Indonesian Journal of Chemical Research

http://ojs3.unpatti.ac.id/index.php/ijcr Indo. J. Chem. Res., 9(1), 57-62, 2021

Pyrolysis Reaction Kinetics of Styrofoam Plastic Waste

Feybi A. G. Kauwo*, I Dewa K. Anom, John Z. Lombok

Chemistry Study Program, Postgraduate School, Universitas Negeri Manado, Matani Satu Street, Central Tomohon, Tomohon-North Sulawesi, Indonesia.

Corresponding Author: feybikauwo@gmail.com

Received: April 2021
Received in revised: April 2021
Accepted: May 2021
Available online: May 2021

Abstract

Pyrolysis at the temperature range of 170 °C-237 °C against polystyrene (Styrofoam) type plastic waste is carried out without a catalyst and added a catalyst. The purpose of this research was to study the reaction kinetics of Styrofoam pyrolysis to liquid smoke products. Pyrolysis using a series of tools made of glass to observe the processes that occur in the reactor. The results showed that Styrofoam pyrolysis for liquid smoke products without catalyst and added catalyst took place in the first-order reaction. The kinetics of the pyrolysis reaction without a catalyst to observe the formation of liquid smoke products obtained by the equation of the reaction constant following the Arrhenius equation $k = Ae^{2111.4 / T}$, with an activation energy value (E_a) of 17.554 x 10^3 kJ/mol and pyrolysis using a catalyst obtained $k = Ae^{10330/T}$, with an activation energy value (E_a) of 85.883x103 kJ/mol. Using catalysts during pyrolysis will reduce the temperature so that the reaction will be slow.

Keywords: Kinetics reaction, reaction order, plastic waste, Pyrolysis, styrofoam

INTRODUCTION

Garbage is an environmental problem in Indonesia (Ningsih, Ariyani, & Sunardi, 2019). In North Sulawesi for the city of Manado, according to data from the Manado City Environment Service, quoted from the Manado Tribune on May 23, 2018, that waste production per day reaches 412.9 tons, not including un transported waste. This waste or garbage is then disposed of in a landfill (TPA) to reduce waste in the middle of the city. Waste based on its form consists of solid, liquid, and gas waste. Solid waste, for example, biomass waste or those originating from living things such as leaves, coconut shells, and rice husks, this type waste is included in waste that can be decomposed by microorganisms, there is also plastic-type solid waste, this waste cannot be degraded by microorganisms, its non-renewable nature takes time to degrade so that accumulation occurs (Sumarni & Purwanti, 2008). In the world, the most widely used plastic materials are Polyethylene (PE), Polyvinilckhorida (PVC), Polypropylene (PP), and Polystyrene (PS) (Marnoto & Sulistyowati, 2012).

In society, plastic waste will be handled by disposing or burning, of course, this method is not a comprehensive way to process waste, on the contrary, breaking down waste by burning it will increase air pollution which will also cause environmental problems (Anom & Lombok, 2020), considering Air pollution also occurs due to the use of fossil fuels (Jelita, Wijayanti, & Jefriadi, 2018). In addition to solving environmental problems, proper waste processing can also have an economic impact on society (Kasim, Ridwan, & Putra, 2018). Processing various kinds of waste or other environmental pollutants requires the right technology, which has no side effects and does not leave new waste and problems to the environment (Maafa, 2021), the technology in question is pyrolysis technology. Products produced from pyrolysis technology include pyrolysis of plastic materials which can produce solids in the form of carbon and produce a liquid that can be processed as fuel. Efforts to treat waste with this technology can overcome environmental problems and produce products such as fuel as alternative energy, given the energy source. The main source currently used comes from fossil fuels, whose energy reserves are increasingly limited (Caturwati, Suhendi, & Prasetyo, 2015).

Styrofoam is a type of Polystyrene (PS) plastic is a plastic material that is widely used as packing material for electronic devices and as a food container (Salamah & Maryudi, 2018) and its use as a greeting board has grown. Styrofoam plastic waste processing using the pyrolysis technique is important because it is part of the action to solve environmental problems.

The process of reactants decomposition that occurs during pyrolysis is important to observe, observations can be made on the effect of temperature, pyrolysis time, and the effect of catalysts on the rate of reaction of the decomposition of reactants in forming products. Knowing the kinetics of the pyrolysis chemical reaction of Styrofoam-type plastics will provide information on how the process of decomposing plastic solids into liquid products. This information can be used to design a more efficient operating unit so that the pyrolysis product will be maximized (Maafa, 2021).

Research conducted by Sumarni & Purwanti, (2008) on LDPE type plastic pyrolysis, the value of activation energy (Ea) in the formation of liquid products is 663.39 kJ/mol, with a rate constant value (k) following the Arrhenius equation. This research also found that the higher the temperature, the more liquid products will be produced. Based on this, it is necessary to conduct research on different types of plastics.

METHODOLOGY

Materials and Instrumentals

Research conducted by Sumarni & Purwanti, (2008) on LDPE type plastic pyrolysis, the value of activation energy (E_a) in the formation of liquid products is 663.39 kJ/mol, with a rate constant value (k) following the Arrhenius equation. This research also found that the higher the temperature, the more liquid products will be produced. Based on this, it is necessary to research different types of plastics.

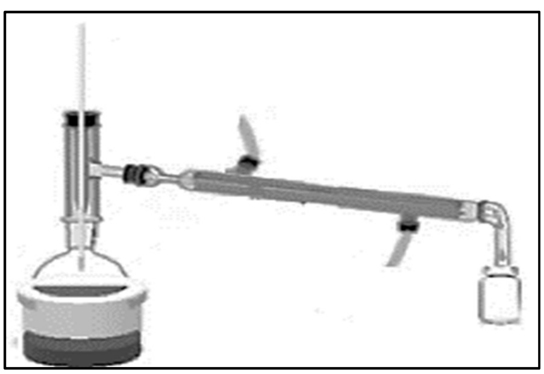

Figure 1. Pyrolsis Instruments

The materials used are Styrofoam which is used as a greeting board and natural Zeolite catalyst which is obtained online.

Figure 2. Styrofoam Sample

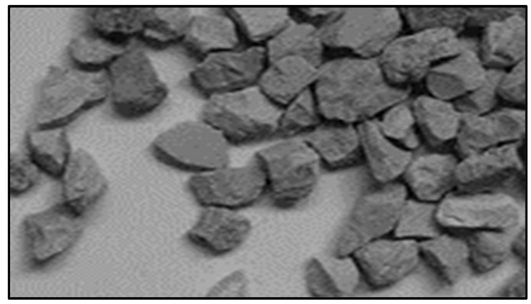

Figure 3. Zeolite Catalyst

Methods

Styrofoam that is not used is collected and then mashed to a size of 3-4 cm. Styrofoam is prepared in two containers, each weighing up to 200 g, then prepare 5 g of Zeolite catalyst which has been dried in the sun. Pyrolysis was carried out twice, namely Styrofoam pyrolysis without a catalyst and Styrofoam pyrolysis using a catalyst. Observations were made every 15 minutes to observe the amount of liquid product produced. Then by knowing the initial sample weight and the weight of the liquid measured at each time interval, the fraction of the weight of the liquid against time is obtained.

Data Analysis

In this research, the mechanism of Styrofoam pyrolysis reaction is considered as the random breakdown of Polystyrene polymer chains into smaller Styrene molecules. This decomposition will produce products in the form of liquids, gases and solids, where changes in the concentration of the reactants to form the product will affect the temperature of the reaction rate. The relationship between reaction rate and concentration can be seen in Table 1.

Table 1. Integrated Rate Law

	Rate Law	Linear equation
Zero Order	$v = -k$	$[A] = -kt + [A_0]$
First Order	$v = -k [A]$	$\ln[A] = -kt + \ln[A_0]$
Second Order	$v = -k[A]^2$	$\frac{1}{[A]} = -kt + \frac{1}{[A_0]}$

The relationship of the reaction rate constant (k) to temperature in Styrofoam pyrolysis in the formation of liquid products was evaluated using the Arrhenius equation (Equation 1).

$$k = Ae^{-Ea/RT} \quad (1)$$

Where Ea is the activation energy (kJ/mol), T is the absolute temperature (K), R is the gas constant 8.314 J/K.mol, e is the exponent and A is the frequency factor. This equation can be made in the form of a linear equation (Equation 2) (Majedi, Wijayanti, & Hamidi, 2015).

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A \quad (2)$$

The plot of ln k against 1/T produces a straight linear equation with the slope of -Ea/R and the intersection of ln A. The constant value of the rate of change of reagents into products can be written as follows Equation (Li, Zhang, Zhang, Ding, & Zhou, 2020).

$$\frac{dm}{dt} = k.f\left(\frac{m - m_a}{m_0 - m_a}\right) \quad (3)$$

dm/dt is the change in mass at each time interval divided by the change in time, where m is the mass in the time interval, m_0 is the mass in the initial state and m_a is the mass in the final state. The mass percent of liquid smoke from pyrolysis (%) obtained using the Equation 4

$$\% = \frac{w_a}{w_0} \times 100\% \quad (4)$$

w_a is the final mass and w_0 is the mass of the sample.

RESULTS AND DISCUSSION

Styrofoam Pyrolisis

The first observation was carried out on pyrolysis without a catalyst. A total of 200 g of Styrofoam is put in the reactor at a temperature of 120 °C, at this temperature the solid Styrofoam has melted. At 140 °C, white smoke was observed, and the sample began to melt. At a temperature of about 198 °C, there is already the first drop of liquid in the container bottle. At about 258 °C the heating begins to be constant. The observations were started at an average temperature of 237 °C i.e. 1 hour after the first liquid dripped when the reaction started to slow down. Heating lasted for 3.5 hours.

The second observation was carried out on pyrolysis plus catalyst. 200 g of Styrofoam and 5 g of Zeolite catalyst were put in the reactor at 100 °C, at this temperature the solid Styrofoam had melted. At 120 °C, white smoke was observed, and the sample began to melt. At about 160 °C there is already the first drop of liquid in the container bottle. At about 180 °C the heating begins to be constant. Then the observations started at an average temperature of 187 °C, that is, 1 hour after the first liquid dripped when the reaction started to slow down. Heating lasts for 3.5 hours.

Pyrolysis of Styrofoam without a catalyst at an average temperature of 235 °C obtained composition of 60% liquid, 35% solids, and 5% gas, while Styrofoam pyrolysis using a catalyst at an average temperature of 182 °C obtained a liquid yield composition of 53.5%, solids as much as 40%, and gas 6.5%. Styrene is the main constituent of Styrofoam in addition to additional additives such as foams and fillers. As a type of plastic that is a thermoplastic, heating Styrofoam at high temperatures causes the random termination of chemical bonds to Polystyrene as a polymer breaks down into Styrene monomers and also several other compounds, such as Toluene, Isopropyl benzene, Benzene and Xylene (Marnoto & Sulistyowati, 2012). The pyrolysis of Polystyrene by (Salamah & Maryudi, 2018) at a temperature of 460 °C without a catalyst obtained 50% Styrene, while pyrolysis with 10% zeolite catalyst obtained 16% Styrene.

The Relation between Mass of Liquid Product and Pyrolysis Time

At the first 60 minutes of the pyrolysis time, the amount of oil production is greater than the subsequent times, this is because at the beginning of heating there are still many polymers as a constituent of Styrofoam which decompose quickly. This data also shows that both Styrofoam pyrolysis without a catalyst or using a catalyst will produce a product that decreases with increasing time. The remaining solid pyrolysis is black in powder form.

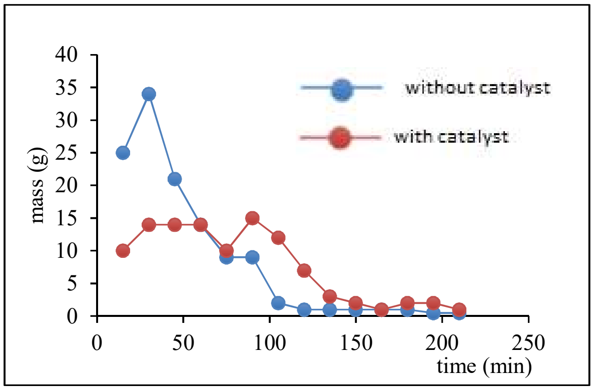

Figure 4. Graph of Liquid Product Mass vs Pyrolisis Time

Reaction Order

The decomposition mass fraction data of Styrofoam to form liquid smoke products is processed using a graphical method by entering the data resulting from the formation of the product in the form of a plot of the reaction product fraction against time then obtained curves and straight-linear equations as in Figures 5 and 6. Data collection starts at 60 minutes because the temperature and reaction rate of oil formation is considered to be constant, indicated by the amount of liquid smoke product that is accommodated. Determination of the reaction order can be determined by paying attention to the value of R square (R^2) in the straight linear equation on each curve, where the R^2 value closest to 1 is the straight-linear equation most suitable for showing the order of the experimental reaction (Puspitasari, Sutijan, & Budiman, 2016). The known reaction order values can be used to calculate the rate constant values based on the rate law (Laily et al., 2019).

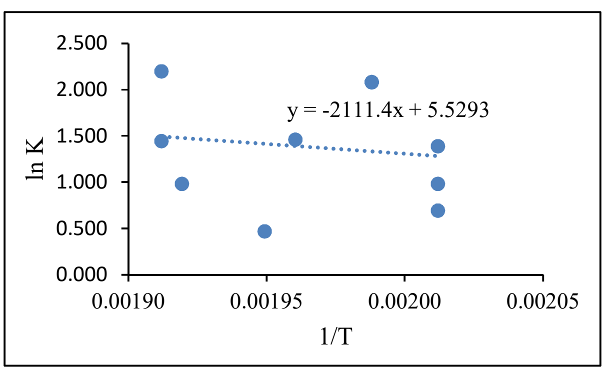

Figure 5. Graph of Linear Equation for First Order Pyrolisis Reaction without Catalyst

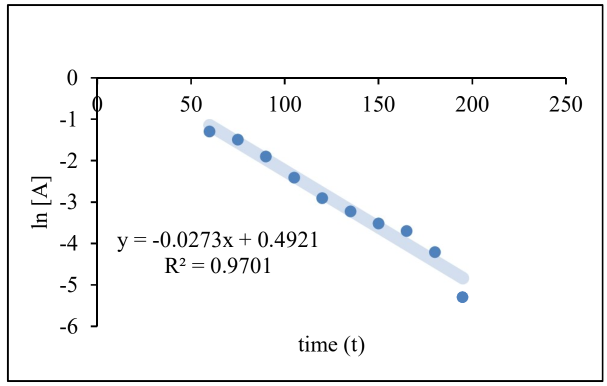

Figure 6. Graph of Linear Equation for First Order Pyrolisis Reaction with Catalyst

Based on the linear equation obtained, it is known that the Styrofoam pyrolysis process to form a liquid smoke product without a catalyst and adding a catalyst follows a first-order reaction. Thus the decomposition reaction rate of Styrofoam to form a liquid product is influenced by changes in concentration.

The Effetct of Temperature

Based on Table 2, by not controlling the temperature, the addition of a catalyst will reduce the heating temperature, so that pyrolysis without the addition of a catalyst will continue at high temperatures so that the reaction will produce more product quantities. The increase in temperature causes the number of colliding molecules to increase so that the reaction takes place faster. The energy involved in a reaction must be greater than the activation energy for a reaction to take place (Haryono, 2017). The increase in temperature will also reduce the activation energy (Hermaw, Hardianto, Suwandon, & Rahmadianto, 2019). Pyrolysis for hydrocarbon polymers requires a large amount of energy because at lower temperatures the reaction will take place slowly and the resulting product will be less (Rahman, Daud, & Reza, 2017)

Table 2. Total Pyrolisis Product

	Liquid	
	Without Catalyst	With catalyst
Average temperature (°C)	235	182
Total product	120 g	107 g

From the data on the process of liquid formation at each time interval, using the equation for the change of reagents into products, the reaction rate parameter is obtained, namely the value of the rate constant (k) at each time interval. After that, using the linear Arrhenius equation, plotting ln K against 1/T, you will get a curve with a straight linear equation for the formation of the product.

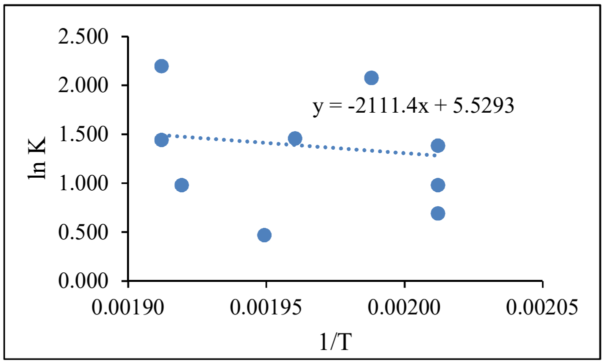

Figure 7. ln k plotted vs 1/T Pyrolisis witout Catalyst

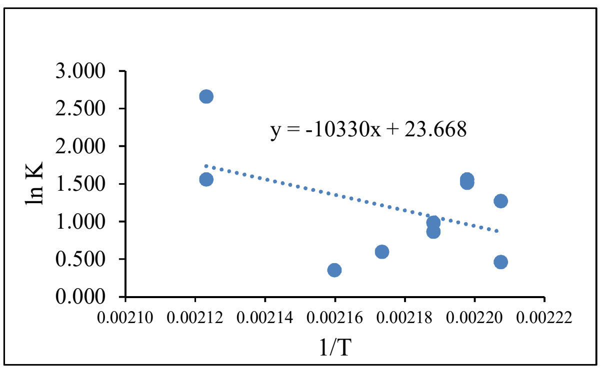

Figure 8. ln K plotted vs 1/T Pyrolisis with Catalyst

Based on the Figures 7 and 8, the Arrhenius equation is obtained as in Table 3. Thus, the exponential equation of the rate constant (*k*) and the value of activation energy (*Ea*) for each pyrolysis can be determined.

Table 3. Exponential Equation of Rate Constant

	Exponentian equation of rate constant (*k*) (minutes^{-1})	Temperature (K)	E_a (kJ/mol)
Without catalyst	$k = \mathrm{A}e^{-2111,4/\mathrm{T}}$	510	17.544,18
With catalyst	$k = \mathrm{A}e^{-10330/\mathrm{T}}$	460	85.883,62

The Effect of Catalyst

The use of a catalyst will reduce the temperature during pyrolysis (Pratiwi & Dahani, 2015), so that it will reduce the amount of product, on the other hand, theoretically, the catalyst will provide a reaction pathway with a lower activation energy value (Purnami, Wardana, & Veronika, 2015; Salamah & Maryudi, 2018). In this study, pyrolysis using a catalyst was not observed in changes in activation energy but was observed at temperature changes, this was possible because this study did not control the temperature to remain constant, therefore it is necessary to control the temperature when using a catalyst. The use of a catalyst must also pay attention to the amount of catalyst used. Research conducted by (Dewangga, Rochmadi, & Purnomo, 2019) obtained results on pyrolysis with a higher amount of catalyst, a higher liquid product was obtained, but according to research by Asmara & Kholidah, (2019) on the excess amount of catalyst will reduce the liquid product resulting from pyrolysis.

CONCLUSION

The pyrolysis of styrofoam to be liquid smoke products can observe at temperature of 170 °C - 237 °C without catalyst and added catalyst takes place in the first-order reaction. The kinetic parameters of the pyrolysis reaction without a catalyst follow the Arrhenius equation $k = \mathrm{A}e^{2111.4\ /\mathrm{T}}$, with an activation energy value (E_a) of 17.554x103 kJ/mol, and pyrolysis added catalyst follows the Arrhenius equation $k = \mathrm{A}e^{10330/\mathrm{T}}$, with the value of activation energy (E_a) of 85.883 x 103 kJ/mol. The use of a catalyst during pyrolysis will reduce the temperature so that the reaction is slow.

REFERENCES

Anom, I. D. K., & Lombok, J. Z. (2020). Karakterisasi Asap Cair Hasil Pirolisis Sampah Kantong Plastik sebagai Bahan Bakar Bensin. *Fullerene Journal of Chemistry*, *5*(2), 96–101. https://doi.org/10.37033/fjc.v5i2.206

Asmara, W., & Kholidah, N. (2019). Pengaruh Jumlah Katalis Zn Terhadap Hasil Pirolisis Limbah Styrofoam Menjadi Bahan Bakar Cair. *Prosiding Seminar Nasional Sains dan Teknologi Terapan*, *2*(1), 1–9.

Caturwati, N. K., Suhendi, E., & Prasetyo, E. (2015). Alat Pirolisis Tempurung Kelapa Sawit Sebagai Bahan Baku Briket Biomassa. *FLYWHEEL : Jurnal Teknik Mesin Untirta*, *2*(1). https://doi.org/10.36055/fwl.v2i1.519

Dewangga, P. B., Rochmadi, & Purnomo, C. W. (2019). Pyrolysis of polystyrene plastic waste using bentonite catalyst. *IOP Conference Series: Earth and Environmental Science*, *399*, 012110. https://doi.org/10.1088/1755-1315/399/1/012110

Haryono, H. (2017). Analisa Kinetika Reaksi Pembentukan Kerak $CaCO_3$-$CaSO_4$ Dalam Pipa Beraliran Laminar Pada Suhu 30 ºC Dan 40 ºC Menggunakan Persamaan Arrhenius. *TRAKSI*, *17*(2). https://doi.org/10.26714/traksi.17.2.2017.

Hermaw, D., Hardianto, A., Suwandon, P., & Rahmadianto, F. (2019). Pengaruh Temperatur Pirolisis Terhadap Energi Aktivasi Pada Tar Limbah Plastik. *Prosiding SENIATI*, 351–357.

Jelita, R., Wijayanti, H., & Jefriadi, J. (2018). Studi Kinetika Pirolisis Sekam Padi: Perbandingan Model Kinetika. *Konversi*, *7*(2). https://doi.org/10.20527/k.v7i2.6496

Kasim, F., Ridwan, M. K., & Putra, M. Y. A. (2018). Pengolahan Sampah Plastik Memakai Teknologi Pirolisis Untuk Pembelajaran dan Konservasi Lingkungan di Pondok Pesantren Al-Anwar Sarang Rembang, Jawa Tengah. *Jurnal Bakti Saintek: Jurnal Pengabdian Masyarakat Bidang Sains Dan Teknologi*, *2*(2), 57–63. https://doi.org/10.14421/jbs.1230

Li, A., Zhang, W., Zhang, J., Ding, Y., & Zhou, R. (2020). Pyrolysis Kinetic Properties of Thermal Insulation Waste Extruded Polystyrene by Multiple Thermal Analysis Methods. *Materials*, *13*(24), 5595. https://doi.org/10.3390/ma13245595

Maafa, I. M. (2021a). Pyrolysis of Polystyrene Waste: A Review. *Polymers*, *13*(2), 225. https://doi.org/10.3390/polym13020225

Majedi, F., Wijayanti, W., & Hamidi, N. (2015). Parameter Kinetik Char Hasil Pirolisis Serbuk Kayu Mahoni (Switenia Macrophylla) dengan Variasi Heating Rate dan 1 Temperatur. *Rekayasa Mesin*, *6*(1), 1–7. https://doi.org/10.21776/ub.jrm.2015.006.01.1

Marnoto, T., & Sulistyowati, E. (2012a). Tinjauan Kinetika Pyrolysis Limbah Polystiren. *Seminar Nasional Teknik Kimia "Kejuangan," D-08*, D-08-1-D08-5.

Ningsih, E. P., Ariyani, D., & Sunardi, S. (2019). Pengaruh Penambahan Carboxymethyl Cellulose Terhadap Karakteristik Bioplastik Dari Pati Ubi Nagara (Ipomoea batatas L.). *Indonesian Journal of Chemical Research*, *7*(1), 77–85. https://doi.org/10.30598//ijcr.2019.7-sun

Pratiwi, R., & Dahani, W. (2015). Pengaruh Penggunaan Katalis Zeolit Alam Dalam Pirolisis Limbah Plastik Jenis Hdpe Menjadi Bahan Bakar Cair Setara Bensin. *Prosiding Semnastek*, Retrieved from https://jurnal.umj.ac.id/index.php/semnastek/article/view/543

Purnami, P., Wardana, I., & Veronika, K. (2015). Pengaruh Pengunaan Katalis Terhadap Laju Dan Efisiensi Pembentukan Hidrogen. *Rekayasa Mesin*, *6*(1), 51–59. https://doi.org/10.21776/ub.jrm.2015.006.01.8

Puspitasari, M., Sutijan, S., & Budiman, A. (2016). Kinetika Reaksi Pirolisis Enceng Gondok. *Eksergi*, *13*(1), 13–16. https://doi.org/10.31315/e.v13i1.1436

Rahman, M. T. A., Daud, S., & Reza, M. (2017). Pengaruh Suhu Dan Persen Katalis Zeolit Terhadap Yield Pirolisis Limbah Plastik Polypropylene (PP). *Jurnal Online Mahasiswa (JOM) Bidang Teknik dan Sains*, *4*(2), 1–7.

Salamah, S., & Maryudi, M. (2018). Proses Pirolisis Limbah Styrofoam Menggunakan Katalis Silika-Alumina. *Jurnal Rekayasa Kimia & Lingkungan*, *13*(1), 1–7. https://doi.org/10.23955/rkl.v13i1.8695

Sumarni, S., & Purwanti, A. (2008). Kinetika Reaksi Pirolisis Plastik Low Density Poliethylene (LDPE). *Jurnal Teknologi*, *1*(2), 135–140.