Research Article

Microwave Assisted Acid Activation of Fly Ash: A Green Process for Enhancing its Physico-Chemical Attributes for Esterification under Dielectric Heating

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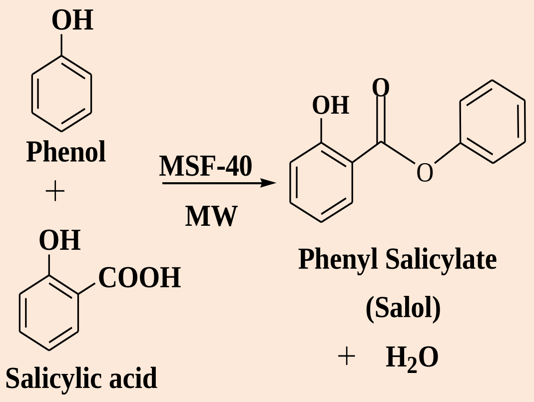
Abstract

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_2SO_4 under microwave irradiation for 20 to 40 min. To determine the physico-chemical attributes of samples, various techniques i.e. XRF, N_2 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^2/g surface area was observed as an efficient solid acid catalyst for solvent-free esterification of phenol and salicylic acid under dielectric heating.

Keywords: Fly ash, Ball milling, Microwaves, Chemical activation, Esterification.



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Introduction

Approaches to address the environmental concerning challenges by application of non-traditional methods such as microwave (μW) irradiation and catalysis has emerged as major tools in green synthesis and engineering. The use of 'μW 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 industrial scale compared to their homogeneous counterparts [2]. Involvement of μW irradiation with activated catalysts (AC) during reaction offer several advantages. AC not only provide active surface for the reaction but also acts as direct selective heating source by absorbing μW. The AC is also capable to serve as medium for reactions, 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 material. In recent years, μW assisted acid treatment of clays has produced equivalent or better results compared to traditional refluxing methodologies. Among μW activation parameters, μW power plays a crucial role in specific 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_2SO_4 (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]. μW assisted 4N H_2SO_4 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 Brönsted 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 encouraged to find a faster technique for FA supported catalyst preparation. μW irradiation heating has been reported earlier in FA sintering [11], zeolite synthesis [12] and curing of FA filled epoxy composites [13]. During the present work, H_2SO_4 activated FA is prepared in microwave reactor possessing stable Brönsted active sites catalyzing μW assisted solvent free synthesis of phenyl salicylate, commercially known as 'salol', widely used as an antiseptic, anodyne analgesic [14] and ultraviolet radiation filters [15].

Experimental

Materials and Apparatus

Coal fly ash (Class F type with $SiO_2+Al_2O_3 > 70$ %) 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 the help of built-in automatic magnetic stirrer. Variable power was supplied by microprocessor-controlled single-magnetron system. The maximum μW irradiation power was utilized during 'ramping time' to attain desired 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_{max}) feature, responsible for maintaining temperature throughout the reaction by simultaneous μW heating and cooling by compressed air. The reaction run was accomplished through the same stages of ramping, holding and cooling time as mentioned in open vessel system.

Preparation of catalyst

For preparation of MSF catalysts, raw FA was mechanically activated in ball mill for 15 h to synthesize MFA-15 having specific surface area (17 m^2/g) according to earlier procedure [16]. For the removal of carbon, sulfur and other impurities, MFA-15 was calcined at 800 °C for 3 h in muffle furnace. Then MFA-15 was refluxed in 5N H_2SO_4 at 1:2 molar ratio in an open vessel system at 90 ºC and 100 W power for 20 and 40 min. Thus prepared slurry was cooled, filtered and washed thoroughly with hot distilled water to achieve pH 7 and make it free from sulphate ions (tested by $BaCl_2$ solution). The activated samples were dried at 110 °C for 24 h followed by calcining at 450 °C for 1 h under static condition in microwave furnace. The prepared samples MSF-20 and MSF-40 are designated according to their microwave irradiation time. **Figure 1** represents the temperature and power monitoring profile for acid activation of MSF-40 catalyst.

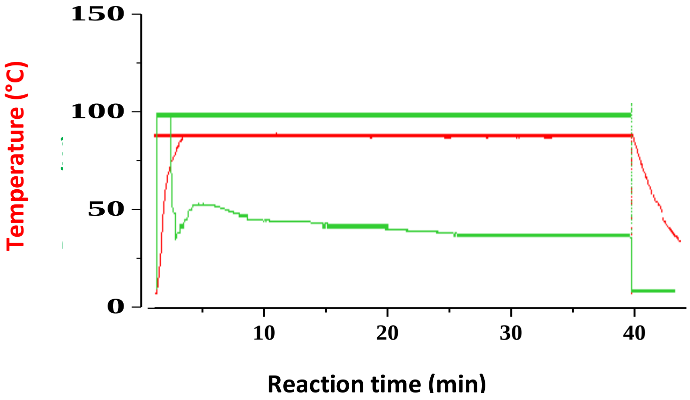


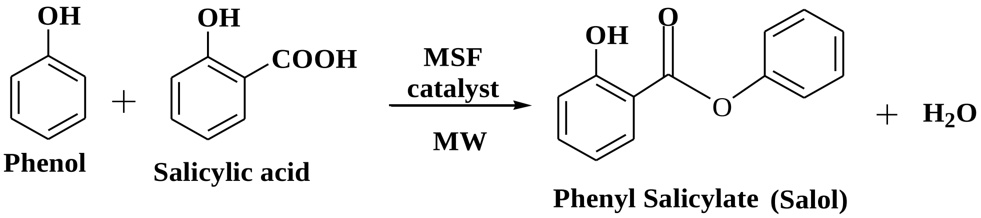
Figure 1 Temperature and Power profile of MSF-40 catalyst.

Characterization Techniques

The physico-chemical and morphological attributes of FA, MFA-15 and MSF samples were analyzed by XRF (Philips PW 1606), Quantachrome NOVA 1000e surface area analyzer (N_2 adsorption-desorption isotherm study), Powder XRD (Bruker diffractometer D8 Advance), FTIR DRS spectrophotometer (Bruker Tensor-27) and SEM (JEOL JEM 5600). The crystalline size of phases and surface acidity measurement by FTIR experiment were determined by the previously reported procedure [17].

Catalytic activity: microwave assisted solvent-free synthesis of salol

The microwave assisted solvent-free esterification reaction using salicylic acid and phenol was carried by MSF catalyst as shown in **Scheme 1**.



Scheme 1 Microwave-assisted solvent-free synthesis of salol over MSF catalyst

In a typical reaction procedure, 20 mmol of phenol, 10 mmol of salicylic acid and catalyst (salicylic acid/ MSF catalyst weight ratio = 5:1) were filled in Pyrex glass vial. Prior to the reaction, catalyst was activated at 450 ºC for 1 h in microwave furnace. After the reaction, acetone was added in the reaction mixture to dissolve the unreacted salicylic acid and filtered to separate out the catalyst. The reaction conditions were varied to obtain maximum yield and conversion into salol. The analysis of salicylic acid conversion was carried out by Gas Chromatograph (Agilent 7820 A) having a flame ionization detector and HP-5 capillary column of 30 m length and 0.25 mm diameter, programmed oven temperature of 70-240 °C and N_2 (25 ml/min) as a carrier gas. The conversion of salicylic acid and yield of salol was calculated by using weight percent method as follows:

$$\text{Conversion (\%)} = 100 \times (\text{Initial wt \%} - \text{Final wt \%}) / \text{Initial wt \%}$$

$$\text{\%Yield of Salol obtained} = \frac{\text{g of Salol obtained}}{\text{g of Salol theoretically obtained}} \times 100$$

Catalyst regeneration

After the initial run, the used catalyst was filtered, washed thoroughly with acetone and dried in oven at 110 ºC for 12 h followed by activation at 450 ºC for 1 h in microwave furnace. Thus, the regenerated catalyst was used in next reaction cycles under the same reaction conditions.

Results and Discussion

The changes in structural and textural properties of FA after mechanical and chemical activation are summarized in **Table 1**. Increment in specific surface area from 17 m^2/g (MFA-15) to 22 m^2/g (MSF-40) was observed due to increased finely dispersed silica components by dissolution of mineral structure. However, further increase in μW activation time didn't produce significant results [18].

Table 1 Characterization of fly ash before and after mechanical and chemical activation

Sample	Silica (wt. %)	Crystalline size (nm)	Specific surface area (m^2/g)
FA	61.90	33	9
MFA-15	64.27	29	17
MSF-20	85.12	15	21
MSF-40	85.79	14	22

FA: Raw fly ash, MFA-15: 15 h mechanically activated fly ash, MSF-20: Chemically activated fly ash under microwave heating for 20 min, MSF-40: Chemically activated fly ash under microwave heating for 40 min

The powder XRD of the raw, MFA-15 and MSF samples have shown mulite ($3Al_2O_3 \bullet 2SiO_2$) phases at 16.4º, 25.8º and 26.2º while 20.73º, 26.55º, 40.68º and 49.95º confirms the presence of quartz (SiO_2) phases as represented in **Figure 2 (a-d)**. The effect of 15 h ball milling of FA has reduced crystallite size from 33 to 29 nm [16] while acid activation under dielectric heating from 20 to 40 min has increased amorphous content and reduced crystalline size to 15 nm (MSF-20) and 14 nm (MSF-40) due to dissolution of some crystalline phases during acid treatment. Dielectric heating at low (100 W) μW power has not altered the basic skeleton of FA which is evident by the resembling XRD patterns of FA and MSF samples. Nevertheless, the surficial structural changes were noticed due to partial destruction of alumino-silicate components evident by the increased silica content as shown in Table 1. Similar results were also reported in the literature signifying the effectiveness of μW heating with low power supply [4, 5].

The FTIR spectra of raw FA and MFA-15 in **Figure 3a** shows a broad band with a maximum centered at 3500-3000 cm^{-1} attributed to surface silanol -OH groups due to physisorbed water. The peak at 1650 cm^{-1} attributed to the bending vibration ($\delta_{O\text{-}H}$) of coordinated water molecule. Ball milling for 15 h broke the quartz structure and formation of more Si-OH groups took place which is evident by broadness in region of 1000-1200 cm^{-1} range corresponding to the valence asymmetric stretching vibrations of the silicate oxygen skeleton [19].

In Figure 3b, FTIR spectra of MSF samples show noticeable increment in broadness at 3500-3000 cm^{-1} compared to FA due to increased silanol groups and adsorbed water molecules on the surface. Instead of remaining isolated these surfacial hydroxyl groups shows extensive hydrogen bonding with their neighbouring hydroxyl groups resulting in broadness of band. The increased amorphous silica in milled and acid activated samples can be characterized by an intense band in the range of 1000-1300 cm^{-1} observed due to asymmetric Si-O-Si stretching which represents a higher shift from 1042 cm^{-1} (MFA-15) towards 1048 cm^{-1} (MSF-20) and 1061 cm^{-1} (MSF-40). The promotion in amorphous silica percentage in MSF catalysts enhanced surface area and increased population of surface hydroxyl groups responsible for the improved surface reactivity of the samples.

The nature of acidic sites of the prepared catalysts was investigated by the presence of the adsorption bands of pyridine in the magnified range of 1650-1400 cm^{-1} as shown in **Figure 4a & b**. The IR peaks at 1598 cm^{-1} and 1540 cm^{-1} in MSF catalysts confirms the presence of sufficient Brönsted acidity due to formation of coordinated pyridine and hydrogen bonded pyridine respectively with surface -OH groups while band at 1490 cm^{-1} shows the pyridine associated with all acidic sites. Another peak at 1450 cm^{-1} assigned for Lewis acid sites as coordinately bound pyridine [20]. The pyridine adsorbed spectrum of MSF-40 catalyst shows more intense peak at 1540 cm^{-1} and 1448 cm^{-1} confirming the presence of higher amount of acidic sites as compared to MSF-20. Microwave heating efficiently facilitates the surface acidity of the materials along with its textural and structural properties in less time under controlled heating [7].

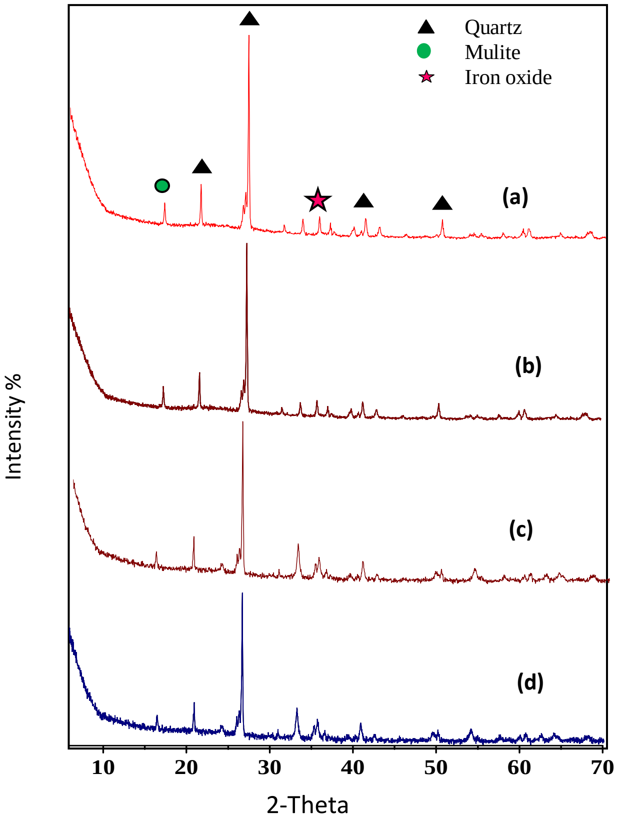
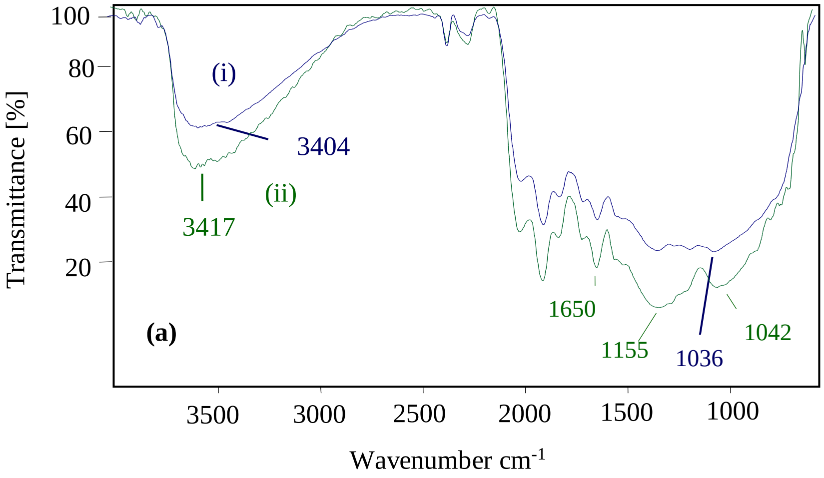


Figure 2 Powder XRD patterns of (a) Raw FA (b) MFA-15 (c) MSF-20 (d) MSF-40.



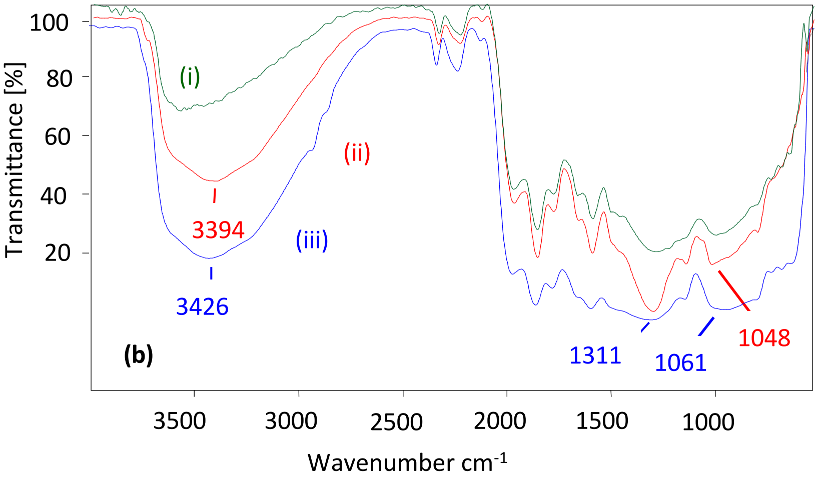


Figure 3 (a) FTIR spectra of (i) FA (ii) MFA-15 (b) FTIR spectra of (i) MFA-15 (ii) MSF-20 (iii) MSF-40.

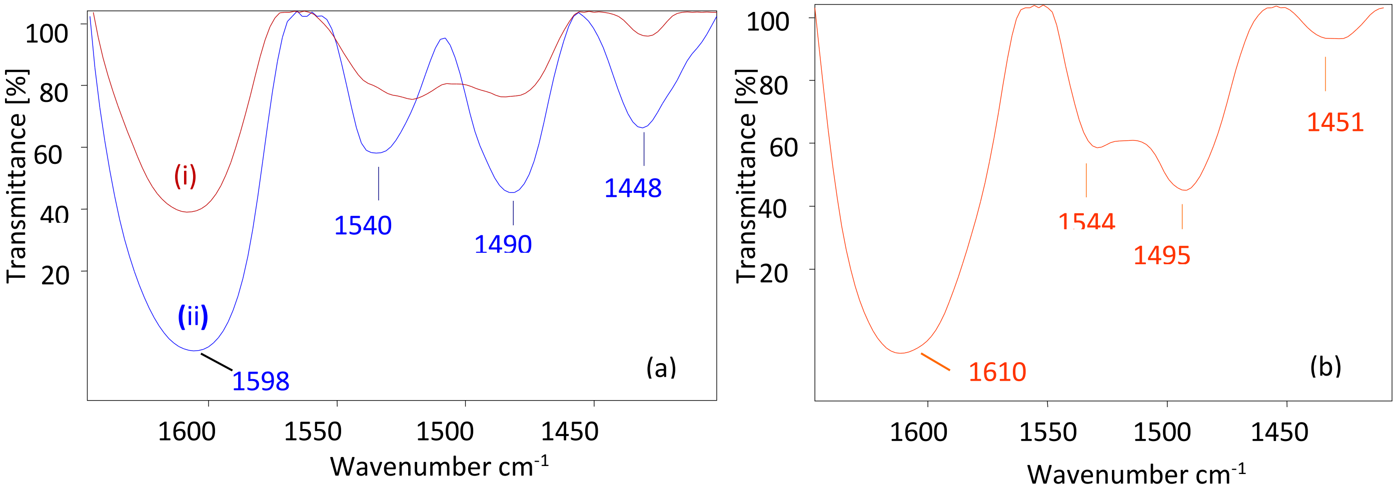


Figure 4 (a) Pyridine adsorbed FTIR spectra of (i) MSF-20 (ii) MSF-40 and (b) Regenerated MSF-40 catalyst.

SEM micrographs of raw FA in **Figure 5A** revealed different shaped, relatively smooth surface hollow cenospheres [21], whereas SEM image of MFA-15 (Figure 5B) shows structural break down of large particles and increased surface roughness due to ball milling. SEM images of MSF-40 revealed increased large gelatinous mass due to partial dissolution of alumino-silicate phases during acid treatment as shown in Figure 5C.

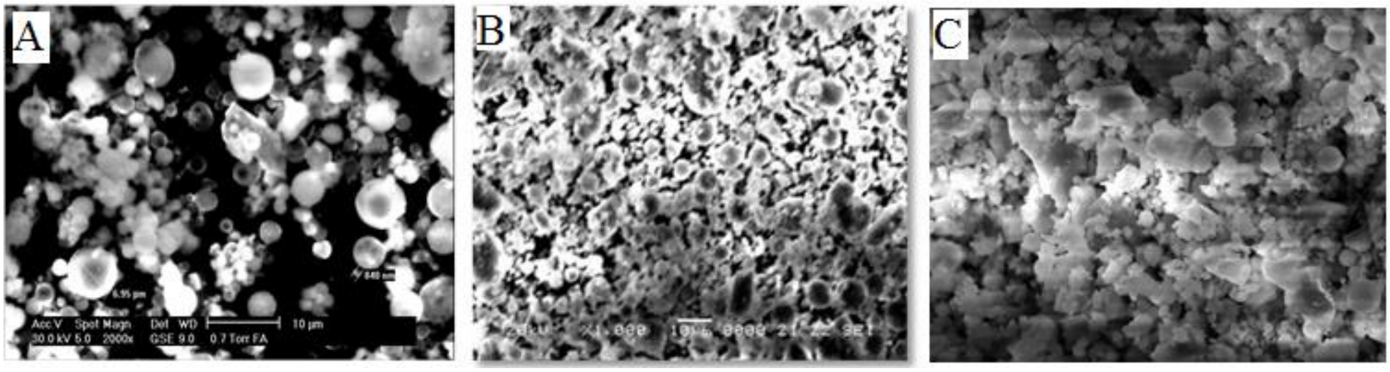


Figure 5 SEM micrographs of (A) FA (B) MFA-15 (C) MSF-40**.**

Catalytic activity- μW assisted solvent-free synthesis of salol

µW assisted solvent-free synthesis of phenyl salicylate (salol) using phenol and salicylic acid was chosen as test reaction to check the catalytic activity of MSF catalysts. The reaction was also preceded only in presence of µW and using MFA-15 as catalyst but conversion of salicylic acid was negligible. Higher conversion (88 %) and yield (90 %) of salicylic acid was obtained by MSF-40 as compared to MSF-20 with 78 % conversion and 82 % yield. Hence, optimization of the following reaction parameters was carried out using MSF-40 catalyst followed by its reusability evaluation.

Effect of reaction temperature

On increasing reaction temperature, conversion % of salicylic acid showed a linear increase upto 120 ºC with maximum 88 % conversion and after which remained almost constant upto 140 ºC **(Figure 6)**.

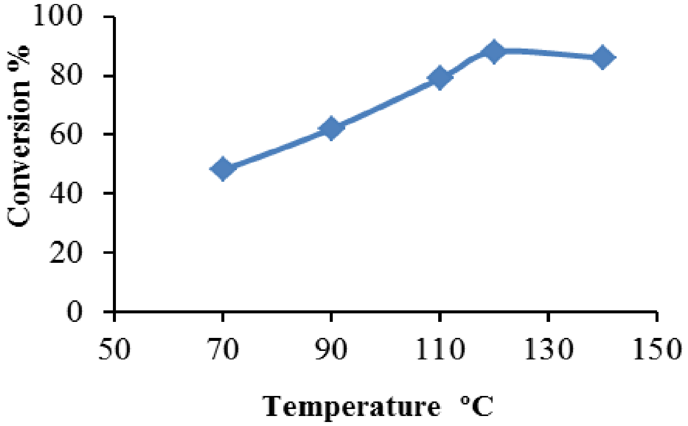


Figure 6 Variation of conversion (%) of salicylic acid over MSF-40 catalyst with temperature.

Effect of reaction period

Optimization of reaction time period was carried to achieve maximum conversion of salicylic acid to salol ranging from 2 to 20 min as shown in **Figure 7** maintaining rest of the reaction parameters same. In the first 10 min, the conversion of salicylic acid increased linearly upto 88 % which remained constant upto 20 min.

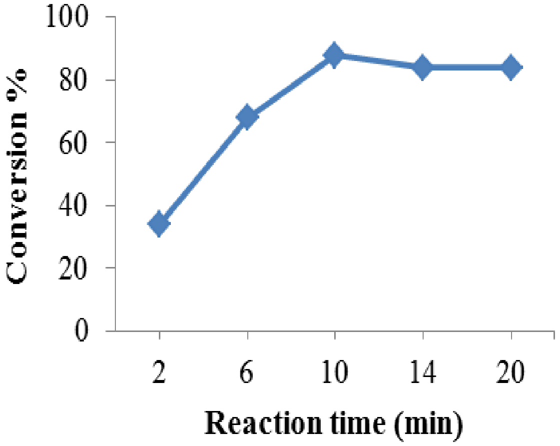


Figure 7 Variation of conversion (%) of salicylic acid over MSF-40 catalyst with reaction time

Effect of reactant molar ratio

The influence of molar ratio of salicylic acid and phenol on conversion % of salicylic acid was monitored at different molar ratios from 1:1 to 1:3 by increasing the amount of phenol only. However, due to solubility restrictions higher concentration studies with salicylic acid could not be conducted [22]. As shown in **Table 2**, on increasing molar ratio of salicylic acid to phenol from 1**:**1 to 1:2, maximum conversion (88 %) and 90 % yield of salol was obtained. The above results show that the yield of product increased with increasing the molar ratio of salicylic acid to phenol. This is mainly due to the reversible nature of the esterification reaction, with the increase in molar ratio salicylic acid to phenol leads to a shift of the equilibrium to the direction of salol ester production. However, further increasing molar ratio to 1:3, decrease in yield % of the salol was observed due diphenyl ether (by-product) formation favored by excess of phenol [14].

Table 2 Effect of molar ratio of salicylic acid/phenol on conversion (%) of salicylic acid to salol over MSF-40 catalyst

Molar ratio (salicylic acid : phenol)	Conversion (%)	Yield (%)
1:1	35	42
1:1.5	64	72
1:2	88	90
1:3	79	82

Reaction conditions under microwave irradiation: Temperature = 120 ºC; Time = 10 min; salicylic acid/MSF-40 catalyst weight ratio=5:1; Power = 100W; P_{max} = ON

Effect of Salicylic acid to MSF-40 weight ratio

The salicylic acid to MSF-40 weight ratio on conversion of salicylic acid was monitored by varying the amount of catalyst under optimized reaction conditions as shown in **Table 3**. Weight ratio of 5:1 gave maximum conversion of 88 % of salicylic acid attributed to availability of sufficient amount of catalytic active sites. On further increase in the amount of catalyst no further change in conversion % was observed.

Table 3 Effect of Salicylic acid to MSF-40 weight ratio on conversion (%) of salicylic acid to salol with MSF-40 catalyst

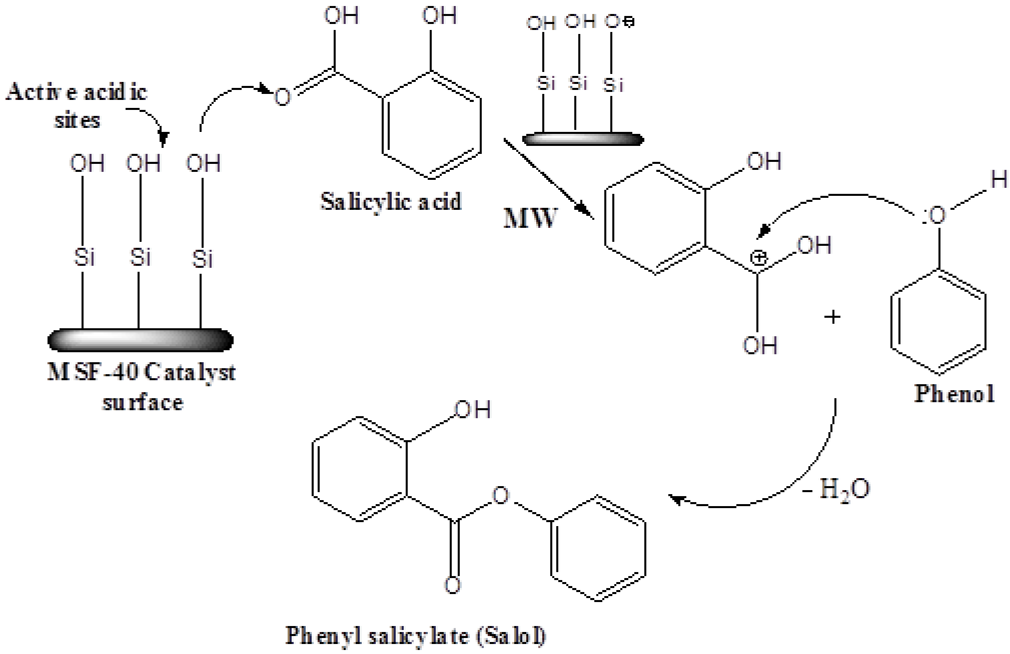
Salicylic acid to MSF-40 weight ratio	Conversion (%)	Yield (%)
10:1	74	76
5:1	88	90
2:1	88	90

Reaction conditions under microwave irradiation: Temperature = 120 ºC; Time = 10 min; molar ratio (Salicylic acid: Phenol) = 1:2; Power = 100W; P_{max} = ON

Proposed mechanism of salol formation over an acidic site

In proposed mechanism of salol synthesis, the salicylic acid gets adsorbed on acidic sites of MSF-40 catalyst and transforms into an electrophile by borrowing a proton from its surface hydroxyl groups. In microwaves, the electric component is responsible for generating heating effects, as it interacts with the polar or charged species (generated electrophile) and in response of this interaction these species start to move or rotate which further resulted as additional polarization of the polar species in the vicinity. When phenol (dipolar species) interacts with the electric field component of microwave it starts oscillating, following the oscillation of the electric field. During such oscillation, the polar species collide with neighboring charged particles i.e. carbonium ion, results as intermolecular friction. This friction generates intense internal heat responsible for the formation of intermediate species which further leads to formation of salol with subsequent removal of water as a byproduct. Microwaves heat only the reactants which avoid the overheating of the reaction walls and help to increase the yield of the product and minimize the side product formation as shown in **Scheme 2**.

The spent MSF-40 catalyst was regenerated by simple microwave regeneration method and retained its activity upto 4th reaction cycle giving conversion 84 % of salicylic acid. The pyridine adsorbed FTIR of the reused catalyst after fourth reaction cycle as given in **Figure 4b** shows similar acidic sites with that of fresh catalyst signifies that active sites remained unaffected by microwaves during the reaction. The significant decrease in conversion was reduced after fourth reaction cycle due to blockage of active sites of the catalyst by the deposition of carbonaceous material [23].



Scheme 2 Proposed mechanistic pathway of microwave-assisted esterification of salicylic acid with phenol over MSF-40 catalyst

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.

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