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Pyrolysis of automotive shredder residue light fraction: maximization of the tar yield using design of experiment

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Abstract. The general aim of this study is the valorisation of Automotive Shredder Residue (ASR) via pyrolysis. Tar, the condensable gases obtained in the pyrolysis process, is an interesting alternative fuel. Thus, the pyrolysis process was investigated in order to maximize the tar yield. The design of experiment approach was used to plan a series of experiments and to identify which operating variables influence the yield of the process. Temperature and carrier gas flow proved to be significant factors affecting the yield, while the influence of ASR light fraction amount pyrolysed was negligible. In the experimental domain, the maximum response was obtained at 500 °C and 100 mL/min.

1. Introduction

Vehicles at the end of their useful life become end-of-life-vehicles (ELVs), a waste. In 2012, Europe (EU 27) produced 6.2 million tons of ELVs [1]. European directives promote the reuse, recycling and recovery of ELVs. During dismantling, ferrous and non-ferrous metals are removed and recovered in secondary smelter plants. Such large-scale thermal processes can be the source of micropollutants [2, 3], giving rise to public concern about their possible health effects. Automotive shredder residue (ASR) is the remainder which is obtained from the ELVs dismantling process. It accounts approximately for 15 wt. % of the total ELVs and is mainly composed (90%) of a light fraction, also called car fluff. Car fluff usually presents heterogeneous composition: plastics (9-35%), rubber (4-12%), textile (8-40%), wood and paper (1-4%), metals (3-8%), wire (1-5%), foam (4-35%) and fines (up to 75%) [2] With a great amount of polymeric materials. On the basis of this composition, pyrolysis can be regarded as a suitable thermal pre-treatment for car fluff [3].

Several studies reported the pyrolysis as a suitable process for reducing the waste stream, obtaining valuable products: gas, i.e. the non-condensable gases; char, i.e. the solid phase; and tar, i.e. the condensable gases [4, 5, and 6]. Some Authors studied the pyrolysis process of ASR [7, 8], producing tar characterized by a high calorific value, 37-40 MJ/kg [9, 10, 11]. On this basis, the use of car fluff-tar as a fuel seems an interesting alternative [11]. Thus, in the present paper, the pyrolysis process was investigated in order to maximize the tar yield.

The use of design of experiment (DOE) allows to get a clear picture of how the process variables, separately and together, affect the experimental responses and how it is possible to control them in order to make the process more effective [12]. This statistical approach was applied in many different areas. For instance Kazemi et al. [13] adopted DOE to investigate the effects of multiple factors and their interactions on the composting performance of municipal solid waste; Mangili et al. [14]

employed DOE to investigate the supercritical CO_2 devulcanization process of ground tire rubber; Kumar and Leech [15] reported a design of experiment methodology to investigate and improve the performance of glucose oxidizing enzyme electrodes. In particular, only few papers [16, 17, 18] applied this statistical approach to the pyrolysis process of waste in order to optimize the experimental conditions maximizing the products yield.

In the present paper, the DOE approach was used to investigate the pyrolysis of the ASR light fraction in a bench scale reactor. We considered the process variables temperature, carrier gas flow and ASR light fraction amount, whereas the tar yield was the response. The process variables were optimized with the aim of maximizing the response.

2. Materials and methods

2.1. ASR sample

ASR light fraction sample (hereafter named car fluff) was collected at a shredder plant in Italy. The sample underwent a quartering procedure and a thorough characterization. Results for elemental and material composition, proximate analysis, and higher heating value were previously reported [19].

2.2. Pyrolysis experiments

Pyrolysis experiments were carried out in a horizontal fixed bed tubular reactor under nitrogen flow (N_2). The tar was collected downstream the oven reactor and weighed. Details about the pyrolysis apparatus and the experimental procedure were described in a previous paper [11].

The tar yield was calculated as the weight percentage with respect to the amount of car fluff pyrolysed.

2.3. Design of Experiment

In order to obtain the maximization of tar yield, a two level full factorial experimental design (FF-ED) [12] was applied. Temperature, N_2 flow and car fluff amount were chosen as process variables or factors and the tar yield was chosen as response.

Table 1 shows maximum (coded as +1), minimum (coded as −1) and central (coded as 0) levels for each factor applied to FF-ED.

Table 1. Factors and levels of the FF-ED.

Factor	Minimum level -1	Maximum level +1	Central level 0
Temperature (T), °C	500	800	650
Flow (Fw), mL/min	100	500	300
Car fluff (CF), g	2	6	3

The temperature levels were chosen considering the usual pyrolysis temperature range [20], the N_2 flow levels were chosen considering the operating condition of the flowmeter and the car fluff amount was chosen on the basis of the pyrolysis reactor dimensions.

To perform the FF-ED, the necessary number of experiments is $N = L^k$, where L represents the number of levels (two in our case) and k represents the number of factors (three in our case). So, eight experiments were carried out to investigate the experimental domain; three more experiments were added to investigate the performance in the centre of the experimental domain and to estimate the model validity, reproducibility and experimental error. A total of eleven experiments were carried out. The experiments were randomly performed to minimize the error due to the planning of the experiments.

The dependence of the experimental response (y) on the n variables (x) was modelled applying following equation [12]:

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

Where β_0 the constant is term, β_i and β_{ij} are the regression coefficients, and ε is the error. For the determination of the coefficients, multiple linear regression was performed on the scaled and centered variables.

The analysis of variance (ANOVA) was applied to determine the factors and interactions that have a significant influence on the process, on the basis of the *P*-value. Furthermore we calculated the coefficient of determination (R^2), the adjusted R^2 (R^2_{adj}) and the coefficient of determination in prediction (Q^2).

The calculations were carried out with MODDE11 software.

3. Results and discussion

The FF-ED experiments and results are shown in Table 2. The evaluated regression includes the three factors and all two-factor interactions [21]. Higher-order interactions were discarded since their importance decreases with increase of the interaction order [12]. On the basis of this assumption, we excluded three- and four-factor interactions. In this way, we privileged the quality of the model and avoided over-fitting [14].

Table 2. FF-ED experiments and results.

Experiment	T (°C)	Fw (mL/min)	CF (g)	Tar Yield (%)
E1	500	100	2	41.9
E2	800	100	2	14.3
E3	500	500	2	35.0
E4	800	500	2	14.4
E5	500	100	6	42.6
E6	800	100	6	15.5
E7	500	500	6	31.5
E8	800	500	6	10.6
Centre 1	650	300	4	22.0
Centre 2	650	300	4	24.0
Centre 3	650	300	4	21.7

In Table 3 we report the regression coefficients and the *P*-value for the experimental response.

Table 3. Regression coefficients and *P*-values.

	Coefficient	*P*-value
Constant	24.9	<0.001
T	**-12.02**	**<0.001**
Fw	**-2.8**	**0.032**
CF	-0.7	0.488
T*Fw	1.6	0.136
T*CF	0.02	0.979
Fw*CF	-1.2	0.263

The factors and their interactions with *P*-values greater than 0.05 can be considered not significant at 95% confidence level. So, just T and Fw prove to be significant factors [22].

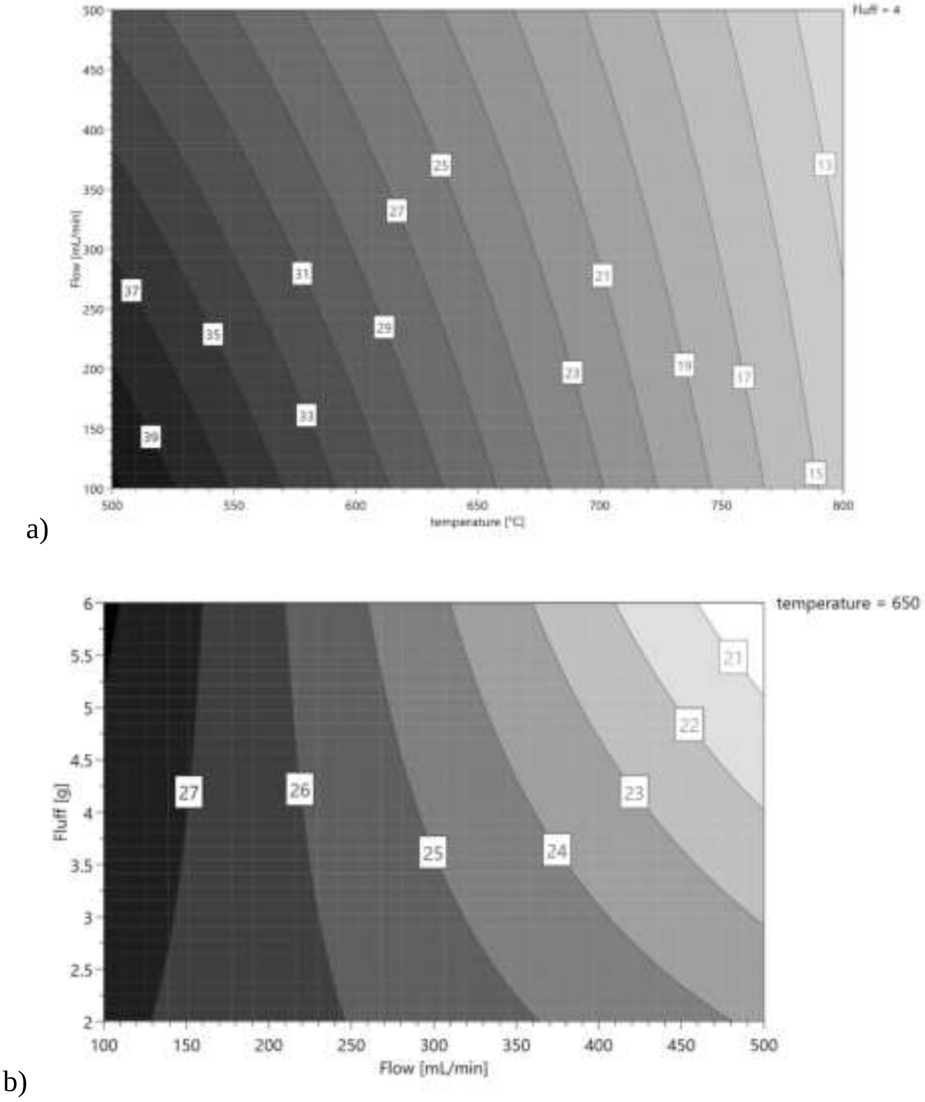
The regression parameters (Table 4) were considered to evaluate the goodness of fit and predictive capacity of the complete model.

Table 4. Regression parameters.

Parameter	
R^2	0.981
R^2_{adj}	0.951
Q^2	0.796

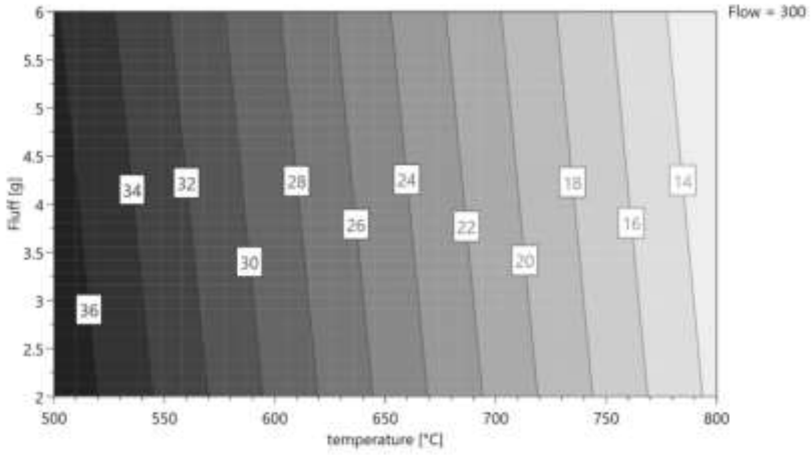
The complete model showed high and comparable R^2 andR^2_{adj}, offering an acceptable explanation of the total variance. Considering the Q^2 value, the predictive ability of the complete model is fair.

The complete model was used to determine the optimal condition range for maximizing the tar yield. To do this, contour plots of tar yield as a function of the temperature, the flow and the car fluff amount are shown in Fig. 1.



a)

b)



c)

Figure 1. Contour plots of tar yield as function of the three factors.

The black colour represents the optimal condition range for the response and 500°C and 100 mL/min were determined as the optimal conditions (Fig. 1a); whereas the negligible influence of the car fluff amount on the tar yield is confirmed in Fig. 1b and 1c.

4. Conclusions

Tar, the oil fraction produced in ASR pyrolysis, is a valuable alternative fuel. In order to maximize the tar yield, a full factorial design of experiment was used for modelling the process and optimizing the process variables. Eleven experiments were performed to explore the experimental domain. Temperature and carrier gas flow proved to be significant factors affecting the yield, while the influence of ASR light fraction amount pyrolysed was negligible. The maximum response was obtained at 500 °C and 100 mL/min.

As the optimal conditions determined are at the lower limit of the experimental domain, further investigation will be performed in a lower temperature range.

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