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Optimization of process parameters by response surface methodology (RSM) for catalytic pyrolysis of waste high-density polyethylene to liquid fuel

Sachin Kumar *, R.K. Singh [1]

National Institute of Technology Rourkela, Orissa, India

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ABSTRACT

Response surface methodology (RSM) was used to optimize the process for catalytic pyrolysis of waste high-density polyethylene to liquid fuel over modified catalyst. The reaction temperature, acidity of the modified catalysts and mass ratio between modified catalysts to waste high-density polyethylene (HDPE) were chosen as independent variables. Face centered central composite (FCCD) design of experiment has been used. Optimum operating conditions of reaction temperature (450 °C), acidity of catalyst (0.341) and catalyst to waste HDPE ratio (1:4) were produced the maximum liquid product yield of 78.7%. The quadratic model obtained fits well to predict the response with a high determination coefficient of R^2 (0.995). The liquid fuel obtained by catalytic pyrolysis of waste HDPE at optimized condition consists of petroleum products range hydrocarbons (C_{10}–C_{25}) with high heating value (40.17 MJ/kg).

Introduction

High-density polyethylene (HDPE) is a thermoplastic material composed of carbon and hydrogen atoms joined together forming high molecular weight products. Methane gas is converted into ethylene, then, with the application of heat and pressure, into polyethylene [1]. The increased demand and production of HDPE has led to the accumulation of large amount of its waste in the final waste stream due to its low useful life. Recycling of plastics already occurs on a wide scale. The most attractive technique of chemical feedstock recycling is pyrolysis [2,3]. Pyrolysis is known to be an environmentally friendly method because no wastes are produced during the process. The effect of temperature and the type of reactor on the pyrolysis of waste HDPE have been studied by different researchers [4–6]. The thermal degradation of waste HDPE can be improved by using suitable catalysts in order to obtain valuable products. The most common catalysts used in this process are: alumina and silica–alumina [7,8], zeolites [9–12], FCC catalyst and reforming catalyst [13]. A number of studies for liquid fuel production from pyrolysis of waste plastics have been reported at various scales and with varying success [14,15]. The yield of liquid from thermal or catalytic pyrolysis depends on the relationship of parameters set in the process. In terms of modeling and optimization of pyrolysis process, there are only few researchers focused on improving the process optimization. A Hybrid Artificial Neural Network-Genetic Algorithm (ANN-GA) method was used for the modeling and optimization of plastic waste conversion to liquid fuels over modified-residual catalytic cracking catalysts by Istadi et al. [16]. Pinto et al. used response surface methodology (RSM) to predict the influence of experimental conditions on product yields formed by waste mixtures pyrolysis. Experiment Factorial Design was used for the optimization of reaction time, temperature and initial pressure to maximize the yield and composition of liquid products for the waste mixture studied [17]. Miranda et al. studied the thermal degradation of waste tyres and waste plastics mixture with the aim of producing liquid fuel. Regression analyses of experimental data were performed according to response surface methodology (RSM). As a result, experimental conditions optimized based on Factorial Design Methodology were 370 °C, 0.48 MPa for initial pressure and 15 min for reaction time. In order to validate the results obtained by the RSM model, three extra runs were conducted sequentially and average values were calculated and found to be: gas yield of 4.9% (w/w), liquid yield of 81.3% (w/w) and solid yield of 12.7% (w/w) with an experimental deviation of 0.95% [18]. Xiong et al. studied for development of an open-source computational tool to help understand the complex phenomena involved with in the biomass fast pyrolysis

* Corresponding author at: C/O Prof. (Dr.) R.K. Singh, Department of Chemical Engineering, National Institute of Technology Rourkela, Orissa 769008, India. Tel.: +91 8895530406.
E-mail addresses: sachin044@gmail.com, sachin.kumar.01@cuj.ac.in (S. Kumar), rksingh@nitrkl.ac.in, raghubansh.singh@rediffmail.com (R.K. Singh).
[1] Address: Department of Chemical Engineering, National Institute of Technology Rourkela, Orissa 769008, India. Tel.: +91 661 2462022; fax: +91 661 2462260; mobile: +91 9861285425.

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process. In this frame work, a multi-fluid model is applied to simulate the multi-phase hydrodynamics while global reaction kinetics is used to describe the physic chemical conversion [19]. Wan Nadhari et al. optimized the manufacturing conditions with RSM for the production of environmental friendly binderless particleboard from waste oil palm trunk [20]. Kumar et al. used computational fluid dynamics (CFD) and response surface methodology (RSM) in combination for the modelization and optimization of photocatalytic degradation of Rhodamine B in an annular photocatalytic reactor [21]. The single and combined effects of operating parameters such as gas velocity, liquid velocity, initial static bed height and average particle size on the adsorption of arsenic (III) from wastewater are analyzed using response surface methodology (RSM) [22].

Response surface methodology (RSM) has an advantage to reduce the number of costly experiments by selecting the right experimental conditions. Therefore, response surface methodology (RSM) can be a method used to solve the optimization problem with the desired goal to maximize the liquid yield. In the present work, catalytic pyrolysis of waste high-density polyethylene was carried out to evaluate the yield and quality of liquid fuel produced. The mass ratio between modified catalysts to waste HDPE, temperature, and acidity of the modified catalysts were chosen as independent variables. The process was optimized by using response surface methodology with the aim of maximizing liquid yield. The liquid obtained was tested for physical properties, gas chromatography–mass spectrometry (GC–MS) and Fourier transform infrared (FTIR).

Materials and methods

Characterization of raw material

Waste HDPE was collected from the National Institute of Technology Rourkela, Orissa, India campus waste yard and used in this experiment. The plastic waste was cut into small pieces (approx. 1 cm^2) and used in the pyrolysis reaction. The ultimate analysis was done by using a CHNS analyzer (ELEMENTAR VARIO EL CUBE CHNSO). Calorific value of the raw material was found by ASTM D5868-10a.

Preparation of catalysts

The kaolin clay used in this experiment is procured commercially from Chemtex Corporation, Kolkata, India. The modification of kaolin using four different acids and one base of 3 M concentration was carried out by adding 50 g of the kaolin clay to 500 ml of acetic acid, hydrochloric acid, phosphoric acid, nitric acid and sodium hydroxide solution of 3 M concentration and refluxing at 110 °C under the atmospheric pressure in a round bottomed flask equipped with a reflux condenser for 4 h. The resulting clay suspension was then quickly quenched by adding 500 ml ice cold water. The content was then filtered, repeatedly washed with distilled water to remove any residual acid, dried in an oven, calcined at 550 °C for 4 h and ground in a mortar pastel to powder form. The untreated sample is referred to as KC and acid treated samples after calcination at 550 °C are referred to as KC (HCl), KC (CH_3COOH), KC (HNO_3), KC (H_3PO_4) and KC (NaOH). The clay samples were characterized for elemental and chemical analysis using X-ray fluorescence (XRF) analyzer (Model-PW2400 of Phillips) with X-ray tube of rhodium anode and scintillation detector with a current 40 mA and voltage 40 mV and acidity using temperature-programmed desorption TPD (ammonia) in Micromeritics 2900 TPD equipment. The acid treated kaolin clay samples were outgassed under He flow (50 N ml/min) by heating with a rate of 15 °C/min up to 650 °C and remaining at this temperature for 30 min. After cooling to 180 °C, the samples were treated with a 30 N ml/min ammonia flow for 30 min. The physisorbed ammonia was removed by passing a He flow at 180 °C for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 650 °C with a heating rate of 15 °C/min, remaining at this temperature for 30 min, and monitoring the ammonia concentration in the effluent He stream with a thermal conductivity detector.

Pyrolysis experimental setup and procedure

The experiment was conducted in a reactor-furnace system in which the temperature was maintained using a PID controller as shown in previous study [2]. The mixture of catalyst and waste HDPE (20 g) in different catalyst to waste HDPE proportion (1:2, 1:4, 1:6) was placed into the 300-ml reactor and the reactor was heated in the furnace to the desired temperature from 400 °C to 500 °C in 25 °C increments at a heating rate of 20 °C/min and the temperature was maintained for the desired length. Vapors were condensed in a condenser at the outlet of the reactor and the condensed liquid was collected in a jar.

Optimization study

The responses and the corresponding factors are modeled and optimized using the response surface methodology. The RSM technique is aimed for: (a) designing of experiments to provide adequate and reliable measurements of the response, (b) developing a mathematical model having the best fit to the data obtained from the experimental design, and (c) determining the optimal value of the independent variables that produces maximum or minimum value of the response. Therefore, RSM was used to determine the optimum and experimental design matrix in this study specified according to the face central composite design (FCCD) method. Three effective parameters (temperature, catalysts to feed ratio and acidity of catalyst) were applied in this study with each parameter being evaluated at fifteen different points. Each point was investigated to select the points that produced the largest volume of pyrolytic liquid. The variables and the experimental domain in this design are specified in Table 1. The CCD consists of 8 cube points, 6 center points in cube, 6 axial points and 0 center points in axial. Therefore, the CCD in this study, resulting in 20 experiments. The CCD matrix for varying 3 variables was constructed in Table 2. All experiments were performed randomly to reduce the effect of unexplainable variance in the observed response caused by unrelated variables. After running the experiments, the results were fitted to a quadratic polynomial model to predict the system response as given in Eq. (1).

$$Y = \beta o + \sum_{i=1}^{n} \beta i \times Xi + \sum_{i=1}^{n} \beta ii \times Xi^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} \beta ij \times XiXj \quad (1)$$

where Y is the predicted response; n is the number of experiments; βo, βi, βii and βij are regression coefficients for the constant, linear, quadratic and interaction coefficients, respectively; and Xi and Xj

Table 1
Range of independent variables and the experimental domain.

Variables	Experimental domain		
	(−1)-level	0-level	(+1)-level
T: temperature (°C)	400	450	500
A: acidity of catalysts	0.109	0.225	0.341
CR: catalysts ratio	2	4	6