



e-ISSN: 2319-8753 | p-ISSN: 2320-6710

# IJRSET

International Journal of Innovative Research in  
**SCIENCE | ENGINEERING | TECHNOLOGY**

# INTERNATIONAL JOURNAL OF INNOVATIVE RESEARCH

IN SCIENCE | ENGINEERING | TECHNOLOGY

Volume 10, Issue 5, May 2021

**ISSN** INTERNATIONAL  
STANDARD  
SERIAL  
NUMBER  
INDIA

**Impact Factor: 7.512**

9940 572 462

6381 907 438

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# Microwave Assisted Acid Activation of Fly Ash: A Green Process for Enhancing Its Physicochemical Attributes for Esterification under Dielectric Heating

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**ABSTRACT:** Fly ash or flue ash, also known as pulverised fuel ash in the United Kingdom, or coal combustion residuals (CCRs), is a coal combustion product that is composed of the particulates (fine particles of burned fuel) that are driven out of coal-fired boilers together with the flue gases. Ash that falls to the bottom of the boiler's combustion chamber (commonly called a firebox) is called bottom ash. In modern coal-fired power plants, fly ash is generally captured by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys. Together with bottom ash removed from the bottom of the boiler, it is known as coal ash. Depending upon the source and composition of the coal being burned, the components of fly ash vary considerably, but all fly ash includes substantial amounts of silicon dioxide ( $\text{SiO}_2$ ) (both amorphous and crystalline), aluminium oxide ( $\text{Al}_2\text{O}_3$ ) and calcium oxide ( $\text{CaO}$ ), the main mineral compounds in coal-bearing rock strata.

Microwave is a form of electromagnetic radiation with wavelengths ranging from about one meter to one millimeter corresponding to frequencies between 300 MHz and 300 GHz respectively. Different sources define different frequency ranges as microwaves; the above broad definition includes both UHF and EHF (millimeter wave) bands. A more common definition in radio-frequency engineering is the range between 1 and 100 GHz (wavelengths between 0.3 m and 3 mm).<sup>[2]</sup> In all cases, microwaves include the entire SHF band (3 to 30 GHz, or 10 to 1 cm) at minimum. Frequencies in the microwave range are often referred to by their IEEE radar band designations: S, C, X,  $K_u$ , K, or  $K_a$  band, or by similar NATO or EU designations.

The prefix *micro-* in *microwave* is not meant to suggest a wavelength in the micrometer range. Rather, it indicates that microwaves are "small" (having shorter wavelengths), compared to the radio waves used prior to microwave technology. The boundaries between far infrared, terahertz radiation, microwaves, and ultra-high-frequency radio waves are fairly arbitrary and are used variously between different fields of study.

Microwaves travel by line-of-sight; unlike lower frequency radio waves they do not diffract around hills, follow the earth's surface as ground waves, or reflect from the ionosphere, so terrestrial microwave communication links are limited by the visual horizon to about 40 miles (64 km). At the high end of the band, they are absorbed by gases in the atmosphere, limiting practical communication distances to around a kilometer. Microwaves are widely used in modern technology, for example in point-to-point communication links, wireless networks, microwave radio relay networks, radar, satellite and spacecraft communication, medical diathermy and cancer treatment, remote sensing, radio astronomy, particle accelerators, spectroscopy, industrial heating, collision avoidance systems, garage door openers and keyless entry systems, and for cooking food in microwave ovens.

## I. INTRODUCTION

Acid activation is a common chemical modification of clays, usually bentonites, with a hot solution of a mineral acid (typically  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ), and it is used for both scientific and industrial purposes. The aim is to obtain partly dissolved material of increased specific surface area, porosity and surface acidity. The product consists partly of the remains of the starting mineral and partly of an amorphous, porous, protonated and hydrated silica phase with a three-dimensional cross-linked framework. Illites containing non-swelling interlayer spaces dissolve more slowly than smectites but the chemical composition of the layers has a greater effect on the process than swellability. The dissolution rate of organoclays decreases with the size of organic cations. Acid activation modifies principal clay properties and thus also their industrial applications. The extent of clay mineral dissolution is derived by many methods, such as chemical analysis, IR or NMR spectroscopy, X-ray diffraction, thermal analysis and microscopic investigation.[1]



It is impossible to imagine modern life without the products manufactured by industries. These products are used in everyday aspects of life, including agriculture, construction, transportation, electronics and well-being. However, their productions generate waste, release toxic chemicals, increase greenhouse emissions and greatly affect human health and the environment. As such, these concerns are driving new priorities that have emphasis on being “green”, ranging from products to processes and technologies. Engineers and scientists from diverse fields are leading the way to solve these issues and challenges. Thus, green engineering has the capability to support and foster this innovation. One of the goals of the modern green process engineering (GPE) community is to design, develop and commercialise industrial processes that are sustainable and economically feasible, whilst minimizing the impact of chemical processes on human health and the environment. GPE is defined as, “the design, commercialization, and use of processes and products, which are feasible and economical while minimizing (a) generation of pollution at the source and (b) risk to human health and the environment. Green engineering embraces the concept that decisions to protect human health and the environment can have the greatest impact and cost effectiveness when applied early to the design and development phase of a process or product [1]. In the past, the objective of process engineering was to minimise product cost and increase profitability without assessing the long-term impacts on the planet and human health. Hence, engineers and scientists should carefully make technical decisions that could have significant impact on the environment. These decisions can lead us either in the direction of sustainability or contribute further to the growing problems. Hence, there is a greater need for engineers and scientists to come together for a common vision of saving the planet by providing new greener technologies and products in an environmentally friendly manner.[2,3]

## II. DISCUSSION

Approaches to address the environmental concerning challenges by application of non-traditional methods such as W irradiation and catalysis has emerged as major tools in green synthesis and engineering. The use of microwave (W flash heating) in synthetic chemistry has emerged as an energy efficient heating source as it reduces processing time by several orders of magnitude by in-core volumetric heating, suppresses side reactions and improves yield, product purity and reproducibility compared to traditional processes [1]. Along with this, encouragement of heterogeneous catalysis in organic synthesis has facilitated greener, safer and non-corrosive route by reduction in waste and easy handling allows the design of continuous flow processes that are economically very attractive at the W irradiation with activated industrial scale compared to their homogeneous counterparts [2]. Involvement of catalysts (AC) during reaction offer several advantages. AC not only provide active surface for the reaction but also W. The AC is also capable to serve as medium for reactions, acts as direct selective heating source by absorbing promotes dry or solvent-free synthesis. Use of different phase catalyst other than reaction substrate provides easy recovery from reaction mixture and reusability of catalyst after simple activation [3].

Acid activation of inorganic materials such as silica, clays and activated carbon etc. with hot mineral acids under reflux condition is one of the widely used techniques to improve surface acidity thus catalytic efficiency of the W assisted acid treatment of clays has produced equivalent or better results compared to material. In recent years, W power plays a crucial role in specific W activation parameters, traditional refluxing methodologies. Among surface area (SSA) enhancement and can affect the basic skeleton during acid treatment. Smectite clay treated with 2M HCl upto 500 W showed increased SSA but didn't change the component structure to any perceptible extent while the samples activated at 650 W showed partial destruction in structure as evident by XRD and also showed reduction in SSA [4, 5]. Upto 600 W, Brazilian bentonite activated with H<sub>2</sub>SO<sub>4</sub> (6N) didn't show any significant alternations and SSA also followed a proportional relationship. Activation above 800 W power gave more drastic reduction and 1000 W showed complete destruction in structure while in SSA sharp declination was observed [6]. W assisted 4N H<sub>2</sub>SO<sub>4</sub> treated Amazon flint kaolin served as an efficient solid acid catalyst for the biodiesel production with 96.4 % conversion rate for esterification confirming sufficient active catalytic sites compared to catalyst prepared under reflux conditions [7]. Recently, fly ash (FA) has been explored as active solid support in synthesis of different heterogeneous Brønsted and Lewis acid catalysts such as FA supported scandium triflate [8], sulphated zirconia [9] and cerium triflate [10] for industrial important organic transformations. All such studies although resulted with increased active acid sites on FA surface, conventional hydrothermal acid digestion and high temperature exposure for a longer time W irradiation heating has been reported encouraged to find a faster technique for FA supported catalyst preparation. earlier in FA sintering [5], zeolite synthesis [6] and curing of FA filled epoxy composites [7]. During the present work, H<sub>2</sub>SO<sub>4</sub> activated FA is prepared in microwave reactor possessing stable Brønsted active sites catalyzing assisted solvent free synthesis of phenyl salicylate, commercially known as 'salol', widely used as an antiseptic, anodyne analgesic [9] and ultraviolet radiation filters [8].



### III. CONCLUSION

*Green Processing and Synthesis* is an open access, single-blind peer-reviewed journal that provides up-to-date research both on fundamental as well as applied aspects of innovative green process development and chemical synthesis, giving an appropriate share to industrial views. The contributions are cutting edge, high-impact, authoritative, and provide both pros and cons of potential technologies. *Green Processing and Synthesis* provides a platform for scientists and engineers, especially chemists and chemical engineers, but is also open for interdisciplinary research from other areas such as physics, materials science, or catalysis. In the present investigation, acid activation of ball milled fly ash was performed under microwave heating. The samples were initially ball milled and then treated with 5N H<sub>2</sub>SO<sub>4</sub> under microwave irradiation for 20 to 40 min. To determine the physico-chemical attributes of samples, various techniques i.e. XRF, N<sub>2</sub> adsorption-desorption, XRD, FTIR, pyridine FTIR and SEM were used. Mechanical activation broke large particles and acid treatment under microwave heating provided in-core volumetric heating of sample to increase surface area and acidity. The prepared MSF-40 catalyst with crystalline size 14 nm and 22 m<sup>2</sup> /g surface area was observed as an efficient solid acid catalyst for solvent-free esterification of phenol and salicylic acid under dielectric heating.

Coal fly ash (Class F type with SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> > 70 %) was collected from Jamshedpur Thermal Power Station (Jamshedpur, Jharkhand, India). Concentrated sulphuric acid (98 %), salicylic acid and phenol were purchased from S. D. fine Chem. Ltd., India and were used as such. Mechanical activation of FA was performed in high energy planetary ball mill Retsch PM-100, Germany. The prepared catalysts were calcined in CEM microwave furnace (Model-Phoenix). The acid activation of milled FA and its catalytic evaluation for esterification reaction was carried out in Microwave synthesis system CEM, USA (Model-Discover) single mode type, using following modes:

#### Open vessel system

Acid treatment of milled FA was carried out under this mode in atmospheric pressure condition. The operating parameters were controlled by software that enables on-line control during the activation. The reaction temperature during the run was monitored with infrared sensor placed aligned just below the reaction vessel and was stirred with W irradiation power was utilized during ‘ramping time’ to attain desired, the help of built-in automatic magnetic stirrer. Variable power was supplied by microprocessor-controlled single magnetron system. The maximum temperature and then, lower power was used to maintain reaction temperature during the ‘holding time’. The reaction mixture was cooled to 50 °C within the instrument in ‘cooling time’.

#### Closed vessel system

Evaluation of catalytic activity of prepared FA samples were performed in closed vessel system using closed Pyrex glass tubes (ca. 10 mL) with teflon-coated septa and teflon stirring bar. The reaction was carried out at desired temperature in solvent-free condition using power maximum (P<sub>max</sub>) feature, responsible for maintaining temperature W heating and cooling by compressed air. The reaction run was throughout the reaction by simultaneous accomplished through the same stages of ramping, holding and cooling time as mentioned in open vessel system. [10]

### IV. CONCLUSION

The present research work provides an energy efficient microwave methodology over traditional thermal refluxing for acid activation of FA under less processing time. Mechanical activation of FA increased surface area by breaking down larger particles while acid treatment under microwave heating further increased surface area, silica content and surface hydroxyl groups resulted as increased surface activity without alternating the basic skeleton of FA to any noticeable extent. Prepared MSF-40 catalyst gave 88 % conversion of salicylic acid and yield 90 % for solvent-free esterification reaction under dielectric heating. This investigation concludes that microwave in-core heating is a clean, fast and innovative source for improving the surfacial properties of FA and provides cost effective pathway for organic transformations with high conversion and better selectivity.

### REFERENCES

1. Website of U.S. Environmental Protection Agency, Washington, D.C. Available online: [http://www.epa.gov/oppt/greenengineering/pubs/whats\\_ge.html](http://www.epa.gov/oppt/greenengineering/pubs/whats_ge.html) (accessed on 3 February 2014).
2. Jenck, J.F.; Agterberg, F.; Droesher, M.J. Products and processes for a sustainable chemical industry: A review of achievements and prospects. *Green Chem.* 2004, 6, 544–556. [Google Scholar] [CrossRef]



3. Anastas, P.T.; Zimmerman, J.B. Design through the 12 principles of green engineering. *Environ. Sci. Technol.* 2003, 37, 94A–101A. [Google Scholar] [CrossRef]
4. Abraham, M.A.; Nguyen, N. “Green engineering: Defining the principles”—Resdts from the sandestin conference. *Environ. Prog.* 2003, 22, 233–236. [Google Scholar] [CrossRef]
5. Patel, D.; Kellici, S.; Saha, B. Some novel aspects of green process engineering. *Chim. Oggi* 2013, 31, 57–61. [Google Scholar]
6. Website of Engineering and Physical Sciences Research Council (EPSRC). Available online: <http://www.epsrc.ac.uk/newsevents/news/2012/Pages/greenengineering.aspx> (accessed on 3 February 2014).
7. Liu, C.; Li, F.; Ma, L.P.; Cheng, H.M. Advanced materials for energy storage. *Adv. Mater.* 2010, 22, E28–E62. [Google Scholar] [CrossRef]
8. Diwekar, U.M. Greener by design. *Environ. Sci. Technol.* 2003, 37, 5432–5444. [Google Scholar] [CrossRef]
9. Grimm, N.B.; Faeth, S.H.; Golubiewski, N.E.; Redman, C.L.; Wu, J.G.; Bai, X.M.; Briggs, J.M. Global change and the ecology of cities. *Science* 2008, 319, 756–760. [Google Scholar] [CrossRef]
10. Lotero, E.; Liu, Y.J.; Lopez, D.E.; Suwannakarn, K.; Bruce, D.A.; Goodwin, J.G. Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.* 2005, 44, 5353–5363. [Google Scholar] [CrossRef]



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