



## Research article

# Statistical prediction and sensitivity analysis of kinetic rate constants for efficient thermal valorization of plastic waste into combustible oil and gases



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## ABSTRACT

Sensitivity analyses of rate constants for chemical kinetics of the pyrolysis reaction are essential for the efficient valorization of plastic waste into combustible liquids and gases. Finding the role of individual rate constants can provide important information on the process conditions, quality, and quantity of the pyrolysis products. The reaction temperature and time can also be reduced through these analyses. For sensitivity analysis, one possible approach is to estimate the kinetic parameters using MLRM (multiple linear regression model) in SPSS. To date, no research reports on this research gap are documented in the published literature. In this study, MLRM is applied to kinetic rate constants, which slightly differ from experimental data. The experimental and statistically predicted rate constants varied up to 200% from their original values to perform sensitivity analysis using MATLAB software. The product yield was examined after 60 min of thermal pyrolysis at a fixed temperature of 420 °C. The predicted rate constant “k(8)” with a slight difference of 0.02 and 0.04 from the experiment revealed 85% oil yield and 40% light wax after 60 min of operation. The heavy wax was missing from the products under these conditions. This rate constant can be utilized to maximize the commercial-scale extraction of liquids and light waxes from thermal pyrolysis of plastics.

## 1. Introduction

Plastics are widely used materials worldwide due to their high strength-to-weight ratio and low cost [1]. Because of their low cost, most regularly used plastic products are discarded after a single use. Inadequate storage space and recycling issues of used plastic result in massive waste [2]. Managing waste materials is a growing challenge, adversely impacting the environment [3,4]. Plastics have

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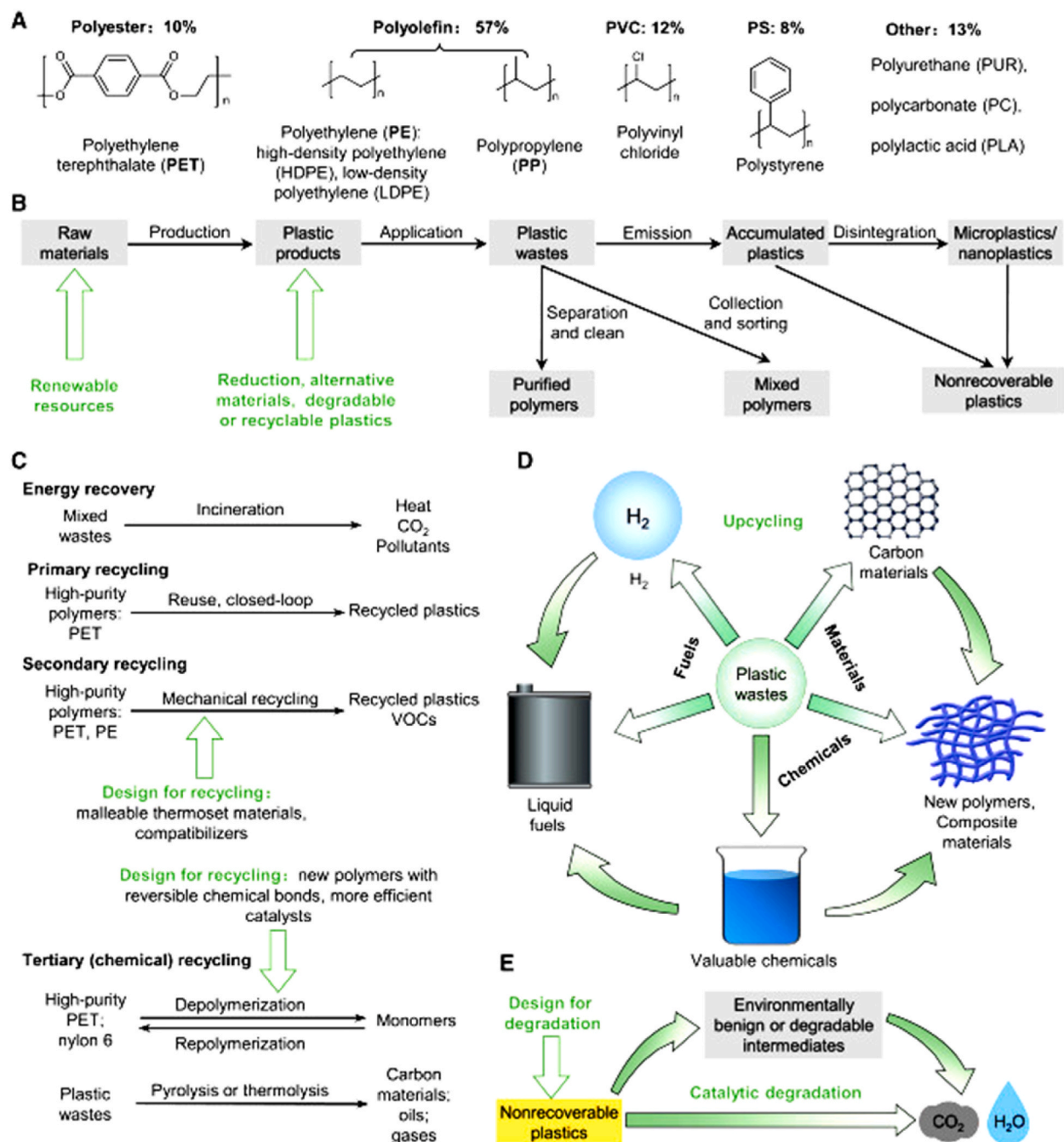
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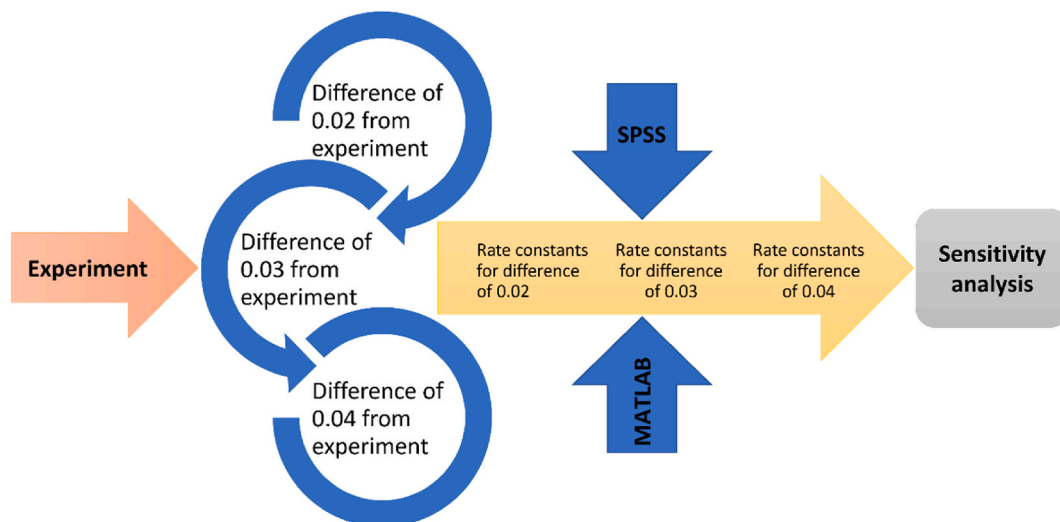


**Fig. 1.** Options for addressing waste management issues based on the plastic waste type and source: (A) classification of plastic waste, (B) production of plastic waste, (C) conventional recycling methods, (D) production of valuable products, and (E) degradation process of plastic waste.

produced nearly 6 billion tons of garbage during the last six decades. Only 9% of this bulk waste was recycled, 60% was dumped in landfills and the rest of the waste was burned or destroyed. By 2025, 12 billion tons of waste plastic are expected to accumulate in the natural environment. Plastic, like fossil fuels, is wreaking havoc on marine life, human health and the ecosystem [5,6]. Managing plastic waste through incineration means wasting a valuable hydrocarbon resource [6]. Therefore, proper waste management and discovering new energy sources must be prioritized to sustain the planet's massive population and ecosystem. Alternatively, waste plastics can be valorized into combustible gases, high-value carbon, chemicals, and monomers [7,8]. Although waste plastic is also being used in construction materials, it is not an environmentally friendly strategy because downsized plastics flow into water bodies and harm marine life. The best strategy is resource recovery through deconstructing plastic waste into liquid and gaseous fuels and waxes [9].

**Table 1**  
MLRM coefficients with a difference of 0.02 for an experiment.

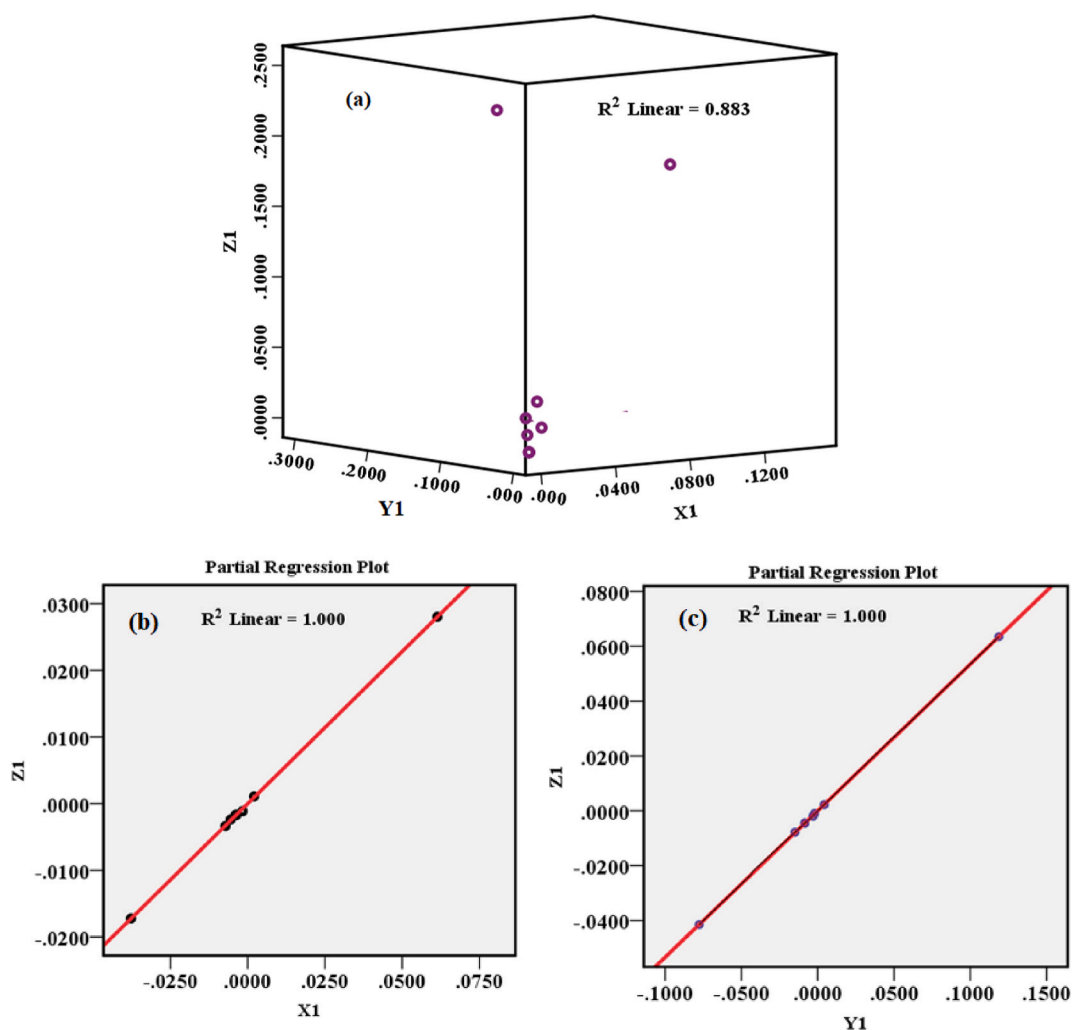
	Estimate	Stand. Error	t-value	P-value
Intercept	$-3.549 \times 10^5$	$7.152 \times 10^{-5}$	-0.496	0.637
X <sub>1</sub>	$4.564 \times 10^1$	$2.439 \times 10^{-3}$	187.139	$1.57 \times 10^{-12}$ ***
Y <sub>1</sub>	$5.346 \times 10^1$	1.240	431.226	$1.05 \times 10^{-14}$ ***



**Fig. 2.** A graphic depiction of the steps involved in sensitivity analysis of kinetic rate constants for thermal degradation of HDPE waste.

Fig. 1(A–E) illustrates the major types of plastic waste, the process production of waste, conventional recycling methods, upcycling to produce valuable products, and degradation or pyrolysis of the plastic waste [10]. The choice of method to address waste management issues depends on the type of waste and process cost. The plastic wastes are categorized into polyolefin, polyester, polystyrene, and polyvinyl chloride. Polyethylene and polypropylene are known as polyolefins, which account for 57% of municipal plastic waste. The high-density polyethylene (HDPE) is extensively used in electrical insulations, bottles, toys, films, pipes, etc [11]. Detailed information on synthesis, characteristics, commercial uses, and associated issues of other plastics are available in the studies conducted by Martín et al. [12] and Rahimi and García [13]. Mostly HDPE and polyvinyl chloride plastic wastes are routinely valorized among the commonly produced plastic wastes, although the recovery rate is far from satisfactory. Various recycling approaches, including closed-loop recycling (primary), mechanical recycling (secondary), chemical recycling (tertiary), and incineration, are being practiced to treat or manage wasted plastic Fig. 1A–E.

The methods of primary recycling and secondary recycling both rely on mechanical operations [13]. Polyethylene terephthalate and polyethylene plastics are commonly recycled by mechanical recycling. Mechanically recycled plastics are still destined for disposal, landfilling, and incineration. Tertiary recycling, on the other hand, refers to the treatment of plastic by chemical processes such as gasification, pyrolysis, and depolymerization. Through thermal cracking, thermolysis, catalytic cracking, and liquefaction, pyrolysis turns plastic into liquids, gases, and light waxes and heavy waxes [14]. Avoiding side reactions and having good product yield, selectivity and distribution are fundamental challenges of the conventional pyrolysis processes [15]. It is necessary to choose deliberately the kinetic model and reaction mechanism for the efficient pyrolysis of plastic waste [16]. Different pyrolysis parameters, such as reactor type, plastic type, pyrolytic temperature, residence time, and ramping rate, may influence the process efficiency and product composition. Because operating conditions can have a substantial impact on product composition and reaction mechanism, kinetic modeling is critical for explaining the reaction mechanism of thermal cracking of plastic molecules [17,18]. Ganeshan et al. [19] performed kinetic modeling of the pyrolysis of Polyethylene terephthalate using the Coats–Redfern technique. In the reported first-order reaction kinetics, the activation energies ranged from  $133 \text{ kJ mol}^{-1}$  to  $251 \text{ kJ mol}^{-1}$  with a low value of  $<0.8$ . Zhang et al. [18] investigated the product evolution and reaction kinetics of pyrolysis polypropylene, polyethylene, and their mixtures. All the reactions were predominantly endothermic and most of the degradation of polypropylene, polyethylene, and mixture happened in the temperature range of  $389.85\text{--}502.17 \text{ }^\circ\text{C}$ ,  $374.91\text{--}495.15 \text{ }^\circ\text{C}$ , and  $368.30\text{--}496.29 \text{ }^\circ\text{C}$ , respectively. Das and Tiwari [20] determined the kinetic parameters of pyrolysis polyethylene terephthalate at different heating rates by using an iso-conversational method. The activation energies of the reaction were reported about  $196\text{--}217 \text{ kJ mol}^{-1}$ . Al-asadi and Miskolczi [21] study both Ni-zeolite catalyzed and thermal pyrolysis of Polyethylene terephthalate at  $600\text{--}900 \text{ }^\circ\text{C}$ . Osman et al. [17] investigated the pre-exponential constant, activation energy and rate of reaction of thermal pyrolysis of polyethylene terephthalate. They used AKTS software in studying the kinetic triplet. Because these values are not impacted by scale, it was determined that the kinetic triplet could be beneficial in process



**Fig. 3.** (a) Data plot between the dependent variable ( $Z_1$ ) and predictors ( $X_1$  and  $Y_1$ ) with a difference of 0.02 (b) partial relation between the dependent variable ( $Z_1$ ) and predictor ( $X_1$ ) and (c) partial relation between the dependent variable ( $Z_1$ ) and predictor ( $Y_1$ ).

**Table 2**

Statistical rate constants were obtained with a difference of 0.02 at 420 °C.

Dependent variable $Z_1$	Independent variable $X_1$	Independent variable $Y_1$	Rate constant $\alpha_1$
0.17	0.15	0.19	$1.70 \times 10^{-1}$
$2.43 \times 10^{-8}$	$2 \times 10^{-8}$	$2.9 \times 10^{-8}$	$-3.55 \times 10^{-5}$
0.0301	0.02	0.04	$3.05 \times 10^{-2}$
0.206	0.1	0.3	$2.06 \times 10^{-1}$
0.0146	0.013	0.016	$1.45 \times 10^{-2}$
0.0104	0.005	0.015	$1.03 \times 10^{-2}$
$2.25 \times 10^{-14}$	$2.00 \times 10^{-14}$	$2.50 \times 10^{-14}$	$-3.55 \times 10^{-5}$
0.0205	0.01	0.03	$2.06 \times 10^{-2}$
$3.48 \times 10^{-10}$	$2.00 \times 10^{-10}$	$5.00 \times 10^{-10}$	$-3.55 \times 10^{-5}$

modeling to comprehend the process at large scale. Because it provides a better understanding of the reaction mechanism, this ultimately aids in the optimization of reactor design at scale. These researchers' predictions can be used to analyze how the reaction rate will change as a function of process temperature and heating rate utilizing stepwise, isothermal, and non-isothermal heating regimes.

For the efficient transformation of plastic waste into useful fuel materials, it is necessary to study the sensitivity of rate constants toward the chemical kinetics of the pyrolysis reaction. From sensitivity analysis, we can individually assess the kinetic rate reaction's effectiveness. The influence of the pyrolysis process on the species can be investigated using this technique by lowering or raising its



**Table 3**  
MLRM coefficients obtained with differences of 0.03 and 0.04 from an experiment.

Difference		Estimate	Stand. Error	t-value	P-value
0.03	Intercept	$3.000 \times 10^{-2}$	$2.074 \times 10^{-9}$	1.446	$2 \times 10^{-16}$ ***
	X <sub>2</sub>	1.000	$3.507 \times 10^{-8}$	$2.852 \times 10^7$	$2 \times 10^{-16}$ ***
	Y <sub>2</sub>	$2.724 \times 10^{-8}$	$3.494 \times 10^{-8}$	$7.800 \times 10^{-1}$	0.465
0.04	Intercept	$4.000 \times 10^{-2}$	$3.168 \times 10^{-9}$	$1.263 \times 10^7$	$2 \times 10^{-16}$ ***
	X <sub>3</sub>	1.000	$3.919 \times 10^{-8}$	$2.552 \times 10^7$	$2 \times 10^{-16}$ ***
	Y <sub>3</sub>	$-4.505 \times 10^{-9}$	$3.990 \times 10^{-8}$	$-1.130 \times 10^{-1}$	0.914

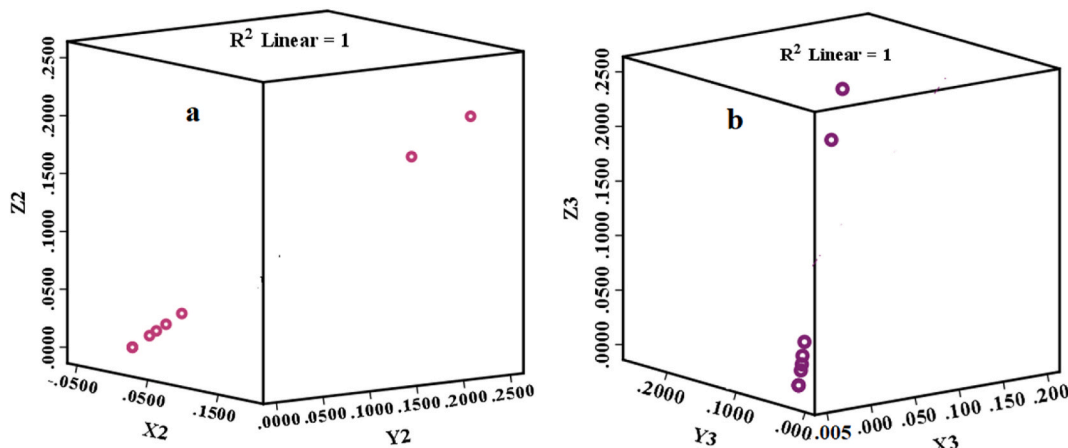


Fig. 4. Correlation between dependent and independent variables with (a) 0.03 difference and (b) 0.04 difference.

**Table 4**  
Statistical rate constants predicted using a difference of 0.03.

Dependent variable	Independent variable	Independent variable	Rate constant
Z <sub>2</sub>	X <sub>2</sub>	Y <sub>2</sub>	α <sub>2</sub>
0.17	0.14	0.2	$1.71 \times 10^{-1}$
$2.43 \times 10^{-8}$	-0.030	0.0300	$2.31 \times 10^{-3}$
0.0301	$1.00 \times 10^{-4}$	0.0601	$3.21 \times 10^{-2}$
0.206	0.176	0.236	$2.06 \times 10^{-1}$
0.0146	-0.0154	0.0446	$1.68 \times 10^{-2}$
0.0104	-0.0196	0.0404	$1.26 \times 10^{-2}$
$2.25 \times 10^{-14}$	-0.03	0.03	$2.31 \times 10^{-3}$
0.0205	-0.0095	0.0505	$2.26 \times 10^{-2}$
$3.48 \times 10^{-10}$	-0.03	0.03	$2.31 \times 10^{-3}$

**Table 5**  
Statistical rate constants were predicted with a difference of 0.04.

Dependent variable	Independent variable	Independent variable	Rate constant
Z <sub>3</sub>	X <sub>3</sub>	Y <sub>3</sub>	α <sub>3</sub>
0.17	0.14	0.2	$1.70 \times 10^{-1}$
$2.43 \times 10^{-8}$	-0.030	0.0300	$2.38 \times 10^{-8}$
0.0301	$1.00 \times 10^{-4}$	0.0601	$3.01 \times 10^{-2}$
0.206	0.176	0.236	$2.06 \times 10^{-1}$
0.0146	-0.0154	0.0446	$1.46 \times 10^{-2}$
0.0104	-0.0196	0.0404	$1.04 \times 10^{-2}$
$2.25 \times 10^{-14}$	-0.03	0.03	$-1.80 \times 10^{-10}$
0.0205	-0.0095	0.0505	$2.05 \times 10^{-2}$
$3.48 \times 10^{-10}$	-0.03	0.03	$-1.80 \times 10^{-10}$

initial value to a certain level where maximum oil output is obtained [2]. To date, no research has been conducted to predict the rate constants and their sensitivity to the products. These two factors can play an essential role in producing oil yield from high-density plastic pyrolysis on a commercial scale. Therefore sensitivity analysis of individual rate constants can provide important

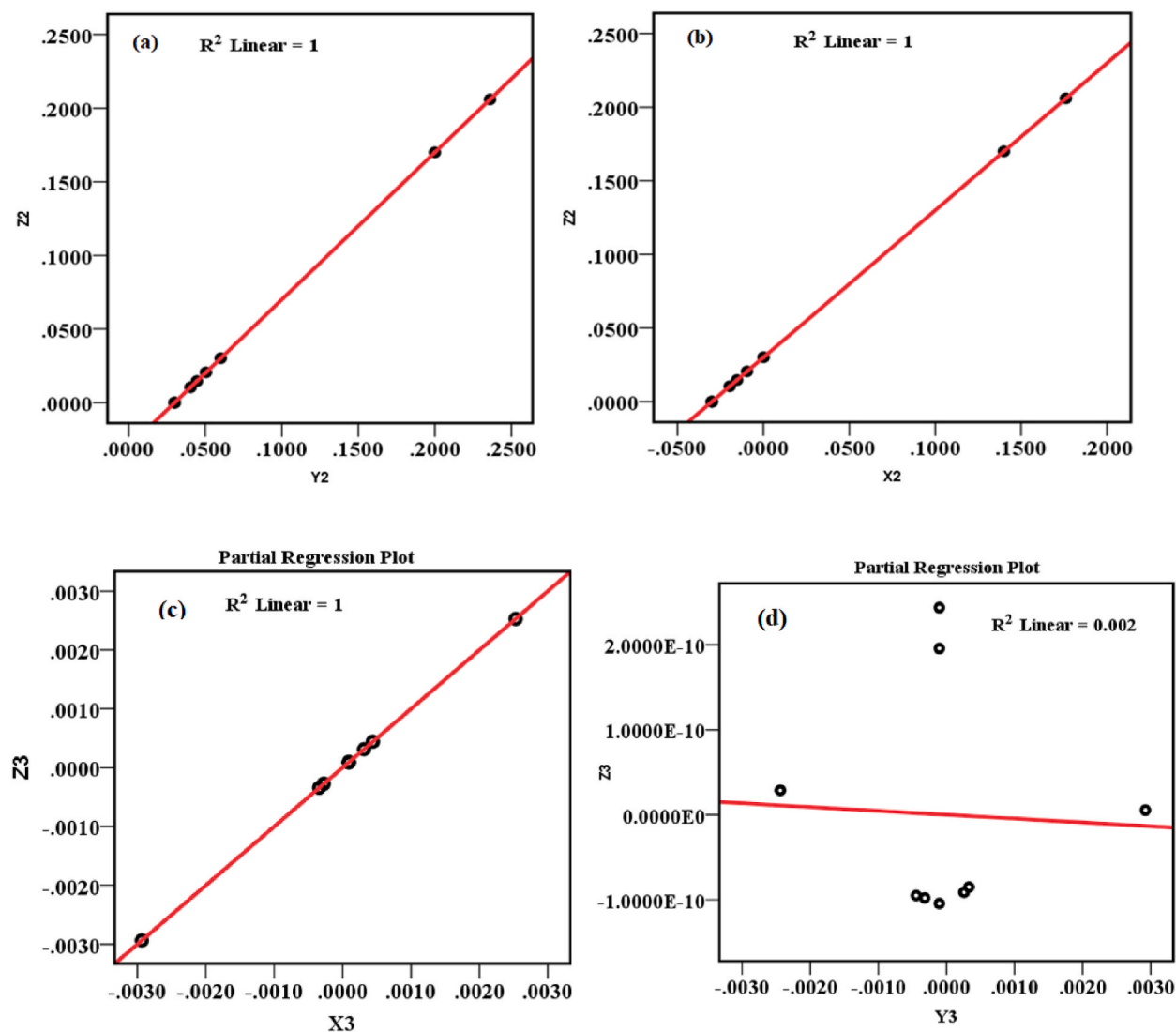


Fig. 5. A relationship between the (a) dependent variable ( $Z_2$ ) and predictor ( $Y_2$ ) with a difference of 0.03 difference, (b) between the dependent variable ( $Z_2$ ) and predictor ( $X_2$ ) with a difference of 0.03, (c) between the dependent variable ( $Z_3$ ) and predictor ( $X_3$ ) with a difference of 0.04, and (d) between the dependent variable ( $Z_3$ ) and predictor ( $Y_3$ ) with a difference of 0.04.

Table 6

Experimental and statistically predicted rate constant with 0.02, 0.03, and 0.04 difference.

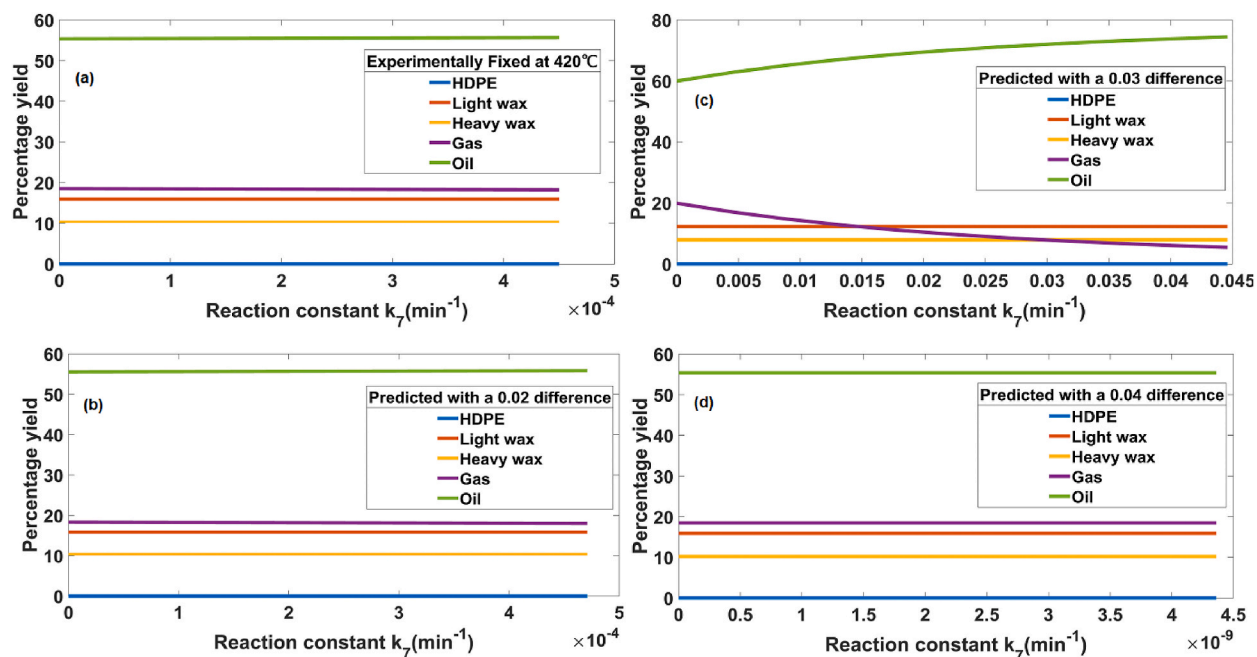
Rate constant	Experimental K	Predicted at 0.02 $\alpha_1$	Predicted at 0.03 $\alpha_2$	Predicted at 0.04 $\alpha_3$
k(1)	0.17	$1.70 \times 10^{-1}$	$1.71 \times 10^{-1}$	$1.70 \times 10^{-1}$
k(2)	$2.43 \times 10^{-8}$	$-3.55 \times 10^{-5}$	$2.31 \times 10^{-3}$	$2.38 \times 10^{-8}$
k(3)	0.0301	$3.05 \times 10^{-2}$	$3.21 \times 10^{-2}$	$3.01 \times 10^{-2}$
k(4)	0.206	$2.06 \times 10^{-1}$	$2.06 \times 10^{-1}$	$2.06 \times 10^{-1}$
k(5)	0.0146	$1.45 \times 10^{-2}$	$1.68 \times 10^{-2}$	$1.46 \times 10^{-2}$
k(6)	0.0104	$1.03 \times 10^{-2}$	$1.26 \times 10^{-2}$	$1.04 \times 10^{-2}$
k(7)	$2.25 \times 10^{-14}$	$23.55 \times 10^{-5}$	$22.31 \times 10^{-3}$	$21.80 \times 10^{-10}$
k(8)	0.0205	$2.06 \times 10^{-2}$	$2.26 \times 10^{-2}$	$2.05 \times 10^{-2}$
k(9)	$3.48 \times 10^{-10}$	$-3.55 \times 10^{-5}$	$2.31 \times 10^{-3}$	$-1.80 \times 10^{-10}$

information on reaction conditions and the quality and quantity of the products [6]. For sensitivity analysis, one possible approach is to estimate the kinetic parameters using MLRM model in SPSS at a fixed pyrolysis temperature. No studies that integrate sensitivity analysis with statistical optimization of rate constants have been published in the literature as of yet [22]. This work aims to address

**Table 7**

The initial values and lower extreme to higher extreme position yields for both experimental and statistically predicted  $k(2)$ ,  $k(7)$ , and  $k(9)$  rate constants.

Rate constant	Initial values				H.W	L.W	Gas	Oil
	Rate constants predicted with a slight difference from experimental values							
	Experimental	0.02 difference	0.03 difference	0.04 difference	%Yield			
K(2)	$2.43 \times 10^{-8}$	$3.55 \times 10^{-5}$	$2.31 \times 10^{-3}$	$2.38 \times 10^{-8}$	0	0	0	0
K(7)	$2.25 \times 10^{-14}$	$2-3.55 \times 10^{-5}$	$22.31 \times 10^{-3}$	$2-1.80 \times 10^{-10}$	0	0	0	74%
K(9)	$3.48 \times 10^{-10}$	$3.55 \times 10^{-5}$	$2.31 \times 10^{-3}$	$1.80 \times 10^{-10}$	0	0	0	0



**Fig. 6.** Trend of the pyrolysis products obtained with (a) experimental rate constant  $k(7)$ , (b) predicted rate constant  $k(7)$  with a difference of 0.02, (c) predicted rate constant  $k(7)$  with a difference of 0.03, and (d) predicted rate constant  $k(7)$  with a difference of 0.04.

**Table 8**

The initial values and lower extreme to higher extreme position yield for experimentally fixed and statistically predicted  $k(1)$  rate constant.

Rate constant	Initial values	H.W	L.W	Gas	Oil
		% yield at lower to higher extreme values			
k(1) Experimentally fixed	0.17	3 to 15	24 to 10	6 to 37	66 to 47
k(1) with a difference of 0.02	$3.55 \times 10^{-5}$	3 to 14	24 to 10	7	72 to 75
k(1) with a difference of 0.03	$2.31 \times 10^{-3}$	3 to 12	18 to 8	7 to 14	72 to 66
k(1) with a difference of 0.04	$2.38 \times 10^{-8}$	3 to 17	24 to 10	0	72 to 74

this research gap so that theoretical studies might improve the discrepancy between the experimental rate constant and the oil content. We developed a statistical model at a fixed temperature of 420 °C and analyzed it after 60 min of reaction time. In this model, we tried to figure out the maximum oil quantity obtained with the original value of the rate constant by hypothetically increasing and decreasing the original value of the experimental and anticipated rate constant by 100%. These methods require statistical tuning of the process parameters to obtain maximum production and superior product selectivity. A factorial design was applied by Wirawan and Farizal [23] to optimize plastic pyrolysis for high grade fuel products. They used a 2k factorial design to optimize the type of plastic, process temperature, and residence time for high liquid fuel yield. It was possible to produce diesel-like liquid products at low or moderate temperatures after statistically optimizing the pyrolysis process. About 175 °C and 3 h were reported as the optimal temperature and residence time, respectively. Joppert et al. [24] used a factorial design methodology to improve the composition of diesel fuel produced through co-pyrolysis of heavy gas oil and HDPE waste. Using this methodology, they optimized the reaction parameters to improve oil fractions' selectivity. Better selectivity and product yield were possible at 550 °C. About 94% of the oil was

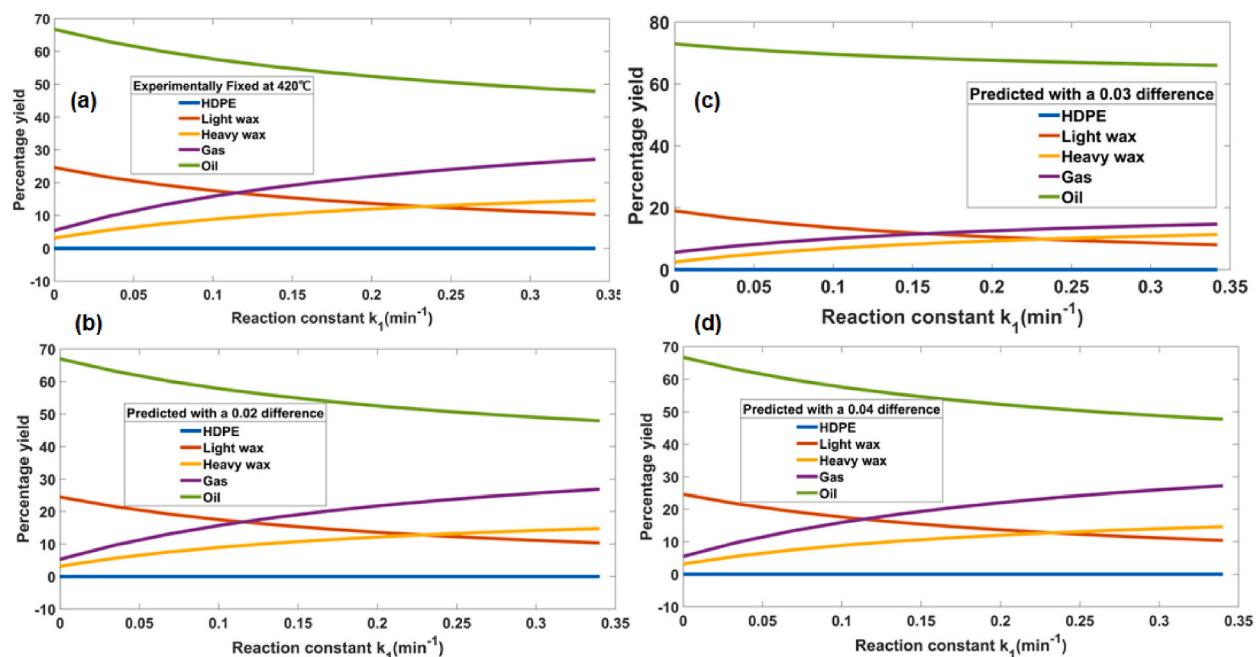


Fig. 7. Trend of the pyrolysis products obtained with (a) experimental rate constant  $k(1)$ , (b) predicted rate constant  $k(1)$  with a difference of 0.02, (c) predicted rate constant  $k(1)$  with a difference of 0.03, and (d) predicted rate constant  $k(1)$  with a difference of 0.04.

Table 9

The initial values and lower extreme to higher extreme position yield for experimentally fixed and statistically predicted  $k(3)$  rate constant.

Rate constant	Initial values	H.W				L.W			
		%age yield at lower to higher extreme values				%age yield at lower to higher extreme values			
k(3) Experimentally fixed	0.0301	11	18	20	52	59			
k(3) Predicted at a variance of 0.02	$3.05 \times 10^{-2}$	11	18	0	71	76			
k(3) Predicted at a variance of 0.03	$3.21 \times 10^{-2}$	9	13	12	68	72			
k(3) Predicted at a variance of 0.04	$3.01 \times 10^{-2}$	11	18	0	72	77			

recovered through these optimizations, with a diesel content of about 93%. Krishna et al. [25] examined the global kinetics for rapid pyrolysis of plastics by determining the pre-exponential factors and activation energy with integral reaction models. They also established a statistical kinetic compensation effect for plastics by taking data from the reported literature. The maximum evolution of vapors was possible within 12–45 s at 500 °C, depending on the plastic type. The evolution time was reduced to 20–22 s at 600 °C. The process temperature and reaction time can be reduced further by performing a sensitivity analysis of rate constants toward the chemical kinetics of the pyrolysis of plastics. This part is missing in the literature and better insight into sensitivity analysis can significantly reduce the process cost by enhancing the product yield at relatively lower temperatures. This study is conducted to explore the above-mentioned research gap.

## 2. Statistical approach to predict rate constants

This study is conducted to establish a relation between reaction rate constants and product yield from the pyrolysis of HDPE waste. This study also addresses the sensitivity of the individual rate constants to the product type and yield. The oil product finds its applications in combustion and energy, while light wax can be used commercially as food coating, packing material, and lamination. With this scope of the study, we developed a statistical model at a fixed temperature of 420 °C and analyzed it after 60 min of reaction time. We tried to figure out the behavior of the kinetic rate reaction by changing the value of both the experimental and predicted rate constants up to 200%. Thermal pyrolysis of HDPE plastic waste with these kinetic parameters was performed using a MLRM model in SPSS software [26].

Eidesen et al. [27] calculated the amount of oil and gas produced by the thermal pyrolysis of HDPE using these empirical rate constants. To forecast the rate constants statistically, we utilized SPSS software. The thermal valorization of HDPE was simulated in MATLAB using the estimated rate constants. Investigations were done into how these rate constants affected oil, gas, and waxes evolved over the course of processing. To establish the best mix of rate constants for high sensitivity, selectivity, and yield, the modeling results were compared to actual data. While the statistically presumed rate constants were utilized as independent or

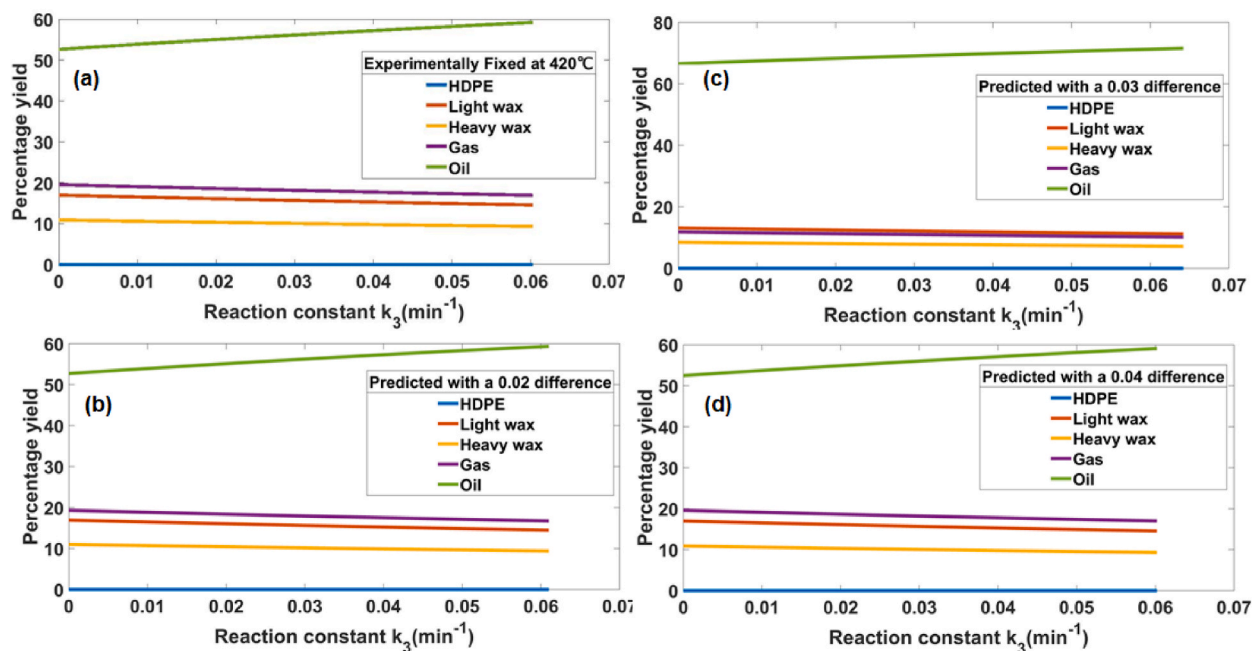


Fig. 8. Trend of the pyrolysis products obtained with (a) experimental rate constant  $k_3$ , (b) predicted rate constant  $k_3$  with a difference of 0.02, (c) predicted rate constant  $k_3$  with a difference of 0.03, and (d) predicted rate constant  $k_3$  with a difference of 0.04.

Table 10

The initial values and lower to higher extreme position yield of experimentally fixed and statistically predicted  $k_4$  rate constant.

Rate constant	Initial values	L.W				Gas	Oil
		%age yield at lower to higher extreme values					
$k_4$ Experimentally fixed	0.206	17 to 22	7 to 18	8 to 30	48 to 60		
$k_4$ Predicted at a variance of 0.02	$2.06 \times 10^{-1}$	6 to 16	5 to 21	0	68 to 76		
$k_4$ Predicted at a variance of 0.03	0.04	5 to 13	4 to 16	8 to 18	65 to 70		
$k_4$ Predicted at a variance of 0.04	$2.06 \times 10^{-1}$	6 to 17	5 to 21	0	72 to 76		

predictor variables, the experimental rate constants were used as dependent or response variables in the statistical model. The correlation between the response and predictor factors was validated using different graphical demonstrations after applying the model. The generic version of MLRM Equation (1) was then applied in the SPSS software on the assumed rate constants [28].

$$Z_n = A_{0n} + C_n X_n + D_n Y_n \tag{1}$$

where, Z is the response variable or statistical rate constant,  $A_0$  is an intercept, C and D are the coefficients of the regression model., X and Y are the independent variables, and n = 1, 2, and 3 are the statistical operations. These coefficients are used to determine an acceptable set of statistical rate constants. In MLRM, the predictor variables were used with slight differences of 0.02, 0.03, and 0.04 from the experimental data. This difference in MLRM is explained using Equation (2):

$$Z_1 = A_0 + C_1 X_1 + D_1 Y_1, Z_2 = B_0 + C_2 X_2 + D_2 Y_2 \text{ and } Z_3 = C_0 + C_3 X_3 + D_3 Y_3 \tag{2}$$

where,  $X_1, X_2, X_3, Y_1, Y_2,$  and  $Y_3$  are independent variables,  $Z_1, Z_2,$  and  $Z_3$  are dependent variables, while  $C_1, C_2, C_3, D_1, D_2,$  and  $D_3$  are the coefficients of the regression model. The rate constants were predicted using an assumed series of activation energies, frequency factors, and fixed temperatures in SPSS software. The rate constants were estimated statistically using a combination of activation energies ( $E_a$ ) and frequency factors ( $A_0$ ). In the statistical model, we do not have exact values of  $E_a$  and  $A_0$  since MLRM does not deal with them and is unable to reveal these values. This is one of the limitations of the tested model. MLR coefficients  $C_1$  ( $-0.04$ ) and  $D_1$  ( $4.56 \times 10^{-1}$ ) and SPSS intercept  $A_0$  ( $5.35 \times 10^{-1}$ ) were first used in the analysis with a difference of 0.02 in the MLRM equation. The symbol ‘\*\*\*’ in Table 1 shows that the p-values for  $X_1$  and  $Y_1$  are  $<0.001$ , which is statistically significant. A graphic depiction of the steps involved in sensitivity analysis of rate constants for thermal pyrolysis of HDPE waste using SPSS and MATLAB is given in Fig. 2.

When  $D_1$  is kept constant, the estimated regression coefficient  $C_1$  reveals 0.456 units increase in  $Z_1$  with variations in predictor variables. Similarly, when  $C_1$  is kept constant, the regression coefficient  $D_1$  indicates an increase of 0.534 units in  $Z_1$ . According to Fig. 3a, the dependent variable ‘ $Z_1$ ’ and predictors ( $X_1$  and  $Y_1$ ) can be used to investigate the nature of the data. The given data plot

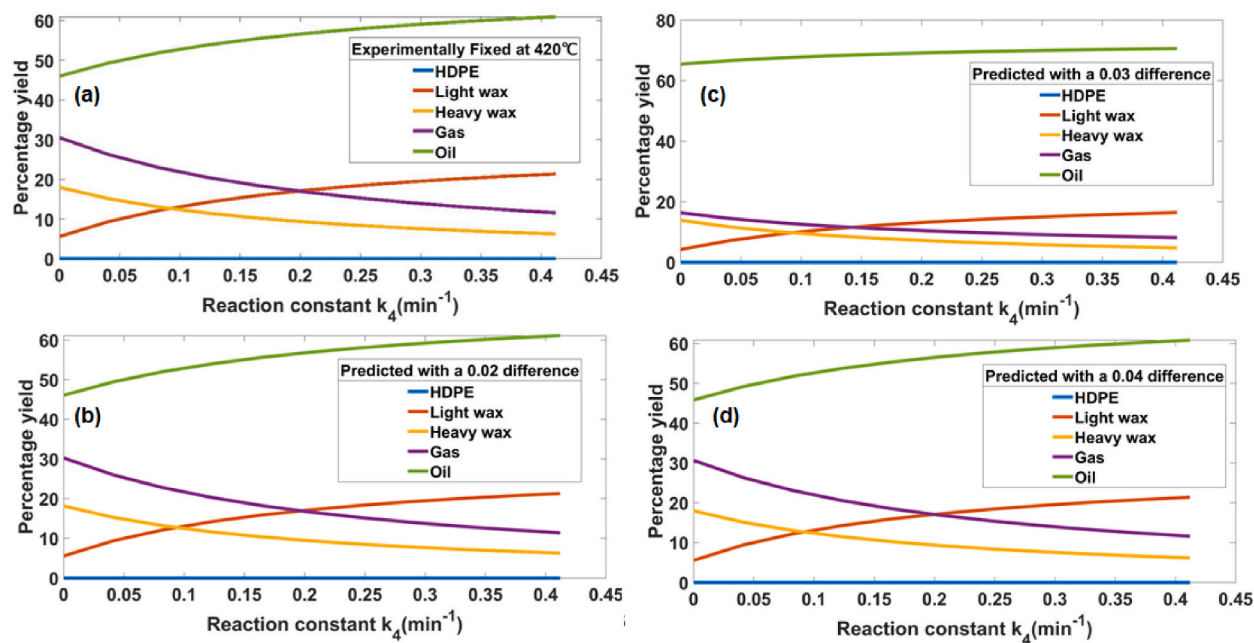


Fig. 9. Trend of the pyrolysis products obtained with (a) experimental rate constant  $k_4$ , (b) predicted rate constant  $k_4$  with a difference of 0.02, (c) predicted rate constant  $k_4$  with a difference of 0.03, and (d) predicted rate constant  $k_4$  with a difference of 0.04.

Table 11

The initial values and lower to extreme position yield of experimentally fixed and statistically predicted  $k_5$  rate constant.

Rate constant	Initial values	H.W	L.W	%age yield at lower to higher extreme values	
				Gas	Oil
K(5) Experimentally fixed	0.0146	3 to 20	15	5 to 28	52 to 60
K(5) Predicted at a variance of 0.02	$1.45 \times 10^{-2}$	3 to 20	17	0	64 to 80
K(5) Predicted at a variance of 0.03	$1.68 \times 10^{-2}$	2 to 16	12	4 to 14	66 to 70
K(5) Predicted at a variance of 0.04	$1.46 \times 10^{-2}$	3 to 20	17	0	64 to 80

between dependent and independent variables is for 0.02 difference between statistically predicted and experimental values. Dependent and predictor variables in the graph with a trend from bottom to top show  $R^2 = 0.883$ , indicating the significance of data ( $P < 0.001$ ) and a positive correlation between variables. Fig. 3b and c partially demonstrate  $X_1$  and  $Y_1$  predictors, which show almost the same data trend. It is a partial relation between dependent and predictor variables with a 0.02 difference from the experiment. This set of rate constants ( $\alpha_1$ ) is generated after running MLRM in SPSS, as summarized below in Table 2.

Table 3 shows MLRM coefficients for the empirical constants at 420 °C with a slight difference of 0.03 and 0.04 from the experiment. In this table,  $C_2(4.56 \times 10^{-1})$ ,  $C_3(1.00 \times 10^0)$ ,  $D_2(5.35 \times 10^1)$ , and  $D_3(-4.51 \times 10^{-9})$  are the coefficients of MLRM, whereas  $C_0(-3.55 \times 10^{-5})$  and  $D_0(4.00 \times 10^{-2})$  are the intercepts estimated using MLRM in SPSS. It is demonstrated that p-values for the predictors  $X_2$  and  $X_3$  are significant ( $p < 0.001$ ), but the p-values for  $Y_2$  and  $Y_3$  are not significant ( $P > 0.001$ ), as shown in a 3D demonstration in Fig. 4(a) and (b).

The results showed a negative relationship between predictor factors  $Y_2$  and  $Y_3$  and responses  $Z_2$  and  $Z_3$ . The findings show that dependent and predictor variables are significant for  $X_2$  and  $X_3$  but not for  $Y_2$  and  $Y_3$  since the data trend does not shift precisely from bottom to top, as illustrated in Fig. 4(a) and (b). Tables 4 and 5 show the estimated rate constants with a variance of 0.03 and 0.04, respectively. A positive correlation for  $X_2$  and  $X_3$  is shown in Fig. 5(a) and (b) since the p-value is greater than 0.001. However, a negative correlation between  $Y_2$  and  $Y_3$  is clear in Fig. 5(c) and (d) since the p-value is less than 0.001.

Table 6 lists the experimental and statistically estimated rate constants. MATLAB version R2020a was used to solve an ODE  $i.e [t,x] = ode23s(@t,x,k)$ , time, C0 for both experimental and statistically forecasted rate constants to study the relationship between rate constants and %age yield across process time [21,22].

### 3. Sensitivity analysis of statistical kinetic rate constants

Sensitivity analysis is a technique for individually assessing the effectiveness of kinetic rate constants. In this strategy, we can examine the influence of the rate constants on the pyrolysis species by lowering or raising their initial values to a certain level, where



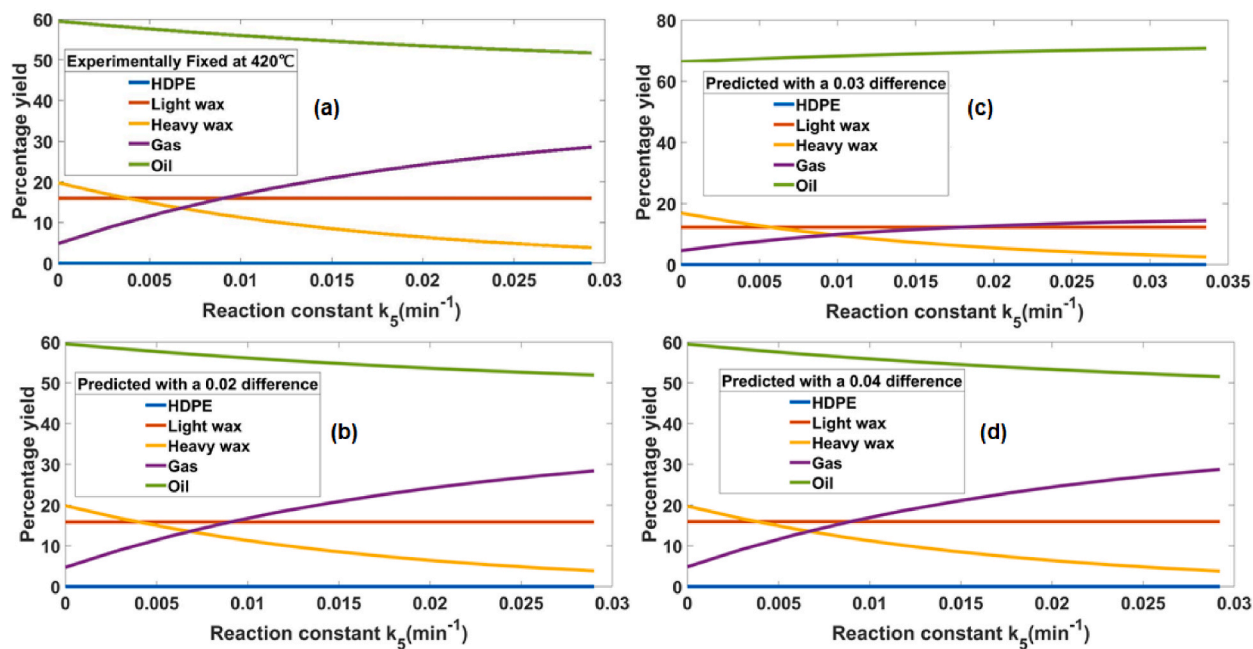


Fig. 10. Trend of the pyrolysis products obtained with (a) experimental rate constant  $k_5$ , (b) predicted rate constant  $k_5$  with a difference of 0.02, (c) predicted rate constant  $k_5$  with a difference of 0.03, and (d) predicted rate constant  $k_5$  with a difference of 0.04.

Table 12

The initial values and lower to higher extreme position yield for experimentally fixed and statistically predicted  $k_6$  rate constant.

Rate constant	Initial values	H.W	L.W	Gas	Oil
		% age yield at lower to higher extreme values			
K(6) Experimentally fixed	0.0104	17 to 3	18 to 19	22 to 25	45 to 64
K(6) Predicted at a variance of 0.02	$1.03 \times 10^{-2}$	17 to 3	18 to 19	0	67 to 78
K(6) Predicted at a variance of 0.03	$1.26 \times 10^{-2}$	14 to 2	12 to 13	14 to 10	59 to 76
K(6) Predicted at a variance of 0.04	$1.04 \times 10^{-2}$	17 to 3	17 to 16	0	67 to 76

maximal oil output is produced. The economy and capacity to produce oil from thermal pyrolysis at a commercial scale largely depend on sensitivity analysis, which is missing from the published literature. We presumed that the reaction would have two extreme values, say the lower extreme and the upper extreme:

$$[t,x] = \text{ode23s}(@(\text{t,x}) \text{test reaction}(\text{t,x,k},\text{time},\text{C0}) \tag{3}$$

$$k_{n\_max} = k(n)+k(n) \tag{4}$$

In this model, Equation (3) is the second-order differential solver used in MATLAB to investigate the individual efficiency of kinetic rate reactions. In this equation, “t” is the process time, which varies from 1 to 240 min, “x” is % yield, “C0” is the number of equations to be solved (initial condition), and “k” is the estimated rate constants. Equation (4) shows a 200% change in the reaction. These changes help find the values of rate constants suitable for producing the maximum amount of oil and light wax as a byproduct, if any. This can be more effective on an industrial scale if the gas yield is added to the oil content. The yield is determined after 1 h of processing at a 100% increment and decrement in the initial values. Eidsen et al. [27] revealed that when the best pyrolysis conditions are met, the production of light wax largely depends on kinetic reaction  $k(1)$ , oil on kinetic reaction  $k(2)$ , gas on kinetic reaction  $k(3)$ , and heavy wax on kinetic reaction  $k(4)$ . The free radicals in the light wax can also be converted to oil by tuning the kinetic rate constant  $k(5)$ , light wax to gas with  $k(6)$  kinetic reaction, heavy wax to gas with  $k(8)$  kinetic reaction, and heavy wax to oil with a  $k(9)$  kinetic reaction [29].

The initial values of experimental and statistically predicted  $k(2)$ ,  $k(7)$ , and  $k(9)$  rate constants and corresponding yields are reported in Table 7. After 1 h of operation, the rate constants  $k(2)$  and  $k(9)$  produced no oil, waxes, or gas for the difference of 0.02, 0.03, and 0.04. In other words, these rate constants could not initiate the pyrolysis process. A similar trend was observed in experimental data where products were almost absent after the said time. The rate constant  $k(7)$  also showed a similar trend except for the difference of 0.3, as shown in Fig. 6. This difference leads to 60%–74% oil yield production. This trend is attributed to sufficient activation energy and, indeed, the frequency factor, both of which are important in kinetic processes [30]. The collision hypothesis states that the

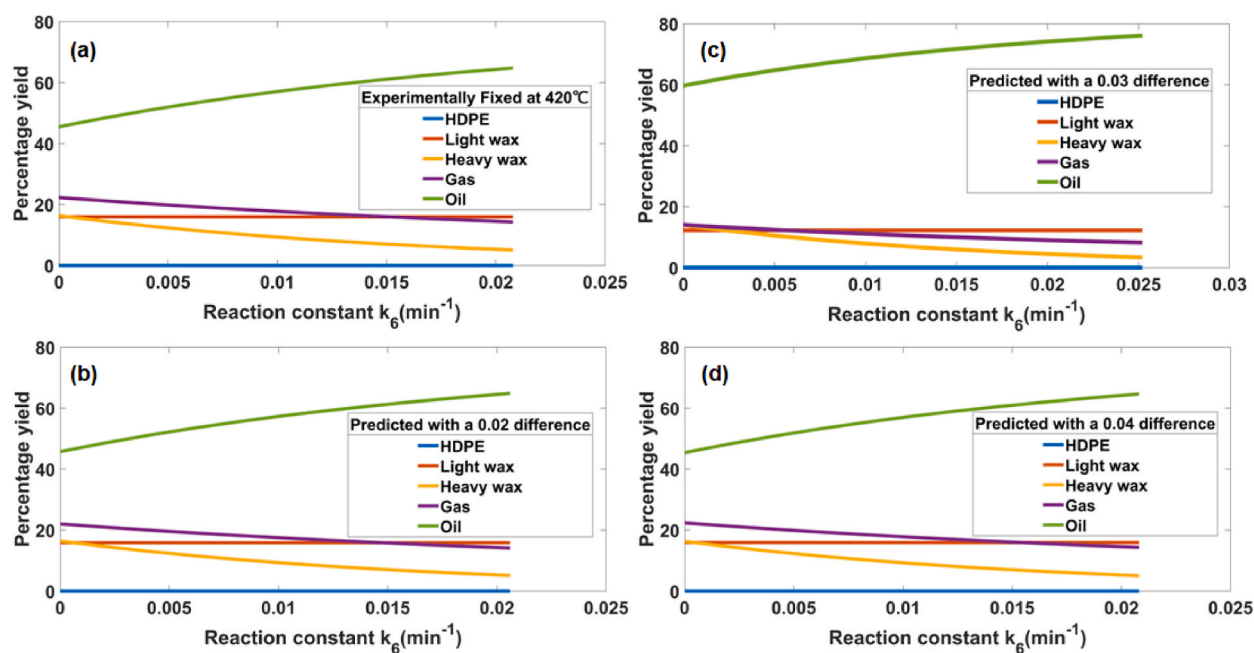


Fig. 11. Trend of the pyrolysis products obtained with (a) experimental rate constant  $k(6)$ , (b) predicted rate constant  $k(6)$  with a difference of 0.02, (c) predicted rate constant  $k(6)$  with a difference of 0.03, and (d) predicted rate constant  $k(6)$  with a difference of 0.04.

Table 13

The initial values and lower to higher extreme position yield of experimentally fixed and statistically predicted  $k(8)$  rate constant.

Rate constant	Initial values	%age yield at lower to higher extreme values			
		H.W	L.W	Gas	Oil
K(8) Experimentally fixed	0.0205	0	40 to 2	18	31 to 67
K(8) Predicted with a 0.02 difference	$2.06 \times 10^{-2}$	0	40 to 2	18	49 to 85
K(8) Predicted with a 0.03 difference	$2.26 \times 10^{-2}$	0	34 to 1	23	45 to 79
K(8) Predicted with a 0.04 difference	$2.05 \times 10^{-2}$	0	40 to 3	0	49 to 85

reaction will proceed slowly if the activation energy is significantly more than the sum of the molecular kinetic energies. There won't be many fast-moving molecules that can interact and create the oil or other products [31]. There will be more molecules with the necessary kinetic energy if the activation energy is significantly lower than the average kinetic energy of the molecules. The reaction rate will be accelerated by the numerous collisions between these molecules [31]. It was found that the value of the  $k(7)$  rate constant, predicted with a 0.03 difference, is higher than the experimental value and other statistically predicted values. It is a possible reason for the occurrence of pyrolysis reaction and the formation of oil.

Table 8 shows the pyrolysis products and their yield obtained with the rate constant  $k(1)$ . As shown in Fig. 7, light wax and oil production experimentally decreased from 24% to 10% and 66%–47%, respectively. Conversely, heavy wax and gas increased from 3% to 15% and 6%–37%, respectively. The trend of light and heavy waxes, predicted statistically, was almost similar to the experimental trend. The gas yield remained at 7%–14% for a difference of 0.03 and no gas was produced for a difference of 0.04. The oil yield remained higher than the experimental yield for all statistically predicted  $k(1)$  values.

Table 9 lists the starting values of  $k(3)$  kinetic rate constants based on experimental data and statistical predictions. Fig. 8 shows that HDPE is wholly converted to oil and other products within 60 min of operation. The experimental and statistical findings suggest light wax of 9–11%. The heavy wax also remained the same both experimentally and statistically at 18% for the rate constants with differences of 0.02 and 0.04 [31,32]. However, the heavy wax was predicted at about 13% when the difference was 0.3. The gas yield was measured at about 20% experimentally, which was reduced to 12% in statistical predictions when the difference was set at 0.3. The statistical forecasts did not show the formation of gas for the difference of 0.2 and 0.4. However, these differences in rate constants produced the highest oil yield of 76–77%. It was found that the experimental  $k(3)$  yielded oil between 52% and 59% [33]. Since the temperature was fixed, moisture can only be the factor to affect the gas yield in the experiment. Gas production increases with the moisture content [34].

The starting values of the  $k(4)$  rate constant based on experimental data and statistical predictions are given in Table 10. Fig. 9 shows that HDPE is wholly converted to oil and other products within 60 min of operation. The experimental data produced 17–22% heavy wax, 7–18% light wax, 8–30% gas, and 48–60% oil. On the other hand, the statistical analysis produced the highest oil yield of

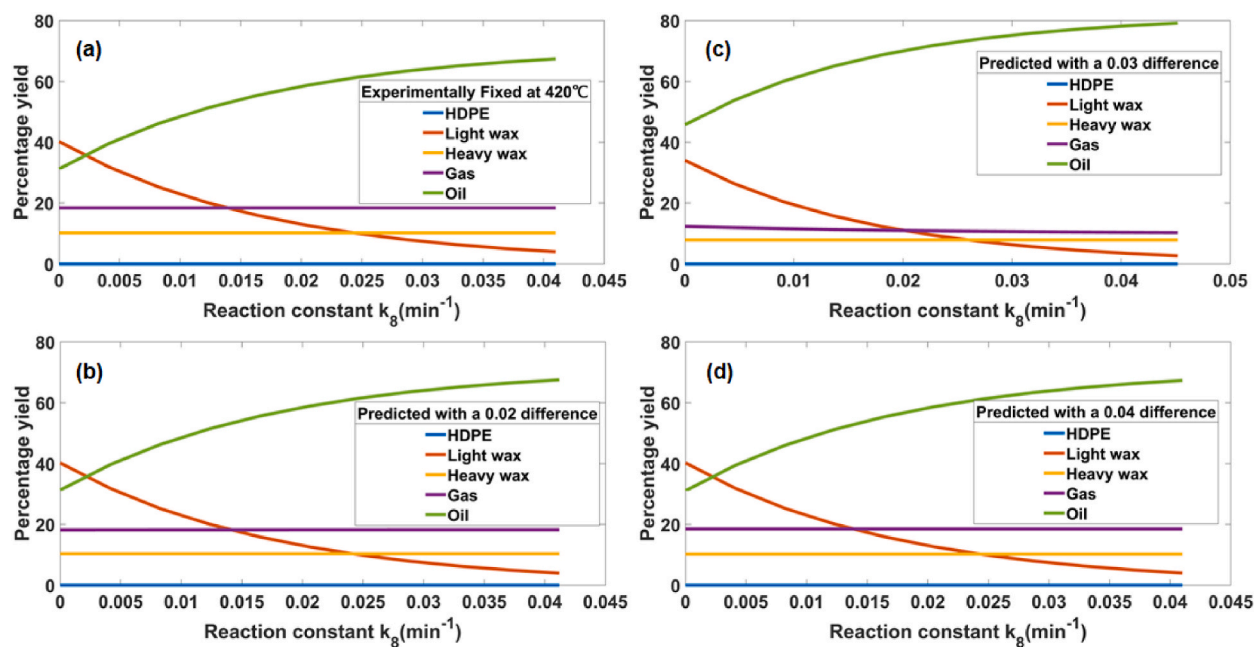


Fig. 12. Trend of the pyrolysis products obtained with (a) experimental rate constant  $k(8)$ , (b) predicted rate constant  $k(8)$  with a difference of 0.02, (c) predicted rate constant  $k(8)$  with a difference of 0.03, and (d) predicted rate constant  $k(8)$  with a difference of 0.04.

72–76%, with the rate constant having a difference of 0.04 from the experiment. This rate constant produced 0% gas and 5–21% light wax, and so does the rate constant having a difference of 0.02 from the experiment. However, the rate constant, having a difference of 0.03, produced slightly different results. For this difference, the heavy wax remained at 5%–13%, light wax remained at 4%–15%, gas yield remained at 8%–18% and oil yield remained at 65%–70% oil [35]. The  $k(4)$  rate constant showed a similar moisture impact as of  $k(3)$ .

For the rate constant  $k(5)$ , the initial values and individual efficiencies are shown in Table 11. For the experimentally determined and statistically estimated rate constants, the heavy wax and light wax were found to be 2–20% and 12–17%, respectively, with a difference of 0.02 and 0.04 in the experimental findings. Although after 60 min of processing time, heavy wax output was found to be 2–17% and light wax yield was 12% lower. The rate constant with a 0.03 difference in the experimental fixed value suggests a downward trend in waxes and gas. There was a decrease in the production of waxes over the processing time, as shown in Fig. 10. The proportion of gas and oil yield after 60 min of processing time was 52–60% for the experimentally fixed-rate constants and 64–80% for the statistically estimated rate constants, with a difference of 0.02 and 0.04, respectively. These findings suggest a significantly high oil yield in statistical predictions. For both the experimental and statistically projected rate constants, the production of gas grows as the process advances by an amount of 8%–28%. The reduction in byproducts has become the cause of an increase in the primary product in both the experimental and statistical rate constants at fixed temperatures [36,37].

For both experimental and statistical (6) rate constants, the initial and time-dependent efficiency of species is shown in Table 12. For both the experimental and statistically estimated  $k(6)$  rate constants, the light wax yield decreased slightly and the heavy wax decreased more drastically after 60 min of processing time, as shown in Fig. 11. The gas yield was expected at 22–25% and 14–10% in experimental work and statistical predictions, respectively, with a difference of 0.03. However, the rate constant, predicted by a difference of 0.02 and 0.04, indicated no gas formation. The oil yield remained about 67%–78% for statistical  $k(6)$  with a difference of 0.02–0.04 and 45%–64% for the experimental and forecasted with a 0.03 difference. The wax formation substantially decreased in both experimental statistical cases, which was the reason for an increase in oil yield [38,39].

The starting values of the  $k(8)$  rate constant based on experimental data and statistical predictions are given in Table 13. Fig. 12 shows some interesting results obtained after 60 min of experimentation. Altering the initial values of experimental and statistical  $k(8)$  enhances the oil output and significantly reduces the formation of light wax. Other kinetic rate constants did not show such a trend. The amount of heavy wax in both experimental and statistical findings remained zero, while the amount of light wax was also negligible.

Rate constants with a difference of 0.02 and 0.04 showed a reduction in light wax from 40% to 2%, whereas the light wax for 0.03 difference decreased from 34% to 1%. Experimental and statistical oil yields differed for 0.02 and 0.04, which increased from 31% to 67% and 49%–86%, respectively, after 60 min of operation. As time passes, less light wax is created, while the percentage of oil rises progressively over time [40]. The light wax production increased in both the experimental findings and the statistically predicted values, with a difference of 0.02 and 0.04. The experimental and statistical  $k(8)$  values with 0.02 and 0.04 difference results in higher reaction rates. Due to the lower activation energy compared to the frequency component, more collisions occur in the reaction [41]. So, the statistical  $k(8)$  rate constant with a difference of 0.02 and 0.04 can be utilized at a commercial scale for better performance.

**Table 14**

Comparison of maximum yield at extreme positions for both the experimental and predicted rate constants.

Rate constants	Initial values	Maximum percentage yield					
		Oil			Light wax		
		At initial	Lower extreme	Higher extreme	At initial	Lower extreme	Higher extreme
<b>Experimental fixed</b>							
k(1)	0.17	55	66	47	14	24	10
k(2)	2.43E-08	66	66	66	17	17	17
k(3)	0.0301	54	52	59	18	18	18
k(4)	0.206	47	45	60	18	5	21
k(5)	0.0146	58	59	51	15	15	15
k(6)	0.0104	58	45	64	12	12	12
k(7)	2.25E-14	58	58	58	17	17	17
k(8)	0.0205	58	31	67	18	40	4
k(9)	3.48E-10	66	66	66	16	16	16
<b>Predicted with a 0.02 difference from the experiment</b>							
k(1)	1.70E-01	73	72	74	14	24	10
k(2)	-3.55E-05	73	73	73	17	17	17
k(3)	3.05E-02	74	71	76	18	18	18
k(4)	2.06E-01	73	76	72	18	5	21
k(5)	1.45E-02	66	64	80	18	18	18
k(6)	1.03E-02	75	67	78	15	15	15
k(7)	23.55E-05	58	58	58	17	17	17
k(8)	2.06E-02	76	49	85	18	40	4
k(9)	-3.55E-05	72	72	72	17	17	17
<b>Predicted with a 0.03 difference from the experiment</b>							
k(1)	1.71E-01	68	72	56	12	18	8
k(2)	2.31E-03	69	69	69	12	12	12
k(3)	3.21E-02	68	66	71	12	12	12
k(4)	2.06E-01	69	65	70	14	4	16
k(5)	1.68E-02	68	66	70	12	12	12
k(6)	1.26E-02	70	59	76	12	12	12
k(7)	22.31E-03	70	69	74	16	16	16
k(8)	2.26E-02	70	45	79	10	34	2
k(9)	2.31E-03	69	69	69	13	13	13
<b>Predicted with a 0.04 difference from the experiment</b>							
k(1)	1.70E-01	73	72	74	14	24	10
k(2)	2.38E-08	73	73	73	18	18	18
k(3)	3.01E-02	68	66	71	18	18	18
k(4)	2.06E-01	73	76	72	18	5	21
k(5)	1.46E-02	66	64	80	18	18	18
k(6)	1.04E-02	75	67	78	15	15	15
k(7)	21.80E-10	58	58	58	17	17	17
k(8)	2.05E-02	76	49	85	18	40	4
k(9)	-1.80E-10	72	72	72	17	17	17

Finally, the rate constants for maximum light wax and oil yield after a 100% increment and decrement in the actual values are summarized in Table 14. The experimental rate constants produced 50–67% oil yield and 12%–18% light wax, while the simulated rate constants with 0.02, 0.03, and 0.04 differences from the experiment values approximated 65%–76% oil yield and 8%–12% light wax. The theoretical findings suggested a 9%–15% higher oil yield than the experimental value of oil yield. The k(8) rate constant is responsible for the conversion of heavy wax to gas. Both experimental and theoretically predicted k(8) constant values revealed an increase in oil and light wax. With this rate constant, the oil yield increased from 49% to 85%, with 40% light wax, as shown in Table 14. In the case of the k(8) rate constant, the amount of gas and heavy wax was almost zero throughout the processing time. These findings suggest that the predicted k(8) rate constant with a 0.02 and 0.04 difference is more useful for producing maximum oil and light wax at large-scale pyrolysis of HPDE waste.

#### 4. Limitations of the model

The statistical model was tested at a fixed temperature of 420 °C. At higher temperatures, the sensitivity analysis using this model may result in more gaseous products than liquid products from high-density plastics. The limited kinetic rate reactions can be examined using this model, while the plastics may undergo several complicated reactions. Some experimental rate constants are needed in this model to predict the new rate constants and to analyze the collinearity of the predicted rate constants. The statistical rate constants are based on a combination of  $E_a$  and  $A_o$ , which implies that this model forecasts the rate constants by default. The presented sensitivity analysis was specific to high-density plastics. In a real case, plastic waste is composed of different plastic fractions. So the reported model needs to be modified for the pyrolysis of mixed plastics.

## 5. Conclusions

The sensitivity analysis of kinetic rate constants with differences of 0.02, 0.03, and 0.04 from experimentally fixed values was conducted for the pyrolysis of HDPE using MLRM in SPSS. The study's primary goal was to analyze the kinetic rate reactions and their sensitivity that might have a major impact on commercial oil production. This approach provides information on the development of primary products during pyrolysis, allowing for the monitoring of the development of those products individually. Much work must be done to better understand experimental and statistical rate constants and their sensitivity behavior when used as an evaluation tool for determining the efficacy of individual kinetic rate reactions. It is concluded that substantial improvements in the oil yield are attributed to the elevation of the kinetic rate constants. It was essential to construct a model to determine the impact that operational factors have on the behavior of the system. The experimental and statistical rate constants demonstrated a positive correlation between dependent and predictor variables. To perform sensitivity analysis, the experimental and statistically predicted rate constants varied up to 200% from their original values. The product yield was examined after 60 min of thermal pyrolysis at a fixed temperature of 420 °C. The statistically predicted rate constant "k(8)" with a difference of 0.02 and 0.04 from the experiment revealed 85% oil yield and 40% light wax after 60 min of operation. The heavy wax was missing from the products under these conditions. This rate constant can be utilized to optimize the commercial-scale production of liquids and gases from the pyrolysis of plastic waste.

### Author contribution statement

Muhammad Irfan, Shazia Shukrullah, Hassan Abbas Khawaja: Analyzed and interpreted the data; Wrote the paper.

Rao Adeel Un Nabi, Hammad Hussain, Muhammad Yasin Naz: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Saifur Rahman, Muhammad Usman Farid: Contributed reagents, materials, analysis tools or data.

### Data availability statement

Data will be made available on request.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e16049>.

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