

# Process Optimization for Pyro-Gasification of Waste Polymer using Hierarchical Catalysts

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The growing environmental concerns and the decrement in the amount of fossil fuels have initiated a global shift towards the use of alternative feedstocks such as biomass and plastics for sustainable energy production. These materials offer a renewable and abundant source, which can be converted into valuable fuels and chemicals. However, their efficient conversion into gaseous with high hydrogen content and low carbon dioxide emissions remains a challenge. Due to their unique properties such as high surface area, thermal stability, Si/Al ratio and acidity, zeolite-based catalysts have proven to be a promising solution in pyrolysis and gasification. Besides, zeolites can help to reduce the CO<sub>2</sub> emission by improving selectivity for production of lighter hydrocarbons. However, the process optimization is highly dependent on many factors, including the zeolite structure, process parameters, feedstocks and reaction kinetics. Therefore, process simulations play a crucial role in understanding and optimizing the catalytic conversion of waste. Simulation tools such as MATLAB based kinetic models are used to investigate the catalyst-feedstock interactions, providing insight into reaction mechanisms and guiding the selection of optimal process parameters. In addition, sensitivity analysis can identify critical parameters that significantly affect the performance of zeolite catalysts. In this work, waste polymers were pyrolyzed in the presence of hierarchical zeolites by TG method.

## 1. Introduction

Thermochemical recycling, which mainly includes pyrolysis, gasification, and incineration, is a promising approach to converting biomass and plastic waste into valuable fuels, chemicals or other high-value products (Zhang et al. 2018 and Arenas et al. 2019). These processes help to degrade complex organic compounds into simpler molecules under controlled conditions, often in the presence of catalysts to increase efficiency and selectivity. Catalysts play a key role in thermochemical recycling as they can reduce the required activation energy for degradation reactions and directly convert the raw materials to the desired products (Wang et al. 2017 and Peng et al. 2022). Among the various catalysts, zeolites are particularly suitable owing to their microporous crystalline aluminosilicate structure, high surface area, strong acidity, and well-defined pore structure that could be effective in selective adsorption and catalytic reactions. Furthermore, zeolites combined with kaolin, a naturally abundant and cost-effective clay material, resulted in a composite catalyst with improved mechanical properties, enhanced fouling resistance, and extended catalyst lifetime. Kaolin functions as a binder and complements the high activity of zeolites, making the mixture flexible and practical for large-scale applications (Aliyu et al. 2023, Asgahari et al. 2019 and Mohan et al. 2023).

One of the most critical parameters is their silica-alumina ratio, which determines the acidity and hydrophobicity of the zeolite. Zeolites with a low Si/Al ratio have a higher density of acid sites, which is important in cracking reactions, making them effective at breaking large polymer chains or biomass molecules. However, these materials may also undergo higher rates of coke deposition and deactivation (Gomes et al. 2018., Gao et al. 2016 and Zhang et al. 2018). In contrary, zeolites with a high Si/Al ratio contain fewer acid sites but have a greater thermal and hydrothermal stability and higher selectivity toward specific lighter products. Optimizing the Si/Al ratio for different feedstocks or reaction conditions is essential to achieve the best balance between activity, selectivity, and durability (Aliyu et al. 2023).

To further improve their performance, zeolites and zeolite-kaolin composites can undergo modifications such as metal impregnation or mechanochemical activation. Metal ions such as nickel, cobalt, or iron can improve cracking and hydrogenation reactions. Furthermore, mesoporous hierarchical structures can improve the accessibility and diffusion of larger molecules such as long-chain polymers or biomass-derived macromolecules. The use of such catalysts significantly impacts the entire thermochemical recycling process. By lowering the activation energy, the required energy for decomposition can be reduced. Catalysts also increase the degradation rate, accelerating the degradation of biomass and plastics into smaller molecules, thereby improving the performance of the process. These advances make the recycling process more efficient, economically viable, and environmentally sustainable (Gomes et al. 2018., Gao et al. 2016 and Zhang et al. 2018). In conclusion, the integration of advanced catalysts such as zeolite-kaolin composites into thermochemical recycling processes helps to solve the most important challenges of sustainable waste management and energy production (Aliyu et al. 2023, Asgahari et al. 2019 and Mohan et al. 2023).

In this work, the degradation of biomass and regranulated plastic waste was investigated by TG method with catalysts utilizing diverse Si/Al ratio. In order to calculate the kinetic parameters and to precise the model three different heating rates were used.

## 2. Materials & methods

In this work, the effect of catalysts with different Si/Al ratio was investigated on biomass and plastic waste in a TG-FTIR equipment. In order to get appropriate information for kinetic calculations, three different heating rates (5, 20, 50°C/min) were used with 800°C end temperature.

### 2.1 Raw material

As raw material, maize and mixed waste polymer granulate was analyzed. The maize biomass was shredded to smaller particles (<3mm), while the waste plastic granulate contained 40% HDPE, 40% PP and 20% PS. The main properties of the materials are shown in Table 1. For each measurement 10-15 mg sample was used.

*Table 1: The main properties of the raw materials*

	Regranulate	Biomass
Composition	40% HDPE, 40% PP, 20% PS	maize
Fixed carbon*, %	-	16.2
Moisture content, %	0.2	6.5
Volatile matter, %	99.6	75.0
Ash content, %	0.2	2.3
C, %	86.1	48.5
H, %	14.5	6.3
N, %	0.01	0.5
S, %	0.2	<1.0
O*, %	-	44.7

\*calculated value

### 2.2 Product analysis

The thermogravimetric analysis of the raw materials was carried out using a Netzsch TG 209 F1 Libra thermogravimetric instrument. During the measurement, a nitrogen atmosphere and heating rates of 5, 20, and 50°C/min were applied which gives further data for more exact calculations of kinetic parameters.

The elemental composition of the catalysts was analyzed using a Shimadzu EDX-8100 Energy Dispersive X-ray Fluorescence spectroscopy.

In order to determine the activation energy, the Arrhenius equation was used, while the model fitting was made by MATLAB R2021b simulation program.

### 2.3 Catalysts

The nickel content was placed to the surface of the catalysts by wet impregnation. During this process, the catalyst supports were impregnated with a 1 M Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution at 80°C for 3 hours. After that, the suspension was filtered and dried at 110°C for 10 hours. Finally, the treated catalysts were calcined at 600°C for 3 hours. Each catalyst contained 25-75% of ZSM-5 and kaolin (Catalyst A), where in case of the modification of Si/Al ratio NaOH (Catalyst B) and HCl (Catalyst C) was used. Table 2 contains the main properties of the used catalysts. As it can be seen in case of the Si/Al ratio, with the use of NaOH solution decrement (1.9), while

with the use of HCl increment (11.0) was achieved owing to the modification of silica and alumina content. Based on the results, the modification of Si/Al ratio was successful, therefore the effect of Si/Al ratio can be investigated during the thermal degradation of different types of wastes.

Table 2: The main properties of the catalysts

	Catalyst A	Catalyst B	Catalyst C
Si	18.2	11.5	19.6
Al	3.0	6.1	1.8
Ni	2.4	2.2	2.0
Na	-	4.0	-
Fe	0.1	0.2	0.1
K	0.1	0.2	0.1
Cl	-	-	1.5
O	76.2	75.8	75.0
Si/Al	6.0	1.9	11.0

### 3. Results & discussion

The following subsections are presenting the results obtained with TG-FTIR equipment, with the utilization of three different catalysts in case of the thermochemical degradation of biomass and plastic waste. Besides, the obtained results from kinetic calculations are also can be found.

#### 3.1 Thermogravimetric analysis

In order to make the kinetic calculations, it is essential to study the thermal degradation of the raw materials. The examined biomass material contained varying amounts of cellulose, hemicellulose, and lignin, while the regranulated polymer waste contained mainly olefins. Thermogravimetric analysis provides information about the thermal degradation behavior of materials, while with derivative thermogravimetric curves, the decomposition stages can be identified, where multiple peaks indicate multiple degradation steps.

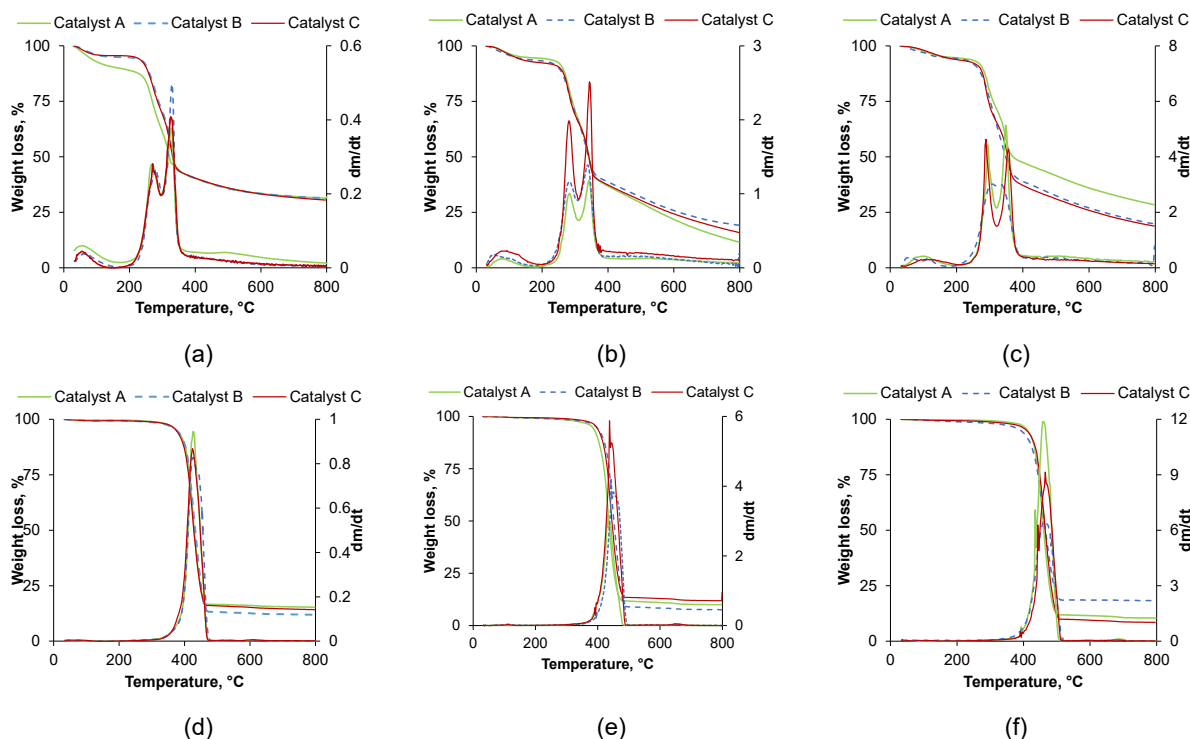


Figure 1: The TG-DTG curves in case of (a) biomass 5°C/min, (b) biomass 20°C/min, (c) biomass 50°C/min, (d) regranulate 5°C/min, (e) regranulate 20°C/min, (f) regranulate 50°C/min

Based on Figure 1, it can be noted that biomass degraded in two main steps, between 211°C and 413°C, with a smaller third degradation step between 30-200°C. The latter one indicates the removal of moisture content of biomass waste, while the greater peaks show the degradation of hemicellulose and cellulose units. Biomass degrades in several steps because its lignocellulose content has unique thermal stability and decomposition characteristics. Nevertheless, secondary reactions, the release of moisture and volatiles further contribute to multiple stages. Besides, it should be mentioned that with the increment of heating rate, the intensity of the DTG peaks were higher, which means that the decomposition rate was higher. The mentioned phenomena can be explained by the higher heating rate, the improved heat transfer and the use of more acidic catalyst as it can be seen in Figure 1 (a) and (b).

Focusing on the regranulated polymer waste (Figure 1 (d)-(f)), it can be observed that it was degraded in one step owing to its homogenous structure and single dominant degradation mechanism such as chain scission and depolymerization. Same results can be seen, in case of the DTG curves, however with the increment of heating rate not only the intensity of degradation was greater, but the degradation temperature ranges were shifted into higher temperatures. At first, the main degradation step occurred between 321-491°C, with 20°C/min heating rate it was between 362-510°C, while that of with 50°C/min was 392-552°C.

### 3.2 Parameter optimization by kinetic model

The thermal degradation of biomass is a highly complex process, which can be attributed to its diverse composition. During thermal degradation, numerous simultaneous reactions occur, making the precise determination of the mechanisms of these reactions challenging. Regarding plastic waste it can be concluded that the degradation mechanism is more simply than that of biomass. Assuming that the transformation of the raw material into the product occurs as a single-step process, the reaction rate can be expressed using the Arrhenius equation as follows (Yan et al. 2019 and Bach et al. 2014):

$$k = Ae^{-\frac{E_a}{RT}} \quad (1)$$

where  $k$  is the reaction rate constant,  $A$  is the pre-exponential factor (1/min),  $E_a$  is the activation energy (kJ/mol),  $R$  is the universal gas constant (8.314 J/molK), and  $T$  is the absolute temperature (K).

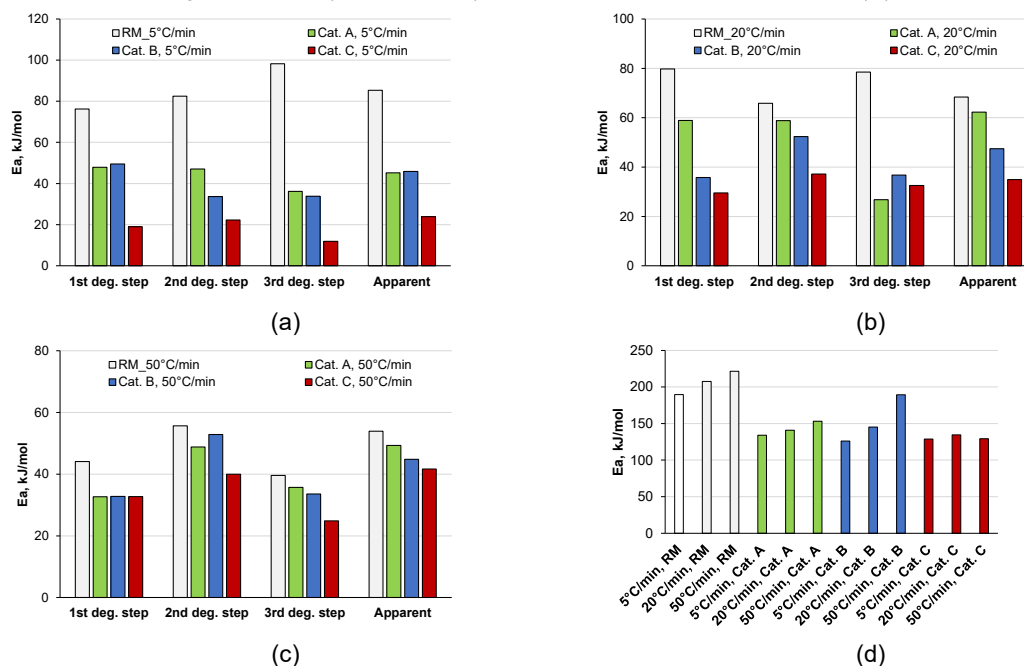


Figure 2: The calculated activation energies with different heating values and catalysts with diverse Si/Al ratio

The calculated results with catalysts using different Si/Al ratios are shown in Figure 2, comparing to the raw data, where no catalyst was used. As it can be seen, in case of biomass waste the activation energies have overall higher values in case of 5°C/min and 20°C/min heating rates than with 50°C/min which can be explained by the longer exposure time, thermal lag and the shift to other decomposition pathways with higher energy requirement. With lower heating rates the decomposition can occur more completely and at closer-to-equilibrium conditions, which may indicate higher energy pathways that require greater activation energy.

Regarding the activation energies, in case of biomass the first degradation step is the moisture content removal, the 2<sup>nd</sup> and the 3<sup>rd</sup> are the degradation of hemicellulose and cellulose units, while the apparent value is

considering the 2<sup>nd</sup> and 3<sup>rd</sup> peak together. Focusing on the catalysts, it can be seen that with the increment of Si/Al ratio the value of the activation energy is decreased significantly. In case of 5°C/min heating rate (Figure 2 (a)) “Catalyst C” eventuated 71-88% lower values than without catalyst (RM\_5°C/min), while that of 20°C/min was 10-65% and with 50°C/min was 8-25%. The explanation of the significant decrement in activation energy with the use of “Cat. C” are its facilitation properties on the reaction mechanism which help to make the reactants easier to convert into products. Acidic catalysts can increase the electrophilicity of the molecule making it more reactive, also, they can stabilize the transition states of reaction, providing alternative reaction pathways and in multiple steps they can reduce the activation energy. However, in case of “Catalyst B” which was treated with NaOH, averagely similar or lessen values were noted than that of “Catalyst A”, especially in case of the apparent activation energies (Figure 2 (a)-(c)), where the deviation was 9-23% compared to the values obtained with “Cat. A”. In Figure 2(d), the change of the activation energy can be seen in case of the degradation of regranulated polymer waste. Similar tendencies can be noted as it was in case of biomass waste. The decrement of the activation energy was followed the same pattern: “Cat B”>“Cat. A”>“Cat.C”, as the Si/Al ratio was increased. Overall, the catalysts helped to reduce the activation energy with a remarkable value, besides, the higher was the Si/Al ratio the greater decrement could be observed.

The behaviour of the biomass conversion with respect to time during the thermal degradation process is reported in Figure 3. Visual inspection of the curve indicates that it can be divided into three distinct phases. In Phase 1, moisture removal and the start degradation reaction occur. Phase 2 is characterized by the primary and secondary degradation steps, during which decomposition and subsequent cracking or recombination reactions take place. In Phase 3, the degree of conversion approaches a plateau, indicating that the reaction rate has effectively reached zero. At this stage, all degradable components are assumed to have been converted into products, and only thermally stable materials, such as solid residues, remain. To quantitatively describe the degradation behavior across these three phases, a kinetic model was used. Each phase was modelled separately to account for the different dominant mechanisms, using distinct kinetic parameters. The kinetic behavior in each phase was described using Equations (2,3)

$$\frac{d\alpha}{dt} = (1 - \alpha)^n \bar{k} \exp\left(\frac{-E}{RT}\right) \quad (2)$$

$$\frac{dT}{dt} = \beta \quad (3)$$

where  $\alpha = \frac{c_0 - c}{c_0}$ ,  $\bar{k}$  is the pre-exponential factor,  $E$  is the activation energy,  $R$  is the universal gas constant,  $T$  is the temperature,  $\beta$  is the heating rate, and  $n$  is the reaction order (Yan et al. 2019, Arenas et al. 2019 and Bach et al. 2014). Model parameters ( $n, \bar{k}, E$ ) were estimated for each phase by minimizing the following objective function (Eq. 4), based on the least squares error between experimental and calculated values:

$$\sum_i^N (\alpha_i^{exp} - \alpha_i^{cal})^2 \quad (4)$$

where  $\alpha_i^{exp}$  and  $\alpha_i^{cal}$  denote the experimental and calculated values of conversion, respectively, and  $N$  is the total number of experimental data points. The optimization was performed using the Nelder-Mead simplex direct search method. The transition points between phases were initially identified through visual inspection of the conversion-time data and subsequently refined by minimizing the error between experimental observations and model predictions.

Figure 3 presents the comparison between experimental and simulated data for both biomass and regranulated plastic waste. The model shows high accuracy, with regression coefficients ( $R^2$ ) close to 0.99 for both materials. These results confirm the reliability of the proposed model for determining kinetic parameters and activation energy values associated with the thermal degradation process.

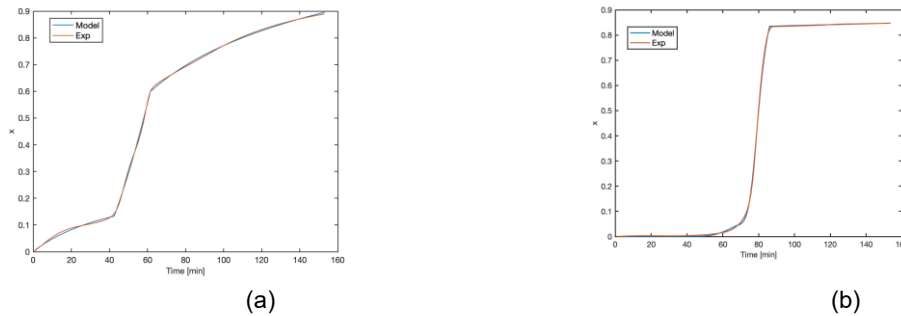


Figure 3: Comparison between model and experimental data in case of (a) biomass waste, (b) regranulated plastic waste

#### 4. Conclusions

This study demonstrated that catalysts with varying Si/Al ratios significantly reduced the activation energy during biomass and regranulated polymer waste degradation. The biomass waste degraded in two main steps while that of regranulated polymer was one. Additionally, higher heating rates increased the intensity of the degradation peaks and shifted the degradation temperature ranges to higher temperatures. At lower heating rates (5°C/min and 20°C/min), the activation energy was higher owing to the longer exposure times and more complete decomposition. The utilization of catalysts with higher Si/Al ratios ("Catalyst A" and "Catalyst C"), resulted in a remarkable reduction of activation energy.

#### Nomenclature

HDPE – high density polyethylene

PP – polypropylene

PS – polystyrene

#### Acknowledgments

Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

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