

Special issue on Sustainable Environmental Processes and Technologies

THERMOLYSIS OF MEDICAL PLASTIC WASTES USING ZEOLITE A CATALYST-KINETIC STUDY, EXPERIMENTAL OPTIMISATION AND VALIDATION

Amar Kumar DAS¹, Saroj Kumar ROUT², Achyut Kumar PANDA^{3*}

¹Department of Mechanical Engg, GIFT, Bhubaneswar, Odisha, India ²Department of IT, Vardhaman College of Engineering, Hyderabad, Telangana, India ³Department of Chemistry, Veer Surendra Sai University of Technology Burla, Odisha, India

Received 27 June 2020; accepted 09 March 2021

Highlights

- Verify the efficacy of Zeolite A catalyst in the thermal degradation of medical plastic waste to fuel oil by kinetic study and subsequently by lab-scale pyrolysis reactor.
- Optimise the reaction conditions including temperature and catalyst concentration to maximising the oil yield and validate the experimental result with Artificial Neural Network.
- ▶ Characterise the composition and fuel properties of the oil obtained in optimum condition.

Abstract. This work reports the thermo-catalytic conversion of medical plastic wastes to fuel oil using the detergent grade Zeolite A as the catalyst. The effect of catalyst on the pyrolysis is ascertained from the kinetic data obtained from thermogravimetric analysis assuming it to be a first-order reaction. A significant reduction in activation energy of the thermal degradation reaction is found in presence of the Zeolite A catalyst. The pyrolysis runs were performed at different temperatures from 400–550 °C in a stainless-steel batch reactor system to obtain an optimum condition for suitable waste to energy process. The highest oil yield of 79% was obtained at 500 °C with 10% catalyst concentration. The thermogravimetric analysis and the batch pyrolysis experimental result indicated a promising effect of the catalyst in terms of the enhanced rate of reaction and conversion. The oil fraction obtained in the optimum condition of catalytic pyrolysis was analysed for its composition and fuel properties. It confirmed the presence of branched alkane and alkene with composition $C_{10}-C_{18}$. Again, the fuel properties of the oil such as specific gravity (0.793), viscosity (3.75Cst@ 30 °C), and flash point (<11 °C) resemble that of the petro fuels. Neural Networks (NNs) are used to recognize patterns, and relationships in data and validate the experimental results of this reaction and the results indicate that the use of ANN in thermo-catalytic degradation of medical waste to fuel oil is a feasible option that should be considered for real-time applications.

Keywords: medical plastic wastes, Zeolite A catalyst, pyrolysis, Artificial Neural Networks.

Introduction

Waste plastics have become a threat to our environment due to their high volume and non-biodegradability. Among the different sources, the health sector also contributes a substantial amount of such waste from the process of diagnosis to treatment. As reported by WHO, about 85% of the wastes produced in hospitals are actually non-hazardous, 10% are infectious and 5% are hazardous but non-infectious. Studies show that the magnitude of bio-medical waste (in kg/bed/day) generated in India is 0.3 to 1.0 is very low compared to a few other developed countries such as the USA (4.5), Latin America (2.63 to 3.8), the Netherlands (2.7), France (2.5). In addition, 50% of the wastes generated in India are collected as infectious wastes, which could further be reduced by effective segregation (Environmental Information System [ENVIS], 2014). In this context, Bio-Medical Waste Management Rules-2016 has taken proactive measures to differentiate types of wastes generated at the source into four coloured categories for better segregation. The red category of the wastes mostly includes infected recyclable primarily plastic waste generated from non-reusable items. Such waste

*Corresponding author. E-mail: achyut.panda@gmail.com

Copyright © 2022 The Author(s). Published by Vilnius Gediminas Technical University

This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited. plastics collected out of the total volume of medical wastes generated imparted a major contribution to MSW (Lee et al., 2002). The most commonly used plastics used in medical application includes high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), acrylonitrile-butadiene-styrene terpolymer (ABS), etc. (Lee et al., 2002). The most common management techniques being adopted in India include incineration/deep burial incineration, autoclaving, microwaving, and disposal by deep burial, including recent techniques like Plasma Pyrolysis, Waste Sharps dry heat sterilization, and encapsulation and shredding cum chemical disinfection to avoid contamination and infection (ENVIS, 2014).

In addition, the waste plastics from medical wastes system could also be recycled by pyrolysis. Plastic pyrolysis has three-fold advantages; viz. firstly it helps manage high volume solid plastic wastes and reduces their environmental menace, secondly, it promotes recovery of alternate fuel and chemicals and thirdly it also has the environmental advantages of no emissions of hazardous gases (Al-Salem et al., 2017; Aguado et al., 2008). As reported, it is a sustainable process is affected by different process conditions such as temperature, pressure, residence time, reactor design, feed composition, catalyst, etc. and these parameters can be altered to achieve the desired product type (Panda et al., 2010). This being an endothermic process, temperature plays a significant role in product distribution and quality (Al-Salem et al., 2017; Aguado et al., 2008; Panda et al., 2010). The effect of pressure is reported to be significant at low temperatures (Panda et al., 2010). Many types of reactor and experimental setups have been reported for plastic pyrolysis. Most researchers have reported the uses of batch reactors and it is good to understand the process in lab scale. But it is not consistent and cost-effective due to the requirement of frequent feeding subsequently escalating the employment cost of the method. Therefore, a continuous pyrolysis process is recommended in favour of higher investment business. Microwave-assisted pyrolysis procedures are reported to be a better alternative to minimize the energy and time required for the pyrolysis process (Butler et al., 2011; Miandad et al., 2016; Kunwar et al., 2016). Thermo-catalytic degradation of waste plastics can be considered better than the thermal pyrolysis process in terms of high reaction rate, superior product yield, and quality. Furthermore, the oil obtained from catalytic cracking using a suitable catalyst yields qualitative by-products intended for automotive as an alternative fuel, simultaneously easing the process in context to energy and time. The effect of the catalyst is more significant among the other parameters and efforts are made to design a cheap but efficient catalyst that is less prone to polluting and deactivating with impurities in the feedstock. Accordingly, a wide range of heterogeneous catalysts was utilized for catalytic cracking of plastics including silica-alumina, conventional zeolites (HZSM-5, HBeta, HY, etc.), nanocrystalline zeolites (n-ZSM-5, n-MOR, n-USY), Lamellar, pillared and hierarchical zeolites with enhanced catalytic activities, fresh and spent FCC catalysts, mesostructured catalysts (MCM-41, FSM-16, Al-SBA-15, Al-MCM-41, Al UTD-1, KFS-16), superacid solids (ZrO₂/SO₄²⁻), gallosilicates, various types of clay such as kaoline, calcium bentonite, montmorillonite, saponite, albite, pyrophyllite, and halloysite restructured smectite clays, acid modified clay, as well as their Al- and Fe/Al-pillared derivatives, metalbased catalysts, and basic catalysts (BaO,K2O, magnesium carbonate, Barium carbonate, calcium carbonate) (Miandad et al., 2016; Kunwar et al., 2016; Serrano et al., 2012; Jan et al., 2010a, 2010b). Zeolites are used as catalysts due to its versatility. The common features that the reported catalyst holds for plastic pyrolysis includes different surface properties including high surface area, mesopore and micropore texture, and acidic and basic surface. Most of the catalysts reported for plastic pyrolysis are acidic in nature because the faulty sites in polymers can be protonated to form on-chain carbocations. On the other hand, basic catalysts act on the polymer by abstracting the proton from its surface giving reactive carbanions. The acidic or basic surface affects the quality of the fuel and the product distribution. As a whole, the occurrence of an appropriate catalyst reduces the cracking temperature and raises the conversion as compared to thermal processes.

In this context, the present work focuses on the thermo-catalytic recycling of medical plastic wastes into value-added fuels using Zeolite A as the catalyst. The major aspects of the work are to study the catalytic performance of the catalyst in the reaction with respect to the kinetics and product distribution. The novelty of the work is to study the catalytic efficacy of Zeolite A in the thermal degradation of medical plastic wastes. The experimental optimization of the process with respect to temperature and catalyst has been validated using ANN approach (Krestinskaya & James, 2018; Aljarah et al., 2018; Montana & Davis, 1989). The analysis of composition and fuel properties of the products of Zeolite A catalysed pyrolysis of plastic wastes is another important aspect of the work.

1. Experimental

During an assessment regarding the kinds and size of medical plastic wastes produced in various healthcare bins located in smart city Bhubaneswar, it is evident that the majority of plastic wastes generated in medical are comprised of the used disposable syringes and exhausted saline bottles. However, other used items are found in small portions. In addition, collected saline bottles and used syringes are found in the total waste as 70:30 by weight. Thus, it is quite obvious to conduct pyrolysis of these wastes by their source availability proportion. So in this matter, these two types of plastic waste materials are collected from different hospitals and subsequently dried and shredded into small sizes of around 2-4 mm and then made ready for pyrolysis in 70:30 (Saline bottles: Syringe) part. The type of polymer used in these items is found to be polypropylene known by the recycling symbol on the items.

Zeolite A is used as the catalyst in this experiment. Detergent grade Zeolite A $[Na_2O(AlO_2.SiO_2.)_{12} 27H_2O]$ procured from NALCO Damonjodi Odisha (NALCO India, n.d.). The XRF composition of this catalyst is Al_2O_3 : 27.98, SiO_2 : 32.87, Na_2O : 16.98, LOI: 22.19. It is a white free-flowing powder with an average particle size of 4–6 micron particle size and a high surface area of 350 to 1000 m²/g have high thermal and hydrothermal stability and can withstand temperatures up to 800 °C even in presence of steam. SEM of the sample confirms the particle has a cubic shape with rounded corners and edges. The XRD of the powder also infers the presence of different phases with a high level of crystallinity (95%) (Patnaik et al., 2020).

The thermogravimetric analysis of the plastic sample was carried out by Perkin Elmer STA8000 at a heating rate of 20 K min⁻¹ in a nitrogen atmosphere with a flow rate of 20 ml per min in the temperature range from 30–600 °C. A definite amount of plastic samples were taken and subjected to thermal degradation in an inert atmosphere. In catalytic experiments, samples are taken in plastic to catalyst ratio of 10:1 by weight and subjected to thermal degradation.

The pyrolysis of the plastic wastes is carried out in a semi batch reactor already reported in our other works (Panda & Singh, 2014). The reactor is heated by an external electric furnace integrated with a thermocouple and a PID controller to maintain the desired operating temperature. Shredded mixed plastic wastes (discarded syringe and saline bottle in 70:30 proportions) of 50 g were loaded in each pyrolysis reaction. In the catalytic pyrolysis, a mixture of catalysts in different concentrations and the plastics samples were subjected to pyrolysis at the desired temperature. The vapours of the pyrolysis experiments are condensed in a water-cooled liebig condenser. The reaction time is recorded from the point of inserting the reactor inside the furnace (after attaining the desired temperature) till the last drop of the oil collected from the condenser. The weight of the oil collected through the condenser and the residue that remains inside the reactor is weighted, while the amount of gas produced is calculated by material balance.

2. Results and discussions

2.1. Kinetics of thermal degradation

The TG and DTG behaviour of the plastics shows a similar weight-loss trend, indicating a comparable degradation pattern at the specified scope of temperature (Figures 1 and 2). However, the degradation temperature differs for thermal and catalytic reactions, which could be attributed to changes in the reaction path and mechanism of the degradation reaction in presence of the catalyst. In the present case, the temperature of degradation pursues the order: Catalytic > Thermal. In addition, temperatures by which weight loss of 50% (T₅₀) transpires are about 463 °C for thermal, while it is 445 °C for the catalytic reaction. The



Figure 1. TG plot of plastic sample in thermal and catalytic experiment



Figure 2. DTG plot of plastic sample in thermal and catalytic experiment

DTG plot shows that there is a significant change in the T_{onset} and T_{max} and the major degradation occurs from 400–500 °C. So, the pyrolysis experiments were conducted in the specified temperature scope of 400–550 °C to optimise process conditions for maximising the oil yield.

Kinetics parameters for the thermal and Zeolite A catalysed degradation of wastes plastic sample is determined from the TG data to comprehend the effect of Zeolite A as catalyst on the reaction. The activation energy (E_a) of thermal degradation can be determined from the weight loss pattern from the thermogravimetric analysis of plastic sample by model fitting kinetic approach using order based Mampel first-order model fitting (Direct Arrhenius plot) method assuming first order kinetics.

Kinetic equation used is:
$$\ln(-\ln (1 - x)) = \ln\left(\frac{ART^2}{\beta E_a}\right) - \frac{E_a}{RT}$$
, where, $x = \text{conversion}\left(=\frac{W_0 - W_t}{W_0 - W_{\infty}}\right)$,

 W_0 , W_t and W_∞ designate the early weight, weight of the sample left after time *t*, and weight after pyrolysis, A = Arrhenius/pre exponential factor, R = gas constant, β = heating rate E_a = activation energy, and *T* = temperature. The kinetic result in the present experiment also provides finest statistical

compatibility by considering the first order kinetic analysis. The value of kinetic energy could be intended from the slope of the straight line obtained for the plot of $\ln[-\ln (1 - x)/T^2]$ vs 1/T shown in Figure 3. From this, the activation energy for both thermal and catalytic reactions are calculated and reported in Table 1. The significance of activation energy meant for the reaction is found to be decreased by 102 KJ/mol/K in presence of Zeolite A catalyst as compared to thermal reaction.



Figure 3. Kinetic plot for the thermal and catalytic degradation plastic sample

Table 1. Kinetic calculation

Reaction	R ²	slope	Peak tem- perature T_p (°C)	Activation energy E _a (KJ/mol/K)
Thermal	0.967	30557.9	469	254.05
Catalytic	0.987	18394.2	454	152.92

2.2. Experimental optimisation of the pyrolysis process

The pyrolysis experiments accomplished in the temperature range from 400 to 550 °C show substantial alteration in the product distribution with varying temperatures (Figure 4). Oil is the main product at the entire the temperatures, raises from a lower yield of 53.7% at 400 °C to the highest value of 71.3% at 500 °C and successively reduces with additional raise in temperature beyond 500 °C. The yield of the gaseous fraction explains a diminishing trend from 44.8% at 400 °C to a least possible value of 27.8% at 500 °C and raises further beyond this temperature. The residual fraction is the lowest (<2%) among all the three portions. The product distribution pattern with temperature can be explained due to the change in reaction time. Higher reaction time aids the secondary cracking of the primary reaction oligomers to lighter fractions yielding high gaseous product at a lower temperature. With the increase in temperature, the oligomers get sufficient energy to come out of the reactor and escape secondary cracking. After an optimum temperature of 500 °C, the very high initial thermal energy intends severe cracking

of the polymer mostly to a gaseous fraction. So, the experimental results conclude the optimising condition for the highest yield of oil is 500 °C. The reaction kinetics was inferred in terms of the completion time of the reaction conducted at a specified temperature. The rate of reaction increases or the completion time of reaction decreases with an increase in temperature. The pyrolysis product distribution with catalyst concentration is summarised in Figure 5. The catalyst illustrates a significant effect on the product yield and kinetics of the reaction (Figure 6). A maximum oil yield of 79.2% is observed with 10% Zeolite catalysts and decreased with a rise in the concentration of catalyst to 20%, simultaneously increasing the gaseous fraction. A considerable change in the physical properties of the oil such as density and viscosity also is viewed in the presence of both catalysts (Table 2). The above results infer that the catalyst accelerates the reaction rate and yield of oil, and also improves the product quality. This can be explained due to the presence of high surface area and surface basicity that make possible the cracking of plastic samples. The basic center on the catalyst facilitates the abstraction of proton from the polymer surface at higher temperatures leading to the formation of active carbanion and stimulating the reaction at a lower temperature (Jan et al., 2010a).



Figure 4. Distribution of pyrolysis products at varied temperature



Figure 5. Distribution of pyrolysis products at varied catalyst concentration



Figure 6. Comparison of reaction rate in thermal and catalytic reaction

Table 2. Pyrolysis experimental results at 500 °C

Pyrolysis reaction	Oil yield (%)	Reaction time (min)	Density at 15 °C (g cc ⁻¹)	Viscosity at 30 °C (cSt)
Thermal	75.3	62	0.864	4.52
Zeolite A catalyst	79.2	55	0.793	3.75

2.3. Validation of the experimental results using Neural Networks

Neural Network plays a important role for optimization of given dataset. The performance of the system depends upon the back propagation algorithm. The dataset given to the system which is execute in Neural Network and produced simulation result with minimal error. The result set produced in a trained network from given input/output pair. Figures 7a and 7b represents the multilayer Neural Network with n number of neurons. This network represents the pattern vector p defines the class value O_i when output of ith network is high but other output values are



Figure 7. a – Graphical description of training multi-layer ANN; b – Graphical description of training multi-layer ANN

low. By using formula we can calculate quantity of nodes in the hidden layer.

$$n = \frac{(i+0)}{2} + y^{0.5},\tag{1}$$

where *n*, *i*, o and *y* are the hidden layer nodes, input features, output features and countable patterns in the training set.

The ANN structure defines input parameter as x_1 and x_2 , after executing the data it gives target output y'. When it passes number of iteration weights coefficients of nodes is modified. The output of each neuron is feed as input the next hidden layer neuron.

2.3.1. Simulation results

MATLAB provides facility for simulation of ANN. The Toolbox supported by MATLAB of ANN which makes a neural system to prepare and validate the information for data classification and prediction. There are a few other neural system tools yet MATLAB NN Tool is large number of functionality support. Here we used Back propagation system in ANN Tool in MATLAB with the dataset, in which the information is defined.

The simulation was performed by help of the NN Tool box provided by MATLAB and it simulates the datasheet of oil yield from various plastic wastes under different conditions to find the result. We have made a neural system by the assistance of the training dataset and with help of activation function related with the layers of the system and the type of different parameters affecting the yield. The performance and execution capacities MSE, MSEREG and SSE with training functions TRANSIG, LOGSIG and PURELIN acquired in the results. The feed forward back propagation algorithm calculation is utilized in arrange compose and LEARNGDM versatile function with 2 layers and 10 neurons. In Statistics, Mean Square Error (MSE) is defined as Mean or Average of the square of the difference between actual and estimated values. MSE is a network performance function. It measures the network>s performance according to the mean of squared errors. MSEREG is a network performance function. It measures network performance as the weight sum of two factors: the mean squared error and the mean squared weight and bias values. The sum of squared errors, or SSE, is a preliminary statistical calculation that leads to other data values. SSE is the sum of the squared differences between each observation and its group's mean.

The ANN biases and activations function is represented the system to validate the result in Figure 7b. Explicitly, we use $b_j^{\ l}$ in bias of the j^{th} neuron of the l^{th} layer. Also use $a_j^{\ l}$ in the activation value of the j^{th} neuron in the l^{th} layer is represented in Equation (2).

$$a_j^{\ l} = \sigma\left(\sum_k w_{jk}^{\ l} a_k^{\ l-1} + b_j^{\ l}\right),\tag{2}$$

where defines sum of overall neurons k in the $l-1^{th}$ layer. This expression is written as *weight matrix* w^l for each layer, l. The complete weight matrix w^l is connected to the ANN l^{th} layer, which defines the system of the entry in the j^{th} row and k^{th} column is w_{jk}^{l} . We also define ANN, for each layer la important *bias vector*, b^l . You can probably guess how this works – the components of the bias vector are just the values b_j^{l} , one component for each neuron in the l^{th} layer. And finally, we define an activation vector b^l whose components are the activations a_j^{l} .

This Figure 8 represents and discussed system model and shows how input parameters such as temperature inside the reactor, blending ratio, presence of catalysts are associated in the ANN system. The system defines how all input parameters are connected to ANN hidden layers and also ANN hidden layers are connected to input layer.



Figure 8. Neural Network Model of the system created by the MATLAB

Figure 9 demonstrates the algorithm analysis and, sort of error chose for preparing in training the network i.e. MSE (Mean Square Error) or, MSEREG or SSE. This figure likewise gives us estimation of the error while preparing the system. In this execution feed forward back propagation method is connected the network using different performance functions such as MSE, MSCREG and SSE and to apply different transfer functions such as TRAN-SIG, LOGSIG and PURELIN. The system gives the final result with different iterations and shows the plots of performance, training state and regression charts.



Figure 9. Trained Neural Network model g by the MATLAB

2.3.2. Results analysis

The Table 3 is Training R (Training Regression) results got under various situations of activation functions. For MSE performance execution work with PURELIN exchange function gives better validation results i.e. 0.98939. For

		Transfer functions (Training)				
Performance		LOGSIG	PURELIN	TRANSIG		
function	MSE	0.46226	0.98939	0.92301		
	MSEREG	0.98404	0.96841	0.93853		
	SSE	0.95861	0.84624	0.97951		

Table 3. Results for various Transfer functions for training R

showing performance of system

MSEREG performance function work with LOGSIG function work gives better validation results with 0.98404. For SSE performance function execution work with TRAN-SIG transfer function gives better results with 0.97951. Relatively MSE execution work with PURELIN transfer function gives better approval of tranning R results, i.e. 0.98939. Figure 10 describes the results for various Transfer functions for Training data where represents MSE execution work with PURELIN transfer function gives better performance as 0.98939.



Figure 10. Results for various Transfer functions for Training

Table 4. Results for various Transfer functionsfor all R of the system

Performance function		Transfer functions (All R)			
		LOGSIG	PURELIN	TRANSIG	
	MSE	0.65059	0.95648	0.90936	
	MSEREG	0.16164	0.90831	0.92296	
	SSE	0.98652	0.82816	0.67882	

The Table 4 is All R (all Regression) results acquired under various situations of activation functions. For MSE execution work with PURELIN exchange work gives better validation results with 0.95648. For MSEREG performance function work with TRAN-SIG function work gives better validation results with 0.92296. For SSE performance function execution work with LOGSIG transfer function gives better results with 0.98652. Relatively SSE execution work with LOGSIG transfer function gives better approval All R results, i.e. 0.98652. Figure 11 describes the results for various Transfer functions for Training data where represents SSE execution work with LOGSIG transfer function gives better performance as 0.98652.



Figure 11. Results for various Transfer functions for all R

Table 5. Results for various Transfer functions for validation R

Performance function		Transfer functions (Validation)				
		LOGSIG	PURELIN	TRANSIG		
	MSE	0.42215	0.97442	0.43124		
	MSEREG	0.22132	0.56235	0.40807		
	SSE	0.054427	0.25673	0.96165		

Table 5 represents the result of the Validation R value acquired under various situations of the performance functions. The execution value MSE along with PURELIN performance function represented better result work with 0.97442. For MSEREG execution work with PURELIN exchange shows better results vale of 0.56235. Also SSE performance function work with TRANSIG exchange work good results with 0.96165. Relatively MSE execution work with PURELIN exchange work good results, i.e. 0.97442. Figure 12 describes the results for various Transfer functions for Training data where represents MSE execution work with PURELIN transfer function gives better performance as 0.97442.

Figure 13 represents the results with execution validation graph for MSE in training data where describes MSE execution work with best validation performance with value 1884.4756 at epoch 19.

Figure 14 shows the execution validation graph with MSEREG function for training data where represents MSEREG execution work with best validation performance is 7576.565 at epoch 10 using transfer function. The train graph and test chart having more difference in performance. The validation is relatively similar to train graph. It is best fitted at epoch 10.



Figure 12. Shows the MSE, MSEREG and SSE Transfer functions for validation



Figure 13. Performance validation chart



Figure 14. Performance validation chart



Figure 15. Training state chart

Figure 15 represents Various graphs such as training state, output and regression were generated from the three activation functions such as logsig, transig and purelin with performance functions such as mse, msereg, and sse supplied by NN tool in MATLAB. It represents the performance of the MSE with respect to TRANSIG activation function which represents the value of the Gradient = 0.806289.5485 at epoch 6, mu = 1e-011 at epoch 6 and the validation checks = 6 at epoch 6. The training state chart gives efficient performance for system model of optimisation and validation of oil production. The chart explains the performance of training states in terms of

highest production of oil under the specified training and test data.



Figure 16. The MSE and TRANSIG activation function's regression analysis chart

Figure 16 describes the performance value of MSE and LOGSIG function during regression analysis. Where the value is represented as tranning R = 1, Test R = 0.16427 and its validation value is 0.3135 along with the all R = 0.98918. The simulation value of this regression analysis, conclude that MSE gives better validation results that other.

2.4. Characterisation of the oil samples

The FTIR of the pyrolysis oil attained from thermal pyrolysis of individual and mixed plastics and also from Zeolite catalysed pyrolysed reaction is reported in Figure 17 and the plots of oil samples obtained indicate the presence of similar types of organic components mostly alkane (2853–2969 cm⁻¹:C-H_{Stretching}, 893 cm⁻¹:C-C_{Stretching}, 1377&1450:C-H_{bending}) and alkene/Aromatics (1600–1640 cm⁻¹:C=C_{stretching}, 711–813 cm⁻¹:C-H_{bending}). Thus it could be concluded that the pyrolysis oil contain only saturated and unsaturated hydrocarbons.



Figure 17. FTIR plot of oil samples



Figure 18. GC-MS plot of the pyrolysis oil

Table (5. Fuel	properties	of oil
---------	---------	------------	--------

Darameters	Test protocol	Gasoline	Kerosene	Diesel	Plastic oil at optimum conditions	
T al allietters	iest protocor				Thermal	Zeolite A catalysed
Colour		Yellow	Faint yellow	Orange	Str	aw yellow
Specific Gravity @ 15 °C/15 °C	I.S.1448: P.16	0.73-0.73	0.78-0.82	0.83-0.85	0.864	0.793
Kinematic Viscosity Cst@ 30 °C	I.S.1448: P:25	1.076-1.03	1.54-2.2	2.4-5.3	4.52	3.75
Gross calorific Value MJ/kg	I.S.1448: P:6	46.86	45.46	42.51	43.87	44.39
Flash Point (°C)	I.S.1448: P:20	-42	50-55	55-60	11	
Fire Point (°C)	I.S.1448: P:20	-37	60	68	14	
Boiling point range (°C)	I.S.1448: P.18	40-205	175-325	150-350	56-365	55-335

The composition of the pyrolysis oil produced at optimum condition was studied using Gas Chromatography-Mass spectrometry (Figure 18). The major components of the oil are saturated and unsaturated branched hydrocarbons with carbon composition C_{10} - C_{18} . The major components being 3,7-Dimethyl-2-Octene, 2,5,5-Trimethylheptane, 4-Methyl Decane, 2,3,7-Trimethyl-2-Octene, 7-Methyl-4-Undecene, 2,4-Dimethyl-2-Decene, 7-Methyl-1-Undecene, 2,2-Dimethyl-3-Decene, 1-Dodecene, 1,5-Diethyl-2,3-Dimethylcyclohexan, 2,3,5,7-tetramethyl-2-Octene and 1-Octadecene. The composition of the oil in the catalytic pyrolysis very much resembles that of diesel range fuel and thus be suitable to be used as a fossil fuel substitute directly or can be a feedstock for petroleum refinery.

Table 6 reports the general fuel properties of the oil derived from waste plastics samples obtained at optimal process conditions of thermal and catalytic thermal degradation. The properties of the oil obtained from both the process is comparable with the properties of different petro fuels (Panda & Singh, 2014). The specific gravity and viscosity of the plastic oils was found superior compared with petrol but within the diesel/kerosene range. These properties are slightly higher in thermal as compared to catalytic reaction. The flash point and fire point of the oils is also within that of different petro-fuels. The heating values of the oils are also high enough and at par with the other fuels of petroleum origin. The boiling ranges of the plastic oils are very broad and can be isolated into different boiling fractions to obtain fuels of desired boiling point range. The higher boiling range fraction may be subjected to further cracking or reformation to yield lighter fractions.

Conclusions

An optimised process for the thermo-catalytic degradation of selected plastic wastes to fuel oil in presence of Zeolite A catalyst has been designed through a series of experiments using a batch reactor. A significant decrease in the activation energy of the reaction in presence of Zeolite A ascertained the effectiveness of the catalyst. It is found to be an effective catalyst for the thermal degradation of plastic wastes in terms of bettering the yield and quantity of oil and process time. An oil yield of about 80% by weight is found following the best possible condition of 500 °C and 10% Zeolite A catalysts. The use of ANNs for validation of thermocatalytic degradation process of medical plastic waste to fuel oil is proposed due to its generalization capability and high processing speed and accustomed to predict the quantity of oil with least error, below 1%, and an utmost correlation coefficient close to 1. The oil produced is found to contain hydrocarbons with matching properties as that of different fossil fuels.

References

- Aguado, J., Serrano, D. P., & Escola, J. M. (2008). Fuels from waste plastics by thermal and catalytic processes: A review. *Industrial & Engineering Chemistry Research*, 47(21), 7982–7992. https://doi.org/10.1021/ie800393w
- Aljarah, I., Faris, H., & Mirjalili, S. (2018). Optimizing connection weights in neural networks using the whale optimization algorithm. *Soft Computing*, 22(1), 1–15. https://doi.org/10.1007/s00500-016-2442-1
- 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 Man*agement, 197, 177–198.

https://doi.org/10.1016/j.jenvman.2017.03.084

Butler, E., Devlin, G., & McDonnell, K. (2011). Waste polyolefins to liquid fuels via pyrolysis: Review of commercial state-ofthe-art and recent laboratory research. *Waste and Biomass Valorization*, 2(3), 227–255.

https://doi.org/10.1007/s12649-011-9067-5

- Environmental Information System. (2014). *Bio-medical waste management: An overview*. http://cpcbenvis.nic.in/envis_ newsletter/BMW%20Newsletter.pdf
- Jan, M. R., Shah, J., & Gulab, H. (2010a). Catalytic degradation of waste high-density polyethylene into fuel products using BaCO₃ as a catalyst. *Fuel Processing Technology*, 91(11), 1428– 1437. https://doi.org/10.1016/j.fuproc.2010.05.017
- Jan, M. R., Shah, J., & Gulab, H. (2010b). Degradation of waste High-density polyethylene into fuel oil using basic catalyst. *Fuel*, 89(2), 474–480. https://doi.org/10.1016/j.fuel.2009.09.007
- Krestinskaya, O., & James, A. P. (2018, July). Binary weighted memristiveanalog deep neural network for near-sensor edge processing. In 2018 IEEE 18th International Conference on Nanotechnology (IEEE-NANO) (pp. 1–4). IEEE. https://doi.org/10.1109/NANO.2018.8626224
- Kunwar, B., Cheng, H. N., Chandrashekaran, S. R., & Sharma, B. K. (2016). Plastics to fuel: A review. *Renewable and Sustainable Energy Reviews*, 54, 421–428. https://doi.org/10.1016/j.rser.2015.10.015
- Lee, B. K., Ellenbecker, M. J., & Moure-Eraso, R. (2002). Analyses of the recycling potential of medical plastic wastes. *Waste Management*, 22(5), 461–470. https://doi.org/10.1016/S0956-053X(02)00006-5

Miandad, R., Barakat, M. A., Aburiazaiza, A. S., Rehan, M., & Nizami, A. S. (2016). Catalytic pyrolysis of plastic waste: A review. Process Safety and Environmental Protection, 102, 822–838. https://doi.org/10.1016/j.psep.2016.06.022

- Montana, D. J., & Davis, L. (1989, August). Training feed forward neural networks using genetic algorithms. In *International Joint Conference on Artificial Intelligence* (Vol. 89, pp. 762– 767). Morgan Kaufmann Publishers.
- NALCO India. (n.d.). Zeolite-A. https://nalcoindia.com/business/products/zeolite-a/
- Panda, A. K., Singh, R. K., & Mishra, D. K. (2010). Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products – A world prospective. *Renewable and Sustainable Energy Reviews*, 14(1), 233–248.

https://doi.org/10.1016/j.rser.2009.07.005

Panda, A. K., & Singh, R. K. (2014). Conversion of waste polypropylene to liquid fuel using acid-activated kaolin. *Waste Management* & *Research*, 32(10), 997–1004. https://doi.org/10.1177/0734242X14545504

- Patnaik, S., Barick, A. K., & Panda, A. K. (2020). Thermo-catalytic degradation of different consumer plastic wastes by zeolite a catalyst: A kinetic approach. *Progress in Rubber, Plastics and Recycling Technology*, *37*(2), 148–164. https://doi.org/10.1177/1477760620972407
- Serrano, D. P., Aguado, J., & Escola, J. M. (2012). Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. ACS Catalysis, 2(9), 1924–1941. https://doi.org/10.1021/cs3003403