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# Techno-economic assessment of the pyrolysis of rubber waste

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## Abstract

Slow rubber pyrolysis was performed at 300-500°C in a horizontal batch mechanically fluidized reactor with 30-60 min holding time, and the products were characterized. The char (yield = 50%-wt) exhibited a high heating value (HHV) around 30 MJ/kg, comparable with bituminous coke, and 84%-wt Carbon. The gas products (yield = 24-31%) had a composition dependent on temperature: 21%-v ethylene, 46%-v propane, and 11%-v butane at 300°C; over 20%-v hydrogen and methane at 400°C; at 500°C hydrogen ranged 46-69%-v and methane 21-36%-v. Oil products (yield = 17-22% yield) consisted of <C14 hydrocarbons (HHV around 41 MJ/kg), similar to unrefined gasoline. At 300°C the oil was mainly composed of C10 (benzene, D-limonene, cyclo-hexadiene, and cyclo-heptane); at 400°C of C7-C10, and benzene compounds had the highest concentration; at 500°C C10 decreased and C7 increased. A techno-economic assessment of the scale-up to 2,500 $kgh^{-1}$ is proposed. The economic sustainability of the processes is demonstrated thanks to the hydrogen production (with a market value 2 USD $kg^{-1}$), whose valorization provides the most advantageous scenario with a payback period of 6-7 years. In conclusion, the results of the economic analysis are quite promising, and further experiments and research are needed to optimize the pyrolysis operating parameters.

**Keywords**: Techno-economic assessment, pyrolysis, rubber, end-of-life tires.

## 1. Introduction

In 2021 3.1 billion tires were sold in Europe, of which 2.8 billion were car tires [1]. Tires have a complex composition made of rubber (natural or synthetic), steel, textiles, filler (carbon black and amorphous silica), and additives [2]. Such composition improves rubber quality resulting in higher tear and abrasion resistance, as well as tensile strength [3]. Sulfur and zinc are also used in the rubber formulation. During vulcanization, sulfur addition helps rubber transformation into a solid and durable material, while ZnO acts as an activator by reducing vulcanization time. Steel wires are used to reinforce the tire case and to reduce wear. Other additives, such as antioxidants and antiozonants, improve the resistance to temperature changes and oxidation by oxygen and ozone [4]. Since the tire components are resistant to heat, electricity, chemicals, and bacteria, they are also difficult to dispose of. Microorganisms need over 100 years to degrade tires, and 75% of their matrix is made of air, which can contain toxic components and increase fire hazards [5]. Fires involving waste tires are difficult to extinguish and can last for several days releasing harmful compounds for human health, such as dioxins, and polluting the air, soil, and water.

Waste tires management in Europe follows the waste hierarchy defined by the Waste Framework Directive 2008/98/EC: prevention, reuse, recycling, and energy recovery, while landfilling has been prohibited by the EU Directive 1999/31. In 2019, recycling accounted for 52% of tires management, and energy recovery (mostly in cement kilns) for 40% [6]. Recycling technologies include granulation, inclusion in cement as an aggregate, and use in civil engineering applications as crumb-rubber modified asphalts, sport courts floorings and garden containers [5], [7]. The utilisation of waste tires as fuels (tire derived fuels) in cement kilns or steam turbines poses environmental problems because of the emissions of SOx, NOx, VOC, PAHs, dioxins, and other harmful compounds [8], [9]. There is an urgent need for new recycling technologies applied to waste tires, and pyrolysis could offer an environmentally friendly and safe route to convert waste tires into added-value products while avoiding hazardous emissions. Being able to produce energy, fuels and chemicals from waste can help countries with short/no fossil fuel reserves to lower their imported quota. Hydrogen, methane, ethylene, tire pyrolysis oil (TPO) and char offer strong market opportunities. Limonene is one of the coimpunds present in the oil, it is a high-vale chemical with a market size of 1.2 billion USD$ in 2017 [10]. The solid residue derived form the process offers high end applications such carbon nanotubes [11] and carbon black from new tires manufacturing [12].

Rubber pyrolysis has been previously investigated, mostly from the point of view of a waste-to-energy (WtE) technology, involving pulverized [13], granulated [14] and shredded tires [15]. Larger particles are used in bigger scale plants due to the lower energy required in the pre-treatments [16]. Rubber degradation process and kinetics are still being investigated [17], and the tested reactors are both batch [18] and continuous [19]. As per reactor type, configuration providing material mixing, as the one used in this study, are better if compare with unmixed vessels that are usually employed at lab scale. In fact, mixing provides better heat transfer and more stable product generation and composition [20]. Li et al.[21] reported yields of 22.59 % gas, 38.29 % liquid, and 36.7 % solid for thermal pyrolysis of granulated ELTs in a batch unstirred reactor at 500 °C; while Choi et al. [14] observed yields of 4.5 % gas, 55 % liquid, and 40 % solid from the same input material and conditions in a continuous stirred tank reactor. Moreover, mechanically fluidized bed reactors do not present defluidization problems, can handle particles with different sizes, design and process control are easy.

Considering the process conditions, temperatures in the range 400-800°C have been investigated [22], with variable reaction times of 30 [15], 120 [14] and 240 min [22]. For temperatures lower than 450°C high concentrations of sticky and gummy heterogeneous solids are obtained identifying a non-compòte devolatilization of the feedstock[23]. The temperatures of 500-600°C are associated with high tire pyrolysis oil yields [24]. If the temperature is increased over 600°C, gas production is increased by secondary reactions [25]. The product yields have been shown to vary within the above specified temperature range: at 350°C in a fixed bed reactor gas accounted for 11.54 %, oil 27.20% and char 61.27% [26]; at 450°C in a fixed bed reactor 19.66% is gas, 43.70% is liquid and 36.64% solid [26]. At the same temperature, in a rotary kiln the reported yields are 10.32 % gas, 51.28% oil, 32.16% char [15].

When 600°C is used as oprating temperature the reported yields are 15.90% gas, 38.74% liquid and 45.36% char in a unmixed batch reactor [27], while a fluidized bed reactor achieved 46% gas, 25.30% oil, and 28.70% char [28].[14], [15], [19], [22] Lab scale studies are the most common, and research at larger scale is urgently needed to transfer optimized process parameters to the industrial sector [29].

Compared to the existing literature, this study has two elements of novelty and objectives. Firstly, pyrolysis is specifically considered not as WtE technology, but, rather, as a process to convert waste rubber into added-value products that may have multiple applications as fuels, chemicals and/or building blocks. The specific focus of this study has been on the pyrolytic conversion of waste tires into high-value gaseous products, “fuel-like” oil, and “char-like” solid products. Secondly, this study is aimed to illustrate a techno-economic evaluation of the economic sustainability of the potential scale-up of the process (to 2500 kg $h^{-1}$ of fed waste rubber), to promote its technological transfer to the industrial world.

## 2. Material and methods

### 2.1. Samples origin and characteristics

The rubber used in the experiments was a common gardening rubber (1-2 cm chunks) derived directly from waste tire shredding and metals removal. It contained visible textile fibers, and exhibited a dark brown color and physico-chemical characteristics (Table 1) consistent with those reported in the literature [30]–[32]. The higher heating value (HHV) of the raw rubber was equal to 37 MJ $kg^{-1}$.

**Table 1**. Ultimate and proximate analysis of the rubber feedstock (values expressed as %-wt of dry material)

| Ultimate analysis | | | | | |
|---|---|---|---|---|---|
| N | C | H | S | $O^a$ | 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 | | | |
|---|---|---|---|
| Moisture | Volatile matter | Ash | Fixed carbon |
| 1.94 ± 0.20 | 64.32 ± 0.43 | 5.79 ± 0.05 | 27.95 |

[a] By difference

### 2.2. Pyrolysis tests

Four pyrolysis tests (runs) have been performed in a horizontal batch mechanically fluidized reactor (MFR) (Figure 1). The reactor is 30 cm long and has a diameter of 20 cm resulting in a capacity of 8.5 L. The body is made of 316 stainless steels. To improve the heat transfer, the material is mechanically mixed by internal paddles. An induction unit is the heating source (5-100 KW, Superior Induction Company, California, US). The MFR was connected to a single-stage condenser immersed in an ice-packed water bath, and the gaseous products are directed into an exhaust line.

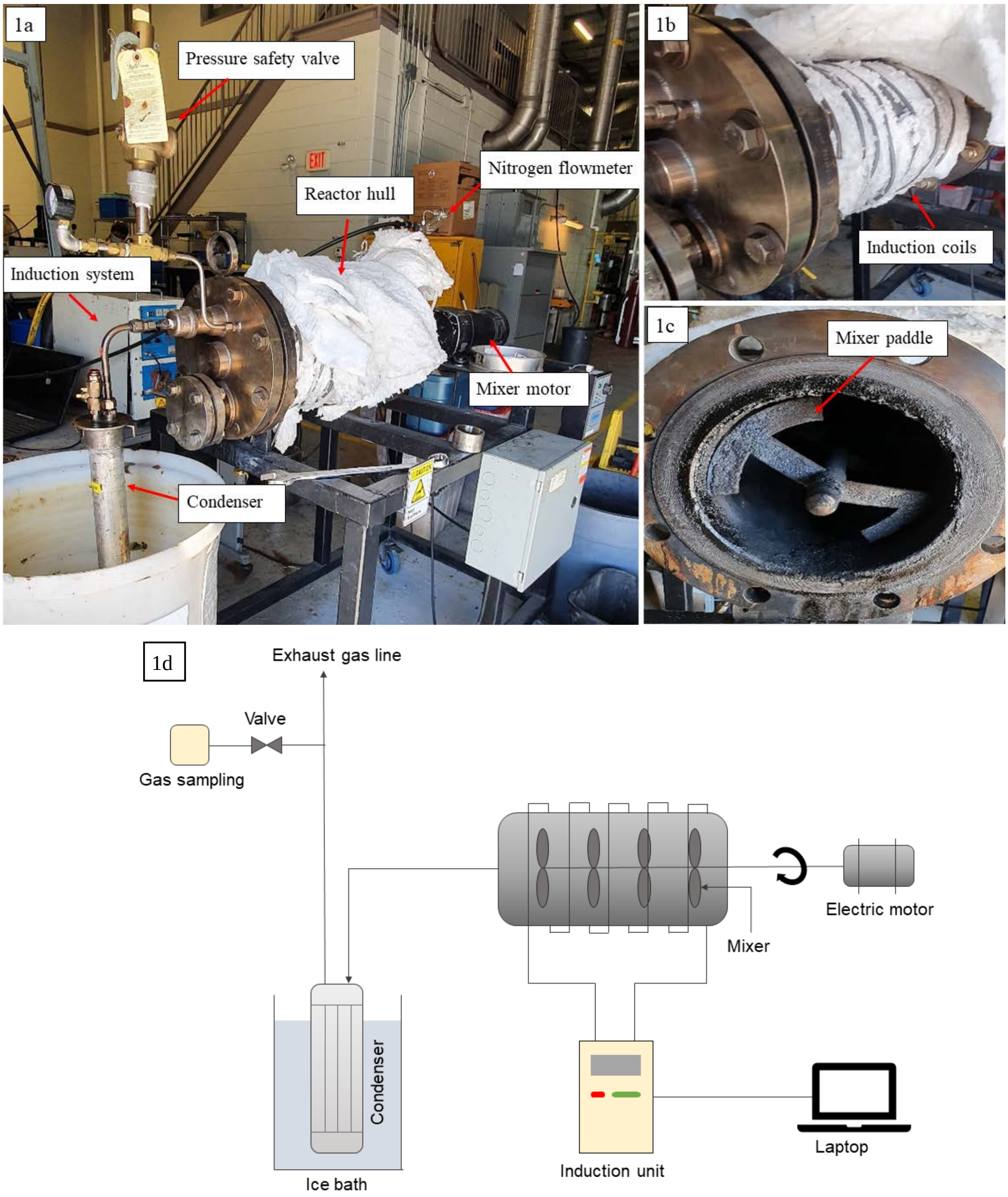

**Figure 1**. The horizontal mechanically fluidized batch reactor: 1a – reactor setup, 1b – induction coils wrapped around the reactor's hull, 1c – inside of the reactor with the mixing paddles, 1d – process flow diagram.

The operating conditions of each test were: 1 kg of rubber, 1 L min$^{-1}$ nitrogen flow, 30 rpm of the paddle mixer, and ambient pressure. In each test the heating rate, target temperature and holding time have been varied (Table 1) (each temperature target was maintained until no gas was produced). The first two runs have been performed at 500 °C, with a 25 °C min$^{-1}$ heating rate and 60 min of holding time at the target temperature. The third and fourth runs aimed at identifing the product evolution with increasing temperatures and to do so different temperatures have been investigated during the same run. The heating rate used was constant and set at 10°C min$^{-1}$, and the holding time for each plateau was defined by the termination of gas production. Specifically, the third run included 3 plateaus selected to investigate the gas and oil compositions at 300, 400, and 500°C. Each target temperature was maintained until little, or no gas was produced - e.g., 45 minutes at 300°C, 30 minutes at 400°C, and 50 minutes at 500°C. The fourth run focused on the product composition at 200, 300, and 400°C. During this last experiment, the time periods required to have no gas production were 15, 30, and 60 minutes, respectively.

**Table 2**. Operating conditions for the pyrolysis tests

| Test | Temperature (°C) | Heating Rate (°C min$^{-1}$) | Holding Time (min) |
|---|---|---|---|
| 1 | 500 | 25 | 60 |
| 2 | 500 | 25 | 60 |
| 3 | 300 | 10 | 45 |
| | 400 | | 30 |
| | 500 | | 50 |
| 4 | 200 | 10 | 15 |
| | 300 | | 30 |
| | 400 | | 60 |

## 2.3. Product analyses

### *2.3.1. Solid rubber feedstock and char product*

The elemental analysis of the rubber feedstock and solid char products of the pyrolysis tests was conducted using a Thermo Flash EA 1112 unit at 900°C in helium.

The proximate analysis (moisture, volatile matter, ash and fixed carbon) consisted of different heating/drying steps performed in sequence on 1 g samples (three replicates): 750°C for 10 min; 105°C for 2 hours; 950°C; and 750°C for 6 hours. After each step, the sample was weighted, and the proximate analysis parameters were calculated as following ASTM D7582-15. All the analysis are conducted in triplicates.

A bomb calorimeter (C200, IKA, Germany) was used to measure the higher heating value following ASTM D240-92. (HHV) A sample mass of 0.3-0.4 g is weighed in a plastic bag and placed inside a quartz crucible. The crucible holder is positioned inside the column, which contains 5 ml DI water, and it is pressurized to 30 bars by oxygen. The column is placed inside the bomb calorimeter filled with water. The instrument returns the HHV by unit mass of sample.

#### *2.3.2. Gas product*

For each test, samples of the non-condensable fraction were collected in gas-tight tedlar sampling bags from the exhaust gas line. A cotton filter was inserted into the line ahead of the sampling port to avoid any contamination of the sample. The gas samples were analyzed using a Micro Gas Chromatograph (Varian mobile CP-4900) equipped with a thermo-conductivity detector (TCD) with a column (Varian, CP-Sil 5 CB) containing a molecular sieve and a polar plot unit to identify hydrogen, methane, carbon monoxide, carbon dioxide, ethylene, ethane, propene, propane, butane, pentane, and hexane. The TCD used helium and argon as carrier gases at 80 psi. Each sample was analyzed in triplicates.

#### *2.3.3. Liquid product*

The primary components of the oil samples are identified using gas chromatography-mass spectrometry. Two milliliters of the solvent, 2-propanol (Caledon Laboratories, 99.5% purity), were used to dissolve a 50 mg sample of each collected oil. To eliminate particles, the samples are shaken for 30 minutes before being filtered three times through a 0.2-micrometer filter. The GC-MS system consists of a gas chromatograph (Agilent 7890A) coupled to a quadrupole mass spectrometer (GC-MS QP 2010, Shimadsu) using a capillary column (DB5MS, 30 m Å~ 0.25 mm i.d.; film thickness: 0.25 μm). Electron ionization (EI) is used with an ion source temperature of 200°C. To establish the identities of the chemicals in EI, the instrument is initially employed in SCAN mode. The split/splitless intake is part of the GC system. The temperature of the injector is 200°C. Injections of 1 liter at a rate of 10 liters per second is made using an AOC-20S autosampler and a 10-liter syringe. Helium (UHP), flowing at a steady rate of 1.5 mL min$^{-1}$, served as the carrier gas. The oven temperature program started at a temperature of 40°C and held it for 10 minutes before increasing the temperature by 10 °C min$^{-1}$ to 300 °C and holding it for 30 minutes, for a total run time of 75 minutes. This temperature program is chosen to offer sufficient separation for the majority of the target chemicals.

### 2.4. Techno-economic analysis

It is important to assess the economic feasibility of new waste treatment technologies and not only their technological practicality. For this reason this second part of this work presents a preliminary techno-economic assessment. By definition, a feasibility study or Class 4 is used to make coarse choices between design alternatives and has an accuracy of ±30% because it is an educated guess based on limited cost data and design detail [33]. The techno-economic analysis (Table 3) considered capital and operating costs, equipment depreciation, taxes, and the net present value (NPV). The total capital investment is composed of 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 with the factorial method; in particular, a Lang factor of 4 has been selected as the optimal for waste tires pyrolysis [34]. The working capital was estimated as percentage (15%) of the fixed costs [34]. Tire pyrolysis oil (TPO) price was defined based on crude oil price - i.e., 0.377 USD kg$^{-1}$ (60 USD /barrel) [35]. The gas price was calculated based on the three most abundant compounds, hydrogen, methane, and ethylene. At the time of the study, the list price of these products was 2 USD kg$^{-1}$ for hydrogen [36], [37], 1.01 USD kg$^{-1}$ for ethylene [38], and 0.077 USD kg$^{-1}$ for methane [39]. 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 in North America (Cabot Corporation) reported 0.066 USD kg$^{-1}$ as CB selling price.

To evaluate the production expenses, annual manufacturing costs and general expenses were considered. The raw material cost was assumed 0$, since wastes were considered. A more accurate techno-economic assessment should include a cost associated with the raw material, particularly if a centralized plant requires gathering and shipping it over certain distances as well as storage and handling costs. To assess labor costs the following assumptions were made: 8 hours shift; 3 shifts per day; average Canadian salary equal to 44,018 USD year$^{-1}$ [40]. The only utility considered was electricity, with a cost of 0.093 USD kWh$^{-1}$ [41]. The power consumption was estimated from the energy balance of the plant. Other voices accounted in the manufacturing cost have been computed as: maintenance and repair (5% of equipment cost) [34], operating supplies (15% of maintenance and repair) [42], laboratory charges (15% of operating labor) [42], taxes (13% for Canadian standards), overhead (50% of total operating labor and maintenance) [34]. General expenses included administrative costs (65% of operating labor), distribution and marketing expenses (5% of total product costs), research and development (1% of sales) [34]. Depreciation was evaluated over a period equal to the total life of the plant (20 years), assuming that the equipment is not going to be replaced during this time.

The annual net cash income was calculated as the sum of annual operating income (after taxes) plus depreciation. The techno-economic analysis was performed based on 6 different scenarios, as follows.

**Table 3.** Outline of the techno-economic analysis approach

| | | | |
|---|---|---|---|
| Fixed capital cost | USD | Lang Factor (=4)*ISBL | [34] |
| Working capital | USD | 15% of fixed capital | [34] |
| Total capital investment | USD | Fixed capital + Working capital | |
| Annual income sales | | | |
| Gas | USD/y | Product yield * selling price | |
| Oil | USD/y | Product yield * selling price | |
| Carbon black | USD/y | Product % * selling price | |
| Annual manufacturing cost | | | |
| Raw material | USD/y | | |
| Operating labor | USD/y | Number of workers * salary | |
| Utilities | USD/y | Factor of the heating source used | |
| Maintenance and repair | USD/y | 5% of ISBL | [34] |
| Operating supplies | USD/y | 15% of maintenance and repair | [42] |
| Laboratory charges | USD/y | 15% of operating labor | [42] |
| Taxes | USD/y | 13% for Canadian standards | |
| Plant overhead | USD/y | 65% of sales | [34] |
| Annual general expenses | | | |
| Administrative | USD/y | 65% of operating labor | [34] |
| Distribution and selling | USD/y | 5% of total manufacturing cost | [34] |

| | | | |
|---|---|---|---|
| Research and development | USD/y | 1% of sales | [34] |
| Annual total product cost | USD/y | Annual manufacturing cost + annual general expenses | |
| Annual operating income | USD/y | Annual income sales - annual total product cost | |
| Depreciation | USD/y | Straight line method and service life of 20 years | [34] |
| Income before tax | USD/y | Annual operating income - depreciation | |
| Income after tax | USD/y | Income before tax - taxes | |
| Annual net cash income | USD/y | Income after tax + depreciation | [42] |
| Discount factor on future cash flows | % | 5% | [42] |
| Total present value | MUSD | $\sum_{i=1}^{20} \frac{Annual\ cash\ flow_i}{(1+disocunt\ factor)^{year}}$ | |
| Annual present value | MUSD | Total present value – total capital investment | |

### 2.4.1. *Base scenario*

The base scenario was referred to the 0.72 kg $h^{-1}$ lab scale plant involved in the actual tests performed in our laboratory. The equipment cost was defined based on the actual price paid for the purchase of our laboratory scale plant. A total amount of 4.5 workers per day was assumed, considering 1 person per shift. 1.5 workers were considered in excess to cover vacation, sick days and overlapping. The final value of the equipment was accounted as 2,000 USD to compute the depreciation.

### 2.4.2. *Scale up*

In 2019, 126,370 tons of end-of-life tires were collected in Ontario of which 107,650 tons were recycled (85%) [43]. Accounting for a 3% of illegal dumping and system losses, 15,000 tons of waste tires were not recycled or valorized, and their value was lost. Therefore, the plant is scaled up to be able to treat 15,000 tons per year - e.g., 2.5 tons per hour, 24 hours per day, 7 days per week, and 240 days per year. The scale-up of the equipment cost was based on the 0.6 power law[34], as follows:

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

where:

$Cost_{equipment,a}$ is the cost of the equipment used for the base scenario,

S is the capacity of the equipment.

The letter ‘a’ refers to the base scenario plant (0.72 kg $h^{-1}$), and the letter ‘b’ relates to the scaled-up process.

The power factor of 0.6 has been found as the most common for the scale-up of chemical processes [42]. The total capital investment was calculated as detailed in section 2.4.

To study the influence of energy price and source and to identify the effect of gas composition changes on the economic feasibility of the project, six different scale-up scenarios were evaluated (Table 4):

Scenario 1, a simple scale-up of the base scenario;

Scenario 2, based on electric energy cost in Québec (0.043 USD $kWh^{-1}$);

Scenario 3, based on natural gas (instead of electricity) as heat source for the plant;

Scenario 4, based on the produced methane recycled as heat source;

Scenario 5, theoretical case based on gas products containing 80%-v hydrogen and 20%-v methane;

Scenario 6, theoretical case based on gas product containing 80%-v ethylene and 20%-v methane. The composition of the gaseous products considered in Scenarios 5 and 6 was based on a theoretical composition to highlight the sensitivity of the overall economic of the process to the gas composition and to define the potential route to follow in future research.

**Table 4**. Scheme of the different scenarios analyzed in the economic assessment

| Case | Processed material (kg $h^{-1}$) | Equipment cost | Gas composition | Methane recycle | Annual manufacturing cost | | |
|---|---|---|---|---|---|---|---|
| | | | | | Operating labor | Utility type | Utility cost |
| Base Scenario | 0.72 | Based on known data | As in experiments | No | 8 hours shifts<br>24 hours per day<br>7 days a week<br>4.5 workers per day | Electricity | 0.093 USD kWh [41] |
| Scenario 1 | 2500 | 0.6 power law | As given in scale up | No | 8 hours shifts<br>24 hours per day<br>7 days per week<br>9 workers per day | Electricity | 0.093 USD kWh [41] |
| Scenario 2 | | | | No | | Electricity | 0.043 USD kWh [41] |
| Scenario 3 | | | | No | | Natural gas | 2.75 USD $MMBtu^{-1}$ [44] |
| Scenario 4 | | | | Yes | | Natural gas if needed | |
| Scenario 5 | | | 80% hydrogen 20% methane | Yes | | Natural gas if needed | |
| Scenario 6 | | | 80% ethylene 20%methane | Yes | | Natural gas if needed | |

## 3. Results and discussion

### 3.1. Pyrolysis yields

The products obtained from the batch rubber pyrolysis were gas, oil, and char and their yields obtained in the four tests performed are illustrated in Figure 2. The char was brittle and black, and accounted for 47.75 to 59%-wt of the products. [21] reported char yields ranging between 40 and 48.67%-wt for pyrolysis performed in a mixed batch reactor. The gas product had an intense odor, and yields ranged between 24.5 and 31%-wt. The gas yields were higher than those reported in the literature for thermal pyrolysis [19], [45] and closer to the value reported for catalytic pyrolysis: 30% gas at 500°C with CaCO$_3$ catalyst [46], 34.4% at 600°C emplying kaolin [47], or 25% at 500°C with ZSM-5 [48]. The oil showed low viscosity and dark brown color, with yield ranging between 17 and 22.5%-wt. These values are comparable to literature rubber pyrolysis studies aimed at gas production [49]. The third run showed the maximum overall production of liquids (22.5%-wt). Comparing the oil production within different temperature intervals, waste tire pyrolysis between 300°C and 400°C generated the highest yield (15.05%-wt) during the fourth run (Figure 3). During the investigation of lower temperatures in run 4, almost no oil was produced at 200°C, meaning that the pyrolysis process had not yet started.

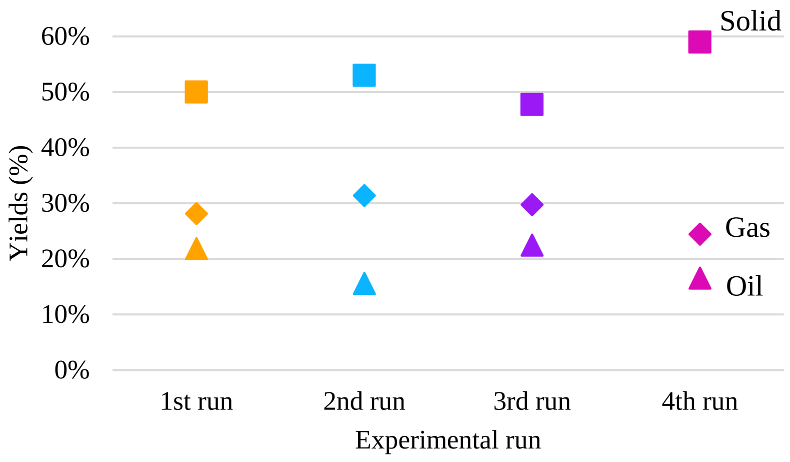

**Figure 2**. Yields of the performed pyrolysis tests: 1st run – 500 °C, 25 °C min$^{-1}$, 60 min; 2nd run - 500 °C, 25 °C min$^{-1}$, 60 min; 3rd run - 500 °C, 10 °C min$^{-1}$, 125 min; 4th run – 400 °C, 10 °C min$^{-1}$, 100 min.

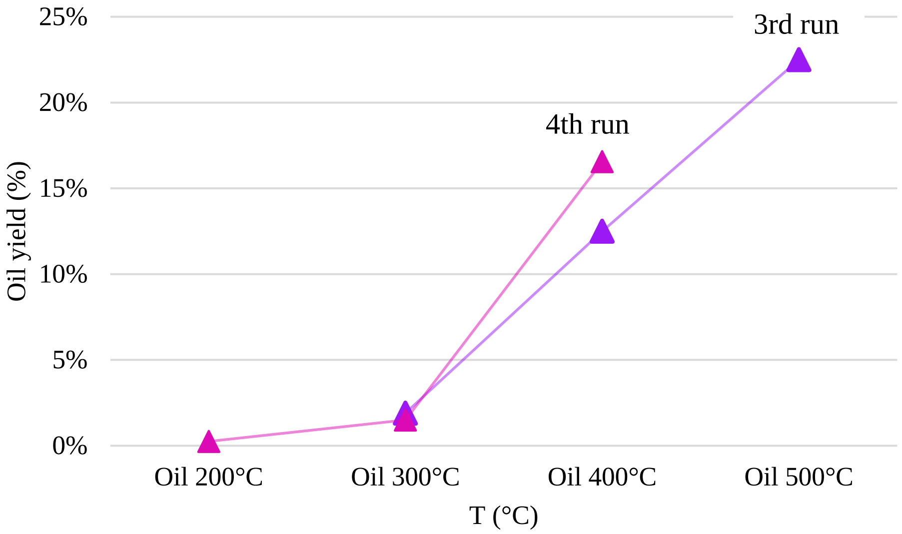

**Figure 3**. Cumulative oil yields obtained within different temperature intervals: 3rd run – 300, 400, 500 °C, 10 °C min$^{-1}$, 45, 30, 50 min; 4th run – 200, 300, 400 °C, 10 °C min$^{-1}$, 15, 30, 60 min.

### 3.2. Products characterization

Char is the main product of the process, and it can greatly influence the overall economic feasibility, depending on its end use. In this case, the proximate analysis' results (Table 5) showed 84.4%-wt fixed carbon, which is promising for a valorization of the product as carbon black substitute [50]. The HHV was 30.8 MJ kg$^{-1}$, comparable with bituminous coke (30.2 MJ kg$^{-1}$) [51].

**Table 5**. Rubber pyrolysis 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 |

The gas production was expected to be the most promising focus of this research. Some differences were identified between the tests at 500°C (Figure 4) due to the intrinsic differences between batches and the achievement of steady state conditions at different times. Despite this, in both experiments carried out at 500°C, the main constituents of the gas were hydrogen and methane, in particular the highest concentrations of hydrogen (59.13 %-v) and methane (36.04%-v) were obtained.

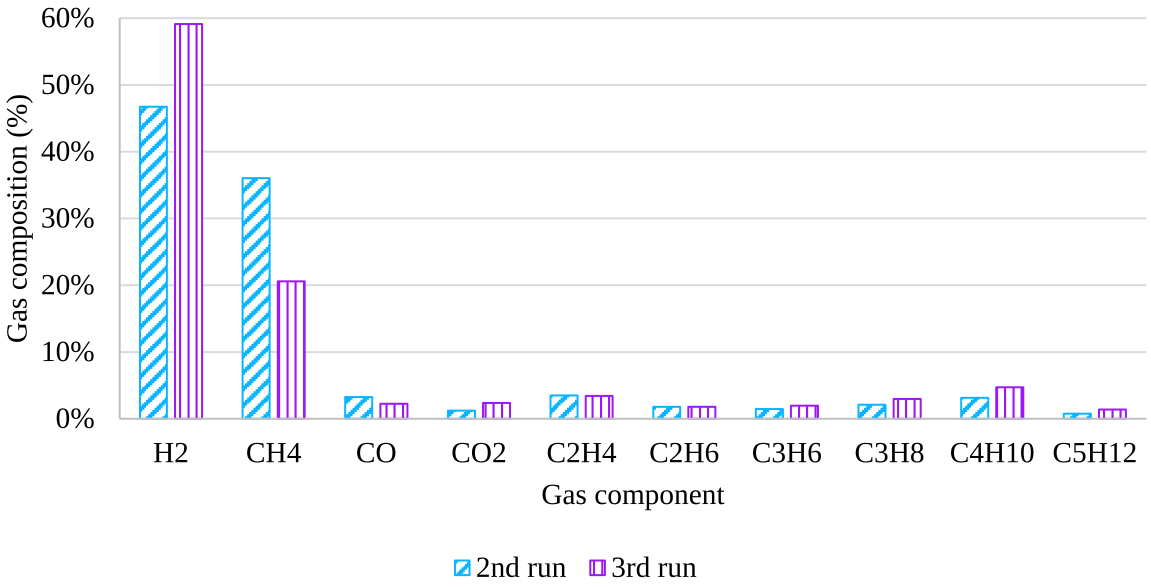

**Figure 4**. Rubber pyrolysis gas composition: 2nd run - 500 °C, 25 °C min$^{-1}$, 60 min; 3rd run - 500 °C, 10 °C min$^{-1}$, 125 min.

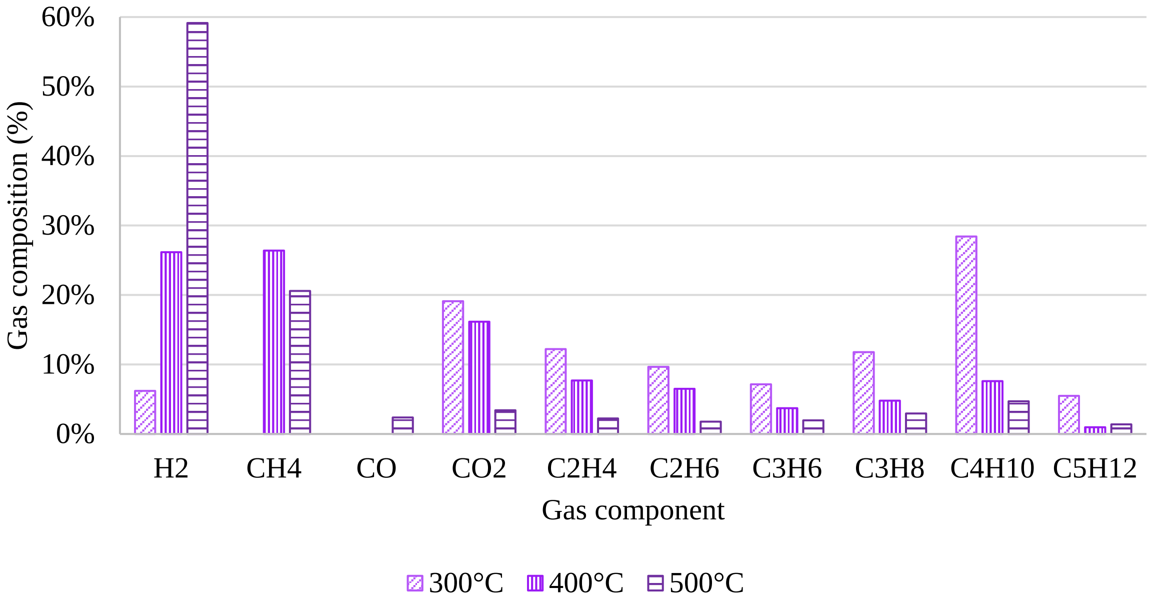

**Figure 5**. Rubber pyrolysis' gas composition at different temperatures: 3rd run - 300 °C, 10 °C min$^{-1}$, 15 min; 400 °C, 10 °C min$^{-1}$, 30 min; 500 °C, 10 °C min$^{-1}$, 50 min.

Gas evolution has been studied by sampling and characterizing the gas content at different temperatures (Figure 5). At 300°C the composition was 12.2%-v ethylene, 11.8%-v propane, and 28.4%-v butane. Increasing the temperature to 400°C lowered butane concentration to 20.8%-v, and hydrogen and methane increased to 26.17%-v and 26.40 %-v, respectively. The quality of non-condensable products depended on the temperature; higher values shifted the gas composition towards more stable compounds, as hydrogen and methane. Comparing the achieved results with literature, [52] reported concentrations of 35%-v hydrogen and 31%-v methane at 500°C in a fixed bed reactor. The higher concentrations obtained in this study can be attributed to better heat transfer to the material due to vigorous mixing. Also, the amount of each individual compound is affected by operating conditiosn and feedstock characteristics [2]. The oil characterization returned over 100 compounds, mostly with less than 14 C atoms, making the oil comparable to unrefined gasoline. At 300°C the oil was mainly composed of C10 compounds (benzene, D-limonene, cyclo-hexadiene, and cyclo-heptane); at 400°C of a mix of C7 to C10 hydrocarbons and benzene compounds; at 500°C was observed a decrease in C10 compounds' concentration and an increase of C7 compounds. The peak relative area (32.7%) registered by the GC-MS was for d-limonene at 300°C, at higher temperatures aromatization was promoted and resulted in indane and quinoline as peak compounds. It has been reported that the maximum d-limonene formation occurs at 380°C when a heating rate of 15°C min$^{-1}$ was applied [53]. Other studies reported 475°C and 20°C min$^{-1}$ as target temperature and heating rate, respectively, to achieve the maximum limonene yield of 7.62-14.14%-wt [26], [54]. The oil exhibited a HHV equal to 40.9 MJ kg$^{-1}$, in agreement with the literature [55], [56]. Increasing the temperature to 500°C led to better conversion of the feedstock and better quality of the products. All the products show interesting compositions and potential applications which make pyrolysis of rubber waste an attractive technology for the production of a variety of products. The possible use of the char as carbon black substitute increases the circularity of the process. The oil end use as fuel substitute is promising for geographic regions with low availability of fossil fuel resources. Based on the experimental results, the gas holds the most appealing end use for green hydrogen production.

### 3.3. Techno-economic assessment

The techno-economic assessment is based on the results of test 3 because it presented the best conversion, including the lowest char formation and the highest hydrogen concentration in the gas. As expected from a small-scale pilot plant, the economic analysis results showed a negative net cash income for the base scenario (1 kg $h^{-1}$), with a resulting NPV adverse throughout the operating life of the plant (20 years). On the other hand, the differences among the scaled-up scenarios (Figure 6) are related to the quantification of manufacturing costs. In particular, a decrease in the manufacturing cost is achieved as the price of electricity decreases by installing the plant in Quebec rather than in Ontario (Scenario 2), as electricity is replaced by natural gas (Scenario 3), and when methane is recycled into the system as process energy source (Scenario 4). Scenario 4 exhibits the highest annual net cash income (3.55 M USD $y^{-1}$). Scenario 5, based on methane recycling and hydrogen production, is the most remunerative (3.95 M USD $y^{-1}$), while Scenario 6 is the least profitable (1.54 M USD $y^{-1}$).

Scenario 1 presents a net profit at the end of the plant's lifetime equal to 11 M USD and the break-even point is reached after about 11 years; this is not advantageous from an industrial point of view, having too high initial investment risk. In Scenario 2 the reduction of energy cost improves the final net profit, and the payback period decreases to 8.5 years, but it is still not interesting for industrial implementation. Scenarios 3 and 4 show the same payback period (7.5 years), but the final remuneration of scenario 4 is greater because the manufacturing costs are lower. Scenario 5 is the most favorable from an economic point of view, with a payback period between 6 and 7 years, and a net profit at the plant's end of life of 28 M USD. The increase in the net profit in this case is due to the hypothesed increase in hydrogen concentration in the gas product. Scenario 6 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 that the plant cannot recover the initial investment.

The market analysis showed that the most interesting product is the gas, in particular its hydrogen content. It plays a major role in the overall profitability of the plant. The sensitivity analysis on the energy source emphasized the importance and the major role of energy price in the economic sustainability of the plant. By recycling some of the methane produced during the pyrolysis process into the system (scenario 4), we achieve an energetically selfsustained process which makes it interesting for industrial implementation. The most outstanding finding of the techno-economic analysis is related to the hydrogen. Due to its high market value in today's economic if we achieve a hydrogen content of 80% in the gas, the economics became even more favorable (payback period of 6.5 years) for actual implementation of rubber waste pyrolysis plants.

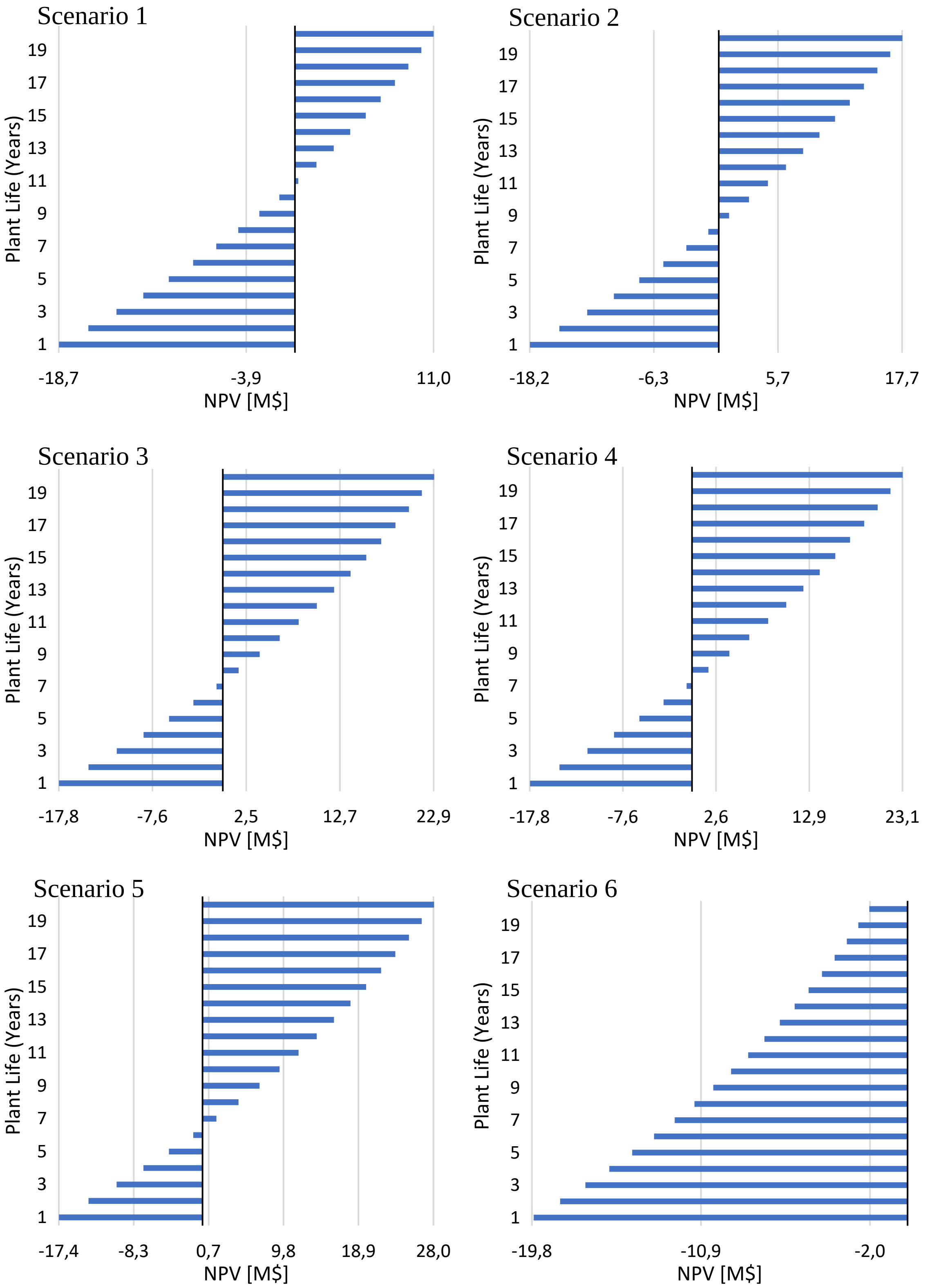

**Figure 6**. Net present value (NPV) over the plant service life (20 years) of the scaled-up pyrolysis process for Scenario 1 – simple scale-up implemented in Ontario, Scenario 2 – Québec electric energy cost, Scenario 3 – natural gas as a heat source, Scenario 4 – methane recycling, Scenario 5 – hydrogen production, Scenario 6 – ethylene production.

## 4. Conclusions

The pyrolysis of waste rubber was experimentally investigated in a lab scale batch mechanically fluidized reactor under different process conditions. The results of the tests showed that increasing the pyrolysis temperature created a double effect: the oil composition shifted to “gasoline-like” lightweight hydrocarbons, and the gas showed higher concentrations of methane due to enhanced cracking. Hydrogen presence in the gaseous products was crucial to reach the economical sustainability of the process due to the high market value of green hydrogen (2 USD kg$^{-1}$). For any of 6 different potential operating scenarios of a scaled-up plant with a capacity of 2.5 tons per hour, rubber pyrolysis required 7-8 years to become profitable. Considering the composition of the different gaseous products (and the different scenarios of the techno-economic analysis), when ethylene production was involved, the pyrolysis plant was not profitable over a work-life of 20 years. Hydrogen valorization led to the most advantageous scenario, exhibiting a payback period equal to 6-7 years. In conclusion, hydrogen production from slow pyrolysis of waste tires is promising for industrial application since it applies mild temperatures, virtually no emissions are produced, and it is profitable over 20 years. Further experiments are required to optimize the operating conditions at the lab scale to achieve 80% hydrogen in the gas product. Moreover, experiments at bigger scales need to be performed.

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