



# Prediction of liquid yields from the pyrolysis of waste mixtures using response surface methodology



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## ABSTRACT

The main objective of this work was to predict the influence of experimental conditions on product yields formed by waste mixtures pyrolysis, using response surface methodology (RSM). Accurate prediction of liquid yields at different experimental conditions and pyrolysis optimisation was achieved. The waste mixture studied contained 10% of pine, 10% of scrap tyres and 80% recycled plastic, whose main components were polyethylene (PE), polypropylene (PP) and polystyrene (PS). Experiment Factorial Design was used for the optimisation of reaction time, temperature and initial pressure to maximise the yield and composition of liquid products for the waste mixture studied. Experimental yields of liquids were fitted with a linear and second order model by the method of least squares with good correlation and high statistical significance. According to the model, the production of total pyrolysis liquids (including those obtained by solvent extraction) was maximised when the following conditions were used: reaction temperature of 350 °C, reaction time of 30 min and initial pressure of 0.2 MPa, leading to liquid yield of 91.3% (w/w). The yield of only decanted liquids (not considering those obtained by solvent extraction) was maximised to the value of 54.9% at 426 °C, 28 min and 0.2 MPa. The total liquid production at these conditions was 79.1%. The results obtained also showed that the approach used may be suitable for optimizing the experimental conditions that favour the formation of chosen gaseous and liquid compounds.

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## 1. Introduction

Modern societies face the challenges of sustainable use of resources and appropriate management of the produced wastes. Tyres, plastics and biomass are examples of materials widely used all over the world, leading to an increasing amount of residues, which have become a problem to humankind, due to their highly negative environmental impact. Land filling and incineration processes used so far to deal with these wastes present several problems. Land filling, the most common disposal route, does not allow the recovery of the organic content of these wastes. Though incineration has the advantage of recovering wastes energetic content, pollutants like light hydrocarbons, nitrous and sulphur oxides, or dusts and dioxins are produced, which degrade air quality and can cause pollution and health problems [1].

The natural raw material for tyre rubber and plastics production is petroleum, whose reserves have a limited lifetime and whose prices are increasing. Therefore, it is important to develop a better management of this resource use. The application of pyrolysis processes to reduce waste load and at the same time to recover their energetic content can have a valuable role in that management.

This technology allows the conversion of organic wastes, namely non-biodegradable, into organic products, which may be used either as raw materials for several industries or for energy production as substitutes of conventional fuels. Plastic pyrolysis has been studied by several authors [2–5]. During pyrolysis, thermal decomposition of wastes occurs in the presence of inert atmosphere under moderate conditions of temperature and pressure [6]. Their polymeric structure is broken down, producing smaller intermediate species, which can further react and produce a complex mixture of smaller hydrocarbon molecules, liquid or gaseous at room temperature.

Some authors have been studying co-pyrolysis of different types of wastes, mainly biomass, mixtures of plastics and used tyres [7–12]. Most of these co-pyrolysis studies were done with binary mixtures. This paper reports the results obtained when a tertiary mixture of tyre rubber, plastic wastes and biomass (pine) was pyrolysed. The main objective was to take profit of the easier decomposition of plastics in these conditions, creating a fluid that could aid in the heat transfer, thus facilitating the pyrolysis of the other two components, which are normally decomposed at higher temperatures.

Pyrolysis of these wastes led to a complex hydrocarbon liquid mixture, whose composition was dependent on experimental parameters, including waste type and content in the mixture. A previous work reported the effect of waste type and content on liquid yield and composition [13]. Possible synergisms between these three types of wastes

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## Nomenclature

$F_{\text{exp}}(z_i)$	Fisher–Snedecor distribution
$MS(z_i)$	Mean of squares
MSE	Mean of squares of experimental deviation
N	Degrees of freedom
R	Correlation coefficient
$SS(z_i)$	Sum of squares of factors
SSE	Sum of squares of experimental deviation
$x_i^+$	Higher level for the natural variable $i$
$x_i^-$	Lower level for the natural variable $i$
Y	Dependent variable or system response
$Y_m$	System response for $m$ conditions
$Y_{t\ 1}$	Total liquids yield estimated by the linear model (first interval)
$Y_{d\ 1}$	Decanted liquids yield estimated by the linear model (first interval)
$Y_{d\ 2l}$	Decanted liquids yield estimated by the linear model (second interval)
$Y_{t\ 2l}$	Total liquids yield estimated by the linear model (second interval)
$Y_{t\ 2q}$	Total liquids yield estimated by the second order model (second interval)
$Y_{d\ 2q}$	Decanted liquids yield estimated by the second order model (second interval)
$z_1$	Coded factor temperature
$z_2$	Coded factor initial nitrogen pressure
$z_3$	Coded factor reaction time

were studied and the results obtained led to the selection of a mixture with 10% of pine, 10% of scrap tyres and 80% recycled plastic to favour the production of liquids. Thus, this paper refers to this single mixture and the main objective is to analyse the effect of temperature, initial pressure and reaction time to optimize liquid yield obtained by pyrolysis of the mixture selected. To avoid doing a huge number of experimental tests, to select the experimental conditions that maximise the production of liquids RSM was selected.

In a previous work the same methodology was also used to optimize pyrolysis of waste plastics and used rubber tyre [14]. A good process optimisation with a reduced number of experiments was achieved. For these dual waste mixtures the experimental conditions optimized based on RSM were 370 °C, 0.48 MPa for initial pressure and 15 min for reaction time. Due to the good results obtained the same procedure was used to optimize the main experimental parameters of pyrolysis of ternary blends, containing waste plastics, used rubber tyre and biomass and the results obtained are reported in the present paper.

The right plan of experimental tests may be achieved by statistic tools like RSM, which allows selecting the right experimental conditions to maximise liquid yields and optimize liquid composition. The innovative feature of this work was the use of a factorial experiment design applied to the study of the pyrolysis of the ternary mixture with rubber tyre, plastic wastes and biomass, enabling a systemization of the experimental work load and the establishment of empirical models which were used to assess the effects of the experimental conditions and then to optimize the production of liquids. This paper demonstrates the usefulness of using RSM to predict pyrolysis yields with a great reduction in the number of experiments. This methodology also showed to be useful to supply information for optimizing the experimental conditions that maximise the production of pre-defined gaseous and liquid compounds. The model developed is expected to be used by other researchers with slight adjustments, depending on experimental devices.

## 2. Material and methods

### 2.1. Procedure

The pyrolysis experiments were conducted at batch conditions in a 1 l autoclave made of Hastelloy C276 (by Parr Instruments). Detailed information about the pyrolysis installation was presented in a previous paper [6]. After the predetermined reaction temperature was reached, the autoclave was maintained at this temperature for the desired reaction time; afterwards the autoclave was cooled down till room temperature and then opened to retrieve the products.

Typical curves of temperature and pressure evolution obtained with the apparatus used, showed that the heating of the mixture was a slow process, as the heat transfer from the furnace to the autoclave interior was not readily done. Average low heating rates of 5.5 °C/min were obtained [13]. As waste mixture heating was a slow process for the equipment used, the residence time of the feedstock inside the autoclave from the start of the heating process until the end of the cooling till room temperature was much longer than the reaction time, which was referred as the time at which the waste mixture was maintained at the desired pyrolysis temperature.

The gaseous product fraction was analysed on a Gas Chromatograph (GC) to quantify the major gas components produced at the several pyrolysis reaction conditions tested. The liquid fraction directly recovered from the reactor (named as decanted liquids) was distilled according to ASTM D86 [15] to yield three fractions: the lighter hydrocarbon fraction distilled below 150 °C, the second distillate fraction with heavier hydrocarbons distilled in the range from 150 °C to 270 °C and the residual fraction had a distillation temperature beyond 270 °C. The first two distillates were analysed by GC (HP 6890) and GC/MS (LECO Pegasus III). Detailed operating conditions for the chromatographic runs were presented in a previous work [16]. The distillation curve of the liquid fraction was also compared to the ones of gasoline and diesel.

The remaining solid fraction inside the reactor was weighted and extracted with dichloromethane (DCM) and tetrahydrofuran (THF) in a soxhlet extractor (by ASTM D5369-93 [17]) to recover the liquids adsorbed in the solid (named as extracted liquids). The dried solid product was weighted to give the effective pyrolysis yield of solids. The extracted liquids were also subsequently analysed by GC and GC/MS.

### 2.2. Raw materials

In this work recycled wastes of polyethylene (PE), polystyrene (PS) and polypropylene (PP) previously pelletized to particles with 5 mm of diameter were used. The biomass used was pine (*pinus pinaster*) in the form of shreds derived from forestry residues with about 2 cm of length and 2 mm of diameter. Filaments of used tyres with the same dimensions were provided by a scrap tyre recycling plant after the removal of the metal and textile parts, their main components were natural rubber (NR), styrene butadiene rubber (SBR) and butadiene rubber (BR). The runs in this work were conducted with the following waste mixture (%w/w): 10% tyre, 10% pine and 80% of plastics mix (56% PE, 27% PP and 17% PS, simulating their composition in the plastics fraction of Portuguese municipal solid wastes). The ultimate and proximate analyses of these wastes are presented in Table 1.

### 2.3. Factorial experimental design

Least-squares were used in the fitting of the dependent variable, which for the present study was either total liquids or decanted liquid yield. The effect of reaction time, temperature and initial pressure on the yield and composition of liquid products for a selected waste mixture composition was studied. The use of RSM allows a response evaluation with the same precision as the one obtained if only a single variable was studied in the same experimental range [18]. In the present case, all  $k$  factors ( $x_i$ ,  $i = 1$  to  $k$ ) represent chosen quantitative variables

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