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Effects of an Inertization System on Waste Plastic Pyrolysis in a Fixed Bed Reactor

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Abstract: This paper reports the results of a study on the significance of the inertization system configuration of a laboratory-scale fixed bed batch reactor with regard to the yield of pyrolysis oil and reactor conversion. Two typical reactor inertization systems were investigated depending on whether the carrier gas (nitrogen in this study) was added from the top or from the bottom of the reactor. Polypropylene (PP) packaging waste (100 g) was used as a model sample. A factorial experimental design was adopted for one categorical parameter, the arrangement of parts of the reactor inertization system. All experiments were conducted at 475 °C, with a carrier gas flow rate of 0.1 L/min and a reaction time of 90 min. Statistical analysis and processing of the results showed that the configuration of the inertization system had a remarkable impact on the pyrolysis oil and gas yield, while its impact on the overall reactor conversion was negligible. When applying the two observed methods of reactor inertization, the average yields of pyrolysis oil and gas differed by 1.7% and 1.8%, respectively. All of the applied statistical treatments had a significance level of 0.05, i.e., there was only a 5% chance of incorrectly rejecting the hypothesis of equality of arithmetic means of pyrolysis yields when the two different methods of reactor inertization were applied. The explanation of this behavior is attributed to the temperature change inside the reactor, which shows that this particular fixed bed reactor suffers from local overheating in its middle part. Local overheating of the middle part of the reactor is more pronounced in the case of inerting the reactor from the bottom, which leads to greater excessive cracking of volatile products compared to the mode of inerting the reactor from the top part and thus greater formation of non-condensable gases, i.e., a reduction in the yield of pyrolytic oil.

Keywords: waste plastic; pyrolysis; fixed bed reactor; inertization effect; carrier gas

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1. Introduction

Pyrolysis is a thermochemical decomposition process that takes place in the absence of oxygen. During the pyrolysis of plastic materials, the decomposition of polymer chains leads to the formation of pyrolysis oil, non-condensable gases, and a small amount of solid residue that remains as ash at the bottom of the reactor. The products are often used as fuels, raw materials in the petrochemical industry, or as monomers [1–7]. Due to the high energy values of gaseous and liquid products, pyrolysis can also be considered as an energy recovery method [8–10]. Reuse of plastic waste is not possible because plastics lose their properties due to contaminants and environmental effects resulting from its use. In addition, internal additives limit its reuse. Therefore, plastic pyrolysis is one of the most adequate processes adopted for the treatment of plastic waste [11]. Furthermore, since this process does not produce residues, or it produces a small amount of them, it is considered environmentally friendly [12–18]. However, depending on the origin, the plastic waste product of pyrolysis may contain some harmful substances resulting from chlorinated and brominated organic compounds contained in e-waste. Particular attention should be devoted to monitoring the amount of such compounds and trying to keep their content as low as possible in an attempt to develop more environmentally friendly systems [19,20]. Therefore, many studies have been focused on the pyrolysis of plastic waste as a promising recycling technique [21–27]. The process temperature is the most significant parameter, since it influences the amount of cracking of polymer chains [17,28–32]. Generally, the relative share of individual pyrolysis products is determined by process conditions such as temperature, reaction time, carrier gas flow stream rate, heating rate, product cooling rate, applied pressure, and particle size of the feedstock material, as well as the nature of the raw material itself and the type of reactor [33–40]. It has been proven that the mass of the raw material, i.e., the filling volume of the fixed bed reactor, has an influence on the pyrolysis oil yield [41]. Furthermore, by simply selecting the appropriate mixture of raw materials, it is possible to modify the heating rate and the overall energy efficiency of the process [42]. Since plastics have low thermal conductivity, it is difficult to achieve rapid and uniform heating in the reaction environment, which has led to different proposals for reactor configuration in the literature [43]. Therefore, a large variation in the obtained results can be observed in the literature in terms of the yield of pyrolysis, the need for catalysts, and the kinetics of the process and quality of the pyrolysis products [44–51]. Several studies were conducted with relatively small samples using thermogravimetric tests which further complicated the comparison of the results of different studies [52–54]. Moreover, in some descriptions of the fixed bed reactor or pyrolysis setup, it is not clear whether a carrier gas is added from the bottom or the top of the reactor or from another side [30,55,56]. The fact is that the carrier gas can be introduced both from the bottom and the top of the reactor, and also from other sides, depending on the reactor configuration [57–59]. Typically, a carrier gas, in addition to its role of creating an inert atmosphere, also has the role of transporting pyrolysis vapors through the reactor [28,59–61]. Therefore, it can be assumed that different carrier gas paths through the system influence the extent of cracking reactions and consequently the yield and distribution of pyrolysis products. Namely, the assumption is that with a change in the carrier gas path, the residence time of the pyrolysis vapors in the fixed bed reactor also changes, which leads to a change in the extent of cracking reactions. Generally, residence is influenced by reactor design and reactor pressure [62]. Furthermore, different carrier gas paths through the reactor could change the heat transfer conditions, which consequently affects the pyrolysis process as a whole. It is known that efficiency of heat transfer is extremely important for achieving high pyrolysis yields, which affects the overall efficiency and economy of the process [63,64]. Therefore, it can be assumed that the way carrier gas enters a reactor can lead to certain changes in the yield of pyrolysis products. The aim of this study is to test the validity of the mentioned hypothesis; analyzing the configuration of the inertization system related to the fixed bed batch reactor at a laboratory scale. For this purpose, two different ways of introducing the inert atmosphere into the fixed bed reactor were examined. All other variables, including the possible effects of different compositions of raw materials, were kept constant throughout all experiments to eliminate their influence and possible mutual interactions.

2. Results and Discussion

Table 1 shows the results of the response measurements (R1, R2, R3), when applying different treatments, with calculated arithmetic means and standard errors for all three responses. The results of this table reveal that there is some variation in individual values depending on the treatment applied. A concrete answer to the question of whether these variations are statistically significant was obtained by analyzing the variance of the assumed factorial model that would describe the influence of Factor A on the responses in question (Table 2).

Table 1. Yield of pyrolysis products (R1, R2, R3) with different modes of inertization of fixed bed reactors.

Factor A Inertization Mode	Response R1 Oil Yield (%)	Response R2 Gas Yield (%)	Response R3 Solid Yield (%)
Bottom inertization	52.11	45.86	2.03
Bottom inertization	51.55	46.52	1.93
Bottom inertization	51.27	46.74	1.99
Arithmetic mean	**51.64**	**46.37**	**1.98**
Standard error	**0.3594**	**0.3962**	**0.0447**
Top inertization	52.45	45.52	2.03
Top inertization	53.58	44.33	2.09
Top inertization	53.92	43.86	2.22
Arithmetic mean	**53.32**	**44.57**	**2.11**
Standard error	**0.3594**	**0.3962**	**0.0447**

Table 2. ANOVA for selected factorial models—Factor A influence (significance level: $\alpha = 0.05$).

Factor A	Response R1	Response R2	Response R3
Sum of squares	4.20	4.88	0.0253
Pure error	1.55	1.88	0.0239
Corrected total sum of squares	5.75	6.76	0.0493
Model F-Value	**10.84**	**10.36**	**4.24**
***p*-value**	**0.0302** **Significant**	**0.0323** **significant**	**0.1087** **not significant**

2.1. Statistical Testing

Table 2 shows that the model F values for responses R1 and R2 are quite similar, and at the same time, they are considerably different from R3. For the case of response R1, the model F value of 10.844 means that the model is significant with respect to noise. There is only a 22.63% chance that such a large F-value could occur due to noise. For the case of response R2, the model F value of 10.36 entails that the model is significant. There is only a 3.23% chance this large F value could be attributed to noise. For the case of response R3, the model F value of 4.24 implies that the model is not significant with respect to noise. There is a 10.87% chance that this large F value could occur due to noise. Similar statements can be made based on looking at the *p*-values. Generally, *p*-values lower than 0.0500 mean that model terms are significant. In this case, Factor A (inertization mode) is a remarkable model term with respect to R1 and R2. Values greater than 0.1000 indicate that the model terms are not significant.

The above statements can be reached by comparing the corresponding I-beams on the graphs presented in Figure 1. The graphs display the average values of the dependent variables with respect to the appropriate treatment (bottom inertization or top inertization), as well as the corresponding LSD intervals, i.e., the 95% intervals of least significant differences (Fisher's LSD test), which are represented by vertical interval lines (I-beams). In order for the two treatments to differ significantly in terms of their impact on the response of interest, there must be no horizontal overlap of the I-bars.

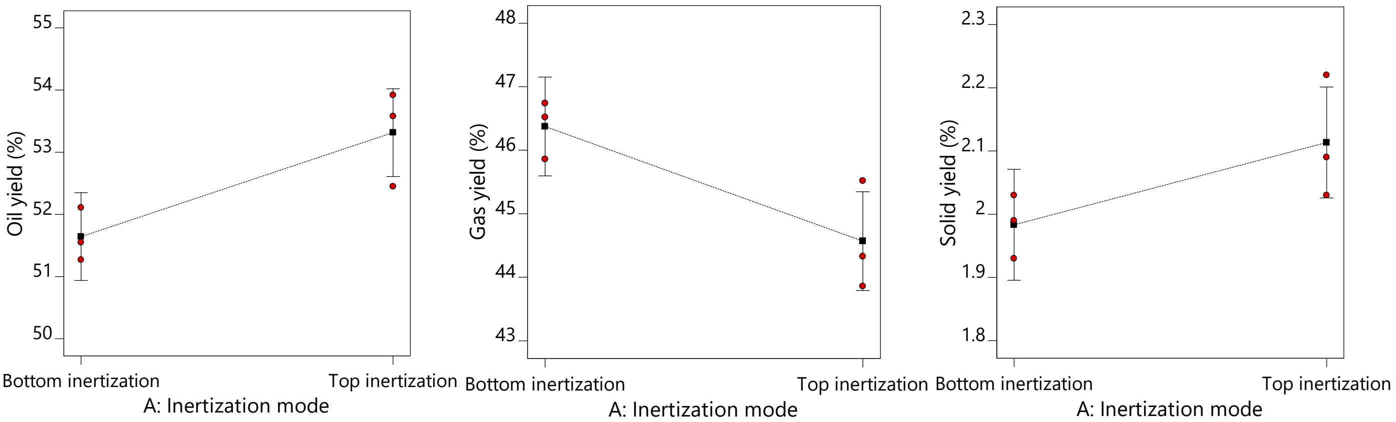

Figure 1. LSD I-beams pairwise comparison of the average response values (significance level: $\alpha = 0.05$).

The plots for the oil and gas yields clearly show that the ranges of values included in the I-beams on the left side of the graph (bottom inertization) do not overlap with the corresponding I-beams on the right side of the graphs (top inertization). The graph for solid yield shows partial overlap of the I-beams. Therefore, one may conclude that there is a significant difference between two fixed-bed reactor inertization modes with respect to both pyrolysis oil and pyrolysis gas yield. As far as the solid yield is concerned, i.e., total reactor conversion, there is no significant influence of the fixed-bed reactor inertizaion mode.

Looking at the size of the impact itself, it should be noted that this impact is relatively small, because the significance of the impact itself was taken as 1.5% (delta signal in Table 3). It is clear that if higher delta signal values were taken (e.g., 2% or more), the above statistics would not show the significance of the impact. Namely, the results summarized in Table 1 revealed that when applying the two observed treatments, the average values of R1 and R2 differ by approximately 2%. However, if the goal is to maximize the yield of pyrolytic oil, it is recommended to investigate different modes of inertization reactors.

Table 3. Statistical power of experimental design.

Responses	Units	Diff. to Detect [1] Delta ("Signal")	Est. Std. Dev. [2] Sigma ("Noise")	Delta/Sigma [3] (Signal/Noise Ratio)	Power [4] for Factor A
Oil yield (R1)	%	1.5	0.48	3.13	81.3%
Gas yield (R2)	%	1.5	0.46	3.26	84.2%
Solid yield (R3)	%	0.5	0.12	4.17	96.1%

[1] Difference to detect or delta signal is the minimum change in the response considered large enough to be a practical change. [2] Estimated standard deviation or sigma noise is an estimate for the run-to-run standard deviation of the response. [3] Signal/noise ratio is used to determine the probability of detecting an effect. [4] Power is reported at a 5.0% alpha level to detect the specified signal/noise ratio. Alpha level corresponds to the significance level (0.05) of rejecting the null hypothesis when it is true, i.e., there is a 5% chance of irregularly rejecting the null hypothesis.

In terms of explaining the influence of the inertization mode on the yield of oil and gas obtained thorough pyrolysis, it is worth noting that the obtained result shows that the application of inertization from the bottom of the reactor leads to a somewhat lower oil pyrolysis yield. Since more efficient (faster) removal of pyrolysis vapors outside the reactor can be envisaged by inerting from the bottom of the reactor, a slightly higher yield of pyrolysis oil may be expected with this inertization mode of the fixed-bed reactor.

Namely, the faster removal of steam from the reactor means a shorter residence time of pyrolysis vapors in the high-temperature area and a smaller extent of cracking reactions and consequently a smaller release of gaseous products, i.e., a higher yield of pyrolysis oil [53,58,65–67]. However, this did not occur, according to the results.

Therefore, it can be concluded that the method of introducing the gas into the reactor does not influence the residence time of pyrolysis vapors in the reactor because the expected increase in oil yield did not occur in the case of inertization from the bottom of the reactor. Most likely, the mass flow of carrier gas, 0.1 L/min, was too small to have a measurable effect on the resident time of the vapors. On the other hand, it is obvious that in this specific case of a reactor with a fixed bed, the effects of changing the heat transfer conditions with a change in the carrier gas path were a more dominant than the expected change in the vapor residence time. This statement is supported by the observation of temperature changes during the pyrolysis process at characteristic points of the reactor (Figure 2).

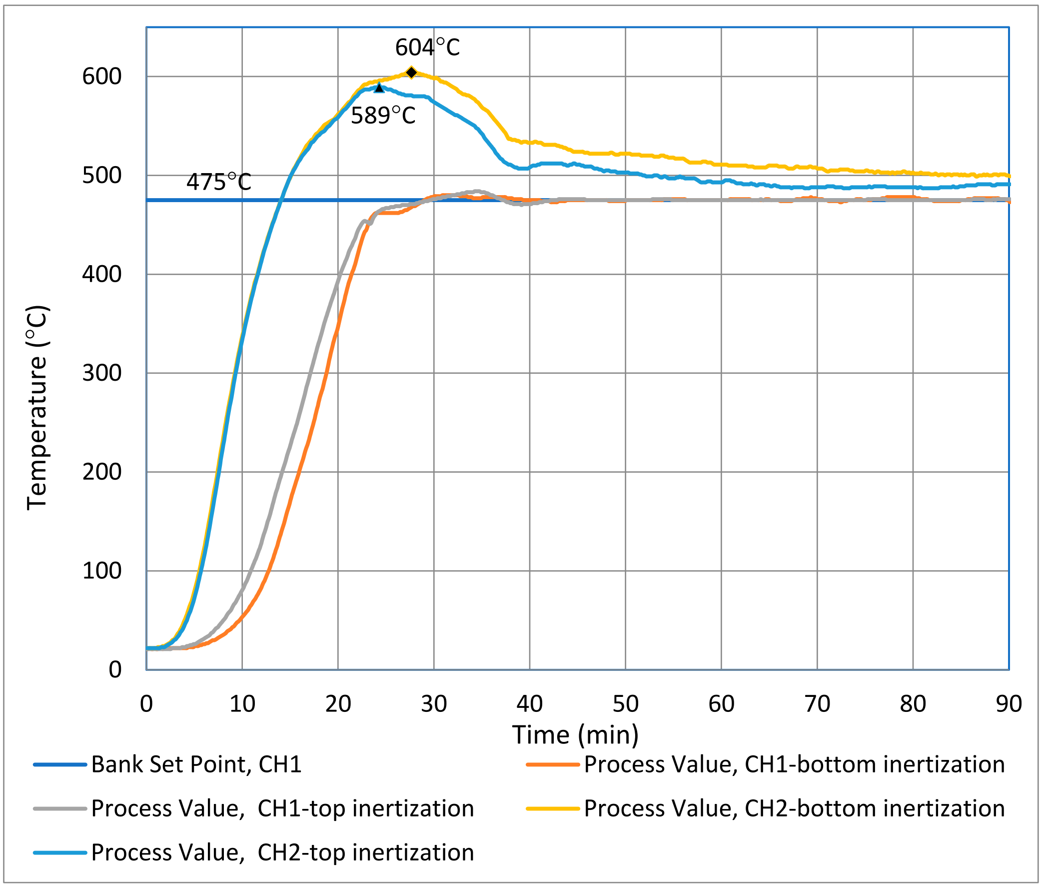

Figure 2. Temperature changes in the bottom and middle parts of the reactor during top and bottom inertization modes.

2.2. Study of Temperature Diagram

In Figure 2, different shapes of the process value–CH2 curves can be seen. These curves show how the temperature varies with time in the middle section of the reactor during reactor inertization in the bottom part (CH2—bottom inertization), i.e., during reactor inertization in the top part (CH2—top inertization). A similar thermal diagram was recorded in the study of Swamardika et al. [68], where the fixed bed reactor was also considered for pyrolysis of PP waste. The CH2—bottom inertization curve reached a slightly higher maximum temperature (604 °C) than the CH2—top inertization curve (589 °C). This behavior of the reactor can be explained by the specific construction of the reactor and the method of temperature control. Namely, this type of reactor has vertically arranged internal heaters, so their operation is PID controlled by the temperature in the lower section of the reactor. In the initial stage of the process, the feed material (PP) occupies approximately 2/3 of the reactor volume, while after the transition to the liquid phase, the feed material occupies only the lower part of the reactor, leaving the middle and upper parts of the reactor empty and exposed to the heaters. After that, the released pyrolytic vapors occupy the middle and upper parts of the reactor, moving towards its outlet, coming into contact with the heaters and being further heated (temperatures of CH2 in Figure 2). The most thermally intensive processes (phase transition and pyrolytic decomposition) occur in the bottom part of the reactor, and the heater operation is temperature-controlled in this part of the reactor, which is practically occupied by pyrolytic vapors and carrier gas. This is the main reason for the higher temperatures in the middle part compared to the bottom side of the reactor. In the case of bottom inertization of the reactor, a subcooling of the feedstock occurs (see Figure 3) together with additional cooling of the heaters, which all together leads to a more intensive operation of the heater in order to meet the set temperature (bank set point—CH1, in Figure 2). Considering the more intensive operation of the heater, a higher temperature increase occurs in the middle part of the reactor compared to the top inertization mode, where the effects of the subcooling of the feedstock do not occur.

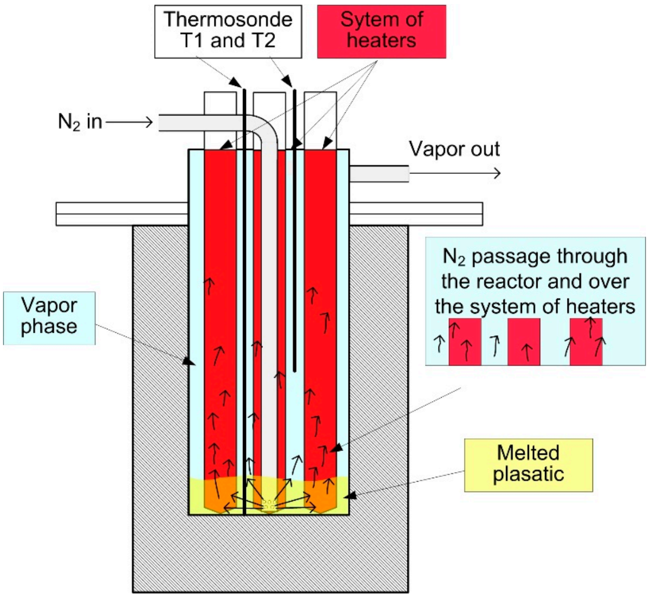

Figure 3. Reactor system subcooling mechanism.

It is known that higher pyrolysis temperatures of plastic materials promote more extensive gas formation due to more intensive secondary pyrolysis reactions, i.e., cracking reactions of macromolecular chains in the vapor phase [6,33,55,69–72]. Since the pyrolytic vapors in the bottom inertization mode have a higher temperature than the vapors in the top inertization mode, more intensive cracking of vapor molecules occurs, providing a higher yield of gaseous products, i.e., less pyrolysis oil.

A similar behavior of a fixed-bed reactor, i.e., excessive overheating of its middle part compared to the bottom part, has been previously reported as well [41,42]. This was observed not only for the case of PP as a model sample [41] but also for the case of a mixture of waste PP, HDPE, and LDPE [42]. However, in this study, we further investigated such behavior under the influence of two different inertization systems.

It is obvious that with a more complex heating control, e.g., two sets of heaters that would be independently PID controlled by corresponding temperatures in the middle and lower sides of the reactor, a somewhat more uniform temperature range could be achieved. This temperature control mode could further influence the yield and distribution of pyrolysis products. This will be the subject of further research and development of the current pyrolysis system in a fixed-bed reactor. However, it should be emphasized that pyrolysis with the current heating method produces completely liquid products (pyrolysis oil), unlike typical PP pyrolysis processes, which at temperature below 500 °C mainly give less-valuable, waxy products [31,59,73,74]. Therefore, further research could examine how heating modes and temperature field uniformity may influence the yield and quality of pyrolysis products.

3. Materials and Methods

3.1. Experimental Setup

Polypropylene (PP) packaging waste (100 g) was used as a model sample. Sample preparation involved washing, drying, shredding, and grinding on a laboratory mill. Pyrolysis experiments were performed in a fixed-bed laboratory reactor. Descriptions of the technique and of the fixed-bed laboratory reactor are available in several studies [41,42,44,75–77]. Based on the results of a previous study [45], a pyrolysis temperature of 475 °C was chosen as the optimum value of pyrolysis oil yield and total conversion in the reactor. The flow rate of the purging gas was 0.1 L/min, and inertization of the reactor prior to the reactor heating sequence took 15 min. Nitrogen with a purity of 99.99%, i.e., the inertization atmosphere, was used as carrier gas. The reaction time for all the experiments was set to 90 min, despite the fact that 60 min had previously been shown to be sufficient for a complete conversion of the raw material below 475 °C [41].

3.2. Experimental Design and Mathematical/Statistical Processing of the Results

The Design-Expert 11 licensed program package (Stat-Ease Inc., Minneapolis, MN, USA) was used for the design of the experiment and the statistical evaluations of the experimental results. To examine the influences of the fixed-bed reactor inertization modes on the yield and distribution of the pyrolysis products, a factorial experimental design was adopted for one categorical parameter with multiple levels of influence (treatments). As a categorical factor of influence, the mode of reactor inertization (Factor A) was observed at two levels of influence:

Level 1 (bottom inertization)—nitrogen enters the reactor at the bottom part, and
Level 2 (top inertization)—nitrogen enters the reactor at the top part (Figure 4).

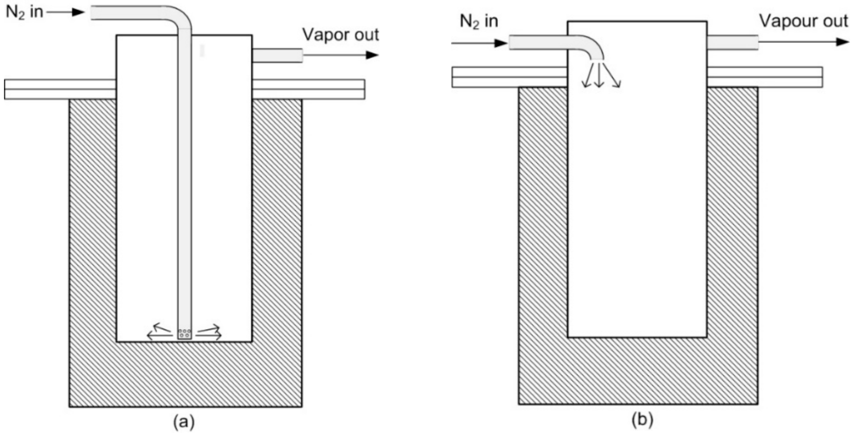

Figure 4. Cross-section of the reactor: (**a**) bottom inertization and (**b**) top inertization.

As dependent variables (measured responses), pyrolytic oil yields (R1), gas yield (R2), and solid residue in the reactor (R3) were monitored, each expressed as a percentage of mass. For each influence level, three experiments were performed, which allowed for a statistically reliable assessment of the tested treatment (Table 3). The statistical power of the experimental design adopted to detect effects of interests (Factor A) on R1, R2, and R3 was 81.3, 84.2, and 96.1%, respectively. These values represent the experiment's success probability, i.e., the probability that a large effect can be considered significant given the expected standard deviation [78]. The power should be about 80% or higher due to the effects one wishes to detect [79,80]. The minimum change that the design should detect as statistically significant and the estimated standard deviation (obtained from previous experiments) were entered for each response.

The significance of the influence of the mode of reactor inertization, i.e., Factor A, was determined using two methods:

1. F test conducted on the model or analysis of variance (ANOVA) of the hypothetical factorial model of influence using the Fisher's statistical test (F test),
2. Fisher's LSD tests.

4. Conclusions

This study is a part of an extended study dealing with the relation between the temperature, reaction time, reactor's feed mass, etc., and the yield of plastic waste pyrolysis performed on a fixed bed reactor. In the present investigation, all efforts were focused on the analysis of the different inertization modes (top, middle, bottom) of a fixed bed reactor while pyrolysis of PP (acting as a model) was occurring. Based on the statistical analysis of the obtained results, it can be concluded that there was a significant difference between the two examined modes of fixed-bed reactor inertization. The bottom inertization mode of the reactor caused a slightly lower yield of pyrolysis oil and slightly higher yield of pyrolysis gases compared to the top inertization mode. There was no significant influence of the examined reactor inertizaion modes on the amount of solid residues in the reactor, i.e., the examined modes of inertization did not influence the total conversion of the reactor.

Looking at the diagram of the temperature changes in the reactor, it was concluded that the two investigated modes of reactor inertization led to different temperature profiles in the middle part of the reactor. This behavior is explained by the specific arrangement of the electric heaters, heating modes, and temperature control inside the reactor, which were affected by the inertization mode. In the case of the bottom inertization mode, slightly higher temperatures occurred in the middle part of the reactor, which led to a higher yield of gaseous products compared to the top inertization mode.

It can be finally concluded that top inertization is certainly more advantageous than the bottom inerting mode in terms of pyrolysis liquid yield, and it is simpler and cheaper to build such an inertization system due to the smaller amount of materials used. Therefore, in the event of a specific fixed-bed reactor with an internal heater arrangement, and in the case where the basic goal of pyrolysis is to obtain as much pyrolysis oil as possible, it is more advanced to use the simpler and cheaper top inertization method. However, we did not perform an economic analysis of these two inertization methods, as such an analysis would be strongly affected by scale issues. The reactor under investigation in this study was quite small, i.e., a laboratory-scale installation, so a cost-effectiveness analysis would be questionable.

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