A new continuous-flow process for catalytic conversion of glycerol to oxygenated fuel additive: Catalyst screening

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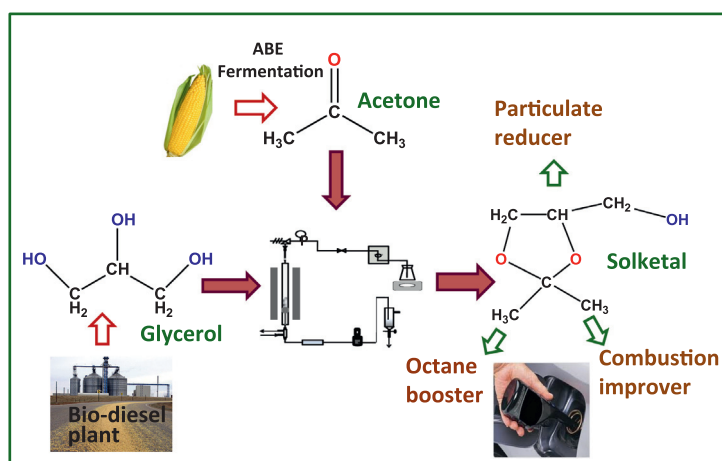[b] Biology Department, Lakehead University, ON P7B5E1, Canada
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HIGHLIGHTS

- A continuous-flow process for catalytic synthesis of solketal from glycerol.
- Six different heterogeneous acid catalysts were studied in the process.
- Glycerol conversion and solketal yield of 90% and 88% respectively were achieved.
- The process has the potential to be scaled-up for industrial applications.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

A new continuous-flow reactor was designed for the conversion of glycerol to solketal, an oxygenated fuel additive, through ketalization with acetone. Six heterogeneous catalysts were investigated with respect to their catalytic activity and stability in a flow reactor. The acidity of the catalysts positively influences the catalyst's activity. Among all the solid acid catalysts tested, the maximum solketal yield from experiments at 40 °C, 600 psi and WHSV of 4 h^{-1} attained 73% and 88% at the acetone/glycerol molar ratio of 2.0 and 6.0, respectively, with Amberlyst Wet. Based on the solketal yield and glycerol conversion results, the activity of all catalysts tested follows the following order of sequence: Amberlyst Wet ≈ Zeolite ≈ Amberlyst Dry > Zirconium Sulfate > Montmorillonite > Polymax. An increase in acetone/glycerol molar ratio or a decrease in WHSV enhanced the glycerol conversion as expected. This process offers an attractive route for converting glycerol, the main by-product of biodiesel, to solketal – a value-added green product with potential industrial applications as a valuable fuel additive or combustion promoter for gasoline engines.

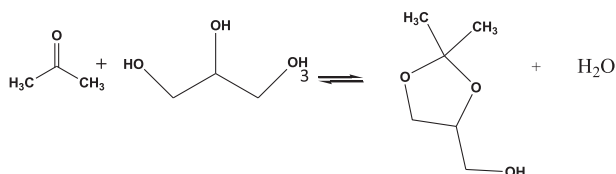* Corresponding authors. Tel./fax: +1 519 661 4016.
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1. Introduction

The booming of biodiesel industry all over the world has led to generation of a huge amount of glycerol as byproduct. It was predicted that by 2020 the global production of glycerol will be 41.9 billion liters annually [1]. In order to avoid the saturation of global glycerol market, it is urgent to develop value-added products to consume the excessive glycerol for the sustainability of biodiesel industry. In this regard, the fuel industry seems to be a suitable market where a high volume of glycerol could be absorbed for value added applications.

The direct use of glycerol as fuel is however not encouraged due to its low calorific value, high boiling point and high polarity. Nevertheless, its conversion into ketals and ethers has demonstrated the potential for being used as oxygenated fuel additives [2–4]. Ketals and ethers can be utilized as oxygenate fuel additive or combustion promoter as the addition of ketals and ethers in gasoline engines improve the octane number, cold flow and ignition properties of the fuel with reduced particulate emission, and gum formation [5–7]. The aquatox fish test requested by the authors' group on the toxicity of the solketal showed that solketal (with a LC_{50} for fish to be as high as 3162 ppm) has demonstrated much less environmental toxicity than the common fuel additive Methyl tert-butyl ether (MTBE) with a $LC_{50} \ll 1000$ ppm.

Conventionally, ketalization of glycerol with acetone in the following reaction scheme was performed under batch reactors in homogeneous liquid phase catalyzed by strong Bronsted acids such as; sulfuric acid, hydrochloric acid, phosphoric acid or p-toluene sulfonic acid, where corrosion, product separation and effluent disposal are high cost and environmental burdens [8–10].

In order to make the ketalization environmentally friendly, many studies were undertaken mostly in batch reactors using heterogeneous catalysts like zeolite [11], amberlyst [12], montmorillonite [5], silica included heterolpoyacids [13], and nafion [2], bio-based reagents, etc. Our previous study [14] reported the thermodynamics and kinetics of the ketalization reaction using a heterogeneous catalyst – Amberlyst 35 in a batch reactor. However, the synthesis of solketal in a batch reactor using either homogeneous or heterogeneous catalysts requires long reaction time (usually exceeding 2 h total reaction time). Moreover, mechanical stirrers are commonly used in batch reactors, which give rise to poorly defined interfacial areas, and hence the yield is strongly dependent on the stirring intensity and efficiency [15]. In addition, a batch process has some major limitations for scale-up.

Clarkson et al. [16] developed a technology for the synthesis of solketal in a semi-batch reactor where acetone was fed continuously but glycerol was fed batch-wisely. The high viscosity of glycerol at low temperatures was found to be the main obstacle in making the process continuous. In another attempt, Monbaliu et al. [17] used a glass reactor for the continuous synthesis of solketal in the presence of a homogeneous catalyst (i.e., sulfuric acid). However, the process is not economical and environmentally friendly due to the aforementioned corrosion and waste disposal problems associated with the use of sulfuric acid. Inspired by the stated landmark papers [16,17], we took an attempt to engineer a continuous flow reactor for the production of solketal using heterogeneous catalysts, which, to the best of our knowledge, is the first work of this kind reported.

It is obvious that the production of solketal in a continuous-flow reactor using heterogeneous catalysts is advantageous because the process has advantages of high heat and mass transfer efficiency, ease of scale-up from laboratory to industrial scale, and high surface to volume ratios [18–20]. To boost the reaction in a flow reactor, the concept of "Novel Process Windows" with respect to temperature, pressure and/or reactant concentration could be exploited and the intrinsic kinetics of the reaction could be fastened [21–23]. In the present study an attempt has been made to use a continuous flow reactor to achieve ketalization of glycerol in a much shorter residence time as compared to that of a batch reactor.

Ketalization of glycerol strongly depends on the experimental conditions used; therefore, it is not easy to make a comparison among the performances of different heterogeneous catalysts reported in literature. In the present study the main objectives were to (1) construct a continuous-flow reactor for the conversion of glycerol to solketal; (2) compare the activities of different solid acid catalysts used in the process under the same experimental conditions for catalyst screening; and (3) investigate the effect of their intrinsic properties on the activity in a continuous flow reactor system.

2. Materials and methods

2.1. Materials

Glycerol and acetone (both >99 wt% purity) were purchased from Sigma Aldrich and used as received. Reagent grade anhydrous ethanol was supplied from Commercial Alcohols Inc. Solketal (1,2-isopropylidene glycerol, 99 wt%), for GC calibration was also obtained from Sigma Aldrich. The catalysts of Amberlyst 35 Dry and Amberlyst 36 Wet were obtained from Rohm and Hass Co. (USA) and used as received. Zeolite beta (CP 814 C) in the acid form was procured from Zeolyst International (USA) and was calcined at 500 °C for 6 h before use. Montmorillonite (K-10) was obtained from Sigma-Aldrich and was dried at 120 °C for 3 h before use. Zirconium sulphate was prepared according to literature [24] from zirconium sulfate hydrate purchased from Sigma–Aldrich. Polymax (845) was provided by Sud Chemie group and was dried at 120 °C for 2 h prior to use.

2.2. Catalyst characterization

The surface area, total pore volume and average pore diameter of the selected catalysts were determined by nitrogen isothermal (at −196 °C) adsorption with a Micromeritics ASAP 2010 BET apparatus. The catalysts zeolite, and montmorilonite were degassed at 120 °C and amberlyst was dried at 90 °C overnight under vacuum prior to the surface area measurements. The acidity of the catalysts were measured by ammonia temperature programmed desorption (NH_3-TPD) test using Micromeritics AutoChem II analyzer. Thermal stability of the catalysts was evaluated using thermogravimetric analyser (TA Q500) at a heating rate of 10 °C/min in N_2 flow of 30 ml/min. Fourier Transform Infrared Spectroscopy (FTIR) (Thermo scientific-Nicolet 6700) was used to identify the functional groups present in the catalysts.

2.3. Synthesis of solketal in a continuous-flow reactor

The synthesis of solketal was carried out in a bench scale continuous down-flow tubular reactor (Inconel 316 tubing, 9.55 mm OD, 6.34 mm ID and 600 mm length) heated with an electric
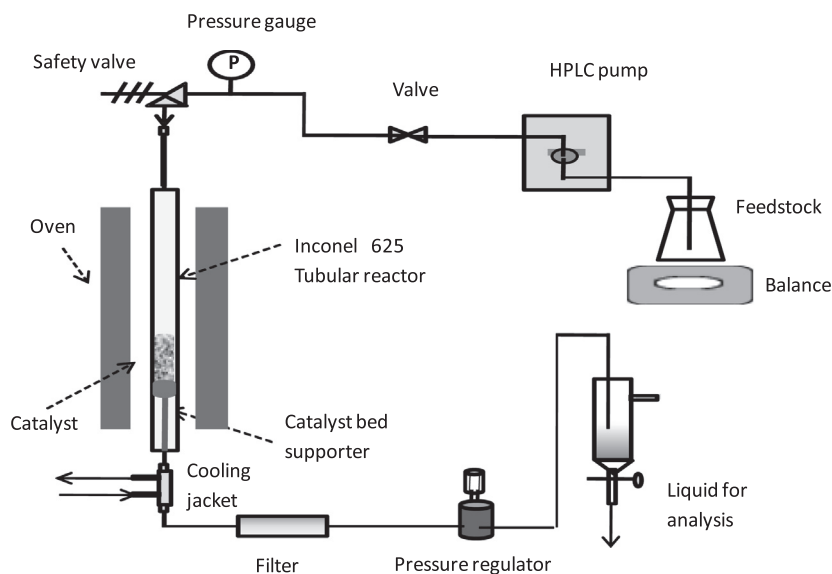
Fig. 1. Schematic diagram of the continuous-flow reactor used for ketalization of glycerol.

furnace. A schematic diagram of the continuous flow reactor system is shown in Fig. 1. The feed – a homogeneous solution of reactants (acetone and glycerol) and solvent (ethanol) at a selected molar ratio, was pumped using a HPLC pump (Eldex) at a specific flow rate into the reactor maintained at a desired temperature and pressure (controlled by a temperature controller and a back-pressure controller, respectively). In a typical run, 116.00 g of acetone, 92.00 g of glycerol and 46.00 g of ethanol (corresponding to 2:1:1 molar ratio of acetone:glycerol:ethanol) were mixed, and the homogeneity of the solution was confirmed by GC–MS analysis. Ethanol was used as solvent mainly to improve the solubility of glycerol in acetone. In each run, a pre-determined amount of catalyst was preloaded into the catalytic bed, in which the catalyst particles were supported on a porous Inconel metal disc (pore size: 100 μm) and some quartz wool. The amount of catalyst in each run was determined by the selected weight hourly space velocity (WHSV, reciprocal of reaction time) defined as follows:

$$\text{WHSV}(\text{h}^{-1}) = \frac{\text{Mass flow of glycerol}(\text{g/h})}{\text{Mass of catalyst used}(\text{g})} \qquad (1)$$

Depending on the feeding rate, compositions of the feed and the amount of the catalyst used in each run, WHSV, varied from 2 to 8 h^{-1}.

2.4. Product analysis

All the components in the reaction mixture were analyzed by GC–MS on a Varian 1200 Quadrupole MS (EI) and Varian CP-3800 GC with VF-5 MS column (5% phenyl/95% dimethyl-polysiloxane, 30 m × 0.25 mm × 0.25 μm), using helium as the carrier gas at a flow rate of 0.5 mL/s. The oven temperature was maintained at 120 °C for 2 min and then increased to 200 °C at 40 °C/min. Injector and detector temperature were 300 °C. Components were identified by NIST 98 MS library. Sample quantification was done on a GC-FID (Shimadzu 2010) using similar separation conditions as mentioned above for the GC–MS.

Solketal was separated and purified from un-reacted reactants and the reaction solvent by distillation. The purified product was identified by Fourier Transform Infrared Spectroscopy (FTIR) and GC-FID.

In all the experiments, the selectivity of solketal was found to be more than 97% with an insignificant amount of undesired products like diethoxy ether and 2,2-diethoxy propane. The reported yield and conversion are values after 4 h on-stream unless otherwise specified. Herewith, the solketal product yield, glycerol conversion and product selectivity are defined as follows:

$$\text{Yield}(\%) = \frac{\text{Moles of solketal formed}}{\text{Initial mole of glycerol}} \times 100 \qquad (2)$$

$$\text{Conversion}(\%) = \frac{\text{Initial mole of glycerol} - \text{Final mole of glycerol}}{\text{Initial mole of glycerol}} \times 100 \qquad (3)$$

$$\text{Selectivity}(\%) = \frac{\text{Moles of solketal formed}}{\text{Initial mole of glycerol} - \text{Final mole of glycerol}} \times 100 \qquad (4)$$

3. Results and discussion

3.1. Fresh catalyst characterization

The fresh catalysts were characterized comprehensively for their textual properties (i.e., specific surface area, pore volume, pore diameter), and chemical properties such as hydrophobicity and acid strength, and thermal stability, as these properties are believed to be critical for determining the catalytic activities and choosing appropriate reaction conditions.

The results of the textual properties (measured by N$_2$ isothermal adsorption) and acidity for the fresh catalysts used in this study (measured by ammonia TPD) are presented in Table 1. It can be seen that zeolite has the maximum surface area (480 m^2/g) with minimum pore size (2 nm), and Amberlyst Wet has the least surface area (33 m^2/g) with maximum pore size (24 nm). The acidity of all the catalysts (Zeolite, Montmorillonite, Amberlyst dry and Amberlyst Wet) are similar in the relatively narrow range of 4.6–5.7 eq/g, while the other two catalysts (Polymax and Zirconium sulphate) were not analyzable after several trials. The textual properties and the acidity of the catalysts will be correlated with the activities of these catalysts for glycerol conversion for solketal synthesis, as reported in the later sections of this paper.

Table 1

Textual properties (measured by N_2 isothermal adsorption) and acidity for the fresh catalysts used in this study.

Catalyst	BET surface area[a] (m^2/g)	Pore volume[a] (cc/g)	Pore size[a] (nm)	Acidity[b] (eq/g)	Mean particle size[c] (μm)
Zeolite	480	0.25	2	5.7	45
Montmorillonite	264	0.36	5.5	4.6	13
Amberlyst dry	35	0.28	16.8	5.4	482
Amberlyst Wet	33	0.2	24	5.6	490

[a] Determined by N_2 isothermal adsorption (77 K).
[b] Determined by ammonia TPD (378 K).
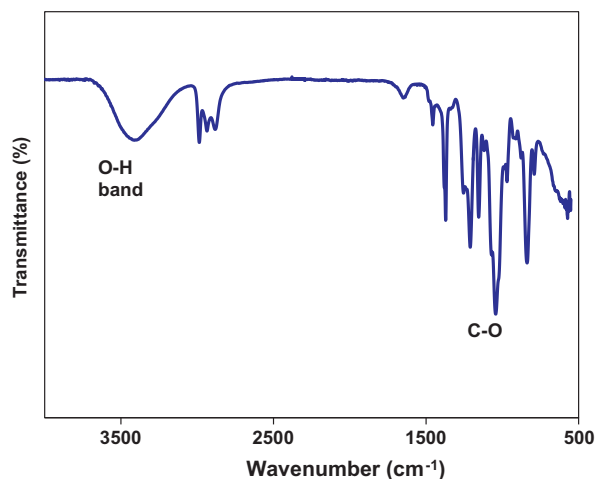[c] From the supplier.

The thermal stability of the catalysts was examined using thermogravimetric analysis (TGA). Fig. 2 illustrates the percentage weight loss results for various catalysts vs. temperature. As shown from the TGA profiles, catalysts such as zeolite, montmorillonite, polymax and zirconium sulfate are very stable at elevated temperatures. Amberlyst Dry and Amberlyst Wet are however temperature sensitive. Temperatures above 100 °C cause thermal degradation of these catalysts. With these results, all our glycerol ketalization experiments were carried out below 100 °C. Characterizations of these two catalysts were also performed below 100 °C for the measurement of their surface area and acidity.

3.2. Product characterization

The FTIR spectrum was employed to confirm the presence of solketal in the purified solketal products. The FTIR spectrum of a typical solketal product is shown in Fig. 3. A strong IR band at around 3400–3600 cm^{-1} was observed which ascribes to the O—H stretching band resulted in the intermolecular and intramolecular hydrogen bonds present in the solketal. The IR absorption peaks at around 1000–1100 cm^{-1} can be attributed to the symmetrical stretching of C—O band in solketal molecular structure [25], confirming the production of solketal in the experiments. In this work, GC–MS and FT-IR were conducted for qualitative analysis of the products. The molecular weight of 132 of solketal is confirmed by MS, and the m/z signal at 43 was assigned to the loss of dioxolane group [26].

3.3. Catalyst activities

In a first set of experiments, the influence of the acetone/glycerol molar ratio on the yield of solketal was investigated. Table 2

Fig. 3. FTIR spectrum of a typical solketal product.

summarizes the glycerol conversion and the solketal yield from the experiments conducted at 40 °C, 600 psi and WHSV of 4 h^{-1} with different acetone/glycerol molar ratio (acetone equivalent ratio) of 2.0 and 6.0. Clearly, increasing of the acetone equivalent ratio resulted in an increase of the solketal yield irrespective of the catalysts used. These results are actually expected as an excess in acetone could drive the reaction in its forward direction thermodynamically to increase the glycerol conversion. A higher concentration of reactant also promotes the reaction rate, leading to a higher product yield. Similar observations in a batch reactor were reported by Agirre et al. [3] In addition, the use of excess acetone could also help enhance the catalytic life time by removing the water formed on the catalyst surface (please be noted that adsorption of water on the catalyst surface would block the catalyst active sites and thus deactivate the catalyst).

Among all the solid acid catalysts tested, the maximum solketal yield was observed with Amberlyst Wet (being 73% and 88% at the acetone/glycerol molar ratio of 2.0 and 6.0, respectively). Based on the solketal yield and glycerol conversion results from Table 2, the activity of all catalysts tested follows the following order of sequence: Amberlyst Wet ≈ Zeolite ≈ Amberlyst Dry > Zirconium Sulfate > Montmorillonite > Polymax.

As well known, ketalization reaction proceeds via acidic catalytic mechanism. As such, catalysts with stronger acidity would lead to higher activities. To examine the dependency of catalyst activity on its acidity, Fig. 4 illustrates the relationship between the product yield and the catalyst acidity using the data from Tables 1 and 2. An approximately linear relationship was observed in Fig. 4, suggesting that catalysts of stronger acidity, such as Zeolite (5.7 eq/g), Amberlyst Dry (5.4 eq/g) and Amberlyst Wet (5.6 eq/g), resulted in a high yield of solketal.

Another set of experiments were conducted to study the effect of WHSV on the solketal yield and glycerol conversion at the
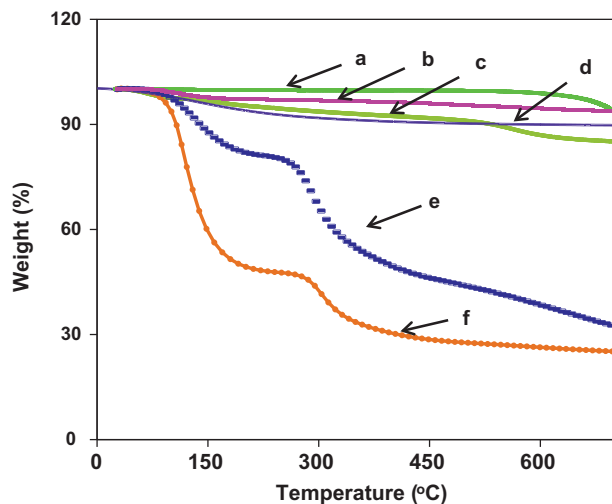

Fig. 2. TGA profiles of fresh catalysts of Zirconium sulfate (a), Montmorillonite (b), Polymax (c), Zeolite (d), Amberlyst Dry (e) and Amberlyst Wet (f).

Table 2
Effect of acetone/glycerol molar ratio at fixed temperature (40 °C), pressure (600 psi) and WHSV (4 h^{-1}).

Catalyst	Acetone equivalent ratio			
	2.0		6.0	
	Yield (%)	Conversion (%)	Yield (%)	Conversion (%)
Zeolite	72 ± 2	73 ± 3	84 ± 2	85 ± 2
Montmorillonite	60 ± 1	60 ± 4	68 ± 1	69 ± 1
Amberlyst Dry	70 ± 1	71 ± 2	86 ± 3	88 ± 3
Polymax	50 ± 1	51 ± 3	60 ± 2	61 ± 2
Zirconium Sulfate	65 ± 3	66 ± 1	77 ± 2	79 ± 2
Amberlyst Wet	71 ± 3	71 ± 3	88 ± 4	89 ± 3

Table 3
Effect of weight hourly space velocity (WHSV, h^{-1}) on solketal yield and glycerol conversion (other reaction conditions: 40 °C, 600 psi and acetone equivalent of 2.0).

Catalyst	WHSV (h^{-1})			
	4.0		8.0	
	Yield (%)	Conversion (%)	Yield (%)	Conversion (%)
Zeolite	72 ± 3	73 ± 2	65 ± 2	66 ± 1
Montmorillonite	60 ± 1	61 ± 2	51 ± 1	52 ± 2
Amberlyst Dry	70 ± 2	72 ± 4	66 ± 2	67 ± 3
Amberlyst Wet	71 ± 2	72 ± 3	65 ± 3	66 ± 2
Polymax	50 ± 1	50 ± 2	35 ± 1	36 ± 2
Zirconium sulfate	65 ± 2	66 ± 3	58 ± 2	59 ± 1

reaction conditions of 40 °C, 600 psi and acetone equivalent of 2.0 under different WHSV (4.0 and 8.0 h^{-1}). The results are given in Table 3. It is evident that increasing the WHSV from 4 to 8 h^{-1}, both the product yield and glycerol conversion decrease irrespective of the catalysts used, simply because for reaction not being at equilibrium a shorter residence time (or larger WHSV) would led to a lower conversion [27].

The effect of temperature on the glycerol conversion to solketal in the continuous-flow reactor was investigated. The experiments were conducted at three different temperatures (40, 70, and 100 °C) while keeping other reaction parameters constant (i.e., acetone/glycerol molar ratio of 2.0, WHSV of 8.0 h^{-1}, pressure of 600 psi, 4 h time-on-stream). The results are presented in Fig. 5. For catalysts such as Zeolite and Amberlyst (both 35 Dry and 36 Wet), the reaction seemed to be mainly thermodynamically controlled: a higher reaction temperature led to a lower yield and lower conversion (exothermic reaction, $\Delta H_{298}^{\circ} = -30{,}058.40 \text{ J mol}^{-1}$). In contrast, for catalysts such as montmorillonite, polymax and zirconium sulfate, the reaction was kinetically controlled: An increase in reaction temperature led to a higher glycerol conversion and larger solketal yield. One can however note from the figure that the yield obtained at 100 °C with the zirconium sulfate is actually higher than that with Zeolite or Amberlyst catalyst at the same temperature. It thus implies that what caused the reduced product yield with increasing temperature for Zeolite or Amberlyst catalyst is not due to the thermodynamic equilibrium, as discussed above, but due to other reasons such as deactivation of these highly active catalysts at an elevated temperature.
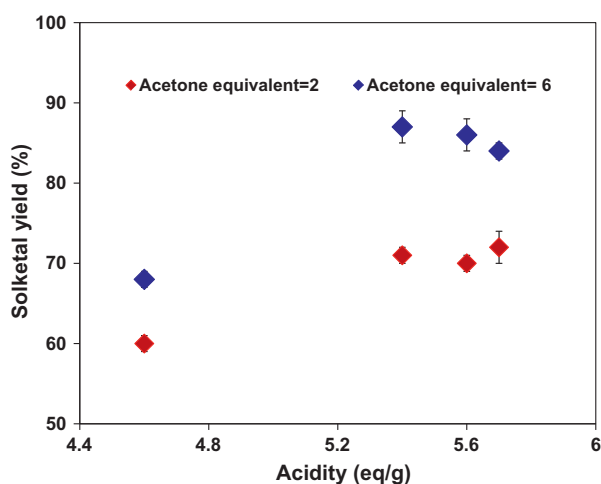
The effect of pressure on the reaction was tested by varying it from 14.7 to 800 psi (or 1–54 atm) under the experimental conditions of 25 °C, acetone:glycerol:ethanol molar ratio of 2:1:1, WHSV of 4 h^{-1} with Amberlyst 36 Wet catalyst, for 4 h time-on-stream). It was found that reaction pressure has a negligible effect on the product yield, as expected for liquid phase reactions. In this study, experiments as reported here were all conducted under elevated pressure (600 psi) to maintain liquid phase of the reaction mixture during reaction. At 600 psi and the maximum operating temperature and the maximum acetone concentration in the feed used in this work, the maximum amount of molecules in gas phase was calculated to be very small (<1%).

The catalyst stability for various catalysts over a longer time-on-stream (up to 24 h) was investigated under the following experimental conditions: 25 °C, 600 psi, 2:1:1 molar ratio for acetone:glycerol:ethanol, and WHSV of 2 h^{-1}. The results are

Fig. 4. Solketal yield vs. acidity for catalysts of Zeolite (6.2 eq/g), Montmorillonite (4.6 eq/g), Amberlyst Dry (5.5 eq/g) and Amberlyst Wet (5.4 eq/g). Experimental conditions: 40 °C, 600 psi and WHSV of 4 h^{-1} with different acetone equivalent ratios of 2.0 and 6.0.
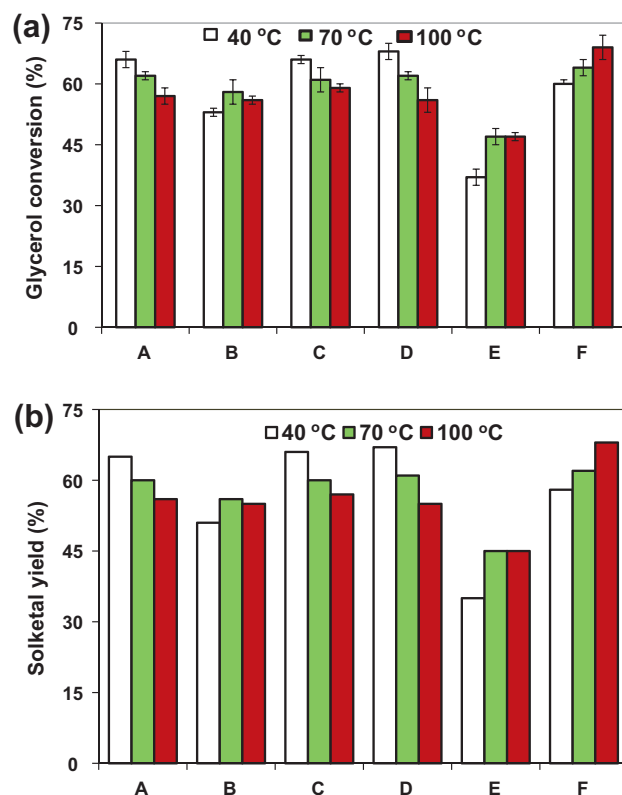

Fig. 5. Variation of glycerol conversion (a) and solketal yield (b) with temperature for various catalysts (A: zeolite; B: Montmorillononite; C: Amberlyst Dry; D: Amberlyst Wet; E: Polymax; F: Zirconium sulfate). Other conditions were: P = 600 psi, molar ratio of acetone:glycerol:ethanol = 2:1:1, WHSV = 4 h^{-1}).
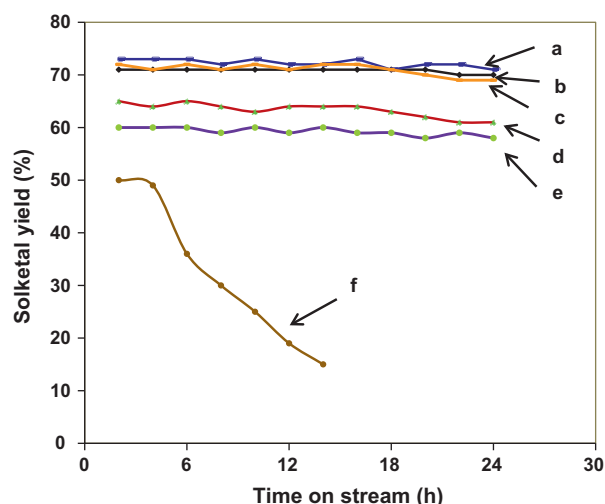
Fig. 6. Solketal yield vs. time-on-stream with catalysts of Amberlyst Wet (a), Zeolite (b), Amberlyst Dry (c), Zirconium sulfate (d), Montmorillonite (e) and Polymax (f).
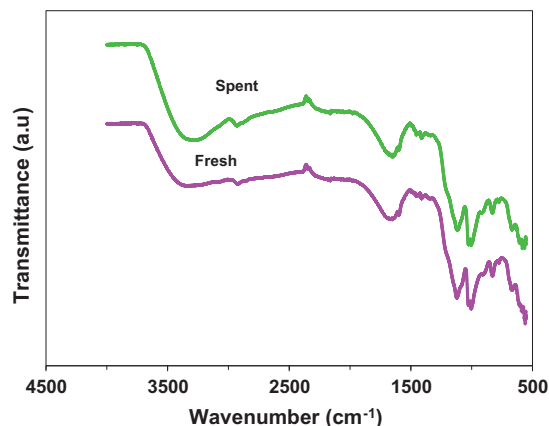

Fig. 7. FTIR spectra of the fresh and spent Amberlyst Wet (experimental conditions: 40 °C, 600 psi and WHSV of 4 h^{-1} with acetone equivalent of 2).

displayed in Fig. 6. The poorest performance was observed with polymax, leading to a drastic declining of activity after 4 h on-stream. The fast deactivation of polymax could be due to the loss of acidity from the catalyst surface by the water produced during the reaction. In contrast, the catalyst of Amberlyst Wet, Zeolite, or Amberlyst Dry exhibited superb stability over a long time-on-stream, producing solketal at a high yield >70% during the whole course of the experiments for up to 24 h on-stream, although it is clear that these catalysts, except polymax, exhibited only a slight decrease in activity with increasing time on-stream. To understand the superb stability of the Amberlyst Wet catalyst, the textual properties and acidity for its spent catalyst after 24 h time-on-stream were measured, and the results are presented comparatively against those of its fresh catalyst in Table 4. In addition, FTIR measurements of the fresh and spent catalyst of Amberlyst Wet after 24 h time-on-stream were measured and the spectra are displayed in Fig. 7. As shown in Table 4 and Fig. 7, it is apparently that the Amberlyst Wet catalyst did not deteriorate significantly in its textual properties (specific surface area and pore structure) during the experiments for 24 h on-stream, which explains its superb stability for the reaction. However, from Table 4, the acidity of the Amberlyst Wet catalyst did decrease slightly from 5.6 eq/g for the fresh catalyst to 5.2 eq/g for the spent catalyst, which might account for the slight deactivation of the catalyst during the experiments for 24 h on-stream.

Reactor clogging is one of the major challenges in operating of a continuous-flow reactor process, particularly with heterogeneous catalysts. During the course of the current investigations, the clogging of the flow reactor was observed for some catalysts including zeolite, montmorillonite and polymax. The increase in flow rate and/or increase in the catalyst loading in the reactor would cause agglomeration of the particles which clogged the reactor resulting

in a sharp increase in the reactor pressure. This suggests that these catalysts may not be suitable for being used for the present glycerol ketalization process using the flow reactor. Admittedly, the reactor clogging phenomenon could be efficiently avoided by diluting the catalyst with inert materials such as glass beads or by minimizing the catalyst bed height. On the basis of the product yield and experimental conditions, the overall results of this study (88% yield for Amberlyst Wet at 40 °C, 600 psi and WHSV of 4 h^{-1}) are better than what reported in literature [12,13].

4. Conclusions

A new continuous-flow process employing heterogeneous catalysts has been developed for the first time for efficiently converting glycerol into solketal. A total of 6 different catalysts were investigated with respect to their catalytic activity and stability at different reaction conditions (e.g., acetone/glycerol molar ratio, WHSV, temperature, pressure, etc.). The increase in the acetone/glycerol molar ratio resulted in an increase of the sloketal yield irrespective of the catalysts used. Among all the solid acid catalysts tested, the use of Amberlyst Wet produced the maximum solketal yield from experiments at 40 °C, 600 psi and WHSV of 4 h^{-1} (being 73% and 88% at the acetone/glycerol molar ratio of 2.0 and 6.0, respectively). It appeared that catalysts with stronger acidity exhibited higher activities: Amberlyst Wet ≈ Zeolite ≈ Amberlyst Dry > Zirconium Sulfate > Montmorillonite > Polymax. Both the solketal yield and glycerol conversion decreased, irrespective of the catalysts used, upon increasing the WHSV. The activities of all the catalysts, except polymax, showed only a slight decrease in its activity for up to 24 h on-stream likely due to the loss of its acidity during a long time on-stream.

Acknowledgements

Table 4
Textual properties and acidity for the fresh and spent catalyst (after 24 h time-on-stream) of Amberlyst Wet.

Catalyst	BET surface area[a] (m^2/g)	Pore volume[a] (cc/g)	Pore size[a] (nm)	Acidity[b] (eq/g)
Amberlyst Wet (Fresh)	33	0.2	24	5.6
Amberlyst Wet (Spent)	32	0.2	25	5.2

[a] Determined by N$_2$ isothermal adsorption (77 K).
[b] Determined by ammonia TPD (378 K).

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