

A Path Exploratory Model on Novel Tactical Synthesis: Paradigmatic Theories on Zeolite Applications

Z. Llarena

Abstract—Synthesized yields of zeolite generated from coal fly ash found in various coal-fired power plants are being utilized as recycling material for catalytic conversion of industrial plastic wastes to synthetic fuel oils, uptake of petroleum hydrocarbons and sequestration of carbon dioxide. Several underlying factors that influence the generation of zeolite are being numerically investigated to explore the path architecture towards optimization of zeolite biomass. This study aimed to explore various path models based on application of zeolites. Model development processes were used for path explorations and further supported by linear algebra. Derivation of degradation kinetics was developed to obtain an equation for the acquisition liquid % yield of gasoline and diesel. Monte Carlo method was developed for the determination of collision probability. Concentration profile was derived for unsteady-state molecular diffusion. Thus, exploratory factor analysis by theoretical establishment of model development processes can be quantitatively derived by synthesis of numerical paradigms.

Index Terms—biosequestration, catalyst, fuel, mass transfer.

I. INTRODUCTION

Coal has various essential utilizations for global applications. Steel production, electricity generation and cement manufacturing are the major important coal purposes. In reference with World Coal Association, an estimate of 7.6 billion tons of coal was globally utilized involving 1 billion tons of brown coal. Since 2000, utilization of coal worldwide has increased rapidly compared to other fuels. Seventy-six percent (76%) of total coal consumption worldwide were accounted to five (5) countries, namely, China, USA, India, Russia and Japan regarded as biggest coal consumers. In 2009, 68.56% of electricity production from coal origins had sourced from India. Being utilized as a fuel, coal regards to all coal types including brown coal of both primary, such as hard coal and lignite-brown coal, and derived, such as patent fuel, gas coke, coke oven gas, blast furnace gas, and coke oven coke, sources. Coal of low quality with high ash result leads in large amounts of fly and bottom ash yields with different features upon coal-fired power plants consumption. Indian power plants utilize its coal that has a general high ash yield of 35-45% and regarded to be of poor quality [1]. Last 2012, the self-sufficiency rate of energy in Japan has decreased to 6.0% subsequent to ceased nuclear power plants due to Great East Japan Earthquake and large tsunami,

leading to an increment in the importation of fossil fuels as alternate options to nuclear energy. Coal has been re-assessed in this event as a significant power supply of base-load due to its economical price per unit of heat energy occurring in all fossil fuels [2].

During 2015, an estimation of more than 580 million tons of fly ash from China coal-fired power plants was produced yearly being accounted to a worldwide yield of greater than 50%. The fly ash disposal became a grave issue due to generation of large quantities of toxic secondary result of coal combustion [3]. Seventy-one (71) million tons of fly ash are being generated yearly in the United States from coal power plants, however, only 45% is being recycled in various utilizations. Different applications described are utilized as polymer fillers, cement-like materials, Portland cement substitute, stabilizing agent, wastewater treatment and asphalt [4]. Affordable power generation with unreliable conformity to fossil fuels following its energy matrix would permit South American countries for fixed-cost reduction and provide a chance for new market entries. In previous years, traditional and non-traditional renewable energies as an integral part of their energy matrix were formed with huge attempts in Chile. As an important attribute, Chile is responsible for native and forest plantations of more than 15 million hectares with an average produce of 20-40 m³/ha/y. Woody residues amounting to almost 4 million tons per year equivalent to 14,000 GWh/y are being generated from forestry pursuits. Replacement of the demand for internal coal as an essential portion for these residues for generation of electricity in coal-fired systems results to an energy matrix that is more sustainable [5].

Subsequent to China, Europe is regarded as the second polymeric producer responsible for the total production of 20.4% worldwide. In 2012, its worldwide utilization resulted to 288 million tonnes, with an augmenting record of 2.8% in comparison with 2011 production, and broadly, in the last 5 decades, the polymeric industry has increased constantly with an outcome of increasing amount of plastic wastes. The amount of polymeric wastes delivered annually to landfill is declining due to positive slope in plastic recovery among its post-consumers. The positive trend is accounted to 61.9% of polymer recovery, 35.6% were utilized for energy recovery and 26.3% were used to polymeric recycling. Although the recycling polymeric rate is still at minimum levels [6].

In the current setting, it is very crucial to recycle/recover/manage polymeric solid waste (PSW) materials. Polymeric manufacturing is a point of interest and gaining popularity among industries, in which plastics are being generated for various products. Polymers have evolved into an essential human need and its worldwide generation has largely augmented within the past 5 decades.

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Conventional polymers are very durable and not easily decomposed in immediate contexts. It is proven that polymers will never decompose and is persistent in the environment for many years, since plastic degradation requires a century in normal atmospheric settings. Polymeric waste is detrimental due to highly toxic pigments of trace elements. As a consequence, synthetic polymers emit environmental pollutants creating a major problem. An enormous scale production of PSW leading to a global generation of 150 million tonnes per annum. An estimation of 8 million tonnes of polymer materials are being utilized in India yearly since 2008 and has increased by 12 million tonnes in 2012. There is a high disposal rate of plasticized PVC due to general manufacturing consumption of window framing, pipes, roofing sheets, floor coverings, and cables. It has a wide scope of utilization including wrapping materials, packaging films, garbage and shopping bags, liquid containers, toys, clothing, building materials, industrial and household products. Virgin polymeric material can be recycled by reusing 2 to 3 times only, because the durability of polymeric material is lessened per recycling owing to thermal degradation. Specifically, solvents capable of donating hydrogen play a role in heat decomposition of plastics influencing hydrocarbon production and distribution. There is no exact approximation available on total polymer production, although, 70% of total polymeric utilization has been disposed as waste, hence, an estimation of 5.6 million tons yearly of polymeric waste has been produced equivalent to 15,342 tons daily [7].

Since polymeric waste is bulkier than other types of waste, an issue has worsened the situation considering that landfill allocation has turned to rare and costly. For energy recovery, incineration generates toxic gaseous products which convert solid waste issue into air pollution problem. Plastic pyrolysis is a possible option for recycling polymeric wastes in which major routes for plastic recovery highlighting chemical importance and energy in comparison to incineration with polymer chemical importance being entirely lost. Pyrolysis of polymeric waste could play an essential key to conversion of waste into cheap and essential hydrocarbons, such as fuels, in the petrochemical industry [8].

Hybrid mesoporous membranes can be fabricated with pore diameters ranging between a few nm to tens of nm with varying geometrical structures and still consider to be challenging with quite significant positive impact on research topics because these materials meet the acceptable criteria for important consideration to various promising utilizations involving size and charge limited separation [9]. Mesoporous zeolites have been greatly applied in recent years as catalytic bases due to their huge even pore sizes, huge pore volumes, and high surface areas. These entities have several structures like SBA-16 with three-dimensional channel cage-like connection and a cubic structure. These properties resulted to higher reactant rates of mass transfer. Furthermore, prevention of metal particle aggregation has been observed with small input of pores. According to a study, SBA-16-supported metal has exhibited its activity suitable for direct hydroxylation of benzene. In reference with the work of Zhu et al., catalytic benzene hydroxylation to phenol in comparison to VO_x/SBA-16 preparation applying an impregnation process resulted to 13.8% benzene conversion and 97.5% phenol selectivity. Recent study involved preparation of co-doping of SBA-16 with an evaporation-induced self-assembly process, resulted to a

28.8% phenol yield and 96.6% phenol selectivity [10].

Fly ash is one of the secondary results of thermal power plant with such appropriate adsorbent that has gained popularity as it is produced in huge amounts as waste entities during worldwide combustion method. It has an approximated worldwide production of 500 Mt per annum of fly ash. Fly ash production from coal-based thermal power plants in India resulted to 131 Mt per annum and it was predicted to augment to 300-400 Mt per annum by this year. The chief end of fly ash is extremely related landfill disposal raising not only economical but also environmental issues. Thus, finding an efficient process becomes essential in order to resolve these problems. Fly ash utilization in varying industrial areas significantly augment, although fly ash production is far larger than its application. Hence, innovation of environmentally friendly applications has driven efforts in creating the best possible utilization for these readily available prolific materials. Although there are extensive investigations and its uses are greatly understood to promote possible environmental impacts in relation to fly ash application. Heavy metals are vulnerable to leach from the ashes having relatively low and thus, its related risks for the liberation of heavy metals into the environment should not exceed beyond its acceptable limits. Fly ash has a promising application in wastewater treatment due to its chief chemical constituents, namely, calcium oxide, magnesium oxide, ferric oxide, silica, aluminum and carbon, and its physical characteristics such as particle surface distribution, surface area and porosity. Fly ash application for the uptake of heavy metals, organics and dyes from wastewater has been cited. Exhibition of low adsorption capacity and fly ash modification can be observed in raw fly ash through physical and chemical treatment leading to adsorption capacity enhancement, thereby, enriching the importance of its utilization. In consideration of several studies, fly ash has been altered through several processes. In the comparative study done by Wang et al., dye uptake utilizing fly ash treated with traditional chemical, sonochemical and microwave techniques. Wang and Zhu investigated fly ash subsequent to sonochemical aqueous solution treatment of methylene blue uptake. In the work done by Pengtham-keerati et al., phosphate removal efficiency with hydrochloric acid (HCl) and sodium hydroxide (NaOH) treated fly ash has resulted to improve its efficiency. The work of Nascimento et al. had investigated on hydrothermally treated fly ash performance for cation adsorption from aqueous solutions, while Sahoo et al., recently assessed the alkali potential of altered fly ash for the metal uptake from acid mine drainage, whereas, Polowczyk et al. observed boron uptake enhancement through application of fly ash agglomerates [11].

Sequestration of carbon dioxide (CO₂) by mineralization is one of the most secured and fixed process for storage of CO₂ liberated by combustion of fossil fuels, and may lead to a viable option of geological storage of CO₂. It is appropriate for emitters of small, medium or impossible geological storage. In comparison to natural minerals, industrial secondary yields such as fly ash have various benefits to be the feedstock involving economical materials, high reactivity of entities, no pre-treatment need, and no difficulty of availability in proximity to CO₂ emission sources. Particularly, fly ash usually has basic oxides such as calcium oxide (CaO) and magnesium oxide (MgO) which are observed to be ideal raw materials for the sequestration of CO₂ due to their high reactivity. Moreover, fly ash is

Since D-operator can also be termed as lambda (λ), substitution of the combined first term of n-degree polynomial and distinct function of liquid % yield resulting to a homogenous solution is expressed by the equation in equation (11).

$$(D - \lambda_1)(y) = L(y) \quad (11)$$

Reaction mechanism for the separation of variables, namely the obtained liquid % yields (y) of synthetic fuels from degraded polymeric materials (c) in respect with change in time (x) and decay constant (λ), is mathematically explained in equations (12)-(22), thus, leading to formula for degradation kinetics, in which D_0 represents the initial % yield and D_1 serves as the target % yield after a distinct time change.

$$\frac{dy}{dx} - \lambda_1 y = L(y) \quad (12)$$

$$\frac{dy}{y} = \lambda_1 dx \quad (13)$$

$$\int \frac{dy}{y} = \int \lambda_1 dx \quad (14)$$

$$\ln|y| = \lambda_1 x + c \quad (15)$$

$$e^{\ln y} = (e^{\lambda_1 x})(e^c) \quad (16)$$

$$y = ce^{\lambda_1 x} \quad (17)$$

Where:

$$\int_{[D_0]}^{[D_t]} d[D] = -k \int_0^t dt \quad (18)$$

$$[D_t] = -kt + [D_0] \quad (19)$$

$$t_{1/2} = \frac{[D_0]}{2k} \quad (20)$$

Since k = degradation constant (λ)

$$\lambda = \frac{[D_0]}{2t_{1/2}} \quad (21)$$

Hence,

$$Y_t = D_0 e^{\lambda x} \quad (22)$$

Monte Carlo method is applied to determine the collision probability of the reaction rate for particle motion. Hydrocarbon particles represented as P_i is investigated for its transfer from one grid (wastewater as P_i) to another local (zeolite as P_j). The particle position is explained as the ratio of the local particle number (n) with simulated wastewater (N), multiplied with its immediate area, radial distribution function, relative transfer velocity and the time difference for the travel of the pollutants. The particle transfer can be numerically explained by equations (23) and (24).

$$P_{ij} = \sum_{j=1}^N P_{ij} \quad (23)$$

$$P_{ij} = \frac{n}{N} 4Ag(r)v_{ij}\Delta t \quad (24)$$

Mass transfer is the molecular diffusion of a substance conducted in z-direction in which partial change in the material concentration of the physical state follows the Fick's second law of unsteady-state diffusion. In order to determine the series of partial change in the amount of carbon dioxide (CO_2) sequestered in the zeolite per partial change in differential time, mass diffusivity is obtained by the increase in partial mass diffusivity in z-direction, in which no chemical reaction takes place in stationary zeolite. The general formula for Fick's second law of unsteady-state diffusion is shown in equation (25).

$$\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2} \quad (25)$$

For the determination of concentration profile, initial condition and two (2) boundary conditions, which can be explained by the statements below, are needed to compute for the partial concentration change per change of time occurring inside the zeolite and at the surface of the zeolite material moving towards the z-direction.

Initial Condition:

$$t = 0, c_A(z, 0) = c_{A,0} \text{ for all } z$$

Two (2) Boundary Conditions:

A. *First Boundary Condition (at the surface):*

$$\text{At } z = 0, c_A(0, t) = c_A \text{ for } t > 0$$

B. *Second Boundary Condition (in the z-direction):*

$$\text{At } z = \infty, c_A(\infty, t) = c_A \text{ for all } t$$

Partial change in initial concentration per unit of time, represented by θ , is equivalent to the initial condition stated above. Hence, interchangeability of the symbols can be done and substitution in the conditions and equations (26) and (27).

$$\theta = c_A - c_{A,0} \quad (26)$$

$$\frac{\partial \theta}{\partial t} = D_{AB} \frac{\partial^2 \theta}{\partial z^2} \quad (27)$$

With

$$\begin{aligned} \theta(z, 0) &= 0 \\ \theta(0, t) &= c_{As} - c_{A,0} \\ \theta(\infty, t) &= 0 \end{aligned}$$

In order to satisfy the two (2) boundary conditions set for the partial change in concentration within the zeolite and its immediate atmosphere going in z-direction, the dimensionless parameter for each concentration change can be applied following Fick's second law of unsteady-state diffusion and their equations are shown in equations (28) and (29).

$$\theta = \frac{c_A - c_{A,0}}{c_{As} - c_{A,0}} \quad (28)$$

(Dimensionless Concentration Change in Respect with Initial Concentration)

$$\theta = \frac{c_{As}-c_A}{c_{As}-c_{A,0}} \quad (29)$$

(Dimensionless Concentration Change in Respect with Surface Concentration)

III. DISCUSSION

Coal-fired power plants gather information regarding the heating and cooling regimes of coal fly ash from several locations and assigned as independent variables classified as subdivisions. Coal burned properties of coal fly ash are subjected to analysis for determination of its composition (anthracite, lignite, bituminous or sub-bituminous). Fig. 1 shows the general model development process for the synthesis of zeolite samples from coal fly ash.

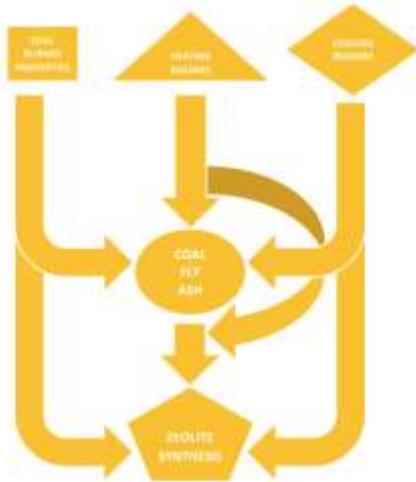


Fig 1. Zeolite Synthesis Pathway

Varying coal burned properties, namely, anthracite, lignite, bituminous or sub-bituminous, serve as independent variables against several other variables influencing the generation of zeolite samples. Other influential independent variables are the amount of coal fly ash produced from each location. Yielded synthetic fuel oils, quantity of petroleum hydrocarbons being taken up and amount of carbon dioxide (CO₂) being sequestered correlates with several determinants for zeolite synthesis. Fig. 2 exhibits the first path exploratory model.

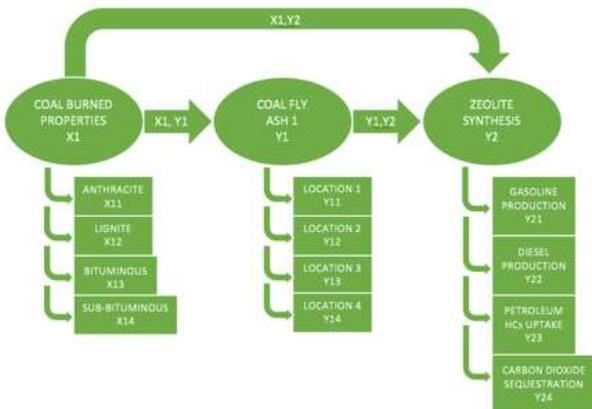


Fig 2. Path Exploratory Model No. 1

Parameters used for the heating regimes of coal fly ash investigate against several other factors to consider for zeolite synthesis. Varying yields of zeolite applications, namely, gasoline, diesel, oil spill uptake and carbon dioxide (CO₂) sequestration correlate with other determining pathways for synthesis of zeolites. Fig. 3 illustrates the second path exploratory model for the generation zeolite materials.

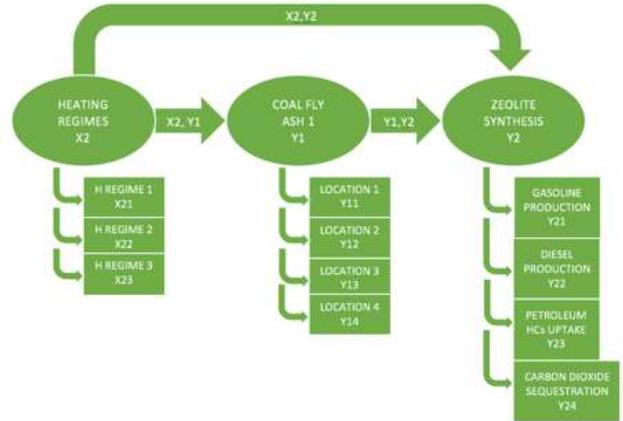


Fig 3. Path Exploratory Model No. 2

Varying factors responsible for the cooling regimes of zeolite synthesis from four local coal-fired power plants correlate for determination of the pathway produced. Quantification analysis from four zeolite applications correlates with other proposed pathways influencing the generation of zeolite particles. Fig. 4 shows the third path exploratory model for evaluation of zeolite pathway synthesis.

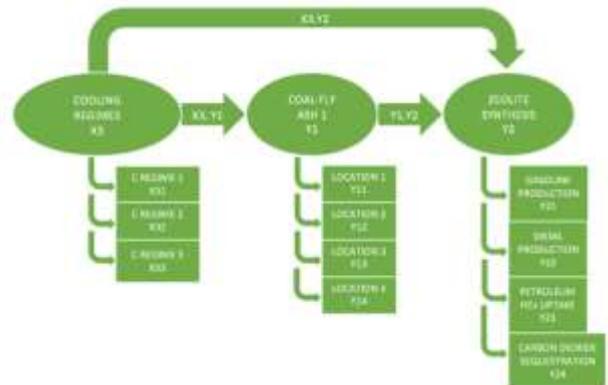


Fig 5. Path Exploratory Model No. 3

IV. CONCLUSION

Exploratory factor analysis (EFA) is an interdependence of several varying processes that possess two main functions. The first is for acquisition of minimum number of parameters containing the maximum possible yield of information involved in the independent variables applied in the model exhibiting greatest possible reliability. The quantity reduction of variables is essential when it has a tendency for data submission to other different variables for analysis procedures, hence, generation of an economical model. Even though there are significant relationships between these determinants, factor analysis secures a level of information from the independent variables. The second function, in relation to the first, is significant for mechanism

identification of indicators applied experimentally and arranged in parameters that are not directly observed, with dimensional representation of the phenomenon being studied. Hence, grounded theory by theoretical assumptions can be numerically established by development of mathematical theories.

REFERENCES

- [1] M. Tiwari, S.K. Sahu, R.C. Bhangare, P.Y. Ajmal, G.G. Pandit. (2014). Elemental characterization of coal, fly ash, and bottom ash using an energy dispersive X-ray fluorescence technique, *Applied Radiation and Isotopes*, 90, 53-57.
- [2] T. Fukasawa, A.D. Karisma, D. Shibata, A.N. Huang, K. Fukui. (2017). Synthesis of zeolite from coal fly ash by microwave hydrothermal treatment with pulverization process, *Advanced Powder Technology*, 28, 798-804.
- [3] L. Ji, H. Yu, X. Wang, M. Grigore, D. French, Y. Gozukara, J. Yu, M. Zeng. (2017). CO₂ sequestration by direct mineralisation using fly ash from Chinese Shenfu coal, *Fuel Processing Technology*, 156, 429-437.
- [4] A.L. Yaumi, I.A. Hussien, R.A. Shawabkeh (2013). Surface modification of oil fly ash and its application in selective capturing of carbon dioxide, *Applied Surface Science*, 266, 118-125.
- [5] R. Perez-Jeldres, P. Cornejo, M. Flores, A. Gordon, X. Garcia. (2017). A modeling approach to co-firing biomass/coal blends in pulverized coal utility boilers: Synergistic effects and emissions profiles, *Energy*, 120, 663-674.
- [6] S. Serranti, V. Luciani, G. Bonifazi, B. Hu, P.C. Rem. (2015). An innovative recycling process to obtain pure polyethylene and polypropylene from household waste, *Waste Management*, 35, 12-20.
- [7] N. Singh, D. Hui, R. Singh, I.P.S. Ahuja, L. Feo, F. Fraternali. (2016). Recycling of plastic solid waste: A state of art review and future applications, *Composites Part B*, xxx, 1-14.
- [8] B. Shi, Y. Wang, C. Chuai. (2011). Pyrolysis of plastic wastes to fuel oil with and without catalyst, *IEEE*, 11, 1-3.
- [9] M. Mekawy. (2016). Fabrication and characterization of mesoporous silica nanochannels inside the channels of anodic alumina membrane, *Arabian Journal of Chemistry*, 9, 269-273.
- [10] M. Jourshabani, A. Badii, N. Lashgari, G.M. Ziarani. (2015). Highly selective production of phenol from benzene over mesoporous silica-supported chromium catalyst: Role of response surface methodology in optimization of operating variables, *Chinese Journal of Catalysis*, 36, 2020-2029.
- [11] S. Banerjee, G.C. Sharma, M.C. Chattopadhyaya, Y.C. Sharma. (2014). Kinetic and equilibrium modeling for the adsorptive removal of methylene blue from aqueous solutions on of activated fly ash (AFSH), *Journal of Environmental Chemical Engineering*, 2, 1870-1880.
- [12] L. Ji, H. Yu, X. Wang, M. Grigore, D. French, Y. Gozukara, J. Yu, M. Zeng. (2017). CO₂ sequestration by direct mineralisation using fly ash from Chinese Shenfu coal, *Fuel Processing Technology*, 156, 429-437.
- [13] S. Luoto, S.A. Brax, M. Kohtamaki. (2017). Critical meta-analysis of servitization research: Constructing a model-narrative to reveal paradigmatic assumptions, *Industrial Marketing Management*, 60, 89-100.



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