Glycerol Derivatives as Fuel Additive: Synthesis of Solketal From Glycerol and Acetone With Various Acid Clay Catalysts

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ABSTRACT
Currently, the huge bulk of glycerol formed during biodiesel production as a by-product offered an abundant and low-cost feedstock. Researchers have shown a growing interest in using glycerol as a sustainable feedstock to produce functional chemicals. In this work, ketalization of glycerol using acetone performed over various acid clay catalysts (montmorillonite, aluminum pillared clay and bentonite) in a batch reactor. Effect of temperature and various catalyst on the solketal yield were observed. Among these heterogeneous clay catalysts at 30°C for 30 min reaction time with acetone/glycerol ratio 2:1 the maximum yield of solketal 60% was attained with aluminum pillared clay catalyst. On the other hand, the solketal yield was 58% with montmorillonite catalyst at 40°C at same other conditions. This method provides an enticing way to convert glycerol to solketal — a green valuable product with possible commercial applications. The solketal obtained could be formulated from renewable resources such as glycerol and acetone extracted from biomass and would like to be a suitable approach for various applications such as fuel additives and in medicine industries.

Keywords: Glycerol, solketal, montmorillonite, aluminium pillared clay

1. INTRODUCTION
The world energy crises have become the most critical topic due to the estimated declining of crude petroleum\textsuperscript{[1, 2]}. Biodiesel release less greenhouse gases during combustion, biodegradable, consists very low sulfur and less toxic and good transportation fuel, named as ‘Future Fuel’ \textsuperscript{[3, 4]}. In biodiesel production, a huge amount of glycerol is produced via transesterification as a byproduct \textsuperscript{[5]}. Rapidly growing concerns about energy and environment related with conventional fossil fuel-based transportation fuels, the production of biofuels escalated worldwide in last decade. Hence a huge bulk of crude glycerol is predicted to be produced from industry of biodiesel. It is estimated that the glycerol worldwide production will be 41.9 billion liters by 2020 as shown in Figure 1 \textsuperscript{[6]}. Currently, the focus is on ecologically friendly catalytic reactions in which waste is turned into commercial products \textsuperscript{[8]}. Glycerol has versatile application due to distinct combination of physio-chemical properties and typical elemental analysis. It is easy to handle and compatible with other substances. It is nontoxic to human health, viscous and stable under different conditions \textsuperscript{[9, 10]}. Glycerol with low molecular weight has wide applications in cosmetics, foods, polymer and plastic industries \textsuperscript{[11]}. Crude glycerol separation from the trans-esterification process has 80% purity. Additionally, a big consumer of glycerol is cosmetic, soap and pharmaceutical industries which also demand purity of glycerol which is not favorable to economically. On the other hand, the excessive quantity of glycerol can create a lot of problems with the disposal and affect the economics of the biodiesel industries \textsuperscript{[12]}. By the acetalization of glycerol with ketones and aldehydes formed cyclic acetals and ketals which is the most favorable application of glycerol \textsuperscript{[13-15]}. Hence, glycerol can be considered as a chemicals platform. Cyclic acetal and ketals are produced as an intermediate during the reaction of glycerol with ketones/aldehydes which are considered to be one of the most promising glycerol applications. In the catalytization of glycerol and acetone where solketal is produced as a product in the presence acid catalyst \textsuperscript{[16-18]}. Solketal (DL-1,2-Isopropylideneglycerol) is a product.

Figure 1 Global production of crude glycerol worldwide \textsuperscript{[7]}.
derived in which the two adjacent hydroxyl groups of glycerol are reacted via condensation with acetone [17]. Solketal is used as a fuel additives by mixing it with gasoline [19] or biodiesel and improves the octane number [20]. It can control the emissions and enhance the cold flow properties. It decreases the gum formation and enhances oxidation stability [21]. It is used as a plasticizer and versatile solvent in the polymer industry [16] and has various applications in many fields especially cosmetics, food, polymer and pharmaceutical industries.

In this research, another promising form of glycerol acetalization with clay is proposed due to its simple and safer handling, it is economically effective, recyclable and environmentally sustainable. The acidity of clay catalyst will be enhanced after treating with strong acid and enhanced the activity. Raw montmorillonite was treated with HCl and nitric acid (6M) for 7 days with constant stirring. Prepared catalyst was separated, washed and dried. The synthesis of solketal was carried out in the presence of prepared catalyst and compared the yield with other catalyst yields.

2. EXPERIMENTAL

Glycerol (99.5%), acetone (99.5+% for analysis), montmorillonite, bentonite, aluminum pillared clay and solketal (1,2-isopropylidene glycerol, 97%) was purchased from Sigma Aldrich to use as standard for GC analysis. The catalyst properties are expressed below in Table 1.

| Catalyst                  | Surface area m²/g | pH |
|---------------------------|-------------------|----|
| Aluminum pillared clay    | 250               | 4  |
| Montmorillonite           | 220               | 3  |

The overall reaction explanation is given below in the figure 2.

![Figure 2](image)

**Figure 2** Graphical explanation of the process.

The schematic diagram of the ketalization reaction of glycerol and acetone was illustrated in the Figure 2.

![Figure 3](image)

**Figure 3** Production of solketal via glycerol and acetone [22].

The ketalization reaction of glycerol and acetone was held in a glass reactor (250ml) consist of magnetic stirrer and reflux condenser as shown in Figure 4. Before reaction the clay catalyst was dried at 110°C for 3h to remove all moisture contents.

![Figure 4](image)

**Figure 4** Batch reactor setup.

Glycerol 10g (0.108 mol), acetone 12.54g (0.216 mol), and clay catalyst (montmorillonite, bentonite and aluminum pillared clay) 1wt.% of total mass of the reactants mixture was added in the reactor. The reaction conditions: acetone/glycerol molar ratio of 2:1, catalyst amount 1wt.%, reaction time: 30 min and runs at temperature (30-60°C). The temperature was maintained with the help of water bath and thermometer. At various time durations, product samples were collected from the reaction mixture and after separation from catalysts by centrifugation were analyzed. The gas chromatography–mass spectrometry (GCMS) was used to identify the reaction product. The
components present in higher amount in the product were identified by using a gas chromatograph, an then equipped with a mass selective detector. Varian CP-3800 GC equipped with VF-5 MS column (30m × 0.25mm × 0.25μm)] and He (helium) was used as a carrier gas. The oven temperature was constantly maintained for 2 minutes at the temperature of 120°C, after that was raised to 200°C with the increasing rate of 40°C/min. Injector and detector block temperature was constantly kept at 300°C [23]. The component identification yield of solketal and conversion of glycerol was calculated by using the NIST 14 MS library. After distillation process solketal is separated and sent for FTIR analysis for the confirmation of solketal presence in the distilled product. The yield of solketal and conversion of glycerol were calculated by using the following equation:

\[
\text{Yield} \, (\%) = \frac{\text{moles of produced solketal}}{\text{initial moles of glycerol}} \times 100
\]

Glycerol conversion \((\%) = \frac{\text{gi} - \text{gr}}{\text{gi}} \times 100\)

\(\text{gi} = \text{initial moles of glycerol}\)

\(\text{gr} = \text{remaining moles of glycerol}\)

The infrared spectra were obtained from a Fourier-transform infrared spectrophotometer, Nicolet model Magna-IR 760. The product samples were analyzed using KBr pellets (500–4000 cm\(^{-1}\)). The analyses were done in the Centralized Analytical Laboratory (CAL).

3. RESULTS AND DISCUSSION

3.1. Solketal Synthesis

The ketalization of glycerol and acetone over various clay catalyst (montmorillonite, bentonite and aluminum pillared clay) obtained for the synthesis of solketal. Reaction time, catalyst number, temperature, acetone / glycerol mol ratio were analyzed to determine the optimum conditions for the reaction. The effect of different clay catalysts on the yield of solketal was investigated as shown in Figure 5. Comparatively lowest solketal yields observed in the presence of bentonite catalyst at 30°C temperature while highest yield of solketal observed in aluminum pillared clay catalyst which is 60% and montmorillonite 49%. By increasing the temperature yield of solketal with aluminum pillared clay catalyst decreased to 45% which depicts that the aluminum pillared clay catalyst is more stable at room temperature then at higher temperatures. Bentonite is showing constantly low yield as compared to other clay catalysts to check the product yield from various natural clays.

During the Ketalization reaction over montmorillonite catalyst, the product yield increase by increasing temperatures. At 40°C, the solketal yield is 58% as shown in Figure 6. Thermodynamically higher reaction temperature results in lower equilibrium yield since the reaction is exothermic, according to the study by Nanda et al. [23].

![Figure 5 Effect of different clay catalysts on the solketal yield (Reaction conditions: acetone/glycerol molar ratio, 2:1; catalyst amount, 1 wt.%; reaction time: 30 min; at 30°C temperature). APC (Aluminum pillared Clay), MM (Montmorillonite), Bt (Bentonite).](image1)

![Figure 6 Effect of various clay catalysts on the yield of solketal (Reaction conditions: acetone/glycerol molar ratio, 2:1; catalyst amount, 1 wt.%; reaction time: 30 min; at 40°C). APC (Aluminum pillared Clay), MM (Montmorillonite), Bt (Bentonite).](image2)

Kinetically, temperature increases the reaction rate, while lower reaction temperature requires longer reaction time to achieve equilibrium output. By increasing temperature, it is expected that the yield of solketal and conversion of glycerol will also increase. In this work, the conversion of glycerol was 85% and 31% over aluminum pillared clay catalyst at 30°C and 40°C. However, the montmorillonite catalyst gives highest conversion of glycerol 77% at room temperature and minimum conversion 15% by increasing temperature till...
At 50°C, solketal yield with aluminum pillared clay was 12% and 8% at 60°C temperature. While montmorillonite reveals the yield 13% at 50°C and by increasing temperature results decline in solketal yield 7% but further increase in temperature lower the yield. For the acetalization process, the preferable temperature was lower than acetone boiling point. The graph depicts that yield of solketal was decreased with rise in temperature as the acetalization reaction is exothermic. As shown in Figure 7 below.

It was concluded that at low temperatures the catalyst gives the best yield of solketal as shown in the Table 2 below. Aluminum pillared clay catalyst gave the good performance during the ketalization of glycerol with acetone while compare to different catalysts.

### Table 2. Effect of catalyst on the yield of solketal.

| Catalyst                  | Conversion of Glycerol % | 2,2-Dimethyl-1,3-dioxolane-4-methanol (5 membered ketal) % | 2,2-Dimethyl-dioxane-5-ol (6 membered acetal) % |
|---------------------------|--------------------------|------------------------------------------------------------|--------------------------------------------------|
| Aluminum pillared clay    | 85                       | 60                                                         | 1.6                                              |
| Montmorillonite           | 77                       | 58                                                         | 1.3                                              |

### 3.2. FTIR Analysis

Analysis of FTIR was used to validate solketal presence in the distilled sample and to equate it with its Sigma-Aldrich standard. Difference in the peaks intensity of product and standard sample was due to presence of impurities in the product. The Figure 8, reveals the presence of solketal in the mixture. The FTIR spectrum of solketal and sigma Aldrich solketal was shown in Figure 8. Figure 8 reveals the axial deformation in hydroxyl bonds and hydrogen bonds (-O-H) at 3432 cm⁻¹ band between solketal molecules. The area consisting of the wave numbers between 2986 and 2983 cm⁻¹ refers to axial deformation of methyl bonds (-C-H). The water angular deformation occurring due to the localized unit at 1456 cm⁻¹ band. The band at 1372 cm⁻¹ belongs to the “umbrella” trend, pointing to the ketone group methylene. Band 1211 cm⁻¹ and 1046 cm⁻¹ represents the dioxolane (five-membered ring) -C=O bonds.

The bands 1158 cm⁻¹ represents to asymmetrical vibrational motion of the solketal bonds (\(-\text{C}=\text{O}-\text{C}-\)). On the other hand, the bands at 912 and 845 cm⁻¹ refers to symmetrical vibrational moment of bands. To sum up, the band at 1047 cm⁻¹ attribute to -\(\text{C}-\text{C}-\text{OH}\) bond of alcoholic group [24].

### 4. CONCLUSION

Glycerol conversion with acetone in the presence of various heterogeneous clay catalyst to solketal was optimized by varying temperature. In the synthesis of solketal from glycerol over Aluminum pillared clay catalysts reveals the best performance with 60% yield without solvent. However, the solketal yield was 58% with montmorillonite catalyst at 40°C for 30 min reaction time. It is expected that by varying the molar ratio of acetone/glycerol and catalyst loading the yield will increase in solvent free process. The solketal obtain can be blended with gasoline to increase the octane number. Comparing it with its commercial counterpart, the solketal developed in this work was distinguished by obtaining very similar characteristics.

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