## Scaling-up of waste tyre pyrolysis process from TRL-5 up to TRL-7 using an auger reactor technology

Alberto Veses<sup>1</sup>, Alberto Sanchís<sup>1</sup>, Juan Daniel Martínez<sup>1</sup>, José Manuel López<sup>1</sup>, Tomás García<sup>1</sup>, Ramón Murillo<sup>1</sup>

<sup>1</sup>Instituto de Carboquímica (ICB-CSIC), C/ Miguel Luesma Castán 4, 50018 Zaragoza, Spain

Presenting author email: ramon.murillo@csic.es

Waste tyres (WTs) are a great source of valuable products. These valuable products can be recovered in a simple way from pyrolysis process. After this process an oil fraction (Tyre pyrolysis oil - TPO), a solid fraction (raw recovered carbon black - raw rCB-) and a gas fraction (Tyre pyrolysis gas - TPG) are produced. In consequence, the economy of the process depends on the quality of these products. The TPO can be used as fuel or be further used as a source of valuable chemicals such as aromatics or limonene. rCB is also a potential product to be used as carbon black, catalyst or activated carbon. Finally, because of its high heating value, TPG can be used to support the energy requirements of the process, since pyrolysis is an endothermic process. This strategy has been studied during years worldwide, specially at laboratory scale. Unfortunately, at higher scales, only limited studied are found in the literature and it should be also stated that only several viable plants at industrial lever are currently implemented. Thus, since the global market of these products is expected to grow up to great levels in next years, the development of the process at industrial levels is of vital importance.

In addition, in order to increase the market opportunities, the optimization of waste tyre pyrolysis processes is crucial. In this step, a reliable scale-up plays the key role. Unfortunately, there is no manuscripts in the literature focused in the scale-up of this process at higher levels. Thus, based in this premise, this manuscript describes the main differences between the properties of the pyrolytic products obtained in a TRL5 pilot plant based on auger technology and the properties of the pyrolytic crude oil obtained in a TRL7 plant under comparable operational conditions. The pilot plant that was used to perform the experiments is located in the Instituto de Carboquímica labs, in Zaragoza, Spain. It is an auger type reactor able to process up to 15 kg/h of shredded rubber. The outer part of the reactor is surrounded with 3 independent electrical resistances that provide the energy for the pyrolysis process. The TRL-7 plant is located at the *Parque Tecnológico de Reciclado* in Zaragoza, Spain. It should be commented that the design and construction of this plant is based in the one at TRL-5 described before. This plant is dimensioned for the pyrolysis of WTs at rates up to of 800 kg/h. The heating system of the auger reactor is carried out the combustion of the pyrolytic gas through an external chamber (countercurrent gas burner), supported by an auxiliary liquefied petroleum gas (LPG) burner.

For the experimental campaign, the operating conditions used in the pyrolysis process at TRL5 tried to mimic the expected ones in the TRL7 plant. Therefore, a tailored temperature profile was used (450 °C, 550 °C and 775 °C) and a short residence time for gases (around 30-40 s) and solid (7 min) was imposed. The raw material used in the pyrolysis was granulated rubber with a particle size comprised between 1 mm and 4 mm coming from truck tyres. The TPO produced during the experiments was collected, filtered and analyzed. The sample was analyzed by gas chromatography (simulated distillation and aromatics and limonene content determination), ultimate composition and several physicochemical properties. rCB was also characterized as well as TPG composition.

Properties	TRL-5 TPO	TRL-7 TPO
C (wt.%)	87.9	87.5
H (wt.%)	10.4	11.3
N (wt.%)	1.5	0.6
S (wt.%)	0.77	0.96
C/H	0.7	0.6
Heating Value [MJ/kg]	42.3	41.5
рН	6.9	7.3
TAN (mg KOH/ g Sample)	6.2	5.4
Density (kg/m <sup>3</sup> )	975.7	960.0
Viscosity (mPa.s)	7.0	5.6

Table 1. Comparison between the properties of both TRL-5 and TRL-7 Auger facilities.

Under these conditions, the following yields were obtained in the TRL-5 plant: 42.9 wt% for raw rCB, 45.8 wt% for TPO and 11.3 wt% for non-condensable gas. Table 1 shows the main properties of the TPOs obtained in the different pyrolysis plants. It should be pointed out that, apparently, similar results were obtained. For both samples, it is observed a similar high carbon content (87.5 - 87.9 wt%). Regarding the sulphur content, it was found also in the same range as the tyre-derived liquids obtained (0.77 - 0.96 wt%). Regarding density, viscosity, pH and TAN, minimum differences can be also observed between both TPOs. These values are also in line with the bibliography (density values between 960.0 and 975.7 kg/m3, viscosity values between 5.6 and 7.0 mPa.s, pH values between 6.9 -7.3 and TAN between 5-7 mgKOH/g sample).

Mass %	TRL-5 TPO	TRL-7 TPO
Benzene	1.70	1.54
Toluene	3.00	4.21
Ethylbenzene	0.54	0.69
(p+m)-Xylene	2.55	3.69
o-Xylene	0.46	1.16
Limonene	6.25	4.15

Table 2. Chromatographic analysis of TPO and HF and LF from real distillation at 235 0C.

Table 2 shows the concentration of benzene, toluene, ethylbenzene, xylenes and limonene for the TPOs samples. It was observed that, although some differences can be observed between both liquids, a remarkable limonene concentration was observed (6.25 wt% for TRL-5 TPO sample and 4.15 wt% for TRL-7 TPO sample). This component together with toluene and xylenes are the main identified components of both TPOs.

From the results found in this report, it has been proved the robust technology of auger reactors in the scalingup of waste tyre pyrolysis. Thus, although there are some differences that could be attached to specific operational parameters, this study shows that similar properties and composition of the products can be obtained. Thus, the main components found in the TPO were limonene and aromatics such as benzene, toluene, ethylbenzene and Xylenes, whilst  $CH_4$  and  $H_2$  were the main components of the TPG.

## Acknowledgements

This work is part of the BLACKCYCLE project (For the circular economy of tyre domain: recycling end of life tyres into secondary raw materials or tyres and other product applications) which has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 869625. The authors would also like to thank the Regional Government of Aragon (DGA) for the support provided under the research groups support programme and CSIC for the interdisciplinary thematic platform SUSPLAST.

## References

Martínez, J.D., Puy, N., Murillo, R., García, T., Navarro, M.V., Mastral, A.M., 2013c. Waste tyre pyrolysis – A review. Renewable and Sustainable Energy Reviews 23, 179–213. <u>https://doi.org/10.1016/j.rser.2013.02.038</u>.

Williams, P.T., 2013. Pyrolysis of waste tyres: A review. Waste Management 33, 1714–1728. https://doi.org/10.1016/j.wasman.2013.05.003.