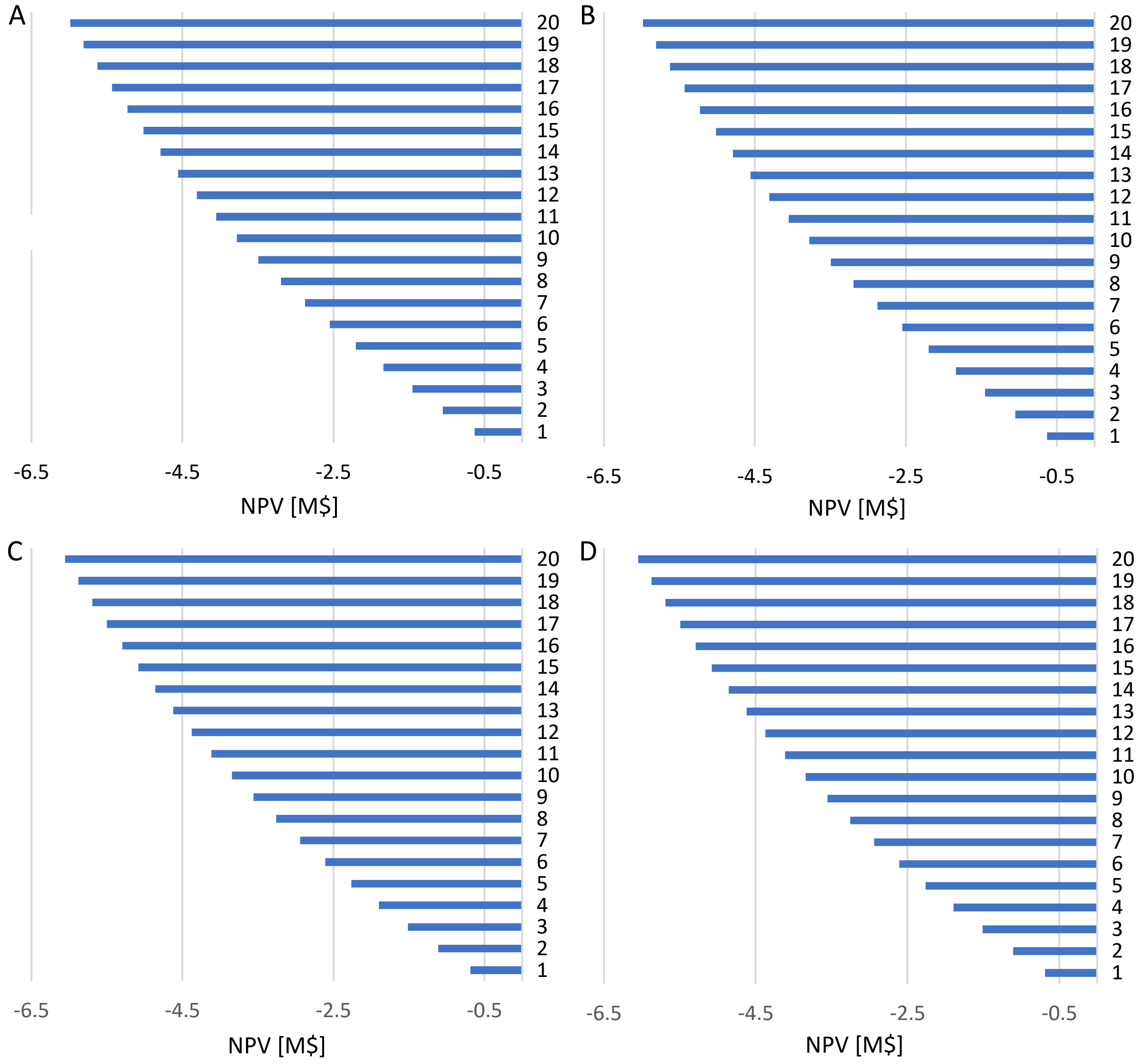
Where $A_{CF}$ is the annual cash flow, d is the discount factor, and n is the reference year of the considered cash flow.

Now, the net present value can be determined using the following equation:

$$NPV = \sum_{i=1}^{N} A_{PV} - C_{TC}$$

Where, $A_{PV}$ represent the annual present value (discounted cash flow), N is the plant lifetime (20 years), and $C_{TC}$ is the total capital investment.

*Figure 28* shows the NPV of HDPE and LDPE base case scenario single and double stage plants. For all the analyzed cases the net present value is negative all along the 20 years of plant operation. So, the plant size is not economically advantageous and does not generate revenues during its working time. All plants set up present a NPV at 20 years around negative (-) 6 million dollars. To better understand if a plant scale up would be remunerative and how some parameters affecting it, different scale up scenarios have been analyzed.



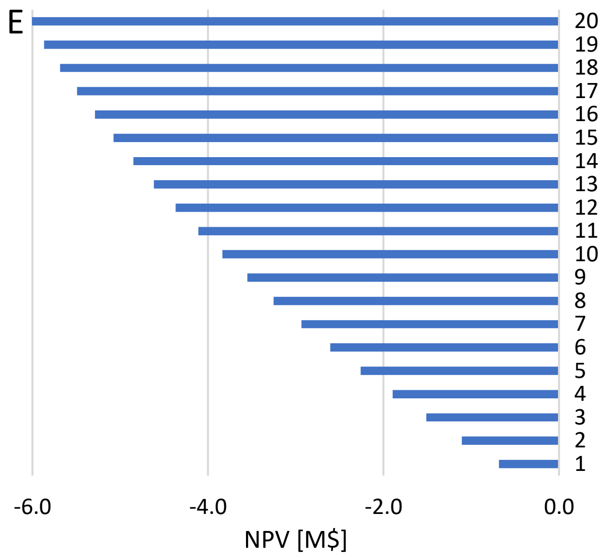


*Figure 28 - Base scenario NPV. A) HDPE 1 stage; B) LDPE 1 stage; C) HDPE 2 stages; D) LDPE 2 stages; E) HDPE 2 stages 480-850 °C 10 LPM*

### 5.1.3 Plant scale-up

The plant is scaled up to be able to treat the annual amount of plastic produced in the city of London, Ontario (Canada). Plastic waste production is about 15000 tons per year, which means an hourly treatment of 2.5 tons of material for a plant working 24 hours a day, 7 days of the week, and 240 days a year.

The scale up of the equipment cost has been done following the 0.6 power law (*Peters et al, 1991)*, which state as follows:

$$Cost_{equipment,b} = Cost_{equipment,a} \cdot \left(\frac{S_b}{S_a}\right)^{0.6}$$

Where, $\mathrm{Cost}_{\mathrm{equipment,a}}$ is equal to the cost of each apparatus in the base scenario plant, S stands for potential and in this case is equal to the capacity of the equipment. If followed by the letter 'a' then it refers to the base scenario plant (0.72 kg/h), the letter 'b' relates to the scale up process. The power factor of 0.6 has been found the most common for chemical processes scale up. Moreover, this estimation method is not rigorous, but it helps us to understand the order of magnitude of the costs. The results obtained are reported in *Table 24*.

The total capital investment has been calculated following the same procedure explained in the previous chapter. Furthermore, the total annual income has been computed based on the percentages of hydrogen, methane, and ethylene in the non-condensable product multiplied by their market price, plus the oil production times its list value. Gas and oil production for these set ups have been calculated as a simple scale up of each components found the stream. As reported in *Table 25* the highest gas selling price is obtained in the HDPE double stage process at 480-850°C with a nitrogen flow of 10 $\mathrm{Lmin}^{-1}$, because it has the highest hydrogen production. This results in the highest annual income of all the processes considered. For the same reason, the single stage process treating LDPE produces the lowest annual income.

*Table 25 - 1 stage and double stages scale up plant equipment cost and total investment analysis*

| Voice | Unit | HDPE 1 stage | HDPE 2 stages | LDPE 1 stage | LDPE 2 stages | HDPE 2 stages 480 - 850 |
|---|---|---|---|---|---|---|
| Extrusion heater | USD | 306261 | 306261 | 306261 | 306261 | 306261 |
| Pyrolizer | USD | 2756353 | 2756353 | 2756353 | 2756353 | 2756353 |
| Furnace | USD | - | 1291624 | - | 1291624 | 1291624 |
| Condenser 1 | USD | 612523 | 612523 | 612523 | 612523 | 612523 |
| Condenser 2 | USD | 612523 | 612523 | 612523 | 612523 | 612523 |
| **Total Equipment Cost** | M$ | **4.3** | **5.6** | **4.3** | **5.6** | **5.6** |
| Installation costs | USD | 1286298 | 1673785 | 1286298 | 1673785 | 1673785 |
| Instrumentation and control | USD | 1071915 | 1394821 | 1071915 | 1394821 | 1394821 |
| Piping | USD | 3430128 | 4463428 | 3430128 | 4463428 | 4463428 |
| Power system | USD | 1286298 | 1673785 | 1286298 | 1673785 | 1673785 |
| Buildings | USD | 1715064 | 2231714 | 1715064 | 2231714 | 2231714 |
| Service equipment | USD | 514519 | 669514 | 514519 | 669514 | 669514 |
| **Total Direct Costs** | M$ | **13.6** | **17.7** | **13.6** | **17.7** | **17.7** |
| Engineering and supervision | USD | 1286298 | 1673785 | 1286298 | 1673785 | 1673785 |
| Legal Fees | USD | 171506 | 223171 | 171506 | 223171 | 223171 |
| Construction and erection | USD | 1286298 | 1673785 | 1286298 | 1673785 | 1673785 |
| Contingencies | USD | 1286298 | 1673785 | 1286298 | 1673785 | 1673785 |
| **Total Indirect Costs** | M$ | **4.03** | **5.24** | **4.03** | **5.24** | **5.24** |
| **Fixed Capital Costs** | M$ | **17.62** | **22.93** | **17.62** | **22.93** | **22.93** |
| **Working Capital** | M$ | **3.52** | **4.59** | **3.52** | **4.59** | **4.59** |
| **Total Capital Investment** | M$ | **21.15** | **27.52** | **21.15** | **27.52** | **27.52** |
| Gas production | kg/y | 4999104 | 11213453 | 5016902 | 13400179 | 12960000 |
| Hydrogen | % | 12 | 17 | 5 | 21 | 28 |
| Hydrogen sale price | USD/kg | 2 | 2 | 2 | 2 | 2 |
| Methane | % | 57% | 63% | 54% | 55% | 3% |
| Methane sale price | USD/kg | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ethylene | % | 31% | 20% | 41% | 24% | 30% |
| Ethylene sale price | USD/kg | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Gas sale price | USD/kg | 0.59 | 0.59 | 0.56 | 0.70 | 0.87 |
| Oil production | kg/y | 9401069 | 3186720 | 9383328 | 999994 | 1440000 |
| Oil sale price | USD/kg | 0.377 | 0.377 | 0.377 | 0.377 | 0.377 |
| **Annual Income (sales)** | M$/y | **6.53** | **7.82** | **6.33** | **9.82** | **11.76** |

Five scenarios have been evaluated. The sensitivity analysis characterizing each scenario concerns the total annual operating cost; it has been investigated how changes in energy supply cost and type affect the economic feasibility of the plant. *Table 26* is a summary of the analyzed scenarios.

*Table 26 - Scheme of the different scenarios analyzed in the economic assessment*

| | | |
|---|---|---|
| | Plastic pyrolysis base scenario | |
| | 0.72 kg $h^{-1}$ | |
| | Plastic pyrolysis scale up scenarios | |
| Scenario 1 | 2500 kg $h^{-1}$ | All the economic parameters are the same in the base scenario |
| Scenario 2 | | Assessment of electrical energy influence. Energy cost is changed to Québec market price: 0.043 $/kWh |
| Scenario 3 | | Assessment of energy source influence. From electrical energy to natural gas as heat source. Utility costs are based on natural gas consumption and cost. |
| Scenario 4 | | Assessment of methane recycling into the system. $CH_4$ is the heat source, utility costs are based on its consumption and price. |
| Scenario 5 | | Theoretical assessment of gas composition influence.<br>Case 1: 80% hydrogen and 20% methane.<br>Case 2: 20% methane and 80% ethylene |

### *5.1.3.1 Scenario 1*

Scenario 1 is the unaltered scale up of the base scenario, meaning that no manufacturing parameters have been changed. A higher number of workers is required to run the plant because of its size. The labor required is estimated to be around 9 workers a day, this value accounts for vacations, medical leave, and shift planning. The analysis highlights that all processes generate a positive annual net cash income, where the double stage configuration treating HDPE (480-850) has the highest profit. *Table 27* reports all the parameters considered in the economic analysis.

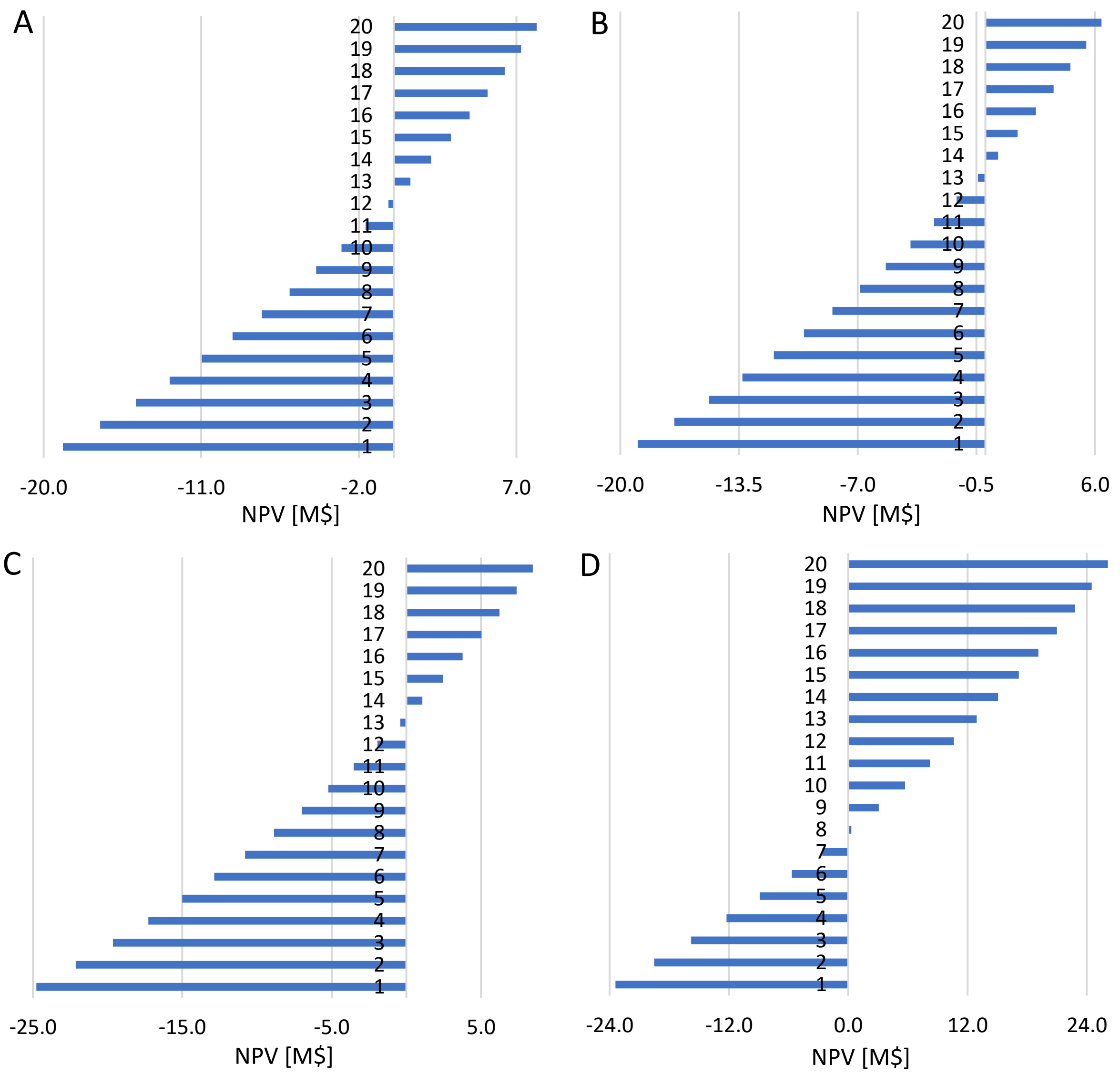
*Table 27 - 1 stage and double stage scenario 1 economic analysis for HDPE and LDPE*

| **Voice** | **Unit** | **HDPE 1 stage** | **HDPE 2 stages** | **LDPE 1 stage** | **LDPE 2 stages** | **HDPE 2 stages 480 - 850** |
|---|---|---|---|---|---|---|
| Raw material | USD/y | 0 | 0 | 0 | 0 | 0 |
| Workers | day | 9 | 9 | 9 | 9 | 9 |
| Salary | USD/y | 44018 | 44018 | 44018 | 44018 | 44018 |
| Operating labor | USD/y | 396162 | 396162 | 396162 | 396162 | 396162 |
| Utilities | USD/y | 993686 | 1224029 | 993686 | 1224029 | 1224029 |
| Maintenance and repair | USD/y | 300136 | 390550 | 300136 | 390550 | 390550 |
| Operating supplies | USD/y | 45020 | 58582 | 45020 | 58582 | 58582 |
| Laboratory charges | USD/y | 59424 | 59424 | 59424 | 59424 | 59424 |
| Taxes | USD/y | 848720 | 1016996 | 822290 | 1276701 | 1528449 |
| Plant overhead | USD/y | 348149 | 393356 | 348149 | 393356 | 393356 |
| **Annual Manufacturing Cost** | M$/y | **3.03** | **3.58** | **3.01** | **3.84** | **4.09** |
| Administrative | USD/y | 79232 | 79232 | 79232 | 79232 | 79232 |
| Distribution and selling | USD/y | 18212 | 21499 | 18053 | 23057 | 24567 |
| Research and development | USD/y | 195859 | 234691 | 189759 | 294623 | 352719 |
| **Annual General Expenses** | UDS/y | **293303** | **335423** | **287045** | **396913** | **456519** |
| **Total Annual Product Cost** | M$/y | **3.33** | **3.92** | **3.30** | **4.24** | **4.55** |
| **Annual Operating Income** | M$/y | **3.20** | **3.90** | **3.03** | **5.58** | **7.21** |
| Annual depreciation | USD/y | 198383 | 262964 | 198383 | 262964 | 262964 |
| Income before tax | USD/y | 3001606 | 3641536 | 2830984 | 5318066 | 6943235 |
| Income after tax | USD/y | 2152886 | 2624539 | 2008694 | 4041365 | 5414787 |
| **Annual Net Cash Income** | M$/y | **2.35** | **2.89** | **2.21** | **4.30** | **5.68** |

*Figure 29* reposts the net present values for all cases considered over the 20 years of operating time of the plant. It is possible to see how all cases at the end of their operating times have produced earning, but they reach the payback period at different times. The single stage

processes (A & B) present similar trends; the HDPE scale up reaches the break-even point between the twelfth and thirteenth year, while the LDPE one in between thirteenth and fourteenth years. The double stage HDPE process (C) also reaches the payback time in between thirteen and fourteen years, it was expected to be lower but apparently the furnace addition does not improve the gas composition sufficiently for it to cover the increase in investment and operating costs. On the other hand, LDPE treated in two stages (D) shows an improvement: payback time lower than eight years. Case E (HDPE 2 stage 480-850) presents the best condition; break-even point is reached between 5 and 6 years of operating life and the final net profit is of 43.2 million dollars. This is due to the higher net cash flow linked to the greater hydrogen and ethylene production.

Cases A, B, C, and D show profitability during their lifetime, but the time they need to reach the brake even point is too long for them to be attractive on an industrial level. On the other hand, case E can be considered for further detailed analysis because it reaches economical sustainability in a short time.



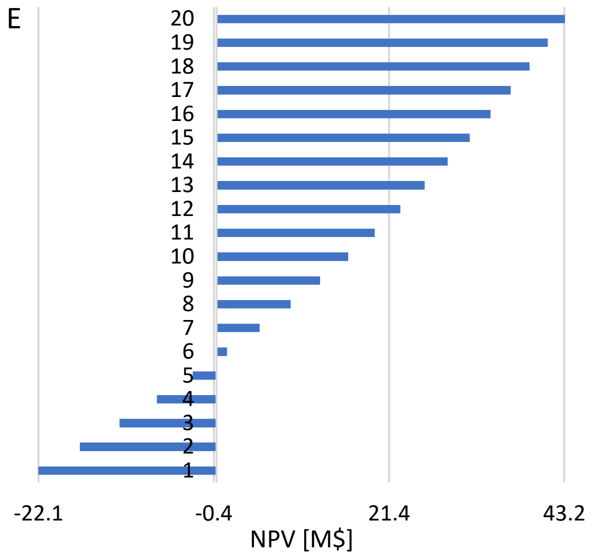


*Figure 29 – Scenario 1 NPV. A) HDPE 1 stage; B) LDPE 1 stage; C) HDPE 2 stages; D) LDPE 2 stages; E) HDPE 2 stages 480-850 °C 10 LPM*

#### *5.1.3.2 Scenario 2*

Scenario 2 has been developed thinking about installing the pyrolysis plant in another Canadian region. Since Québec has a lower electrical energy cost, due to plenty hydropower plants, this is the geographic area selected. Hence, the selection of Québec as site to develop the plastic waste pyrolysis plant allows to determine the influence of the energy demand and cost on the feasibility and profitability of the plant. *Statista (2021b)* reported an electrical energy price for Québec of 0.043 USD $kWh^{-1}$.

*Table 28* shows all the parameters considered in the economic assessment of the scale up plant. As expected, the net cash income resulting in all cases is higher than Scenario 1. This is highlighting how a small change in the energy cost can significantly affect the overall remuneration of the plant, especially if electrical energy is the main source of power as in this case.

*Table 28 - 1 stage and double stage scenario 2 economic analysis for HDPE and LDPE*

| Voice | Unit | HDPE 1 stage | HDPE 2 stages | LDPE 1 stage | LDPE 2 stages | HDPE 2 stages 480 - 850 |
|---|---|---|---|---|---|---|
| Raw material | USD/y | 0 | 0 | 0 | 0 | 0 |
| Workers | day | 9 | 9 | 9 | 9 | 9 |
| Salary | USD/y | 44018 | 44018 | 44018 | 44018 | 44018 |
| Operating labor | USD/y | 396162 | 396162 | 396162 | 396162 | 396162 |
| Utilities | USD/y | 459446 | 565949 | 459446 | 565949 | 565949 |
| Maintenance and repair | USD/y | 300136 | 390550 | 300136 | 390550 | 390550 |
| Operating supplies | USD/y | 45020 | 58582 | 45020 | 58582 | 58582 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Laboratory charges | USD/y | 59424 | 59424 | 59424 | 59424 | 59424 |
| Taxes | USD/y | 848720 | 1016996 | 822290 | 1276701 | 1528449 |
| Plant overhead | USD/y | 348149 | 393356 | 348149 | 393356 | 393356 |
| **Annual Manufacturing Cost** | M$/y | **2.50** | **2.92** | **2.47** | **3.18** | **3.44** |
| Administrative | USD/y | 79232 | 79232 | 79232 | 79232 | 79232 |
| Distribution and selling | USD/y | 15007 | 17550 | 14848 | 19109 | 20619 |
| Research and development | USD/y | 195859 | 234691 | 189759 | 294623 | 352719 |
| **Annual General Expenses** | UDS/y | **290097** | **331474** | **283840** | **392964** | **452570** |
| **Total Annual Product Cost** | M$/y | **2.79** | **3.26** | **2.76** | **3.58** | **3.89** |
| **Annual Operating Income** | M$/y | **3.74** | **4.57** | **3.57** | **6.24** | **7.87** |
| Annual depreciation | USD/y | 198383 | 262964 | 198383 | 262964 | 262964 |
| Income before tax | USD/y | 3539052 | 4303564 | 3368429 | 5980094 | 7605264 |
| Income after tax | USD/y | 2690331 | 3286568 | 2546139 | 4703394 | 6076815 |
| **Annual Net Cash Income** | M$/y | **2.89** | **3.55** | **2.74** | **4.97** | **6.34** |

Comparing the net prevent values and payback periods of scenario 2 *(Figure30)* with scenario 1 it is possible to notice how a small variation in the energy price can influence the overall economic feasibility of the plant. In all cases the payback period decreases and therefore the net profit at the end of the plant life increases. As before, from an economical point of view the best configurations are for LDPE the double stage process reaching the BEP between six and seven years of operating life, for HDPE is the double stage process with the reactor operating at 480°C and the furnace at 850°C. This last configuration (Case E) reports a payback period of five years.

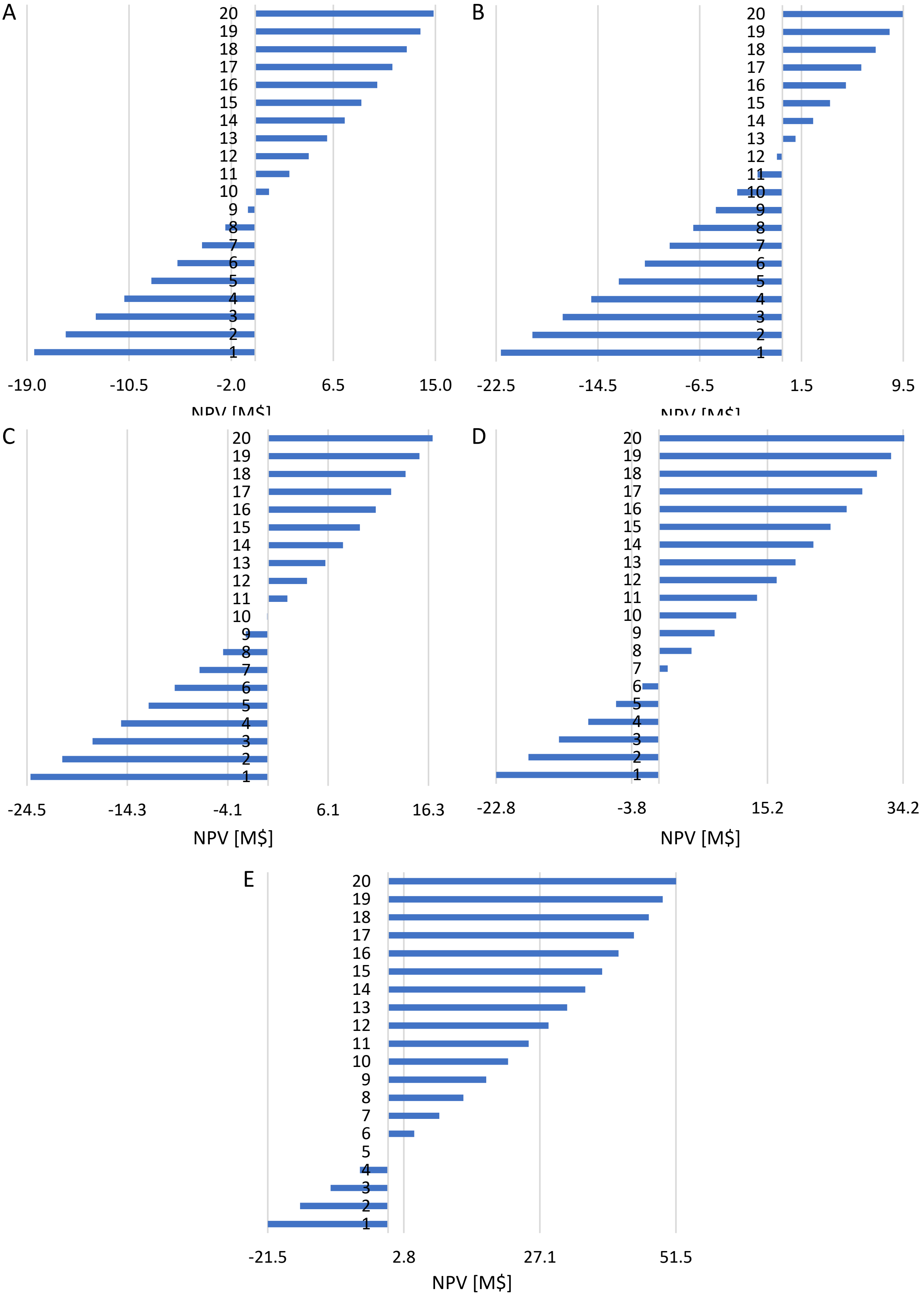


*Figure 30 - Scenario 2 NPV. A) HDPE 1 stage; B) LDPE 1 stage; C) HDPE 2 stages; D) LDPE 2 stages; E) HDPE 2 stages 480-850 °C 10 LPM*

#### *5.1.3.3 Scenario 3*

Scenario 3 aims to evaluate the influence of the heating utility on the overall process. The economic analysis for this case has been performed using natural gas as heating source instead of electrical power.

*Table 29* reposts the electrical energy demand to perform pyrolysis and its conversion in metric million British thermal unit for both single and double stage set ups. Moreover, the natural gas price in Canada is around 2.91 USD MMBtu$^{-1}$.

*Table 29 - Natural gas consumption and total utility cost for single and double stage processes*

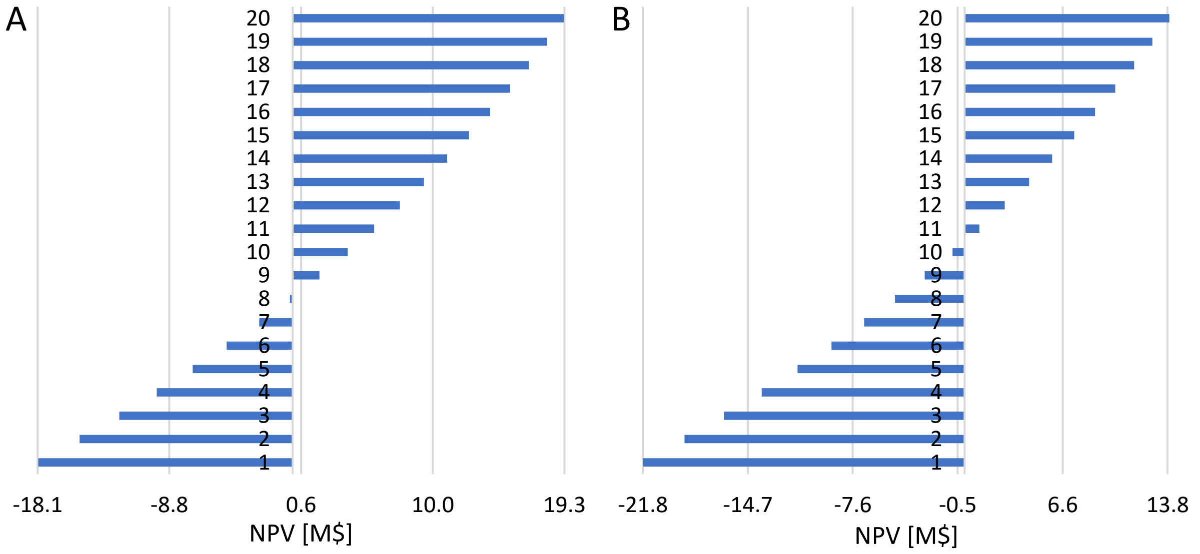
| | | **Single stage** | **Double stage** |
|---|---|---|---|
| Total plant consumption | kWh | 1855 | 2285 |
| | MMBtu/h | 6.32 | 7.79 |
| | MMBtu/y | 36430 | 44874 |
| Natural gas price | USD/MMBtu | 2.91 | 2.91 |
| Utility cost | USD/y | 106011 | 130585 |

Using the value obtained in the previous table as utility parameter for the estimation of the annual manufacturing cost a significant increase in the total annual net cash income can be observed if compared to the scenario 1: all plants show a gain of around 1 million dollars when natural gas is used as heat source *(Table 30)*.

*Table 30 - 1 stage and double stage scenario 3 economic analysis for HDPE and LDPE*

| **Voice** | **Unit** | **HDPE 1 stage** | **HDPE 2 stages** | **LDPE 1 stage** | **LDPE 2 stages** | **HDPE 2 stages 480 - 850** |
|---|---|---|---|---|---|---|
| Raw material | USD/y | 0 | 0 | 0 | 0 | 0 |
| Workers | day | 9 | 9 | 9 | 9 | 9 |
| Salary | USD/y | 44018 | 44018 | 44018 | 44018 | 44018 |
| Operating labor | USD/y | 396162 | 396162 | 396162 | 396162 | 396162 |
| Utilities | USD/y | 106011 | 130585 | 106011 | 130585 | 130585 |
| Maintenance and repair | USD/y | 300136 | 390550 | 300136 | 390550 | 390550 |
| Operating supplies | USD/y | 45020 | 58582 | 45020 | 58582 | 58582 |
| Laboratory charges | USD/y | 59424 | 59424 | 59424 | 59424 | 59424 |
| Taxes | USD/y | 848720 | 1016996 | 822290 | 1276701 | 1528449 |
| Plant overhead | USD/y | 348149 | 393356 | 348149 | 393356 | 393356 |
| **Annual Manufacturing Cost** | M$/y | **2.15** | **2.49** | **2.12** | **2.75** | **3.00** |

| | | | | | | |
|---|---|---|---|---|---|---|
| Administrative | USD/y | 79232 | 79232 | 79232 | 79232 | 79232 |
| Distribution and selling | USD/y | 12886 | 14938 | 12727 | 16496 | 18007 |
| Research and development | USD/y | 195859 | 234691 | 189759 | 294623 | 352719 |
| **Annual General Expenses** | UDS/y | **287977** | **328862** | **281719** | **390352** | **449958** |
| **Total Annual Product Cost** | M$/y | **2.44** | **2.82** | **2.40** | **3.14** | **3.45** |
| **Annual Operating Income** | M$/y | **4.09** | **5.00** | **3.92** | **6.68** | **8.31** |
| Annual depreciation | USD/y | 198383 | 262964 | 198383 | 262964 | 262964 |
| Income before tax | USD/y | 3894608 | 4741540 | 3723985 | 6418071 | 8043240 |
| Income after tax | USD/y | 3045888 | 3724544 | 2901695 | 5141370 | 6514791 |
| **Annual Net Cash Income** | M$/y | **3.24** | **3.99** | **3.10** | **5.40** | **6.78** |



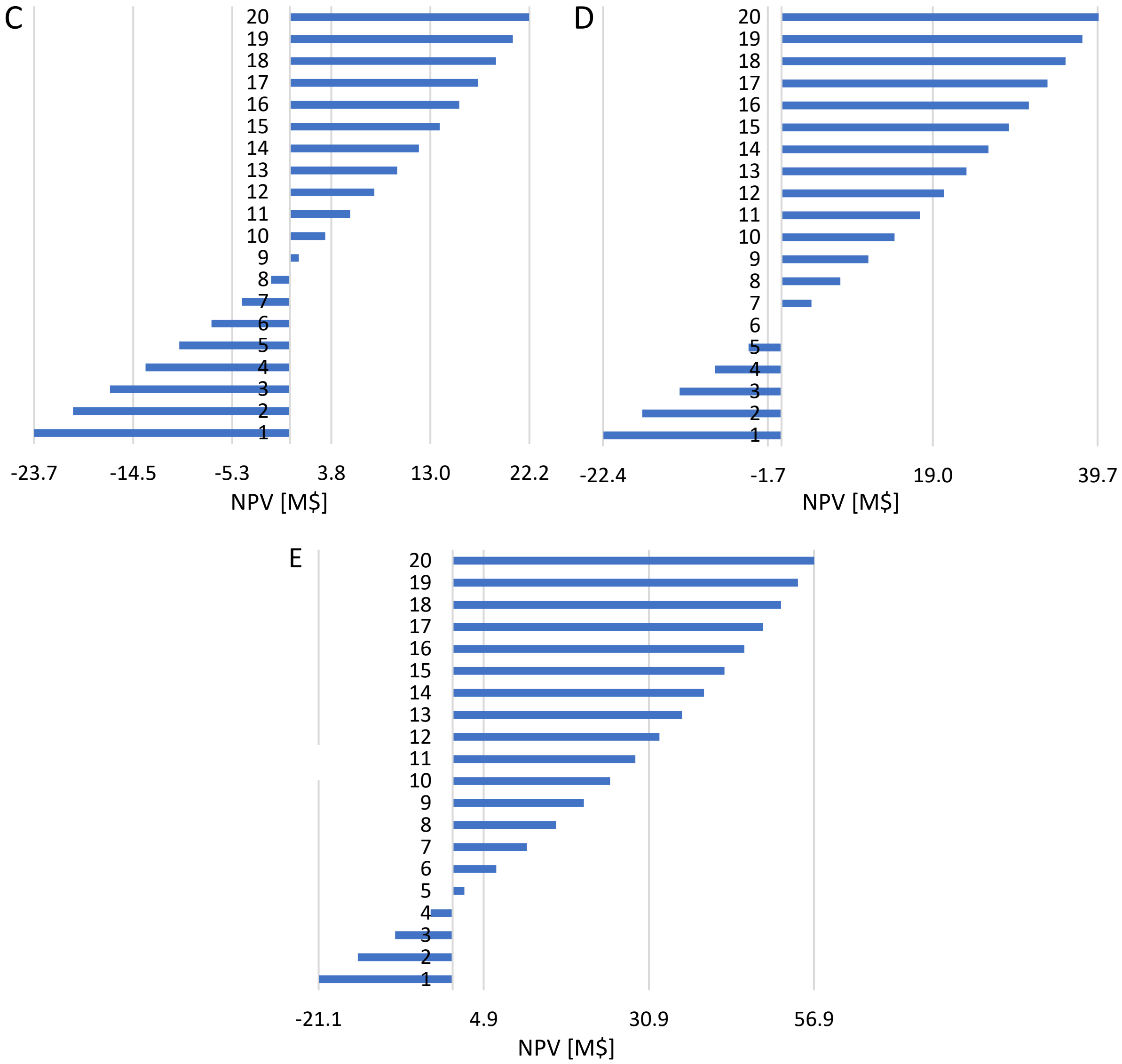


*Figure 31 - Scenario 3 NPV. A) HDPE 1 stage; B) LDPE 1 stage; C) HDPE 2 stages; D) LDPE 2 stages; E) HDPE 2 stages 480-850 °C 10 LPM*

*Figure 31* highlights how changing from electrical power to natural gas as source of heat increases the industrial feasibility of the pyrolysis process. This is due mainly to the lower cost of natural gas. In scenario 3, the payback period for HDPE pyrolysis is reached after 8 years in the single stage and after 8.5years for the double. Considering LDPE, the break-even point is achieved after 10.5years in the single stage and after only 6 years for the double stage process. As always, the best prospect is presented by HDPE double stage (480-850) where the plant starts to be profitable after 4.5 years.

### *5.1.3.4 Scenario 4*

The goal of scenario 4 is to assess the economic feasibility and profitability of a scale up pyrolysis plant using as heating source the methane produced by the process itself. A part of the methane produced by the pyrolysis is recycle into the system to generate the heat required by the process. To simplify the calculations no additional treatments to separate the gaseous fractions has been considered.

*Table 31* shows the calculation carried out to quantify how much stream needs to be recycled into the system. The amount of methane produces is converted into thermal energy by means of volume and density. Then the available thermal energy is compared with the theoretical value obtained. The difference between these values is the additional amount of methane produced and it is going to be sell. It must be noted how in the double stage HDPE pyrolysis process at 480 and 850°C the amount of methane produced is not sufficient to cover the thermal energy requirements of the plant. The negative value is equal to the quantity of natural gas that must be integrated by external sources; it is the quantity that needs to be bought. This value is going to be used to quantify utility costs.

*Table 31 - Methane recycling computation for all scale up processes*

| **Voice** | **Unit** | **HDPE 1 stage** | **HDPE 2 stages** | **LDPE 1 stage** | **LDPE 2 stages** | **HDPE 2 stages 480 - 850** |
|---|---|---|---|---|---|---|
| Methane produced | kg/y | 2042951 | 5723643 | 2265074 | 6049958 | 578016 |
| Produced thermal energy | MMBtu/y | 103026 | 288643 | 114228 | 305100 | 29149 |
| Theoretical thermal energy required | MMBtu/y | 36430 | 44874 | 36430 | 44874 | 44874 |
| Methane available for sale | kg/y | 1320567 | 4833806 | 1542690 | 5160122 | -311820.6 |
| | % | 37 | 53 | 37 | 47 | 0 |
| Methane recycled | % | 20 | 10 | 17 | 8 | 0 |

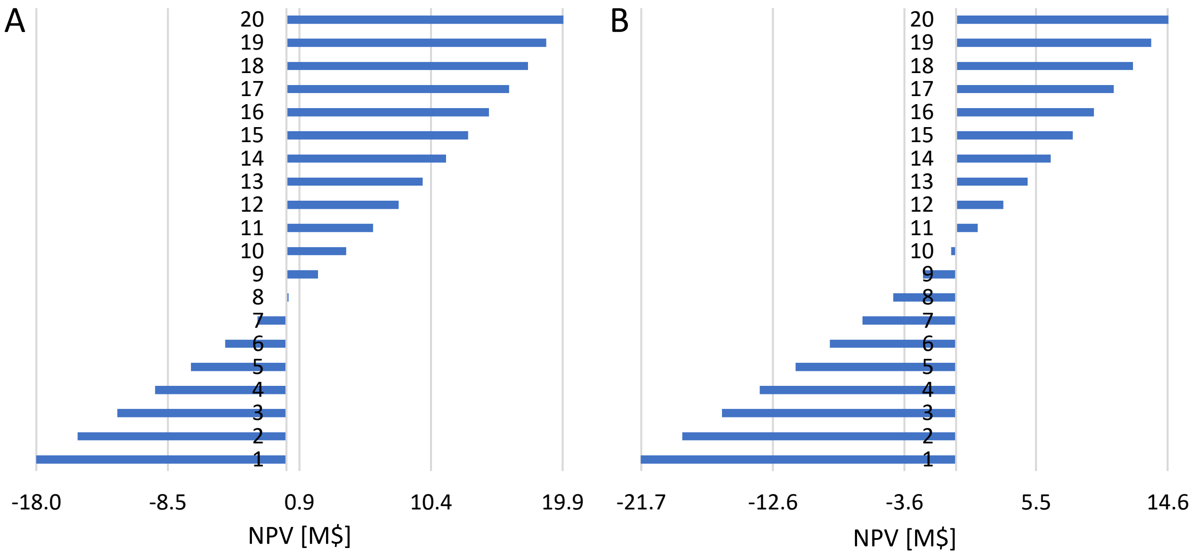
Using the aforementioned values, it was possible to process the economic analysis for this scenario *(Table 32)*. As expected, this case produces the highest annual cash income because the utility cost is completely or partially covered by the methane recycle. The value of the heating cost is not equal to zero because the startup time was accounted. During this time, which was supposed of about 2 hours, the plant needs to reach the operating conditions, so it requires a heating source. Natural gas is considered as heating source for its lower price and adaptability of the equipment used. The last set up considered (HDPE 2 stages 480-850) shows the highest utility cost because the methane amount produced is not enough to cover the plant request so an integration with natural gas from an external source is required. Nevertheless, this is still the case generating the highest annual net cash income.

*Table 32 - 1 stage and double stage scenario 4 economic analysis for HDPE and LDPE*

| **Voice** | **Unit** | **HDPE 1 stage** | **HDPE 2 stages** | **LDPE 1 stage** | **LDPE 2 stages** | **HDPE 2 stages 480-850** |
|---|---|---|---|---|---|---|
| Gas production | kg/y | 4999104 | 11213453 | 5016902 | 13400179 | 12960000 |
| Hydrogen | % | 12 | 17 | 5 | 21 | 28 |
| Hydrogen sale price | USD/kg | 2 | 2 | 2 | 2 | 2 |
| Methane | % | 37 | 53 | 37 | 47 | 0 |
| Methane sale price | USD/kg | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| Ethylene | % | 31 | 20 | 41 | 24 | 30 |
| Ethylene sale price | USD/kg | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Gas sale price | USD/kg | 0.58159 | 0.58281 | 0.54259 | 0.69859 | 0.863 |
| Oil production | kg/y | 9401069 | 3186720 | 9383328 | 999994 | 1440000 |
| Oil sale price | USD/kg | 0.377 | 0.377 | 0.377 | 0.377 | 0.377 |
| **Annual Income (sales)** | M$/y | **6.45** | **7.74** | **6.26** | **9.74** | **11.73** |
| Raw material | USD/y | 0 | 0 | 0 | 0 | 0 |
| Workers | day | 9 | 9 | 9 | 9 | 9 |
| Salary | USD/y | 44018 | 44018 | 44018 | 44018 | 44018 |
| Operating labor | USD/y | 396162 | 396162 | 396162 | 396162 | 396162 |
| Utilities | USD/y | 55 | 68 | 55 | 68 | 45760 |
| Maintenance and repair | USD/y | 300136 | 390550 | 300136 | 390550 | 390550 |
| Operating supplies | USD/y | 45020 | 58582 | 45020 | 58582 | 58582 |
| Laboratory charges | USD/y | 59424 | 59424 | 59424 | 59424 | 59424 |
| Taxes | USD/y | 838712 | 1005772 | 822290 | 1265970 | 1524557 |
| Plant overhead | USD/y | 348149 | 393356 | 348149 | 393356 | 393356 |
| **Annual Manufacturing Cost** | M$/y | **2.03** | **2.35** | **2.02** | **2.61** | **2.91** |
| Administrative | USD/y | 79232 | 79232 | 79232 | 79232 | 79232 |
| Distribution and selling | USD/y | 12190 | 14088 | 12092 | 15649 | 17475 |
| Research and development | USD/y | 193549 | 232101 | 189759 | 292147 | 351821 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Annual General Expenses** | UDS/y | **284971** | **325421** | **281083** | **387028** | **448528** |
| **Total Annual Product Cost** | M$/y | **2.32** | **2.67** | **2.30** | **3.00** | **3.36** |
| **Annual Operating Income** | M$/y | **4.13** | **5.06** | **4.03** | **6.74** | **8.37** |
| Annual depreciation | USD/y | 198383 | 262964 | 198383 | 262964 | 262964 |
| Income before tax | USD/y | 3936591 | 4800379 | 3830577 | 6480097 | 8103449 |
| Income after tax | USD/y | 3097879 | 3794607 | 3008287 | 5214127 | 6578893 |
| **Annual Net Cash Income** | M$/y | **3.30** | **4.06** | **3.21** | **5.48** | **6.84** |

Scenario 4 presents the most favorable cases *(Figure 32)* because heating utilities have been considerably reduced by the recycling the methane produced by the process. Both single stage processes (HDPE & LDPE) present to long payback periods to be considered favorable from an economical point of view. The HDPE double stage reported a break-even point higher than the single stage process; it is not economically feasible because the investment presents a great risk. On the other hand, the 480-850 doble stage set up presents the fastest return on the investments, after 4.5 years the pyrolysis plant starts to generate profit. Concerning LDPE, the double stage process is the most advantageous with a payback period lower than 6 years.



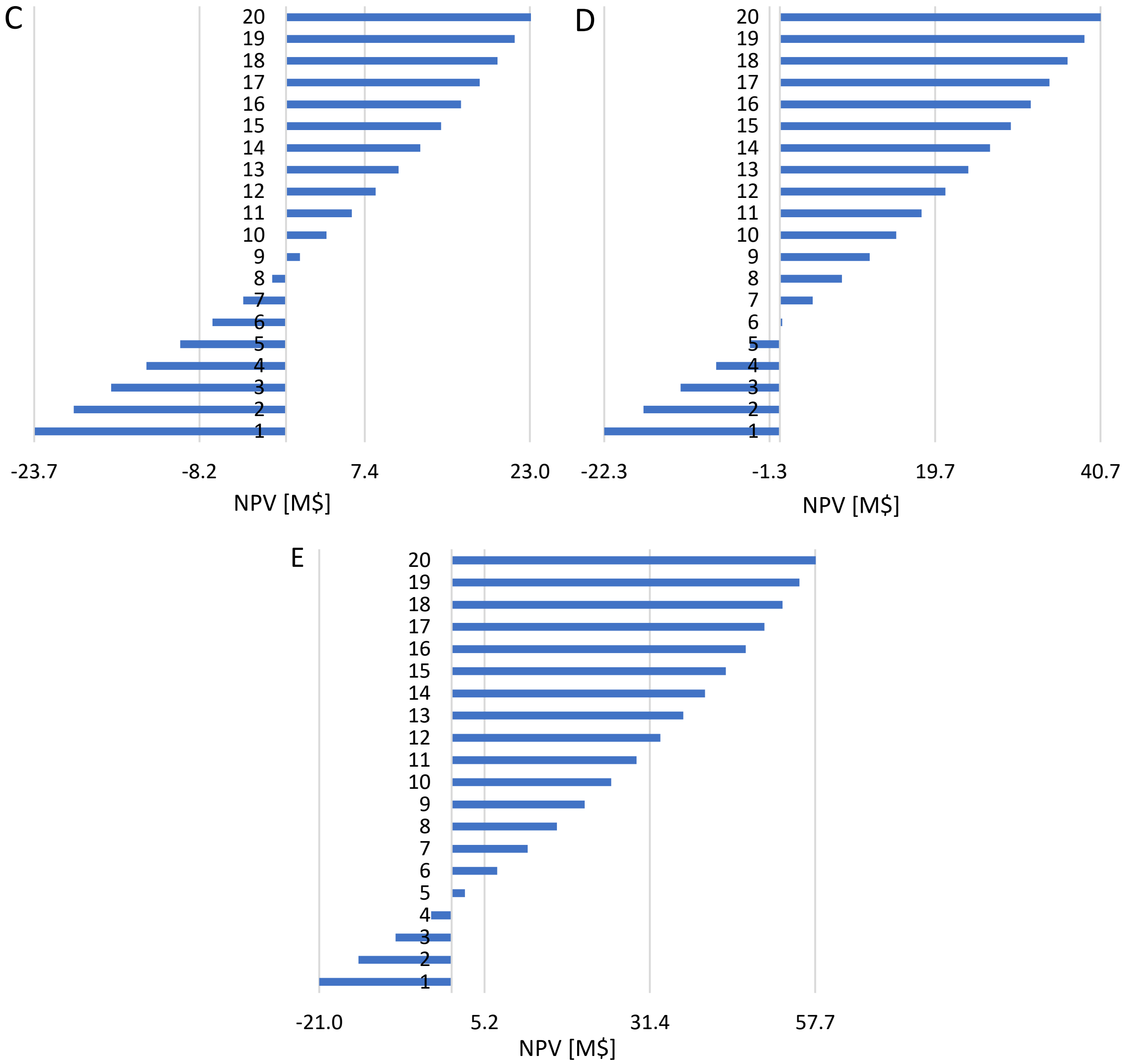


*Figure 32 - Scenario 4 NPV. A) HDPE 1 stage; B) LDPE 1 stage; C) HDPE 2 stages; D) LDPE 2 stages; E) HDPE 2 stages 480-850 °C 10 LPM*

#### *5.1.3.5 Scenario 5*

The influence of the heating source on the economic feasibility of the process is strong and the outcome improves when methane recycling is considered. The next step in the sensitivity analysis is to understand which other parameters affect the net profit of the process. After some investigation it turned out that the other main parameter influencing the economics of the process is the gas composition.

Scenario 5 aims to identify the target gas composition which renders the pyrolysis process advantageous, or else which present the lowest payback time. Two cases have been analyzed:

- Hydrogen production, where the gas product is composed by hydrogen and methane, 80% and 20%, respectively.
- Ethylene production, where the gas stream contains methane and ethylene, 20% and 80%, respectively.

In both cases methane production is considered to overcome the energy requirements of the process.

The following *Figures 33 & 34* report net present value and payback period for hydrogen and ethylene production, respectively. Both cases show a better economic prospect than the previously analyzed. Hydrogen production seems to be economically advantageous from an industrial point of view because the BEP is lower or equal to 4 years in all processes. This is due to hydrogen high selling price. Ethylene production is also profitable with payback periods ranging between 4 and 7 years. Comparing the double stage HDPE theoretical case (Case D) with HDPE (480-850) form the previous scenario, it is possible to see how high ethylene and hydrogen concentrations (30 and 28%) in the gas product improve the overall sustainability of the process lowering the payback period and making it comparable with the theoretical case.

In conclusion, at this time the most profitable pyrolysis set ups are the ones producing hydrogen. Further research should be performed to see which parameters can maximize both ethylene and hydrogen to have payback periods lower than four years.

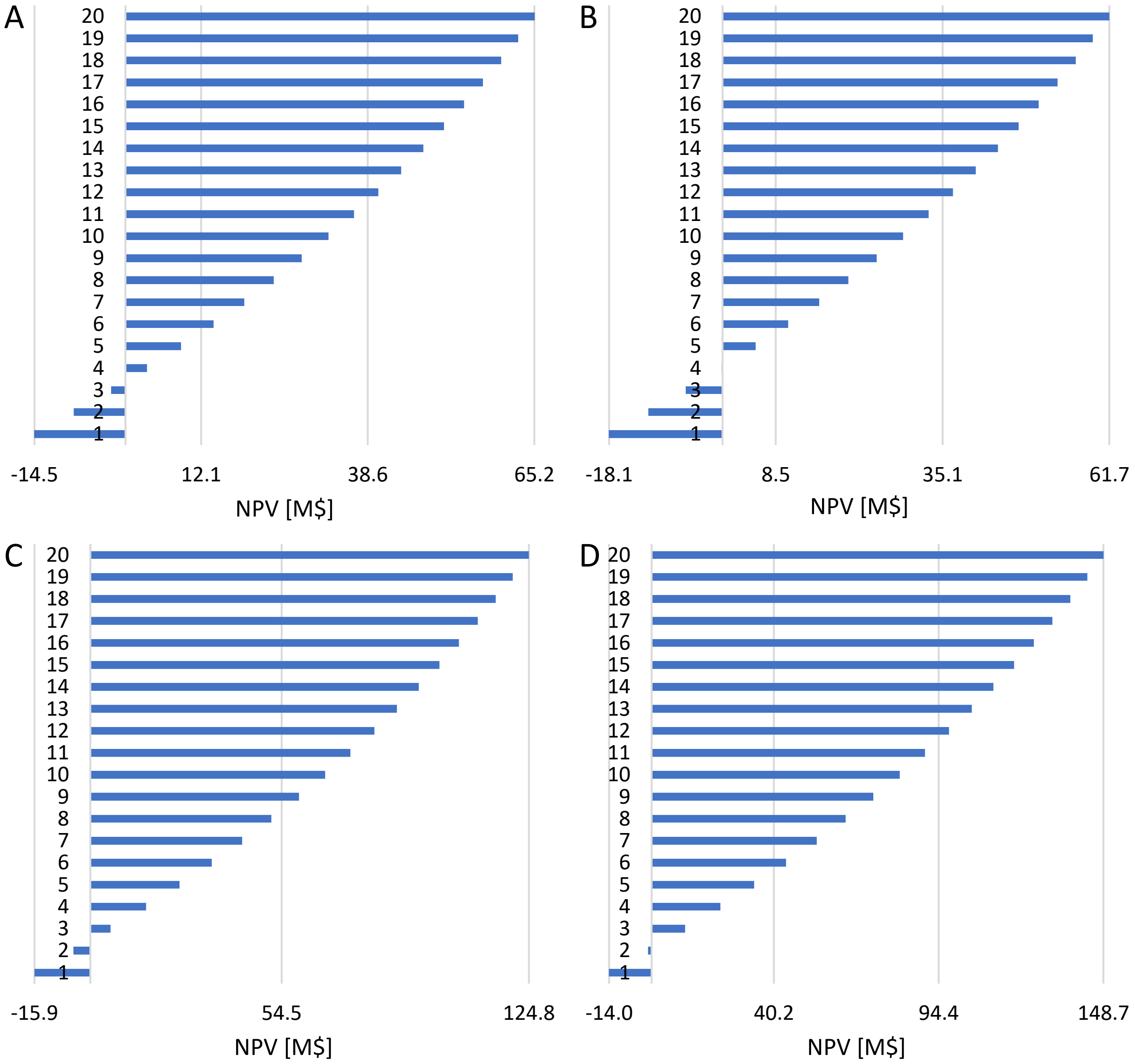


*Figure 33 - Scenario 5 Hydrogen production NPV. A) HDPE 1 stage; B) LDPE 1 stage; C) HDPE 2 stages; D) LDPE 2 stages*

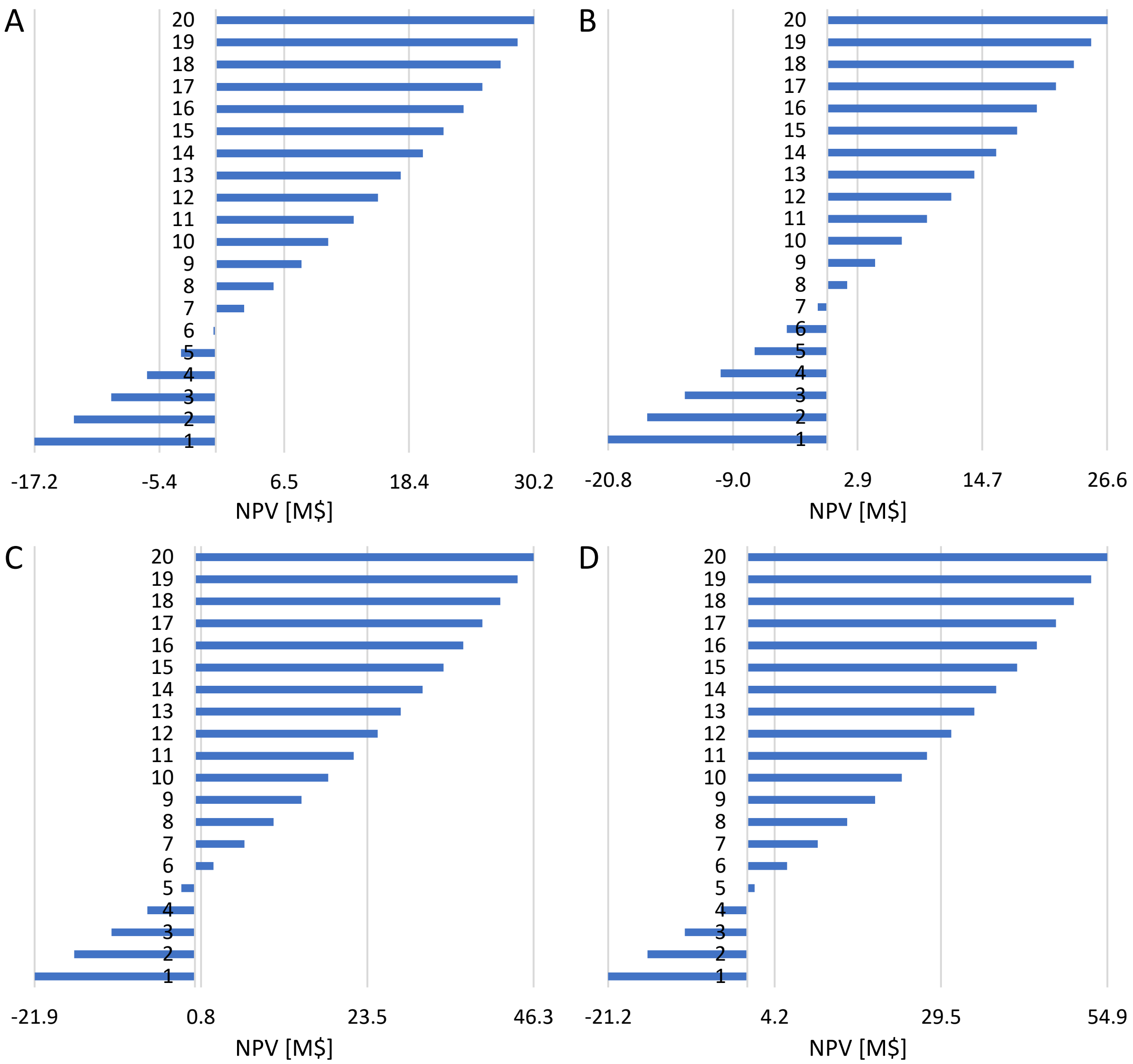


*Figure 34 - Scenario 5 Ethylene production NPV. A) HDPE 1 stage; B) LDPE 1 stage; C) HDPE 2 stages; D) LDPE 2 stages*

## 5.2 Rubber pyrolysis

The goal of the following chapter is to define the economic sustainability and profitability of a rubber pyrolysis plant. The analysis is based on results obtained by tests performed with rubber feedstock as explained in previous chapters. The results used in the economic analysis are those obtained from the third run; temperature 500°C, heating rate 10°C/min, mixing rate 30 rpm and nitrogen flow of 1 L/min.

### 5.2.1 Base scenario

To be able to perform a comparison between plastic and rubber pyrolysis a main assumption has been done in the economical assessment of the rubber process. The hypothesis is that same results are achieved is rubber is pyrolyzed in a continuous process; the results obtained from the batch unit have been consider equal to the results obtained with a vertical MFB operating in continuous. Unser this assumption the economic analysis has been performed and the results are reported in *Table 33*. The estimation off all the parameters follows the same procedure used for the plastic pyrolysis, reported in chapter 5.1.2. The main difference with plastic waste pyrolysis analysis is that in the following case we consider only a single stage process and char sale is taken into consideration to determine the annual sales income. As explained before char is the main product of rubber pyrolysis and it has a great influence on the overall profitability of the plant. Due to its high content of carbon rubber char can be further upgraded to obtain carbon black. In 2020, one of the largest carbon black (CB) producers of North America (Cabot Corporation) reported 0.066 USD $kg^{-1}$ as CB selling price.

As result of the economic analysis the net cash income for the base scenario (1 kg/h plant) is negative and the resulting net present value is adverse throughout all operating life of the plant *(Figure 35)*. So, the plant is not profitable as is.

*Table 33 - Rubber pyrolysis base scenario economic analysis*

| Voice | Unit | Rubber |
|---|---|---|
| Extrusion heater | USD | 2300 |
| Pyrolizer | USD | 20700 |
| Condenser 1 | USD | 4600 |
| Condenser 2 | USD | 4600 |
| **Total Equipment Cost** | M$ | **32200** |
| Installation costs | USD | 9660 |
| Instrumentation and control | USD | 8050 |
| Piping | USD | 25760 |
| Power system | USD | 32200 |
| Buildings | USD | 12880 |
| Service equipment | USD | 3864 |
| **Total Direct Costs** | M$ | **124614** |

| | | |
|---|---|---|
| Engineering and supervision | USD | 9660 |
| Legal Fees | USD | 1246 |
| Construction and erection | USD | 9969 |
| Contingencies | USD | 9969 |
| **Total Indirect Costs** | M$ | **30844** |
| **Fixed Capital Costs** | M$ | **155458** |
| **Working Capital** | M$ | **31092** |
| **Total Capital Investment** | M$ | **186550** |
| Gas production | kg/y | 1716 |
| Hydrogen | % | 72% |
| Hydrogen sale price | USD/kg | 2 |
| Methane | % | 25% |
| Methane sale price | USD/kg | 0.077 |
| Ethylene | % | 3% |
| Ethylene sale price | USD/kg | 1.01 |
| Gas sale price | USD/kg | 1.490 |
| Oil production | kg/y | 1296 |
| Oil sale price | USD/kg | 0.377 |
| Char production | kg/y | 2753 |
| Carbon Black sale price | USD/kg | 0.066 |
| **Annual Income (sales)** | M$/y | **3227** |
| Raw material | USD/y | 0 |
| Workers | day | 4.5 |
| Salary | USD/y | 44018 |
| Operating labor | USD/y | 198081 |
| Utilities | USD/y | 49796 |
| Maintenance and repair | USD/y | 2254 |
| Operating supplies | USD/y | 338 |
| Laboratory charges | USD/y | 29712 |
| Taxes | USD/y | 420 |
| Plant overhead | USD/y | 100168 |
| **Annual Manufacturing Cost** | M$/y | **424791** |
| Administrative | USD/y | 39616 |
| Distribution and selling | USD/y | 2549 |
| Research and development | USD/y | 97 |
| **Annual General Expenses** | UDS/y | **42262** |

| | | |
|---|---|---|
| **Total Annual Product Cost** | M$/y | **467053** |
| **Annual Operating Income** | M$/y | **-463825** |
| Annual depreciation | USD/y | 1510 |
| Income before tax | USD/y | -465335 |
| Income after tax | USD/y | -465755 |
| **Annual Net Cash Income** | M$/y | **-464245** |

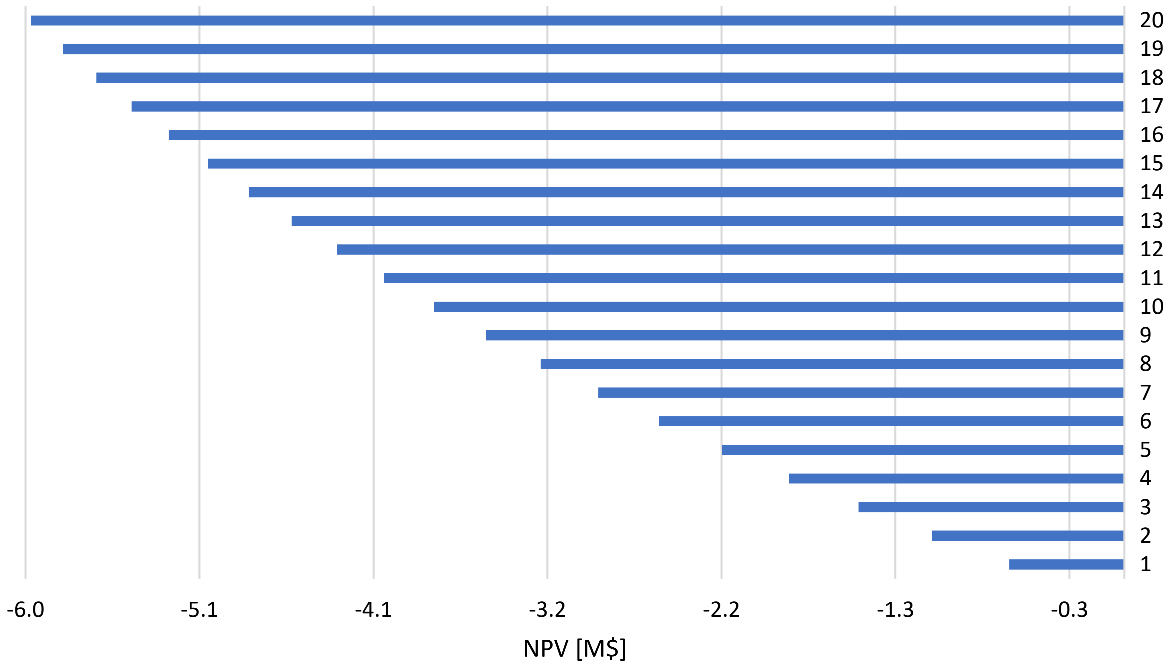


*Figure 35 - Rubber pyrolysis base case scenario NPV*

### 5.2.2 Plant scale-up

To be able to continue the confrontation with the plastic pyrolysis process the scale up considered is 2500 kg $h^{-1}$. As previously reported the plant scale up costs follow the same procedure used for the plastic assessment.

#### *5.2.2.1 Scenarios*

The following chapter aims to provide an idea of the different influence that parameters, such as electrical energy or heat source, have on the overall plant feasibility and remuneration. Six different scenarios have been taken into consideration:

- Scenario 1, simple scale up with all parameters equal to the base scenario.
- Scenario 2, scale up using Québec electrical energy cost (0.043 USD $kWh^{-1}$).
- Scenario 3, scale up using natural gas as heat source instead of electricity.
- Scenario 4, scale up using the produced methane as heat source.

- Scenario 5, theoretical case producing a gas fraction containing 80% hydrogen and 20% methane.
- Scenario 6, theoretical case producing a gas fraction containing 80% ethylene and 20% methane.

*Table 34* reports the economic analysis of all the scenarios considered for the rubber pyrolysis scale up process. Equipment costs and total capital investment are the same for all evaluations because process set up does not change and so all the correlated costs. The first four cases all show the same annual sales income since in these scenarios no variation of the gas composition is supposed. The difference between these cases is focused on the manufacturing cost quantification. It is possible to identify a decrease in the manufacturing cost as the price of electricity is lowered (Case 2), as electrical power is replaced by natural gas (Case 3), and at last when methane is recycled into the system (Case 4). As consequence the scenario including gas recycling into the system as source of energy is the one presenting the highest annual net cash income. Based on Case 4, two other scenarios have been evaluated. As is reported in *Table 34*, Case 5 which consider methane recycle and hydrogen production is the most remunerative of all. On the other hand, scenario 6 which simulates the production of a gas stream composed by methane and ethylene is the least profitable.

*Table 34 - Scenario 1,2,3,4,5, & 6 of rubber pyrolysis scale up economic analysis*

| Voice | Unit | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 | Case 6 |
|---|---|---|---|---|---|---|---|
| Extrusion heater | USD | 306261 | 306261 | 306261 | 306261 | 306261 | 306261 |
| Pyrolizer | USD | 2756353 | 2756353 | 2756353 | 2756353 | 2756353 | 2756353 |
| Condenser 1 | USD | 612523 | 612523 | 612523 | 612523 | 612523 | 612523 |
| Condenser 2 | USD | 612523 | 612523 | 612523 | 612523 | 612523 | 612523 |
| **Total Equipment Cost** | M$ | **4.29** | **4.29** | **4.29** | **4.29** | **4.29** | **4.29** |
| Installation costs | M$ | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 |
| Instrumentation and control | M$ | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 |
| Piping | M$ | 3.43 | 3.43 | 3.43 | 3.43 | 3.43 | 3.43 |
| Power system | M$ | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 |
| Buildings | M$ | 1.72 | 1.72 | 1.72 | 1.72 | 1.72 | 1.72 |
| Service equipment | USD | 514519 | 514519 | 514519 | 514519 | 514519 | 514519 |
| **Total Direct Costs** | M$ | **13.59** | **13.59** | **13.59** | **13.59** | **13.59** | **13.59** |
| Engineering and supervision | M$ | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 |
| Legal Fees | USD | 171506 | 171506 | 171506 | 171506 | 171506 | 171506 |
| Construction and erection | M$ | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 |
| Contingencies | M$ | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 | 1.29 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Total Indirect Costs** | M$ | **4.03** | **4.03** | **4.03** | **4.03** | **4.03** | **4.03** |
| **Fixed Capital Costs** | M$ | **17.62** | **17.62** | **17.62** | **17.62** | **17.62** | **17.62** |
| **Working Capital** | M$ | **3.52** | **3.52** | **3.52** | **3.52** | **3.52** | **3.52** |
| **Total Capital Investment** | M$ | **21.15** | **21.15** | **21.15** | **21.15** | **21.15** | **21.15** |
| Gas production | kg/y | 4291200 | 4291200 | 4291200 | 4291200 | 4291200 | 4291200 |
| Hydrogen | % | 72% | 72% | 72% | 72% | 80% | - |
| Hydrogen sale price | USD/kg | 2 | 2 | 2 | 2 | 2 | - |
| Methane | % | 25% | 25% | 25% | 13.8% | 13.6% | 13.6% |
| Methane sale price | USD/kg | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| Ethylene | % | 3% | 3% | 3% | 3% | - | 80% |
| Ethylene sale price | USD/kg | 1.01 | 1.01 | 1.01 | 1.01 | - | 1.01 |
| Gas sale price | USD/kg | 1.49 | 1.49 | 1.49 | 1.480926 | 1.610472 | 0.818472 |
| Oil production | kg/y | 3240000 | 3240000 | 3240000 | 3240000 | 3240000 | 3240000 |
| Oil sale price | USD/kg | 0.0007 | 0.0007 | 0.0007 | 0.0007 | 0.0007 | 0.0007 |
| Char production | kg/y | 6883200 | 6883200 | 6883200 | 6883200 | 6883200 | 6883200 |
| Carbon Black sale price | USD/kg | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 | 0.066 |
| **Annual Income (sales)** | M$/y | **6.85** | **6.85** | **6.85** | **6.81** | **7.37** | **3.97** |
| Raw material | USD/y | 0 | 0 | 0 | 0 | 0 | 0 |
| Workers | day | 9 | 9 | 9 | 9 | 9 | 9 |
| Salary | USD/y | 44018 | 44018 | 44018 | 44018 | 44018 | 44018 |
| Operating labor | USD/y | 396162 | 396162 | 396162 | 396162 | 396162 | 396162 |
| Utilities | USD/y | 993686 | 459446 | 40228 | 21 | 21 | 21 |
| Maintenance and repair | USD/y | 300136 | 300136 | 300136 | 300136 | 300136 | 300136 |
| Operating supplies | USD/y | 45020 | 45020 | 45020 | 45020 | 45020 | 45020 |
| Laboratory charges | USD/y | 59424 | 59424 | 59424 | 59424 | 59424 | 59424 |
| Taxes | USD/y | 890307 | 890307 | 890307 | 885496 | 957764 | 515942 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Plant overhead | USD/y | 348149 | 348149 | 348149 | 348149 | 348149 | 348149 |
| **Annual Manufacturing Cost** | M$/y | **3.08** | **2.54** | **2.12** | **2.08** | **2.15** | **1.71** |
| Administrative | USD/y | 79232 | 79232 | 79232 | 79232 | 79232 | 79232 |
| Distribution and selling | USD/y | 18461 | 15256 | 12741 | 12471 | 12904 | 10253 |
| Research and development | USD/y | 205455 | 205455 | 205455 | 204345 | 221022 | 119064 |
| **Annual General Expenses** | UDS/y | **303149** | **299944** | **297429** | **296048** | **313159** | **208549** |
| **Total Annual Product Cost** | M$/y | **3.38** | **2.84** | **2.42** | **2.37** | **2.46** | **1.92** |
| **Annual Operating Income** | M$/y | **3.47** | **4.01** | **4.43** | **4.44** | **4.90** | **2.05** |
| Annual depreciation | USD/y | 198383 | 198383 | 198383 | 198383 | 198383 | 198383 |
| Income before tax | M$/y | 3.27 | 3.81 | 4.23 | 4.24 | 4.71 | 1.85 |
| Income after tax | M$/y | 2.38 | 2.92 | 3.34 | 3.35 | 3.75 | 1.34 |
| **Annual Net Cash Income** | M$/y | **2.58** | **3.12** | **3.54** | **3.55** | **3.95** | **1.54** |

*Figure 36* shows the net present value for the different scenarios along the plant operating time (20 years). Case 1 present a net profit at the end of the lifetime of 11 million dollar and the break-even point is reached after about 11 years. This scenario is not advantageous from an industrial point of view, the initial investment risk is too high. In Case 2 the reduction of the energy cost improves the final net profit, and the payback period lowers to 8 and a half years, but it still is not interesting for industrial implementation. Case 3 and 4 show the same payback period, around 7 and a half years, but the final remuneration of scenario 4 is greater because its manufacturing cost is lower (methane recycle in the system). The theoretical case 5 is the most favorable from an economic point of view, payback period between 6 and 7 years and net profit at plant end life of 28 million dollars. It can be concluded that as of now hydrogen production is the most favorable for the overall economics of the plant. At last, case 6 is the theoretical scenario where the gas stream produced is composed by ethylene (80%) and methane (20%). This is the only scale up case where the plant is not economically feasible and the NPV at the end of the operating life is negative, so the plant has not recovered the initial investment.

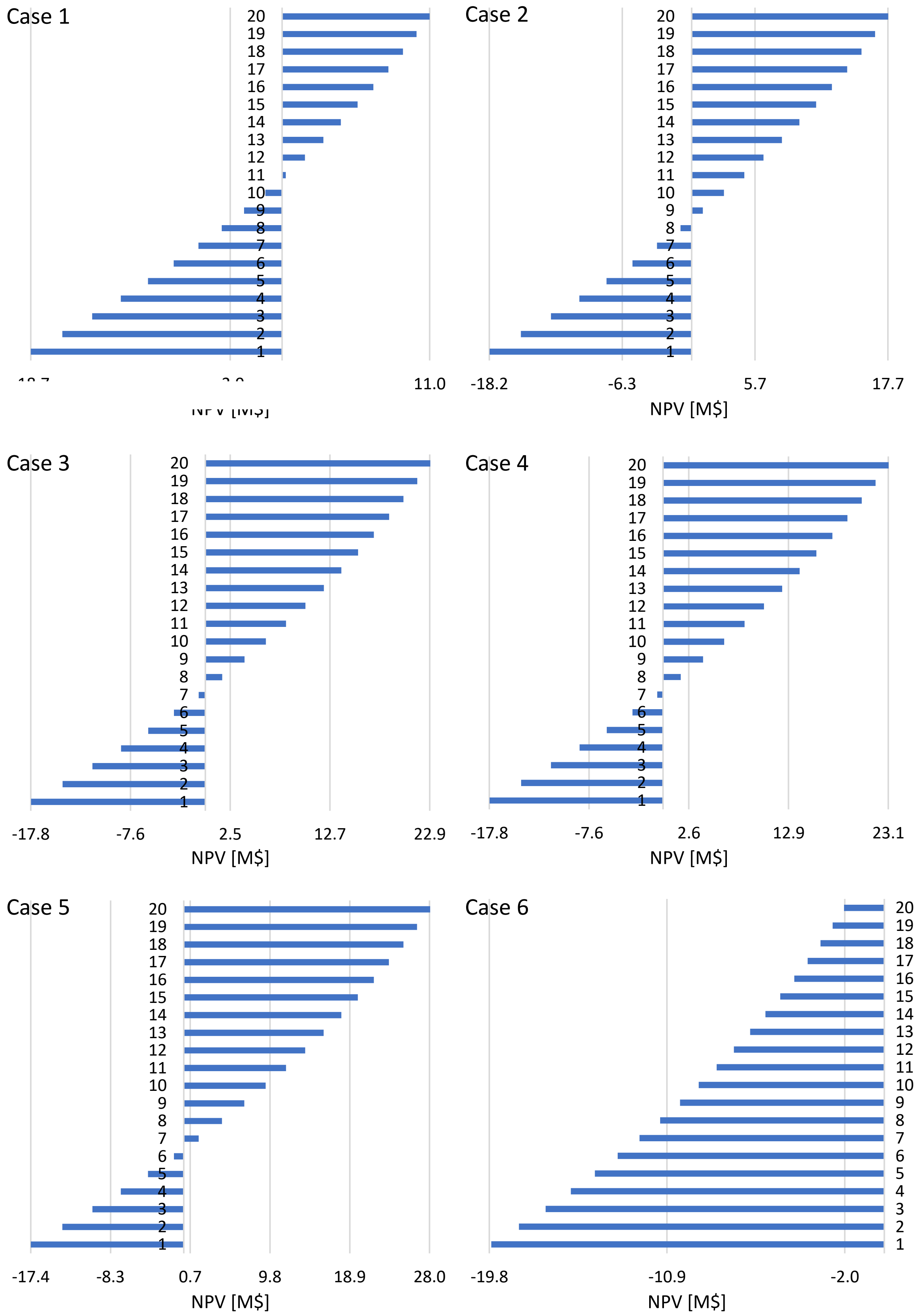


*Figure 36 - Scenario 1,2,3,4,5, & 6 of rubber pyrolysis scale up Net Present Value*

# 7. Conclusions

The literature review on the pyrolysis of waste plastic and rubber showed that both processes are feasible and can support a circular economy system. Moreover, thermochemical processes are preferable compared to incineration for these feedstocks, because they allow to recover chemicals and at the same time produce energy, enabling the valorization of the whole potential value of the waste materials.

Pyrolysis can be performed on all types of plastic with some challenges:

- Polyethylene terephthalate (PET) produces oil containing benzoic acid, which makes it unsuitable for application due to its corrosivity.
- Polyvinyl chloride (PVC) during pyrolysis produces corrosive and toxic compounds such as hydrogen chloride. PVC can be pyrolyzed after dechlorination, but additional pre-treatments result in high process costs.

Different rectors were used and investigated in literature, and many challenges are posed when the equipment is scaled up. First, continuous process is favorable from an economical point of view compared to batch. To avoid feeding problems, bed defluidization, complex design, and poor heat transfer mechanically fluidized bed reactors seem to be the best option. Furthermore, each reactor/feedstock combination needs a carefully tuned combination of process parameters; finally, pyrolysis conditions are case specific.

Plastic waste pyrolysis products are valuable and there is market for them. The gas fraction is reach in hydrogen, methane, ethylene, and other hydrocarbons; they can be sold to petrochemical industries or when monomers are achieved to plastic production industries. Hydrogen and methane can be used in situ or sold for energy generation. Concerning the oil, it can be sold to by petrochemical industries for further treatment and production of petroleum derivatives. The use of pyrolysis oil as fuel is favorable and it shows physical properties comparable with diesel.

Rubber pyrolysis is also feasible, and the main challenges are posed by the presence of nitrogen, sulfur and chlorine in the feedstock which could lead to the formation of acid gasses (equipment corrosion), SOx, NOx, and dioxins. Another challenge is given by achievable the particle size. Rubber is difficult to grind and to reach its brittle point very low temperatures must be achieved (- 70°C or lower). So, the reactors used at industrial scale are mainly kiln reactors which allow coarser particles treatment. Rubber pyrolysis parameters must be tuned case to case, also depending on the desired product.

As for plastic pyrolysis gas fraction, rubber gasses are rich in hydrogen, methane, and ethylene. The waste tire pyrolysis oil (TPO) is a mixture of over a hundred compounds, it can be sold to petrochemical industries, which will mix it with the incoming crude oil and treat it to produce petroleum derivatives. TPO cannot be used alone successfully used in vehicles engines; problems rise in blends with concentration higher than 70%. In all blends, higher emissions of NOx, hydrocarbons, and particulates are measured. Rubber char has different applications such as activated carbon or carbon black substitute. Further research should be done on the application of rubber char for the extraction of electrode material for energy storage.

All the experimental activities conducted on both plastic and rubber have reported results in line with literature. The influence of temperature, given by the addition of the secondary furnace in the plastic pyrolysis set up, is seen by an overall increase in the gas fraction produced and greater methane concentrations. Meaning that enhanced cracking is achieved in the furnace which leads to the formation of stable compounds. When the reactor temperature is lowered and the furnace one is increased the highest hydrogen and ethylene concentration are obtained meaning that in the first stage liquid conversion is maximized and subsequently it is cracked to its monomeric stage. The same temperature effect can be identified in the gas fraction of rubber pyrolysis, at 500°C the main gas composition is given by hydrogen and methane. For both processes further experiments and research is needed to customize the pyrolysis parameters and maximize the desired products. Rubber pyrolysis should be investigated at different residence time and, if feasible, in a continuous process. Moreover, further investigation of the products is needed; identify possible upgrading technologies to increase products quality.

The results obtained in the economic analysis are quite promising in both scale up scenarios. The economical sustainability of the processes is mainly given by the hydrogen content of the gas product, this is due to green hydrogen high market value (2 USD $kg^{-1}$). The major findings can be summarized as follows:

- Base scenarios are not economically feasible either for plastic pyrolysis or rubber pyrolysis.
- Both HDPE and LDPE single stage processes scale up are profitable but not sustainable because they present too long payback periods.
- HDPE double stage pyrolysis is not favorable at industrial level in all scenarios. This is due to little improvement in gas composition which does not cover the increase in investment and operating cost produced by the addition of the furnace.
- LDPE double stage process is promising from an economic point of view, when methane recycle is considered; payback period lower than 6 years.
- HDPE double stage pyrolysis at 480-850°C with nitrogen flow of 10 L min-1 is the most promising case due to high concentration of hydrogen and ethylene. The payback period of this set up is about 4.5 years when methane recycle into the system is considered.
- Rubber pyrolysis payback period with methane recycle is between 7 and 8 years. Further experiments should be carried out to improve the total conversion and gas composition.

Considering the two theoretical cases, hydrogen-methane and methane-ethylene, in all set ups the hydrogen production is more economically advantageous with respect to ethylene. The hydrogen production scenario in the plastic waste pyrolysis analysis reported payback period lower than 4 years in all configurations. The payback time is between 6 and 7 years for rubber pyrolysis. Rubber pyrolysis ethylene production scenario is the worst of all, it is not profitable. In fact, at the end of the operating life the initial investment has not been recovered.

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