



# Microwave-assisted rapid valorization of glycerol towards acetals and ketals



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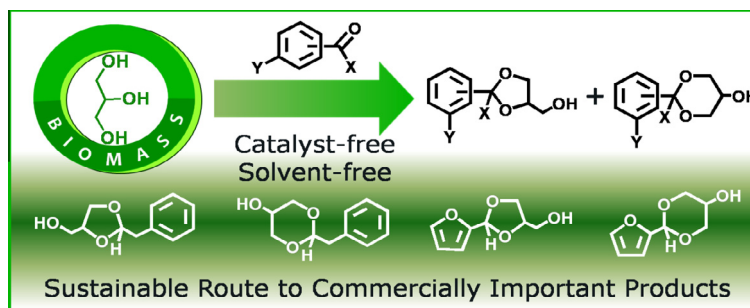
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## HIGHLIGHTS

- Valorisation of glycerol: acetalization reaction with carbonyl compounds.
- Catalyst and solvent free approach for synthesis of glycerol acetals and ketals.
- Microwave irradiation assisted rapid synthesis of hyacinth fragrance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Biodiesel appears as one of the most promising and feasible alternatives among the non-conventional sources of energy; however, its production ends up with a huge amount of glycerol, a financial shortcoming for the expansion of its production. In this context herein we demonstrated an unprecedented catalyst- and solvent-free protocol for the microwave assisted acetalization of glycerol and carbonyl compounds to achieve high yields of cyclic acetals or ketals including commercially valuable hyacinth fragrance and fuel additive precursors. Comparative studies with conventional heating suggest that microwave irradiation plays a crucial role for the acetalization reactions. Moreover, several heterogeneous catalysts on the acetalization reaction have also been screened. The present work thus dispenses with excessive amount of solvents, precious catalysts and provides a clean and green approach towards the valorization of glycerol. Considering the commercial importance of the acetalization reactions the model reaction was scaled up to 150 ml, is evidence for  $90 \pm 5\%$  conversion and consistent selectivity.

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## 1. Introduction

The requirement of bio-fuels is continuously growing due to diminishing fossil fuel reserves [1]. Biodiesel appears to be one of the most promising and feasible alternatives among the non-conventional sources of energy; however, the biodiesel production ends up with a huge amount of glycerol [2,3]. Therefore, it is

essential and timely to develop viable methods to dispense or utilize this anticipated huge quantity of glycerol and to add value to the biodiesel production chain [4–6]. The inherent non-toxic and edible nature of glycerol further encourages its industrial utilization. These motives have triggered rigorous research in recent years to find out the novel applications of this cheap and off grade chemical [6–9]. As a matter of fact, glycerol derivatives such as acetal, ketal (acetalization of glycerol with aldehydes and ketones gives respective 1,3-dioxalane and 1,3-dioxane, commercial important compounds) ether, and ester find applications in the cosmetics, plastic, pharmaceuticals, detergents, fuel additives and fine chemical industries [6,10–13]. So far several catalytic systems

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feasible with or without solvents have been developed to perform the acetalization of glycerol ranging from harsh mineral acids like  $\text{H}_2\text{SO}_4$  and mild organic acids like *p*-toluenesulfonic acid (PTSA) to solid acid catalysts such as alluminosilicates, resins, zeolites and MMT-K10 [6,10–13]. In addition to prolonged reaction time and tricky work up protocols, these systems suffer either stringent environmental regulations or operational disadvantages like moisture-sensitivity of solid acid catalysts [12,14].

On the contrary, microwave (MW) heating is proficient and swift route to carry out chemical transformations and has become a widely accepted non-conventional protocol for organic synthesis. While the conventional reflux set up is relatively slow and inefficient to transfer the energy into a reaction mixture as it relies on convection currents and on the thermal conductivity of medium (reaction vessel, reactants and solvent phase etc.); MW irradiation works through ‘in-core’ volumetric heating (direct coupling of MW energy with reaction mixture) which results in rapid and uniform temperature attainment [15–20]. Considering the aforementioned requirements of glycerol valorisation we have utilized the MW irradiation to perform the acetalization of several aldehydes and ketones with glycerol in catalyst and solvent free conditions. To the best of our knowledge there are no reports on catalyst- and solvent free approaches towards the acetalization of glycerol.

Herein we report the catalyst and solvent free MW-irradiated reactions of glycerol with a number of aldehydes or cyclic ketones to produce corresponding acetals or ketals in high yields (Scheme 1 and 2). Moreover, we have successfully utilized this sustainable and green protocol to achieve commercially valuable hyacinth fragrance as well as furan based fuel additive precursors in good yields.

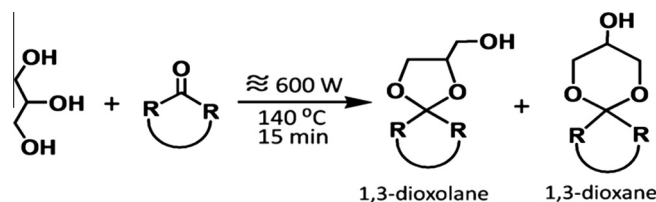
## 2. Experimental

### 2.1. Chemicals

All the reagents viz., glycerol, aldehydes, ketones and solvents used for the experiments were of analytical reagent (A.R.) grade and were obtained from Merck, s.d. Fine (India), Spectrochem and Sigma–Aldrich. All the chemicals were used without further purification. K10-Montmorillonite acid activated clay, Nafion<sup>®</sup> SAC-13, *p*-Toluenesulphonic acid monohydrate (PTSA) and Amberlyst<sup>®</sup> 15 (hydrogen form strongly acidic, cation exchanger, dry) were obtained from Sigma Aldrich. ZSM-5 and Na-Beta (Na $\beta$ ) zeolite were obtained from Zeochem L.L.C Uetikon, Switzerland. Other catalysts were synthesized by following the literature protocols. Detailed synthesis methodology and the PXRD profiles of synthesised catalyst are given in Supporting information (S1.1–S1.5 and Fig. S1) [21–25].

### 2.2. Physical measurements

The synthetic manipulations were conducted on SINEO M-II microwave synthesis assembly with variable MW frequency and temperature.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AX 200 or 500 MHz spectrometer at ambient temperature using



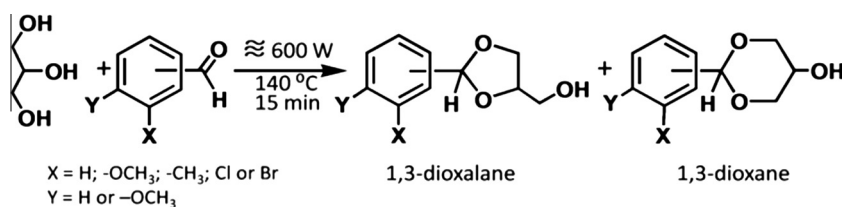
**Scheme 2.** Microwave assisted catalyst/solvent free reactions of glycerol with cyclic ketones.

TMS as an internal standard and  $\text{CDCl}_3$  as solvent. The reaction products were analyzed on a gas chromatograph (Varian, GC-450), equipped with a Factor-4 capillary column (30 m long and 0.32 mm internal diameter) employed with a flame ionization detector. The oven temperature was varied from 80 °C to 240 °C programmed at the ramp rate of 10 °C  $\text{min}^{-1}$ . GC oven programmed in the temperature range 40–200 °C with helium as a carrier gas and MS in EI mode with 70 eV ion source. The calibration of GC peak areas was carried out by taking solution of known compositions with tetradecane as an internal standard. Product identification was done using a gas chromatograph mass spectrometer (Shimadzu GCMS-QP-2010 Japan) equipped with a RTX-5 fused silica capillary column.

### 2.3. Reaction procedure

The synthetic manipulations were conducted using SINEO M-II microwave in a 25 ml RB flask synthesis assembly with variable MW frequency and temperature provision. The typical acetalization reactions were carried out with a neat mixture of glycerol and aldehyde or ketones with stirring under microwave irradiation without solvent or catalyst for pre-set time as required to complete the reaction. The reaction products were efficiently separated from excess of glycerol by solvent extraction using toluene and water. The toluene–water mixture was added to the reaction mixture, wherein glycerol goes into water media and the products are extracted in the toluene. Then the toluene extract was analyzed by GC. Thus, we believe that the toluene extraction used by us only improves the ease of analysis and does not affect the end results. The reaction performance was studied with respect to conversion of aldehydes or ketones. Conversion and selectivity of desired components was estimated by gas chromatograph coupled with mass spectrometer. In all experiments, *n*-tetradecane was used as an internal standard. The crude mixture as well as purified fraction of the products mixtures with different isomers were confirmed with  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The calibration of GC peak areas was carried out by taking solution of known compositions with *n*-tetradecane as an internal standard. The conversion and selectivity were calculated as per the formulas (i) and (ii) respectively.

$$\% \text{ Conversion}_{(\text{substrate})} = \frac{\{C_i - C_f\}_{(\text{substrate})}}{\{C_i\}_{\text{substrate}}} \times 100 \quad (\text{i})$$



**Scheme 1.** Microwave assisted catalyst/solvent free acetalization of glycerol with aldehydes.

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