Experimental Study on Two-Step Pyrolysis of Automotive Shredder Residue

Letizia Marchetti, Federica Annunzi, Federico Fiorini, Cristiano Nicolella

Abstract—Automotive shredder residue (ASR) is a mixture of waste that makes up 20-25% of end-of-life vehicles. For many years, ASR was commonly disposed of in landfills or incinerated, causing serious environmental problems. Nowadays, thermochemical treatments are a promising alternative, although the heterogeneity of ASR still poses some challenges. One of the emerging thermochemical treatments for ASR is pyrolysis, which promotes the decomposition of long polymeric chains by providing heat in the absence of an oxidizing agent. In this way, pyrolysis promotes the conversion of ASR into solid, liquid, and gaseous phases. This work aims to improve the performance of a two-step pyrolysis process. After the characterization of the analysed ASR, the focus is on determining the effects of residence time on product yields and gas composition. A batch experimental setup that reproduces the entire process was used. The setup consists of three sections: the pyrolysis section (made of two reactors), the separation section, and the analysis section. Two different residence times were investigated to find suitable conditions for the first sample of ASR. These first tests showed that the products obtained were more sensitive to residence time in the second reactor. Indeed, slightly increasing residence time in the second reactor managed to raise the yield of gas and carbon residue and decrease the yield of liquid fraction. Then, to test the versatility of the setup, the same conditions were applied to a different sample of ASR coming from a different chemical plant. The comparison between the two ASR samples shows that similar product yields and compositions are obtained using the same setup.

Keywords—Automotive shredder residue, experimental tests, heterogeneity, product yields, two-step pyrolysis.

I. INTRODUCTION

THE global growth of waste production poses significant challenges to both waste management and environmental sustainability. Among other kinds of wastes, the ASR is a heterogeneous material derived from end-of-life vehicles (ELVs) [1], [2]. ELVs are made up of ASR fraction (25%) and metal fraction (85%), this second one is easy to recycle. Instead, ASRs have been for many years mainly disposed of in landfill or incinerated [3], causing serious environmental problems in terms of emissions. The European Union has answered this problem with the European Directive 2000/53/CE, with which it established a minimum threshold value of ELVs recycle. This intervention by the European Union has led to an increasing attention to thermochemical treatments including pyrolysis. Despite this, the problem of GHG emissions has not been completely solved and this has led to the 2009 Renewable Energy Directive (RED), refused in 2018 (REDII). The REDII introduced two new fuels considered as renewable fuels: renewable fuels of non-biological origin (RFNBOs) and recycled carbon fuels (RCFs). Recycled carbon fuels are gas and liquid produced from solid or liquid wastes. However, to be considered an RCF, a fuel must provide for saving in emissions above a certain threshold value. The methodology for calculating the saving and the threshold value is both provided in the 2022 delegated acts. If a fuel is classified as RCF, it can therefore benefit from economic incentives. In this way, the European Union is pushing the treatment of this waste, counteracting its disposal in landfills. All this has led to a growing interest in pyrolysis.

Pyrolysis is a thermochemical treatment that takes place in the absence of an oxidizing agent [4]. High temperatures lead to a breaking of the bonds that make up the long polymer chains achieving the generation of molecules with simpler chains. By subjecting the plastic waste material to the pyrolysis process, it is possible to obtain a liquid, a gas and a solid product. The first two products may be used as fuels. The solid product is composed of char and inert fraction, and it can be subjected to further treatments, such as gasification, a largely studied treatment [5]. In general, pyrolysis products depend on many factors, including fed material, temperature [6], residence time [7], pressure [8] and other operative conditions.

Focusing on industries that generate small amounts of waste may be inconvenient to focus on producing the liquid fraction (pyrolysis oil). Indeed, the oil produced would require expensive and complex refining treatments. Rather, it might be convenient to invest in electricity production feeding the pyrolysis gas in an internal combustion engine (ICE) [9].

Therefore, this study contributes to the development of a two-step pyrolysis process of ASR mainly aimed at gas production. Following the characterization of the tested ASR, experimental tests were carried out with different setup configurations to investigate the effect of the residence time on product yields and quality. The configuration that maximizes the gas yield has been set as the optimal configuration. A second sample of ASR from another plant was tested with the optimal configuration to verify the versatility of the setup used, despite the strong heterogeneity that distinguishes the ASR.

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II. MATERIALS AND METHODS

A. Automotive Shredder Residue

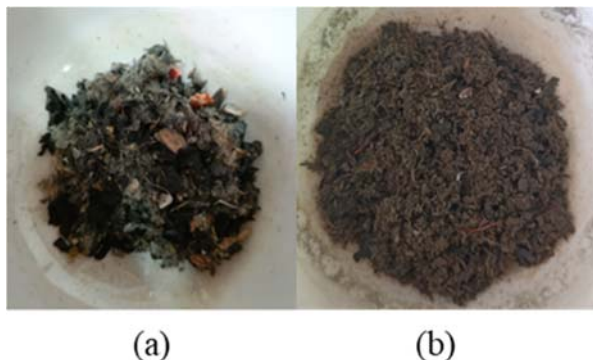Two samples of ASRs supplied by different industries were tested in experimental setup (Fig. 1).

Fig. 1 Pictures of sample 1 (a) and sample 2 (b) of tested ASRs

The two samples were characterized with thermogravimetric analysis (TGA) in order to estimate the mass fraction of inert components. The analysis was carried out in nitrogen (50 mL/min), heated from 25 ºC to 800 ºC (heating rate of 10 ºC/min). The LECO TruSpec CHN analyser and the Elementar Vario Macro CHNS analyser were used for the elemental analysis. The high heating value (HHV) and low heating value (LHV) were calculated using (1) and (2) respectively.

$$HHV = 2.326[146.58C + 568.78H + 29.4S - 6.58A(O + N)] \quad (1)$$

$$LHV = (HHV - 206H) \quad (2)$$

where H, C, N, S, A and O represent the mole percentages of hydrogen, carbon, nitrogen, sulphur, ash and oxygen, respectively. H, C and N were obtained with elemental analysis; S was procured with composition analysis, supplied by the industry; A was determined by burning the sample for 3 h at 600 °C; and O was consequently evaluated as the quantity necessary to achieve 100% of mole percentage of ASR.

B. Experimental Setup

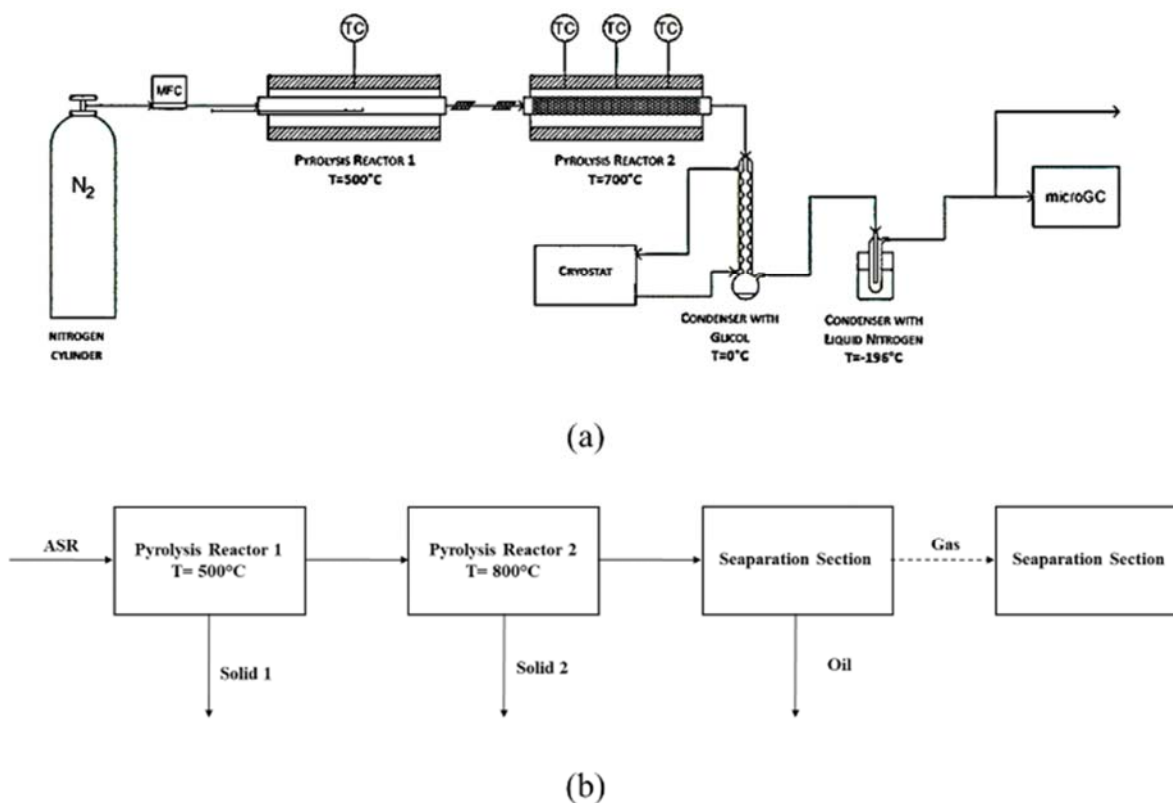The experimental tests were caried out using the batch setup shown in Fig. 2.

Fig. 2 Experimental setup diagram (a) and simplified block scheme (b)

This setup was constituted of three sections: the reaction section, the separation section, and the analysis section. The first one was composed of two reactors in which pyrolysis and homogeneous cracking occurred respectively. In the first reactor solid, vapor and gas phase were produced. The solid phase remained trapped in the first reactor (solid 1); the other two phases left the first reactor to reach the second. In the second reactor, the vapor fraction chains were further broken, generating more gas production and the formation of solid carbonaceous residue (solid 2). The vapor and gas products were fed to the second section of the setup: the separation section. In the separation section, the condensation process was used, which allowed the separation of the liquid phase from the gas. In the third section the products were characterized.

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The reaction section was in detail made of:

- Two inner tubes made of Hastelloy steel with a diameter of 30 mm, one of which with a feeding basket (tube 1) and the other one without it (tube 2).
- One tubular electric furnace model Carbolite TZF 12/65/550 with a length of 650 mm and temperature control in three points of the furnace (furnace 1).
- One tubular electric furnace model Carbolite MTF 12/38/250 with a length of 200 mm and temperature control in the central point of the furnace (furnace 2).

The two furnaces had a maximum temperature of 1200°C. The temperature is measured by J type thermocouples and regulated using PID controllers.

Two different configurations were used for the sample 1 of ASR. In the first configuration, tube 1 was inserted in furnace 1 (constituting reactor 1), and tube 2 was inserted in furnace 2 (constituting reactor 2). Moreover, reactor 1 was positioned before rector 2, and steel balls (AISI 304) with a diameter of 3.2 mm were inserted inside the second reactor; with a measured void fraction of 0.34. In the second configuration, tube 1 was inserted in furnace 2 (constituting reactor 1), and tube 2 was inserted in furnace 1 (constituting reactor 2). Reactor 1 was still positioned before rector 2 and steel balls (AISI 304) with a diameter of 3.2 mm were still inserted in the second reactor. The void fraction was equal to 0.34. Table I summarizes the size of the reactors in the two configurations.

TABLE I
DIMENSIONS OF THE TWO REACTORS IN THE TWO TESTED CONFIGURATIONS

	Configuration #1		Configuration #2	
	Reactor 1	Reactor 2	Reactor 1	Reactor 2
Diameter (mm)	30	30	30	30
Length (mm)	650	200	200	650
Volume (L)	0.46	0.14	0.14	0.46
Void fraction	1	0.34	1	0.34

The reaction environment had to be inert. Therefore, nitrogen gas was fed (300 ml/min) using a flow regulator (MFC, Mass Flow Controller). During the tests, the two reactors worked at 500 °C and 800 °C respectively. Once the furnaces had reached the desired temperature, about 5 g of ASR sample were fed into the midpoint of the first reactor, by using a feeding basket, and the material was pyrolyzed for 30 min. The second configuration was equipped with a reactor 2 bigger than that in the first configuration, and this entails a higher residence time of pyrolysis products at 800 °C. The experimental tests on sample 2 were carried out only with the second configuration.

To separate the condensable phase from the gas, condensers were used. The two cold utilities were ethylene glycol at 0 °C and liquid nitrogen at -196 °C respectively. The operative conditions are summarized in Table II.

TABLE II
SUMMARY OF THE OPERATING CONDITIONS OF THE EXPERIMENTAL SETUP

	Reactor 1	Reactor 2	Condenser 1	Condenser 2
Temperature [°C]	500	800	0	-196
Pressure [bar]	2	2	2	2

The mass of liquid and solid (solid 1 and solid 2) fractions was evaluated by weighing the quantities collected at the end of each test. The mass and composition of gas fraction were determined by using a microGC (Agilent 990) located downstream of the two condensers in the product analysis section.

The described tests were carried out three times for each configuration and sample, and the mass of products was evaluated as an average of all collected value obtained with the same conditions. Once the tests were completed, it was possible to calculate the percentage yields of each product (Y_i) as the ratio between the mass of the product (M_i) and the mass of ASR fed to the setup (M_f) multiplied percent.

$$Y_i = \frac{M_i}{M_f} * 100 \tag{3}$$

The LHV of Gas fraction was determined, knowing its composition and the LHV of each component. Moreover, an energy efficiency of the process (η_P), defined as the ratio between the produced gas energy and the tested ASR energy was evaluated with (4):

$$\eta_P = \frac{Mf * LHVf}{Mg * LHVg} * 100 \tag{4}$$

where the numerator was composed of the product between the mass of ASR fed to the setup (M_f) and its low heating value (LHV_f), otherwise the denominator was the product between the mass of produced gas (M_g) and its low heating value (LHV_g).

III. RESULTS AND DISCUSSION
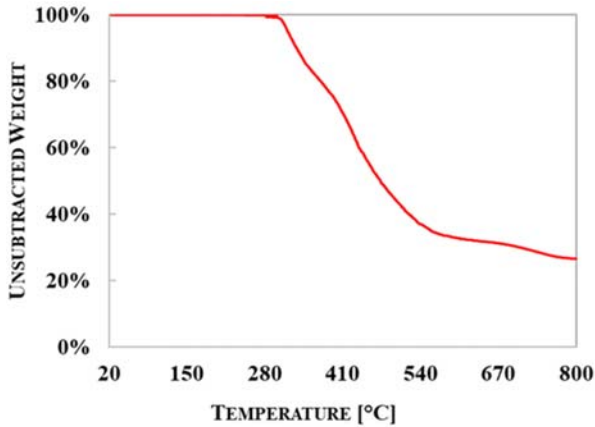
A. ASR Samples Characterization

This part summarizes the main results obtained from the characterization of the two samples of ASR. The TGA was carried out three times for each sample. Fig. 3 shows a comparison between the TGA results for the two ASR samples.

From the comparison between the two TGA results emerged that sample 1 and sample 2 had a solid inert mass fraction of 32 wt% and 44 wt% respectively. Moreover, in Fig. 3 (b) a mass loss between 0 °C and 100 °C underlined that the sample 2 was wet, unlike the sample 1. Both the samples had the major mass loss in correspondence of 500 °C, corresponding to the temperature at which the reactor 1 was set in each experimental test. These results are similar to that obtained in literature [10].
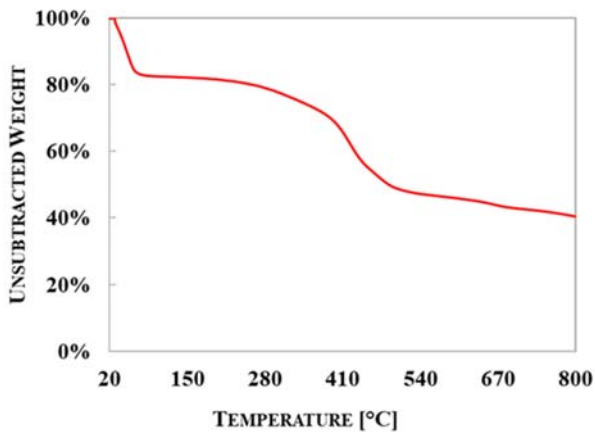
The elemental analysis and the evaluation of LHV made on sample 1 and sample 2 led to the average values collected in the first two columns of Table III, instead the last column displays the value discovered in the literature [11].

B. The Effects of the Residence Time

The effect of residence time on the products yields and gas composition was evaluated testing the sample 1 with the configuration 1 and configuration 2 of the batch setup. The results were collected in Fig. 4.

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TABLE III
CHN ANALYSIS RESULTS

	Concentration [wt%]		
	Sample 1	Sample 2	Literature
Carbon	53.0	47.5	37.2-58.9
Nitrogen	6.0	6.0	4.67-7.48
Hydrogen	1.0	1.5	1.2-1.9
Sulfur	0.6	0.6	0.2-0.9
Oxygen	14.6	8.3	1.5-21.9
HHV	24.0	22.5	17.4-28.1
LHV	22.7	21.3	19.9

Loss is the mass needed to reach 100%. The value of loss was about 12 wt% and 11 wt% for the two configurations, this can be mainly due to two factors: underestimation of the gas phase produced and underestimation of the liquid phase.

With a comparison between the two configurations, it was evaluated the effect of the variation in the residence times on the products. Although passing from the first to the second configuration the residence time in the first reactor decreased a lot, the gas yield increased whereas that of liquid decreased. This result led to the conclusion that the products obtained were more sensitive to residence time in the second reactor (800 °C) than in the first (500 °C). Moreover, the yield of solid in the second reactor (solid 2) was increased with the arise of the residence time in reactor 2, as the chains of vapor phase tend to break up more strongly giving rise to gas and carbon residue.

The two configurations influenced not only the mass of the products but also their compositions. By paying special attention to the gas, the results shown in Fig. 5 were obtained.

The volume content of more volatile substances, as CH_4 and C_2H_2, increased passing from configuration 1 to configuration 2, i.e., increasing the residence time in the second reactor at 800 °C. Indeed, by spending more time at higher temperatures, the chains break further giving rise to more volatile components. Moreover, the lower heating value (LHV) went from 38.3 MJ/kg to 38.5 MJ/kg.
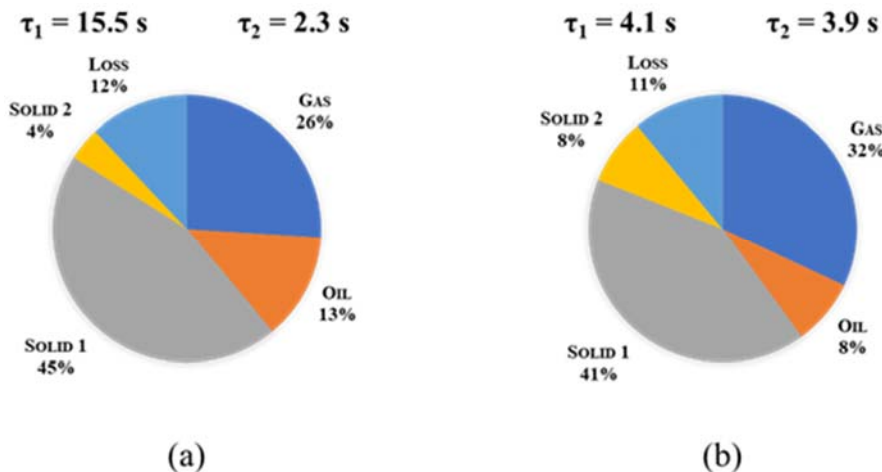
Fig. 3 Comparison between thermogravimetric analysis results of ASR sample 1 (a) and sample 2 (b)

Fig. 4 Comparison between the yields in wt % of products obtained for different residence times in reactor 1 (τ1) and reactor 2 (τ2)
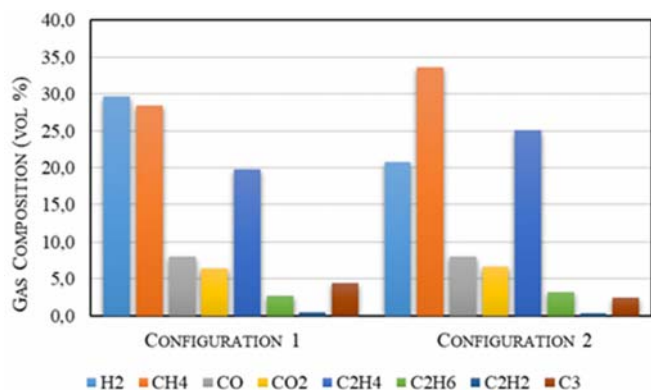
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Fig. 5 Comparison between gas composition obtained by testing the sample 1 with the two configurations

The energy efficiency of the process (η_P), defined as the ratio between the produced gas energy and the tested ASR energy (4), was equal to 43.9% and 54.2% for configuration 1 and configuration 2, respectively.

A. Comparison between Different Samples of ASR

Given the higher efficiency gained with the second configuration, the sample 2 was tested with that one in order to verify the versatility of the studied setup. The yields and the gas composition obtained by testing this second sample of ASR were collected in Fig. 6.

With this type of ASR, the loss fraction was minor. The value of products yields was similar for the two different samples as well as the gas composition. The value of gas PCI was equal to 31.2 MJ/kg and the efficiency of the process was 45.4%.
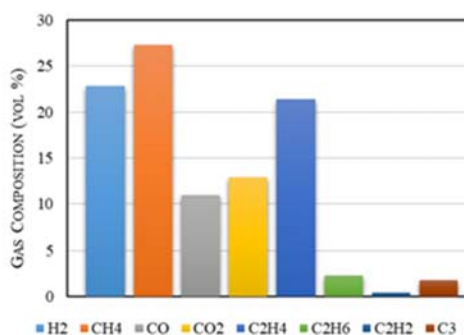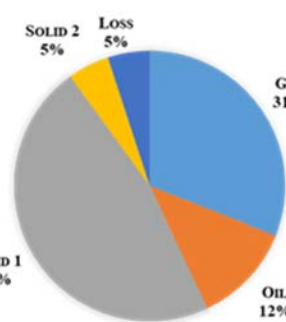

(a)

(b)

Fig. 6 Yields and gas composition obtained by testing the sample 2 with configuration 2

IV. CONCLUSION

The present work has investigated the two-step pyrolysis process applied to ASR. The experimental setup made it possible to reproduce on a small scale the two main sections of the process: the reaction section and the separation section. By performing tests under equal operating conditions but varying the size of the two reactors, gas, liquid and solid yields and the composition of the gas produced have been studied. The results showed that the residence time of the second reactor strongly affects not only the yields of the products but also their compositions. More specifically, an increase in gas yield and a reduction in liquid yield were observed as the residence time increased. The composition of the gas produced achieved more volatile fraction for longer residence times. These results allowed us to confirm what could have been expected, namely that increasing the time spent at 800 °C the chains undergo further fragmentation, leading to the production of more volatile substances and that the residence time in second reactor. The yields of the individual fractions produced are much more influenced by the residence time in the second reactor than by that in the first. In conclusion, despite the heterogeneity of the ASR, setting the operating conditions, the setup led to similar results in the case of different ASR.

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