

Numerical sensitivity analysis of temperature-dependent reaction rate constants for optimized thermal conversion of high-density plastic waste into combustible fuels

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Abstract

The use of experimental rate constants for producing a high yield of liquid fuels from the pyrolysis of plastic waste is not widely accepted owing to a lack of compatibility between the different kinetic rate constants responsible for successful conversion reactions. In R software, the Arrhenius law can forecast the ideal combination of reaction rate constants and frequency factors and then perform sensitivity analysis on individual rate constants to estimate the selectivity and quantity of primary pyrolysis products. Sensitivity analysis is a way of determining the effectiveness of individual rate constants in the reaction. This research element is currently lacking in the literature for the cost-effective valorization of plastics into combustible fuels. We are the first to use R software to perform sensitivity analysis on specific rate constants by reducing or raising their initial values to a point where maximum oil yield is attainable in the temperature range of 340°C to 370°C. The primary focus was to save time and cost of extracting empirical rate constants from experiments to produce commercial-scale pyrolytic oil. The H-abstraction, chain fission, polymerization, and scission reactions were chosen due to the high availability of free radicals for maximum oil production. The oil recovery rate improved drastically to 90% at the end of processing time, while the number of byproducts gradually decreased. The k₈ rate constant driven reaction is the best-suited condition for industrial-scale pyrolysis of high-density plastics into liquid fuels, with 74% improvement in oil production and 14% improvement in light wax during sensitivity analysis.

Keywords: Thermal pyrolysis; high-density polyethylene; numerical analysis; sensitivity analysis; kinetic rate reactions; R software.

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1. Introduction

The dramatic rise in living standards and the use of plastic products significantly impacted the environment. Plastics are currently regarded as essential materials, and demand is rising due to their variety and appealing application areas in industry and household [1]. Thermoplastic polymers, in particular, contribute significantly to trash, and the amount is rapidly increasing globally. As a result of their substantial amount and the fact that thermoplastics do not decompose for a long time, waste plastics offer a severe environmental challenge [2]. Plastics are composed of hydrocarbons derived from petroleum, but they also contain additives such as antioxidants, colorants, and other stabilizers. Furthermore, when these compounds are used and discarded in plastic products, they harm the environment and contribute to pollution. The incineration of plastics causes severe air pollution by releasing harmful gases, including dioxins, hydrogen chloride, and carbon dioxide [3].

Recycling has emerged as a viable solution to the environmental issues plaguing the plastics sector. Recycling can be divided into primary, secondary, tertiary, and quaternary levels. Tertiary recycling lowers polymers to their constituent monomers or basic petroleum fuel [4]. Tertiary recycling breaks down polymer molecules into smaller organic molecules or monomers. Pyrolysis is the most essential and extensively utilized tertiary recycling process, in which polymers are heated without oxygen. Tertiary recycling of waste plastics should not be viewed solely as a solution for waste plastics disposal but also as a source of ecologically friendly transportation fuel or feedstock for producing plastics [5, 6]. The thermal degradation of polyolefins has been intensively studied during the last few decades [7, 8]. There have been reports on the pyrolysis of polyolefins into aromatic hydrocarbons using activated carbon-supported metal catalysts, cracking of polystyrene and polyethylene on silica-alumina, and reformation of heavy oil from waste polymers using zeolite catalysts, among other things [9]. A substantial amount of research has been conducted on the pyrolysis of individual and combined polymers to produce liquid fuels [10].

The liquid fuels can be produced commercially from the pyrolysis of high-density plastic using an appropriate combination of kinetic rate constants. Few studies have investigated the commercial role of experimental fixed rate constants for liquid fuels. Using experimental rate constants to achieve a valuable amount of liquid fuels is still not generally acknowledged due to a lack of incompatibility between the rate constants and the percentage of oil production. In R

software, the Arrhenius law can estimate the type and quantity of primary products such as oil, gas, and waxes. There have been no studies on the prediction of statistical rate constants by assuming activation energies (E_a) and frequency factors, nor has even a single report documented the sensitivity of experimental and statistically predicted rate constants for the pyrolysis of plastics. Sensitivity analysis is a way of determining the effectiveness of an individual rate constant in the reaction. In this work, we investigated the effect of the pyrolysis process on the species by lowering or raising its initial value to a certain level where maximum oil output is possible. These two aspects can play a crucial role in enhancing the production of liquid fuels. We are the first to design a statistical model that predicts the rate constant using R software.

Since operating conditions can drastically alter the product composition and process conditions, kinetic modeling is essentially required for characterizing the reaction mechanism of heat cracking of plastic molecules [11]. Ganeshan et al. [12] used the Coats-Redfern technique to predict the decomposition of polyethylene terephthalate. The activation energies of the first-order reaction kinetics ranged from 133 kJ/mol to 251 kJ/mol, with a low R^2 value of 0.8. Zhang et al. [13] examined the reaction kinetics and product evolution from the pyrolysis of polyethylene, polypropylene, and their composites. The investigated processes were largely endothermic, and most of the breakdown of polyethylene, polypropylene, and mixture occurred between 389.85-502.17°C, 374.91-495.15°C, and 368.30-496.29°C, respectively. Das and Tiwari [14] used an iso-conversational technique to assess the reaction kinetics of pyrolysis of polyethylene terephthalate at varied heating rates and estimated activation energy in the range of 196-217 kJ mol⁻¹. Al-asadi and Miskolczi [15] investigate the thermal and Ni-zeolite catalyzed decomposition of polyethylene terephthalate at 600-900°C temperature range. Osman et al. [16] studied the effect of A_o and E_a on the reaction rate of polyethylene terephthalate pyrolysis. The kinetic triplet was studied using AKTS software. The kinetic triplet was beneficial in model development to comprehend the operation at a scale since these values are unaffected by the scale. These 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.

The primary objective of this study is to increase the production of liquid fuels at a commercial scale through the prediction of statistical rate constants and their sensitivity analysis. The experimental rate constants for extracting liquid fuels from HDP are well-known. However,

the literature indicates that commercial oil and gas extraction using experimental rate constants is not economical. For this reason, it is necessary to predict statistical rate constants. To date, R and MATLAB haven't been used in the literature to forecast statistical rate constants and the individual efficiency of rate reactions by sensitivity analysis. An assumed combination of E_a and A_o , which are the potential factors for estimating kinetic rate constants, is predicted to improve yields on a commercial scale. Sensitivity analysis provides deeper insight into the individual behavior of the kinetic processes. The effects of temperature on the kinetic rate constants were explored, and several ideas for boosting yields were proposed.

2. Statistical Analysis Scheme

The background of this research layout is that experimentally derived rate constants have been used to model the HDPE pyrolysis process [17]. Extracting the empirical rate constants from the experiment involves time and cost. However, the literature has also revealed that the amount of oil and gas obtained from experimental rate constants at the industrial level is not profitable. To better understand the efficacy of large-scale liquid fuel production, we should predict statistical rate constants by using suitable combinations of E_a and A_o and estimate the number of liquid fuels and gases that can be obtained at the industrial level with minimal time, complexity and cost. We assumed E_a and A_o and used them in R software by applying the Arrhenius law to predict statistical rate constants. These predicted rate constants were then used in MATLAB code by selecting the main reactions from the literature [18]. A second-order differential equation solver was used to analyze the percentage of oil yield during the processing time. The sensitivity analysis of these predicted rate constants was also performed by changing the initial value of rate constants at 200% for better insight into the individual behavior of kinetic rate reactions. A logical combination of E_a and A_o was assumed by the comparison of the Arrhenius equation 1 and the slope equation 2 as follows:

$$k = A_o \times e^{\frac{-E_a}{RT}} \quad (1)$$

$$y = mx + c \quad (2)$$

The values of E_a and A_o were needed to predict rate constants from equations (1) and (2). We ran 9 statistical reactions and obtained statistically significant values of E_a and A_o . The statistical rate constants were calculated using these values in R software. According to our model, a small temperature window is applied to avoid forming gaseous products. As the

temperature rises, the average speed of the chemical processes increases. As more molecules collide, the number of molecules going fast enough to react well increases, resulting in faster product synthesis. The production process also depends on the type of reactor and the nature of the heading. We recommend using a short window temperature based on our observations in the HDPE pyrolysis process. The higher temperatures result in the formation of gaseous products. The Arrhenius equation (3) in R software is applied to the assumed factors and b_n , in particular, to predict rate constants k_1 to k_9 . The values of assumed E_a , A_o , and predicted rate constants are reported in Table 1.

$$k_{-N} = a_n \times \exp(-b_n \times ((\frac{1}{T_1} + \frac{1}{T_2}))) \quad (3)$$

where ‘k’ represents the rate constant, ‘a’ represents the frequency factor, ‘b’ represents the activation energy, $(1/T_1 - 1/T_2)$ represents the absolute temperature from 340°C to 370°C, ‘N’ represents the number of rate constants from 1 to 9, and ‘n’ represents the number of supposed values of E_a and A_o from 1 to 9. The reactants must have enough energy to break over the barrier for the reaction to proceed. It is possible to determine the temperature of the particles by examining how the energy is distributed throughout the system [19]. Since they have enough energy, more particles can overcome the barrier at high temperatures. The Arrhenius equation assumes that there will be an increase in the rate constant with the temperature. As T continues to increase, the value of the A_o of the equation becomes less negative, resulting in an increase in the value of k.

Table 1. Combination of the assumed activation energies, frequency factors, and predicted rate constants.

Activation Energy (J/mol)	Frequency factor (L-mol/s)	Predicted rate constants (k)
153644.526	19.186	$k_1 = 2.346211 \times 10^{15}$
23953.294	20.030	$k_2 = 0.0662060$
23428.778	18.945	$k_3 = 0.0709646$
24432.033	20.242	$k_4 = 0.0596878$
26805.276	22.726	$k_5 = 0.0380519$
30317.189	25.997	$k_6 = 0.0188382$
36390.031	31.265	$k_7 = 0.0053239$
24540.545	21.419	$k_8 = 0.0615456$
42106.010	35.660	$k_9 = 0.0015536$

3. Analysis of Species using Predicted Rate Constants

3.1. Reaction Mechanism of HDPE Pyrolysis

The plastic structure is highly complicated, and multiple reactions are involved in its deconstruction. Since we are interested in producing liquid fuels, the main reactions are H-abstraction, β -scission, polymerization, and chain fission [20]. As represented by (*) in Figure 1, many free radicals collide with the plastic molecules. These collisions and involved reactions expedite the decomposition of the plastic molecules. Among these three reactions, the β -scission reaction is more prominent since free radicals formed during this reaction are more prevalent, reactive, and short-lived than those produced in the other two reactions. When these free radicals break C-C bonds, olefins or alkenes (containing H and C) and primary free radicals are produced with two or fewer C-C bonds [21].

Figure 1. 2D and 3D depiction of reaction mechanism and free electron to bind ethylene with single and double C atoms.

This phenomenon repeats itself during plastic decomposition and works like a chain reaction. Two ethylene molecules collide to form a row of four CH₂ units. As a consequence of this mechanism, unpaired electrons exist at both ends of the chain. These are known as free radicals. The unpaired electrons at the ends of CH₂ chains are particularly reactive and contribute to new chemical bonds. The dots in Figure 1 show electrons that originated through one of the electron pairs within the double bond and became available for binding ethylene molecules together. X is an atom that reacts with the free electrons available after polymerization [22].

3.2. MATLAB Analysis

Model equations (6-10) for 150 Kg HDPE were solved in MATLAB (R2020a) using 23s solver for ordinary differential equations [18]. The variables "t" (1–240 min), "x" (%yield), and "C0" (initial condition) were used to complete equation 4 of this model. Equation 5 is for sensitivity analysis, where "c" stands for species and "n" indicates the number of species analyzed in this model. The involved equations and pyrolysis reactions were elaborated using a method reported in the published literature [23, 24]. In Equations (6)-(10), $\frac{dA}{dt}$ is the mass rate, S

is the amount of HDPE used as a reactant, p indicates heavy wax, Q is low wax, and R represents the oil yield.

$$[t, x] = \text{ode23s}(@\text{reaction}, \text{time}, C0) \quad (4)$$

$$dcdt = \text{reaction}(t, c_n) \quad (5)$$

$$\frac{dA}{dt} = -k_1A - k_2A - k_3A - k_4A \quad (6)$$

$$\frac{dHW}{dt} = k_4S - k_8P - k_9P \quad (7)$$

$$\frac{dLW}{dt} = k_1S - k_6Q - k_5Q \quad (8)$$

$$\frac{doil}{dt} = k_2S + k_5Q + k_9P - k_7R \quad (9)$$

$$\frac{dGas}{dt} = k_3S + k_6Q + k_7R + k_8P \quad (10)$$

3.3. Primary Analysis

Under optimal pyrolysis conditions, light wax, oil, gas, and heavy wax are the most anticipated products using reaction constants k_1 , k_2 , k_3 , and k_4 , respectively. Free radicals are responsible for the oxidation reactions that convert light wax to oil using constant k_5 , light wax to gas using constant k_6 , heavy wax to gas using constant k_8 , and heavy wax to oil using constant k_9 . It was also discovered that with k_7 reaction constant, some of the oil directly transformed into gas, as shown in Figure 2 [25]. This study was conducted at 340°C to 370°C temperature to evaluate the effect of predicted rate constants on product yield over process time. High-density plastic may yield oil, gas, and carbon black when subjected to thermal disintegration during additional extraction procedures. HDPE changes to several organic compounds, such as light and heavy waxes, before the process reaches its steady state. The process produces a mixture that includes roughly 1% of residual material. Today's three most common waxes are kerosene, paraffin, and aromatics. Some of these waxes may proceed to degrade into progressively smaller molecules at high temperatures, eventually leading to the creation of carbon black. This carbon black mostly contains carbon but also includes other smaller particles. However, carbon is the predominant component of this carbon black. Carbon black is highly stable; therefore, no further chemical changes will occur during high-temperature processing [26, 27].

Figure 2. Demonstration of the possible relationship between model parameters.

3.4. Secondary Analysis

After 25 minutes of processing, most of the feedstock is converted into oil, gas, and waxes. The effect of rate constants on the species indicates the breaking of HDPE into smaller particles, which then change into heavy and light waxes [17]. During secondary analysis, the time-dependent conversion revealed that residue is approximately 1%, and the light wax is 18%. On the other hand, the heavy wax disappeared over the processing time at 340°C to 370°C. After 60, 120, and 180 minutes of processing, the gas yield was predicted as 25%, 18%, and 13%, respectively. The gas yield was reduced to half after 180 minutes. As illustrated in Figure 3, the oil yield was predicted as 73%, 81%, and 86% at 60, 120, and 180 minutes of processing. After 180 minutes, the light and heavy waxes are converted to oil [28]. After 180 minutes of processing, gas production dropped from 13% to 9% and oil yield improved from 86% to 90%. Figure 3 also indicates that at a fixed temperature, the gas yield declines and the oil yield rise over time. Some of the vapors in the gas phase also condense into the liquid with time. This conversion is notably high for low A_0 values [17, 18]. At the end of the processing (240 minutes), the amount of species except oil dropped.

Figure 3. The decomposition of HDPE and percentage yield of species throughout the process.

The obtained oil can be used in turbines and refinery furnaces. The properties of pyrolytic oil differ significantly from the properties of mineral oil. The oil shows a polar character with high concentrations of oxygenated components and does not mix easily with hydrocarbons [29]. The aromatics content of pyrolysis oil has also been estimated to be around 40% [30]. The aromatic concentration of diesel is typically less than 35% [31]. In addition, pyrolysis oil has greater thermal efficiency than diesel [32]. Due to limited heating value, low cetane number, high water content, and increased susceptibility to re-polymerization, direct use of pyrolysis oil in diesel engines is problematic. Several new fuels were developed from pyrolysis oil to use in diesel engines. The emulsion and tertiary blends were developed through mechanical and chemical treatment procedures. Modified fuels generally burn more efficiently by reducing CO emissions. However, all such fuels are acidic and require a new fuel injection system. From an economic standpoint, it may not be easy to justify the engine and fuel modifications.

4. Sensitivity Analysis

Sensitivity analysis is a better insight into determining the efficacy of a kinetic rate reaction. In this strategy, we can investigate the effect of the pyrolysis process on the species by reducing or raising the starting values of the rate constants to a specific level where maximum oil output is possible. A change in the rate constant upto 200% is recommended in the literature for sensitivity analysis [33]. The reference values for the rate constants are taken from the experimental work [17]. We assumed an arbitrary range of rate constants from 0 to 200% to visualize the sensitivity of the product yield to the rate constants.

The presented model predicts that the yield at 100% is the initial yield of assumed rate constants. The lower and upper extreme values for rate constants are taken with ± 100 change in the initial values of the rate constants. The lower and upper values are chosen to check the actual role of rate constants in the reaction. The behavior of the rate constants can be better understood using this approach. It will give us a better understanding of how kinetic rate reactions behave as a function of time. To date, no research has been attempted on sensitivity analysis for kinetic rate constants, even though sensitivity analysis is essential in producing oil commercially. Equation 11 in this model represents the second-order differential solver used in MATLAB to study the effectiveness of individual kinetic rate reactions, whereas equation 12 represents 200% change in each process. In these equations, "t" represents time, "x" represents percentage yield, "k" represents the reaction constant, "C0" represents the initial condition, and "N" represents a 200% increase in the initial values. The industrial-scale production of oil is more practical if the light wax production is coupled with the oil yield. Even if large-scale oil production is not straightforward, this approach can reduce cost by improving the light wax combined oil throughout the pyrolysis process by considering k_8 reaction constant. In this investigation, the percentage yield is calculated after 60 minutes of process time with a 100% increase and decrement in the starting values.

$$[t_n, x] = \text{ode23s} (@(t_n, x) \text{ test reaction}(t_n, x, k_n), \text{time}, C0) \quad (11)$$

$$k_N_max = k(N) + k(N) \quad (12)$$

The amount of species obtained with all predicted rate constants is reported in Table 2. The effect of $k(1)$, $k(5)$, $k(6)$, and $k(9)$ rate constants on the product yield is reported in Figure 4. The rate constant $k(1)$ is responsible for the conversion of HDPE into light wax, $k(5)$ for light

wax into oil, k(6) for light wax into gas, and k(9) for heavy wax into oil. These rate constants did not produce any oil, gas, or waxes after 60 minutes of operation and the products' trend became steady after the said time. The reported values of factors "Ea," "Ao," and "k" indicate that the activation energy is much higher than the average kinetic energy of the molecules colliding and crossing the potential barrier. At the beginning of the process, the temperature seems to have a negligible effect on molecular collisions. It does not contribute to polymer breakdown to move into the initial phase cracking [34].

Table 2. The efficiency of species at actual, lower, and higher extreme positions.

Rate constant	Initial value	Oil	Gas	HW	LW	Initial values	Oil	Gas	HW	LW	Initial value	Oil	Gas	HW	LW
	Yield (%)					Yield (%)					Yield (%)				
	At actual value					At a lower extreme position					At a higher extreme position				
k(1)	0.000000	73	25	1	0	0	73	25	1	0	0.0000	73	25	1	0
k(2)	0.066206	70	28	0	0	0	90	7	1	0	0.1324	59	39	0	0
k(3)	0.070964	74	24	0	0	0	61	36	1	0	0.1419	81	17	0	0
k(4)	0.059689	74	24	1	0	0	65	33	0	0	0.1194	79	19	1	0
k(5)	0.038052	73	25	1	1	0	73	25	1	1	0.0761	73	25	1	1
k(6)	0.018838	73	25	1	1	0	73	25	1	1	0.3768	73	25	1	1
k(7)	0.005324	74	24	1	0	0	66	32	1	0	0.0106	80	18	1	0
k(8)	0.061546	73	25	0	0	0	58	26	14	0	0.1231	74	25	0	0
k(9)	0.001554	73	25	1	0	0	73	25	1	0	0.0031	72	26	0	0

Figure 4. Effect of k(1), k(5), k(6), and k(9) rate constants on the product yield.

The effectiveness of the rate constant k(2) is reported in Figure 5(a), which transforms HDPE into oil and then oil into gas. The oil and gas yields were 70% and 28% for the actual value of this rate constant. The heavy and light waxes were not observed with this rate constant after 60 minutes of processing. When the initial value of k(2) rate constant is decreased to a lower extreme value, it reveals 90% oil and only 7% gas yield. However, when the initial k(2) rate constant values increased to higher extreme positions, the oil and gas production was 59% and 39%, respectively. This behavior is confirmed in Figure 5(a), which shows that k(2) positively impacts both oil and gas yields.

In Figures 5(b) and 5(c), the behavior of k(3) and k(4) rate reactions was nearly the same but contradicted the k(2) reaction constant. The k(3) reaction rate was responsible for converting

HDPE to gas and then gas into oil, while the $k(4)$ reaction constant was responsible for converting HDPE into heavy wax and then into oil. Based on these rate constants, initial oil and gas yields were 74% and 24%, respectively. Both $k(3)$ and $k(4)$ rate constants show the same trend of oil and gas yield at the lower and higher extreme positions, as shown in Figure 5(c). This trend is attributed to a negligible difference in E_a and A_o values for these constants. HDPE transforms into gas and vapors over time. Over extended periods, the vapors change to liquid by increasing the oil yield [35].

Figure 5. The efficiency of $k(2)$, $k(3)$, and $k(4)$ kinetic rate reactions.

The behavior of $k(7)$ rate constant is depicted in Figure 6(a). This rate constant is responsible for converting gas into oil. Before altering its initial value, this rate constant gives oil and gas about 74% and 24%, respectively. At the lower extreme, the oil and gas yields were 66% and 32%. However, at a higher extreme position, the gas yield decreased to 18% and oil yield increased to 80% [36]. The explanation for this upward trend in oil yield and a downward trend in gas yield after 60 minutes of process time is that the waxes get degraded into oil over time due to the high kinetic energy of molecules. More and more molecules under inelastic collisions with high kinetic energy and expedite the pyrolysis reaction [37]. Figure 6(b) reveals some intriguing findings for $k(8)$ kinetic reaction after 60 minutes, which are attributed to the conversion of light wax into gas and gas into oil. The oil yield was 73% at the starting value of the rate constant, whereas the gas was roughly 25% throughout the operation. Changing the starting value of $k(8)$ rate constant will result in an increase in oil yield and a decrease in the production of light wax. Other kinetic rate constants did not exhibit this pattern.

Figure 6. The individual response of $k(7)$ and $k(8)$ rate constants.

The $k(8)$ rate constant revealed a drop in light wax from 14% to 0% and an increase in oil content from 58% to 74% after 60 minutes of processing. No unspent plastic material was observed at this stage of processing. After 60 minutes of processing, the light wax decomposes into oil products [38]. More collisions of molecules occurred in the reaction because of the lower activation energy relative to the frequency factor [39]. This reaction, among all the reactions,

resulted in an increase in light wax over time. These findings suggest that $k(8)$ rate constant may be used for commercial-scale processing of HDPE into oil and gas.

Figure 7 provides a comparison of products obtained with initial values, lower extreme values and upper extreme values of reaction rate constants. At a lower extreme point, the reaction rate constants reach to zero value. So rate constants were from upto 200% from this point to get better insight into the reaction mechanism. It is the best way to assess the sensitivity of the kinetic rate reaction. The presented model required a combination of assumed E_a and A_o predicting rate constants. The Arrhenius law predicted the reaction rate constants by fixing the temperature window of 340-370°C. It shows that the presented model works well at lower temperatures. This model results in a high yield of waxes at higher temperatures instead of producing oil. Also, the reported model is limited to high-density polymers and may not be applied effectively to other types of plastic. A second-order differential solver is required for numerical analysis [28].

Figure 7. Graphical depiction of species at the initial, lower extremity, and higher extreme positions.

5. Conclusions

The statistically estimated rate constants derived using an optimal combination of E_a and A_o , can improve commercial-scale oil yield from the pyrolysis of high-density plastics. The sensitivity of the rate constant affects the commercial-scale production of oil. Sensitivity analysis is the best way of estimating the efficiency and effectiveness of individual rate constants in the reaction. This research element is currently lacking in the literature for the cost-effective valorization of plastics into combustible fuels. At the end of the processing time, the oil recovery rate increased dramatically to 90%, while the quantity of byproducts gradually reduced. During sensitivity analysis, the $k(8)$ rate constant driven reaction was found to be the best-suited condition for industrial-scale pyrolysis of high-density plastics into liquid fuels, with 74% improvement in oil output and 14% improvement in light wax. For predicting the rate constants $k(1)$, $k(5)$, $k(6)$, and $k(9)$, E_a values were almost the same and higher than the average kinetic energy of the

molecules. The $k(8)$ rate constant dominated the other predicted rate constants since the value of E_a was significantly lower than the average kinetic energy of the molecules. The $k(8)$ rate constant was economically sustainable since it produces 74% oil yield and 14% light wax.

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References

1. Seghiri, M., Boutoutaou, D., Kriker, A., and Hachani, M. I. "The possibility of making a composite material from waste plastic." *Energy Procedia* 119 (2017): 163-169
2. Nabi, R.A.U.; Naz, M.Y.; Shukrullah, S.; Ghamkhar, M.; Rehman, N.U.; Irfan, M.; Alqarni, A.O.; Legutko, S.; Kruszelnicka, I.; Ginter-Kramarczyk, D.; Ochowiak, M.; Włodarczak, S.; Krupińska, A.; Matuszak, M. (2022). Analysis of Statistically Predicted Rate Constants for Pyrolysis of High-Density Plastic Using R Software. *Materials*, 15, Article 5910. <https://doi.org/10.3390/ma15175910>
3. Abba, H. A., Nur, I. Z., & Salit, S. M. (2013). Review of agro waste plastic composites production. *Journal of Minerals and Materials Characterization and Engineering*, 1(5), 271-279
4. Qureshi, M. S., Oasmaa, A., Pihkola, H., Deviatkin, I., Tenhunen, A., Mannila, J., Minkkinen, H. Pohjakallio, M., Laine-Ylijoki, J. (2020). Pyrolysis of plastic waste: Opportunities and challenges. *Journal of Analytical and Applied Pyrolysis*, 152, 104804
5. Armenise, S., SyieLuing, W., Ramírez-Velásquez, J. M., Launay, F., Wuebben, D., Ngadi, N., Rams, J., & Muñoz, M. (2021). Plastic waste recycling via pyrolysis: A bibliometric survey and literature review. *Journal of Analytical and Applied Pyrolysis*, 158, 105265
6. Davidson, M. G., Furlong, R. A., & McManus, M. C. (2021). Developments in the life cycle assessment of chemical recycling of plastic waste—A review. *Journal of Cleaner Production*, 293, 126163
7. Al-Salem, S. M., Antelava, A., Constantinou, A., Manos, G., & Dutta, A. (2017). A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). *Journal of Environmental Management*, 197, 177-198

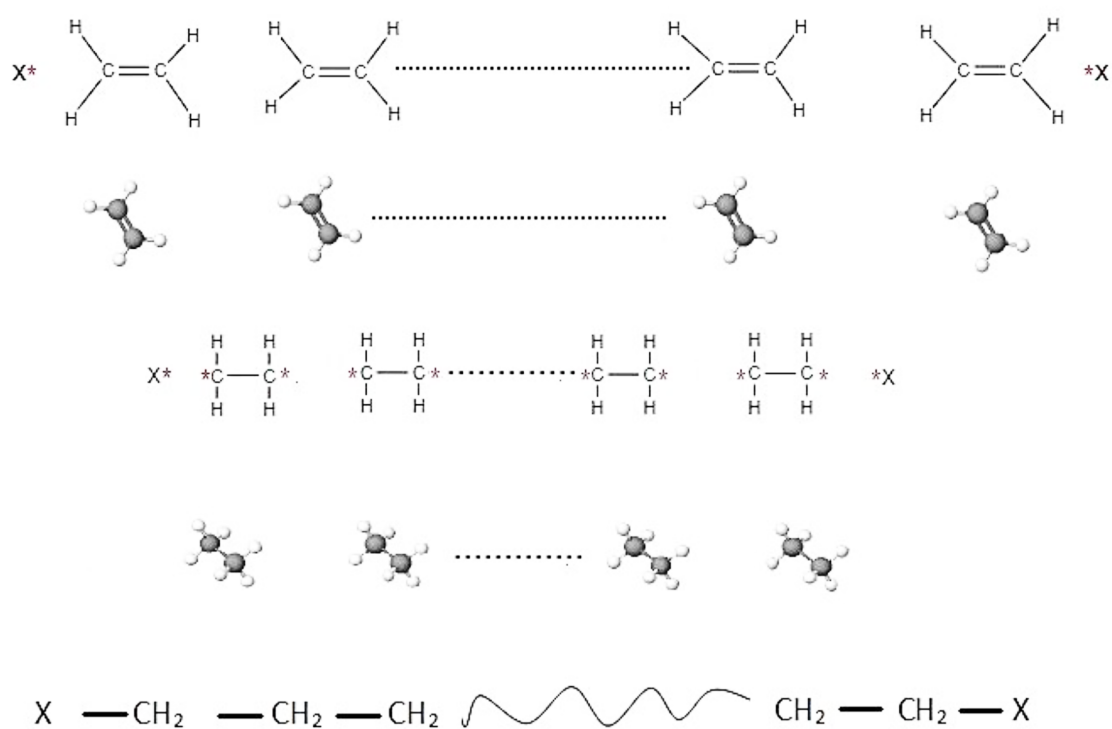
8. Alqarni, A.O.; Nabi, R.A.U.; Althobiani, F.; Naz, M.Y.; Shukrullah, S.; Khawaja, H.A.; Bou-Rabee, M.A.; Gommosani, M.E.; Abdushkour, H.; Irfan, M.; Mahnashi, M.H. (2022). Statistical Optimization of Pyrolysis Process for Thermal Destruction of Plastic Waste Based on Temperature-Dependent Activation Energies and Pre-Exponential Factors. *Processes*, *10*, 1559. <https://doi.org/10.3390/pr10081559>
9. Canopoli, L., Fidalgo, B., Coulon, F., & Wagland, S. T. (2018). Physico-chemical properties of excavated plastic from landfill mining and current recycling routes. *Waste Management*, *76*, 55-67
10. Muhammad, C., Onwudili, J. A., & Williams, P. T. (2015). Thermal degradation of real-world waste plastics and simulated mixed plastics in two-stage pyrolysis–catalysis reactor for fuel production. *Energy & Fuels*, *29*(4), 2601-2609
11. Zhang, J., & Ghosh, S. (2013). Molecular dynamics-based study and characterization of deformation mechanisms near a crack in a crystalline material. *Journal of the Mechanics and Physics of Solids*, *61*(8), 1670-1690
12. G. Ganeshan, K. P. Shadangi, and K. Mohanty, (2018) Degradation kinetic study of pyrolysis and co-pyrolysis of biomass with polyethylene terephthalate (PET) using Coats–Redfern method, *Journal of Thermal Analysis and Calorimetry*, *131*, 1803-1816
13. Y. Zhang, Z. Fu, W. Wang, G. Ji, M. Zhao, and A. Li, (2022) Kinetics, Product Evolution, and Mechanism for the Pyrolysis of Typical Plastic Waste, *ACS Sustainable Chemistry & Engineering*, *10*, 91-103
14. P. Das and P. Tiwari, (2019) Thermal degradation study of waste polyethylene terephthalate (PET) under inert and oxidative environments, *Thermochimica Acta*, *679*, 178340
15. M. Al-asadi and N. Miskolczi, (2018) Pyrolysis of polyethylene terephthalate containing real waste plastics using Ni loaded zeolite catalysts, *IOP Conference Series: Earth and Environmental Science*, *154*, 012021
16. A. I. Osman, C. Farrell, A. H. Al-Muhtaseb, A. S. Al-Fateh, J. Harrison, and D. W. Rooney, (2020) Pyrolysis kinetic modeling of abundant plastic waste (PET) and in-situ emission monitoring," *Environmental Sciences Europe*, *32*, 112
17. Safadi, Y., Zeaiter, J., & Ahmad, M. (2013). Advanced Modeling of High Density Polyethylene Pyrolysis. *Int. J. of Thermal & Environmental Engineering*, *5*(2), 123-128.

18. Eidesen, H., Khawaja, H., & Jackson, S. (2018). Simulation of the HDPE Pyrolysis Process. *The International Journal of Multiphysics*, 12(1), 79-88
19. Aquilanti, V., Mundim, K. C., Elango, M., Kleijn, S., & Kasai, T. (2010). Temperature dependence of chemical and biophysical rate processes: Phenomenological approach to deviations from Arrhenius law. *Chemical Physics Letters*, 498(1-3), 209-213
20. Rodríguez Lamar, Y., Noboa, J., Torres Miranda, A. S., & Almeida Streitwieser, D. (2021). Conversion of PP, HDPE, and LDPE plastics into liquid fuels and chemical precursors by thermal cracking. *Journal of Polymers and the Environment*, 29(12), 3842-3853
21. Long, F., Zhang, X., Cao, X., Zhai, Q., Song, Y., Wang, F., Jiang, J., & Xu, J. (2020). Mechanism investigation on the formation of olefins and paraffin from the thermochemical catalytic conversion of triglycerides catalyzed by alkali metal catalysts. *Fuel Processing Technology*, 200, 106312
22. Norsk kjemisk selskap, "Polymerisasjonskjemi," 2007. [Online]. Available: <http://www.naturfag.no/artikkel/vis.html?tid=689055>. [Accessed 18. 10. 2022].
23. Kruse, T. M., Woo, O. S., Wong, H. W., Khan, S. S., & Broadbelt, L. J. (2002). Mechanistic modeling of polymer degradation: a comprehensive study of polystyrene. *Macromolecules*, 35(20), 7830-7844
24. Eidesen, H. Khawaja, H., Jackson, S. (2018). Simulation of the HDPE Pyrolysis Process, *The International Journal of Multiphysics* 12(1): 79-88.
25. Khaghanikavkani, E., & Farid, M. M. (2011). Thermal pyrolysis of polyethylene: a kinetic study. *Energy Science and Technology*, 2(1), 1-10
26. Ramzan, F., Shoukat, B., Naz, M. Y., Shukrullah, S., Ahmad, F., Naz, I., Makhlof, M. M., Farooq, M. U., Kamran, K., Single step microwaves assisted catalytic conversion of plastic waste into valuable fuel and carbon nanotubes, *Thermochimica Acta*, 715, 179294, 2022.
27. Debecker, D. P., Le Bras, S., Boissière, C., Chaumonnot, A., & Sanchez, C. (2018). Aerosol processing: a wind of innovation in the field of advanced heterogeneous catalysts. *Chemical Society Reviews*, 47(11), 4112-4155
28. M. Irfan, R. A. U. Nabi, H. Hussain, M. Y. Naz, S. Shukrullah, H. A. Khawaja, S. Rahman, A. A. J. Ghanim, I. Kruszelnicka, D. Ginter-Kramarczyk and S. Legutko, Response Surface Methodology Analysis of Pyrolysis Reaction Rate Constants for

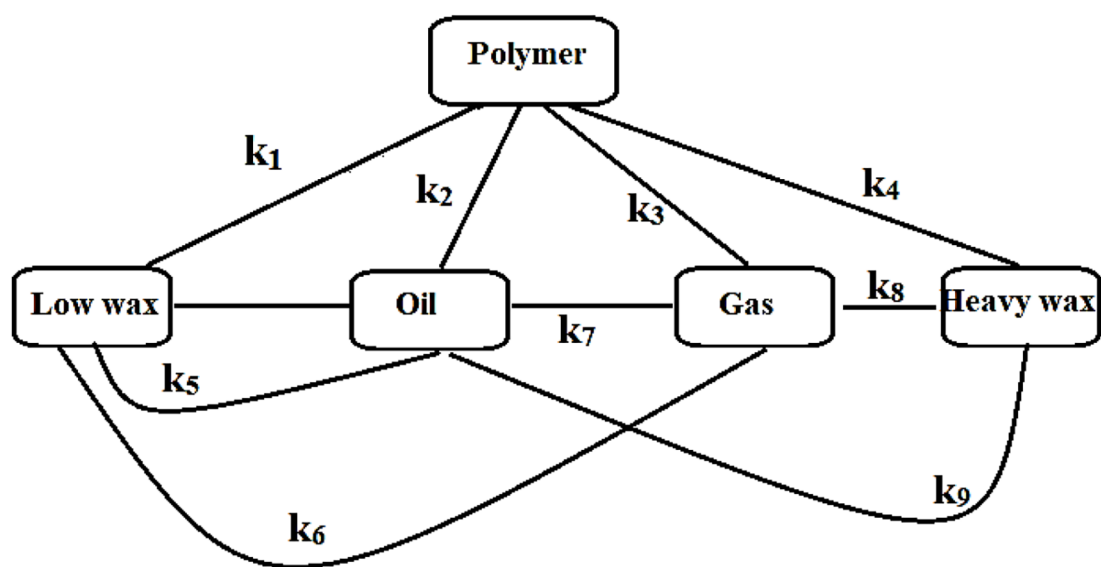
- Predicting Efficient Conversion of Bulk Plastic Waste into Oil and Gaseous Fuels. *Energies*, Vol. 15, Article 9594, pp. 1-17
29. Van de Beld, B., Holle, E., & Florijn, J. (2013). The use of pyrolysis oil and pyrolysis oil-derived fuels in diesel engines for CHP applications. *Applied Energy*, *102*, 190-197
30. Mahfud, F. H., Melian-Cabrera, I., Manurung, R., & Heeres, H. J. (2007). Biomass to fuels: upgrading of flash pyrolysis oil by reactive distillation using high boiling alcohol and acid catalysts. *Process Safety and Environmental Protection*, *85*(5), 466-472
31. Chiaramonti, D., Rizzo, A. M., Peruzzi, N., Bonini, M., Fratini, E., & Baglioni, P. (2011). Preliminary investigation of pyrolysis oil upgrading via emulsification with biodiesel. In *19th European biomass conference and exhibition* (pp. 1666-1671)
32. A. V. Bridgwater, (2011). Upgrading Fast Pyrolysis Liquids. In *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*, R. C. Brown (Ed.), John Wiley & Sons Ltd, New York, UAS, 157-199
33. McKenzie, P. F., Duvencek, M. J., Morreale, L. L., & Thompson, J. R. (2019). Local and global parameter sensitivity within an ecophysiological based forest landscape model. *Environmental Modelling & Software*, *117*, 1-13.
34. Ng, Q. H., Chin, B. L. F., Yusup, S., Loy, A. C. M., & Chong, K. Y. Y. (2018). Modeling of the co-pyrolysis of rubber residual and HDPE waste using the distributed activation energy model (DAEM). *Applied Thermal Engineering*, *138*, 336-345
35. Pathak, G. (2020). Permeable persons and plastic packaging in India: from moral substance exchange to chemotoxic transmission. *Journal of the Royal Anthropological Institute*, *26*(4), 751-765
36. Antonyuk, S., Heinrich, S., Tomas, J., Deen, N. G., Van Buijtenen, M. S., & Kuipers, J. A. M. (2010). Energy absorption during compression and impact of dry elastic-plastic spherical granules. *Granular Matter*, *12*(1), 15-47
37. Zhou, Y. (2011). A theoretical model of collision between softspheres with Hertz elastic loading and nonlinear plastic unloading. *Theoretical and Applied Mechanics Letters*, *1*(4), 041006
38. Colantonio, S., Cafiero, L., De Angelis, D., Ippolito, N. M., Tuffi, R., & Cipriotti, S. V. (2020). Thermal and catalytic pyrolysis of a synthetic mixture representative of

packaging plastics residue. *Frontiers of Chemical Science and Engineering*, 14(2), 288-303

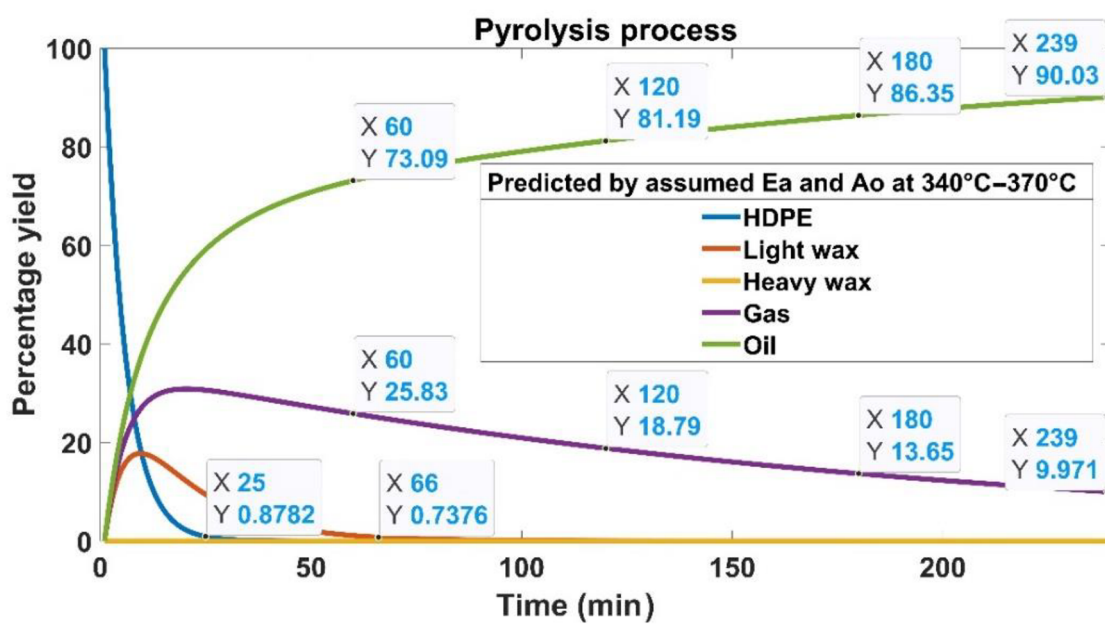
39. Milani, G., & Milani, F. (2021). Relation between activation energy and induction in rubber sulfur vulcanization: An experimental study. *Journal of Applied Polymer Science*, 138(12), 50073.



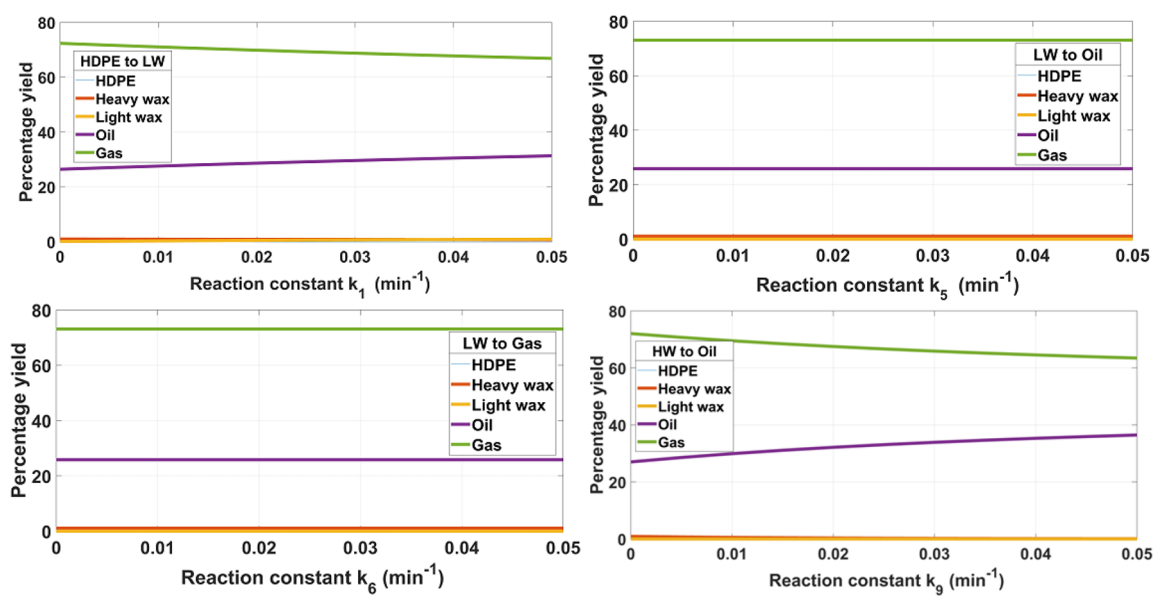
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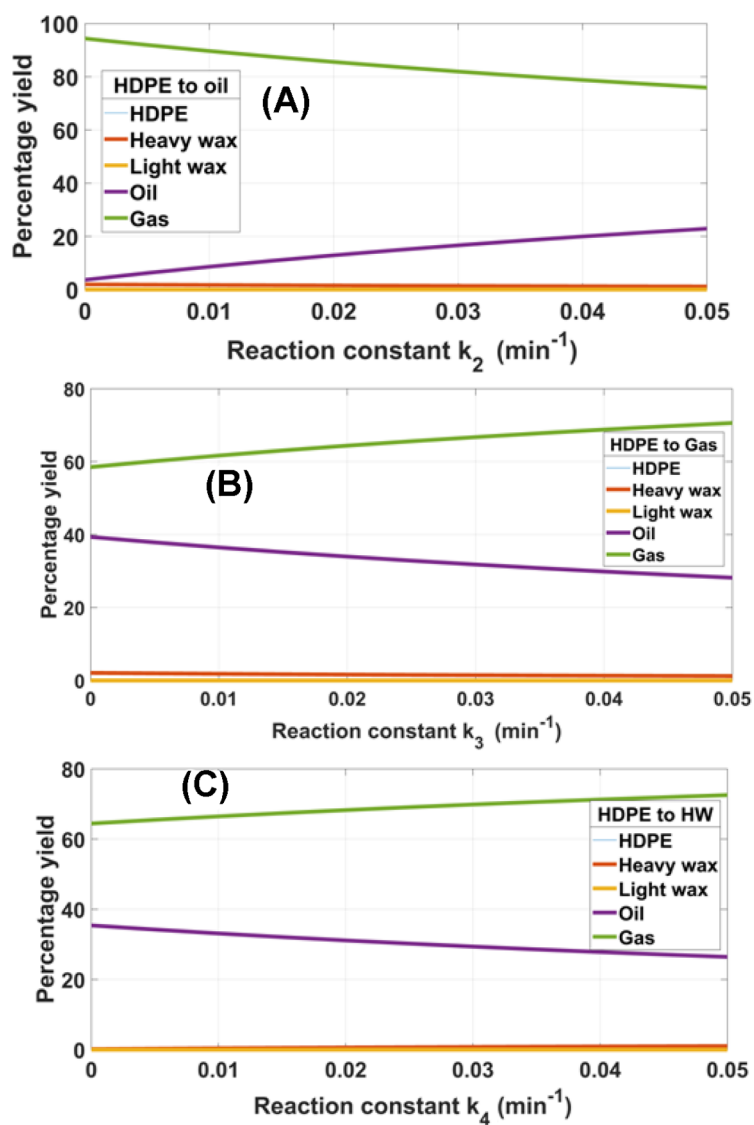
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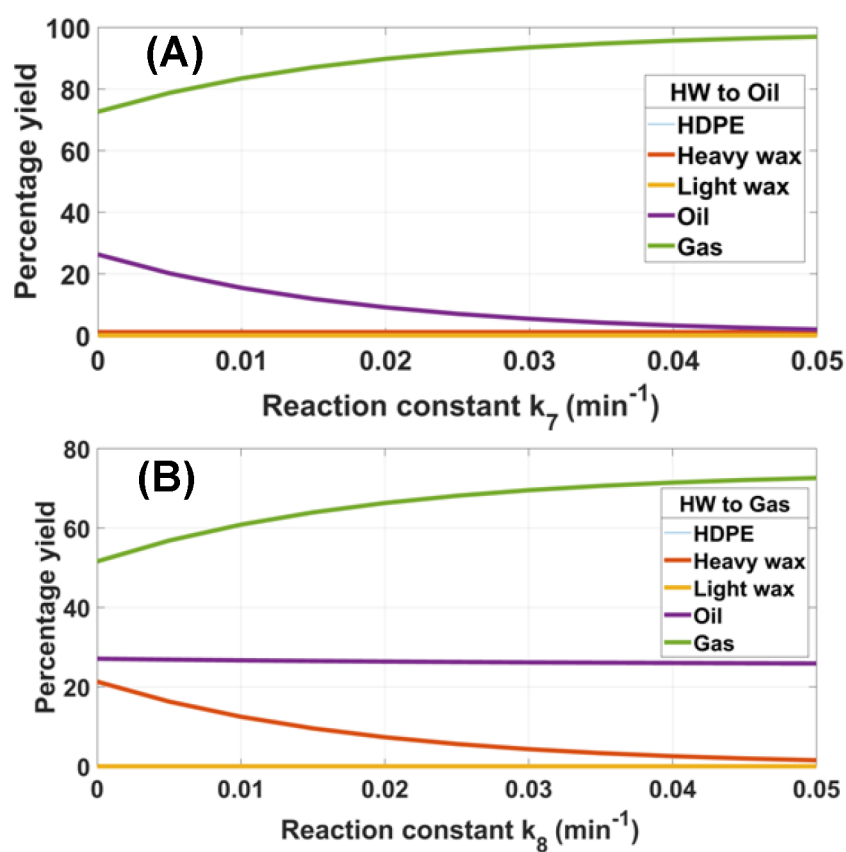
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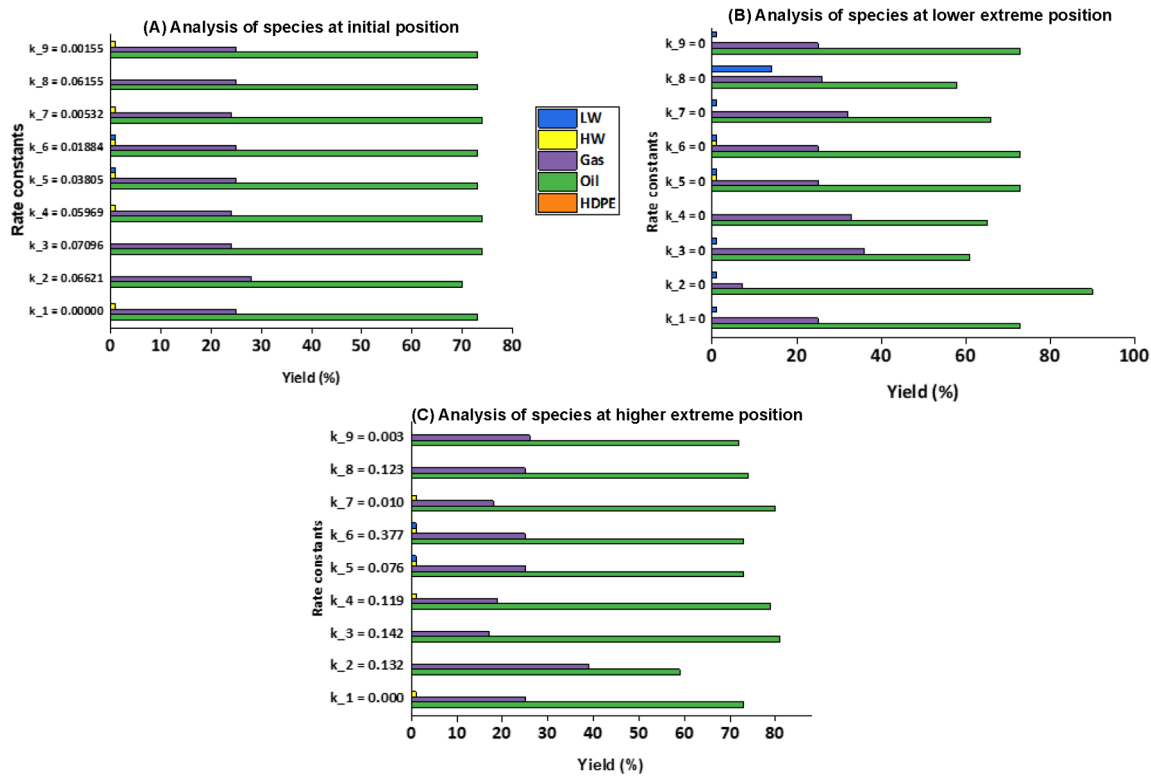
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CJCE_24883_CJCE-22-0608.R1_Figure 5.tif



CJCE-22-0608.R1_Figure 6.tif



CJCE-22-0608.R1_Figure 7.tif