

# Heterogeneous catalytic reaction of glycerol with acetone for solketal production

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**Abstract.** The rapid growth of biodiesel industries has also increased the production of glycerol as side product. Without proper treatment, glycerol may cause serious problem for the environment. Glycerol can be reacted with acetone to produce solketal as a fuel additive. The aim of this research was to study the glycerol ketalization with acetone using Amberlyst-15 as catalyst. Experiments were undertaken in a batch reactor. A set of experiment was conducted at varying temperature (35 to 60°C), initial mole ratio of acetone to glycerol (2 – 6) and catalyst loading (1,3,5 and 7% w/w). Sample was analyzed every 30 minutes. The results showed that optimal condition was achieved at temperature of 60 °C, initial mole ratio of acetone to glycerol of 3, and the catalyst load of 3%. The highest glycerol conversion achieved was 87.41 % at 60°C for 3 hours reaction. The Pseudo Steady State Hypothesis (PSSH) has been developed as  $r_{net} = \frac{k_4 \cdot C_G \cdot C_{Ac}}{1 + k_5 \cdot C_G}$ . Parameter estimation of  $k_4$  and  $k_5$  were evaluated from experimental data at various temperatures. It appears that the model predicted the experimental data well at high conversion (above 80 min) and showed relatively poor prediction below 80 min.

## 1 Introduction

Glycerol is known as a byproduct from biodiesel production. As a result of the increasing biodiesel production, there has been a surplus of glycerol supply. Utilization of glycerol to produce oxygenated compounds such as acetal and ketals is a potential pathway for glycerol conversion. Solketal is one of the chemical compound which can be synthesized from glycerol by acetalization with acetone. Solketal can be used as fuel additives to improve the octane number and cold flow properties, reduce particulate emission and gum formation [1]. As a fuel additive, it is common to blend solketal at 3, 5, 7 and 10vol % with oxygenate free gasoline. When compared to unblended gasoline, the higher value of octane number is obtained with blended ones [2]. Meanwhile Dmitriev et al. [3] mentioned that gasoline with solketal as oxygenated have improved detergent properties, combustion characteristic and form smaller amount of CO and hydrocarbons during combustion.

For solketal production, some researchers have used solid catalyst due to better separation aspect and reusability of solid catalyst. Reddy et al. [4] investigated ketalization of glycerol using promoted zirconia catalyst and exhibited promising catalytic activity. When Amberlyst-46 as catalyst load was increased from 0.5% to 1.00%, solketal yields increased significantly from 59% to 84% [2]. Mallesham et al. [5] found that among the solid catalyst, the Amberlyst-15 acid resin catalyst exhibited the highest glycerol conversion within 0.25 hour of reaction time. Manjunathan et al. [6] has

investigated the use of modified zeolite beta catalysts of 5wt% to obtain the glycerol conversion of 87.5%.

In order to study the kinetics of glycerol ketalization using zeolite H-BEA as catalyst, Rosa et al. [7] expressed the kinetics in the pseudo homogeneous model such as reversible kinetics model. The equilibrium constant for a range of temperature 40 – 80°C the forward and reverse reaction energy activity were similar. The impacts of temperature on the reaction rate, conversion and selectivity were discussed. It was shown that the solketal yields was reduced when the temperature was increased. When temperature is too high, acetone is prone to vaporization while the glycerol is in the liquid phase on the surface of active catalyst [8,9]. In addition, Samoilov et al. [10] expressed the elevation of the temperature led to a decrease in selectivity for solketal formation. Esteban et al. [11] expressed the temperature higher than 313K was required to facilitate removal of water for shifting the reaction equilibrium to the product.

Agirre et al. [12] investigated ketalization glycerol with formaldehyde from 1:1 to 1:3 using amberlyst-47 catalyst. By increasing the molar ratio of glycerol, the equilibrium conversion of the formaldehyde increased as well. As the acetone to glycerol molar ratio increased from 4:1 to 8:1, glycerol conversion was found to increase from 52% to 100% associated with decreasing the selectivity to solketal and increasing that of 6-acetal [13]. Manjunathan et al. [6] mentioned that glycerol conversion increased with the increase of acetone to glycerol molar ratio from 1:1 to 3: 1. It was found that the acetone to glycerol molar ratio of 2:1 appeared to be the optimum condition. The aim of present work was to

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undertake the Pseudo Steady State Hypothesis (PSSH) model of solketal synthesis from glycerol and acetone using Amberlyst 15 as catalyst. For that purpose, glycerol conversion was evaluated by varying systematically, temperature, catalyst loading and acetone to glycerol ratios.

## 2 Materials and methods

### 2.1 Material

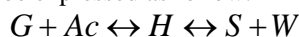
The reactants were glycerol and acetone. Glycerol technical grade was used with further purification. Acetone 99wt% purity were purchased from Merck. The catalyst used in the study was Amberlyst -15 which was purchased from Sigma Aldrich.

### 2.2 Experimental method

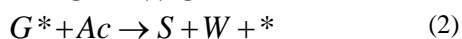
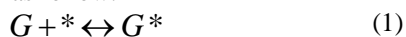
The synthesis of solketal was conducted in a three neck flask reactor with round bottom and equipped with stirrer, heater, condenser, thermometer and sampling apparatus. Glycerol was filled into the reactor, then stirred and heated to attain the required temperature. Subsequently, acetone as reactant and Amberlyst 15 as the catalyst were added to the reactor. Samplings were conducted every 30 minutes which was followed by separation of catalyst by filtration. The samples were analyzed using periodic acid.

### 2.3 Modelling method

The reaction rate mechanism for the ketalization reaction between glycerol and acetone has been proposed by Trifoi et al. [1] and Mallesham et al. [5]. The reaction mechanism can be expressed as follow:



H is hemiacetals which is known as the intermediate. Assuming that the intermediate product of H was formed and disappeared spontaneously, one may simplify the reaction mechanism as follow:



From site balance, we may infer that:

$$C_{G^*} + C_v = C_{tot} \quad (3)$$

By assuming equilibrium in Eq. 1, we obtain:

$$0 = k_1 \cdot C_G \cdot C_v - k_2 \cdot C_{G^*}$$

$$0 = k_1 \cdot C_G \cdot (C_{tot} - C_{G^*}) - k_2 \cdot C_{G^*}$$

$$C_{G^*} = \frac{k_1 \cdot C_G \cdot C_{tot}}{k_2 + k_1 \cdot C_G} \quad (4)$$

$$r_{net} = k_3 \cdot C_{G^*} \cdot C_{Ac}$$

$$r_{net} = k_3 \cdot \frac{k_1 \cdot C_G \cdot C_{tot}}{k_2 + k_1 \cdot C_G} \cdot C_{Ac}$$

The concentration of acetone is typically in excess compared to the glycerol. Thus, the change of acetone concentration followed stoichiometric relationship with the amount of glycerol converted. As a result, by using Pseudo Steady State Hypothesis (PSSH) model, the reaction rate can be modified as follow:

$$r_{net} = \frac{k_4 \cdot C_G \cdot C_{Ac}}{1 + k_5 \cdot C_G} \quad (5)$$

$$k_4 = A_4 \cdot \exp\left(\frac{-Ea_4}{R.T(K)}\right) \quad (6)$$

$$k_5 = A_5 \cdot \exp\left(\frac{-Ea_5}{R.T(K)}\right) \quad (7)$$

The reaction rate as in Eq. 5 was evaluated with the batch reactor data. Parameter k4 and k5 were assumed to follow Arrhenius equations as shown in Eqs. 6 and 7. Hence, there are 4 parameters to fit namely: pre-exponential factor (A) and activation energy (Ea) as described in Eqs. 6 and 7.

The batch reactor was modeled as:

$$-r_{net} \cdot W = V \frac{dC_G}{dt} \quad (8)$$

All parameters were estimated to the experimental data from temperature variation. Gradient search methods as well as ODE solver in MATLAB have been used for parameter fitting and simulation, respectively. The objective function was to minimize the SSE from residuals of glycerol concentration from simulation and experimental data.

For simulation, the initial concentration of acetone and glycerol used were 10.8 M and 2.7 M, respectively. The liquid volume (V) was kept constant at 370 ml. Similarly, the weight of catalyst was maintained at 2.76 gr which corresponds to 3 wt.% of catalyst.

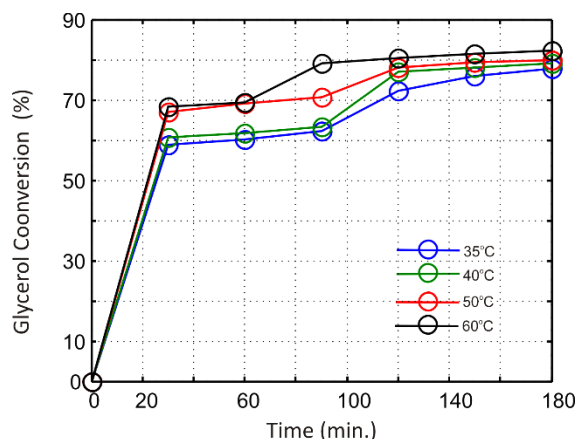
## 3 Results and discussion

Solketal synthesis from glycerol with acetone over Amberlyst 15 catalyst was investigated. In order to attain the optimum reaction condition, temperature, catalyst loading, acetone to glycerol molar ratio were studied. The time of reaction and stirrer speed were fixed at 3 hours and 500 rpm, respectively. The stirrer speed has been set constant at 500 rpm. Nanda et al. [[8] carried out the experiments of solketal synthesis from glycerol with acetone under stirring speed 400 and 1100 rpm and there was negligible influence of stirrer speed on the reaction time and glycerol conversion. The same conclusion was reached by Agirre et al. [14] when reacting glycerol with acetaldehyde at 700 to 1250 rpm and aldehyde to glycerol molar ratio of 3:1.

### 3.1 The effect of reaction temperature

The effect of the reaction temperature on ketalization of glycerol with acetone was presented in Fig 1. As shown in Fig 1, the highest glycerol conversion was attained as high as 82.26 % at 60°C. The same result was also reported by Ilgen et al. [2] which showed the glycerol

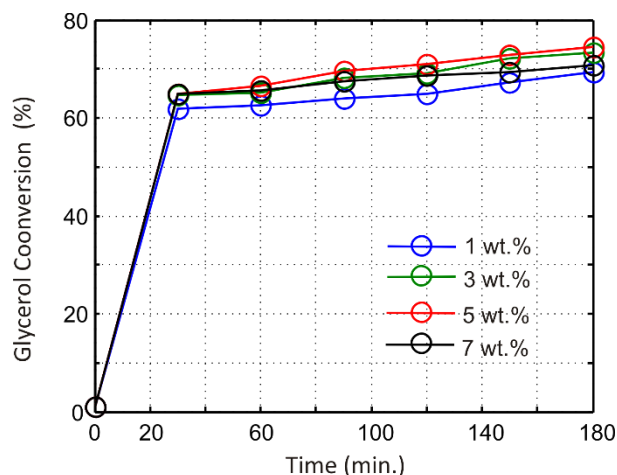
conversion of 84% was attained at 60°C. Generally, one may infer that the glycerol conversion decreases with the increase of temperature. It was probably caused by vaporization of acetone when approaching the acetone boiling point [10]. When the temperature increased, acetone would vaporize and more acetone would present in the gas phase while the glycerol is in the liquid phase on the surface of the catalyst [1, 8, 9]. The synthesis of solketal using Ni-Zr supported on activated carbon catalyst has been reported by Khayoom and Hameed [12] and they found that 45°C was the best temperature. At 45°C, complete glycerol conversion was obtained with selectivity of 74%.



**Figure 1.** The effect of reaction temperatures to the glycerol conversion

### 3.2 The effect of catalyst loading

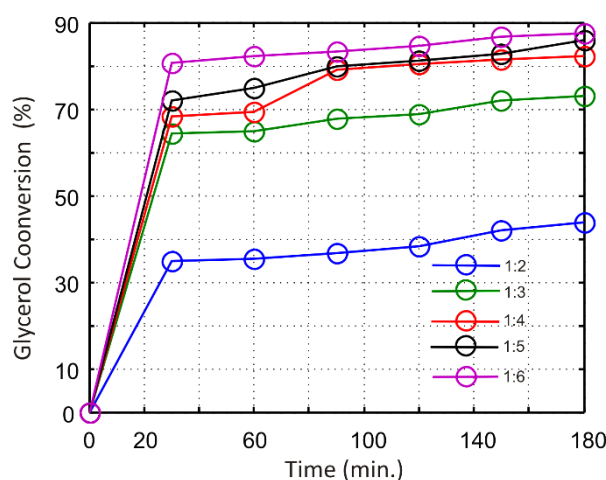
The effect of catalyst loading to glycerol conversion has also been conducted by varying the loading of Amberlyst 15 from 1, 3, 5 and 7 wt% to glycerol weight. For this variation, acetone to glycerol ratio of 3:1 and temperature of 60°C were maintained. Fig. 2 displayed the glycerol conversion by varying catalyst loading. As shown in Fig. 2, the glycerol conversion was increased from 69.16 to 74.15% with the increase of catalyst loading. It can be concluded that no influence of catalyst loading on reaction rate lead to glycerol conversion. When catalyst loading increase to 7%, the glycerol conversion decrease to 70.40%. This might be due to deposition of catalyst which settle down on the bottom of reactor. By using H-βeta-1 as catalyst for glycerolysis with acetone, Manjunathan et al. [6] found that the maximum glycerol conversion of 87.10% for 7.5 wt% of catalyst amount. Meanwhile, Reddy et al. [4] investigated acetalisation reaction by using zirconia and promoted zirconia as catalyst by varying the catalyst loading from 1 to 5 wt%. The promoted zirconia catalyst exhibited higher catalytic glycerol conversion. The glycerol conversion over zirconia and promoted zirconia catalyst were 10 and 98%, respectively. As the catalyst amount increased from 0.15 to 0.20 g, glycerol conversion reached 100% and selectivity to 6-acetal was raised from 16 to 26% [12].



**Figure 2.** The effect of catalyst loading to the glycerol conversion

### 3.3 The effect of acetone to glycerol molar ratio

In order to study the influence of acetone to glycerol ratio, we have set the catalyst loading of 3% Amberlyst 15 and temperature of 60°C. The following investigations were aimed to evaluate the optimum acetone to glycerol molar ratio. Fig. 3 presents the results of glycerol conversion obtained using several acetone to glycerol molar ratio. As the increase of acetone to glycerol molar ratio would cause the increase of glycerol conversion. Increasing the molar ratio of acetone to glycerol from 2 to 6 gave an increase of conversion from 43.92 to 87.41%. An excess of acetone employed in this reaction would drive the forward reaction and enhanced the complete conversion of glycerol. As shown here, the ratio of 3:1 gave the glycerol conversion of 73.15%. Increasing the molar ratio to 4, 5 and 6 gave the glycerol conversion of 82.26%, 85.80% and 87.41%, respectively. It could be concluded that the molar ratio of 3:1 was the optimum condition.



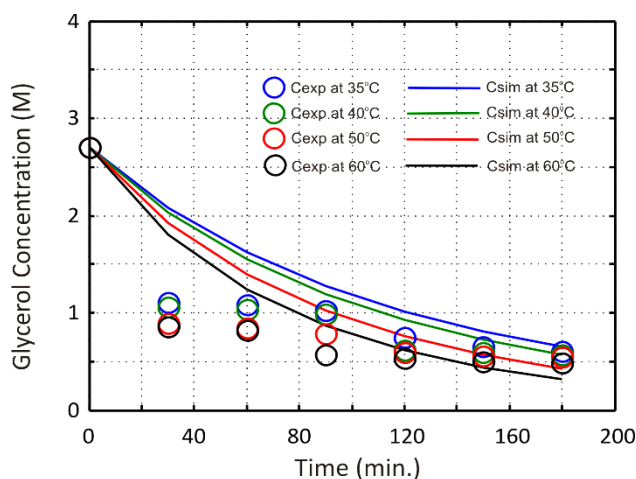
**Figure 3.** The effect of glycerol to acetone molar ratio to the glycerol conversion

By using promoted zirconia catalyst on acetalisation of glycerol Reddy et al. [4] found the glycerol conversion increased from 62% to 98% at molar ratio of 1:1 to 6:1. If the catalyst was used without promoted zirconia or

zirconia only the glycerol conversion attained was less than 10%. da Silva et al. [14] undertaken acetylation in the presence of SnF<sub>2</sub> catalyst, an increase the molar ratio of acetone to glycerol resulted higher glycerol conversion which range from 58 to 97%. The mass balance showed that the glycerol was converted to solketal. Manjunathan et al. [6] used variation of molar ratio from 1 to 3 and it was found that acetone to glycerol molar ratio of 2:1 turned out to be the optimum for the catalytic transformation of glycerol to solketal. The glycerol conversion remained almost the same with further increase in mole ratio to 3:1. Some researchers [4, 6, 15] observed as the acetone to glycerol molar ratio increase, the glycerol conversion also increase. In addition, it is worth noting that the increase in molar ratio of acetone to glycerol does not influence the selectivity to solketal and remained almost the same that greater than 90%.

### 3.4 Kinetic modelling result

A kinetic model based on PSSH mechanism has been proposed as in Eqs. 1 - 7 with reactor model as in Eq. 8. Comparison between the simulation and experimental results is presented in Fig. 4. It should be mentioned here that the simulation was only based on the effect of temperature as it was found that the glycerol conversion was sensitive to the temperature variation. The model parameters of A<sub>4</sub>, A<sub>5</sub>, Ea<sub>4</sub> and Ea<sub>5</sub> were estimated at various temperatures. From parameter estimation, preexponential factor of 0.04 L<sup>2</sup>.mol<sup>-1</sup>.kg<sup>-1</sup>.min<sup>-1</sup> and 0.81 were obtained for A<sub>4</sub> and A<sub>5</sub>, respectively. The activation energy of 15.3 kJ/mol and 26.8 kJ/mol were obtained for Ea<sub>4</sub> and Ea<sub>5</sub>, respectively. Parameter estimation based on gradient search method also obtained the SSE of 49.04.



**Figure 4.** Comparison of glycerol concentration between simulation and experimental data for various temperatures.

It appears that the model predicted the experimental data well at high conversion (above 80 min) and showed relatively poor prediction below 80 min. The poor prediction below 80 min might also indicate that more

experimental data is needed to allow the model to capture better the rapid reaction that occurred in the beginning of reaction. However, with present technique, collecting data under 30 min could be challenging and hence required more advanced analytical technique.

## 4 Conclusion

The acetalisation of glycerol with acetone was carried out over Amberlyst 15 as catalyst. The influence of various parameters such as reaction temperature, catalyst loading, acetone to glycerol molar ratio have been conducted to evaluate the glycerol conversion. It was observed that the Amberlyst 15 exhibit good performance as a solid catalyst which gave the highest glycerol conversion of 87.41%. The acetone to glycerol molar ratio gave more influence to the glycerol conversion especially for the molar ratio of 2:1 to 3:1.

A kinetic model based on experimental data at of 35-60°C has been developed with PSSH approach as:

$$r_{net} = \frac{k_4 \cdot C_G \cdot C_{Ac}}{1 + k_5 \cdot C_G}$$

with k<sub>4</sub> and k<sub>5</sub> were described as

Arrhenius equations. From parameter estimation, preexponential factor of 0.04 L<sup>2</sup>.mol<sup>-1</sup>.kg<sup>-1</sup>.min<sup>-1</sup> and 0.81 were obtained for A<sub>4</sub> and A<sub>5</sub>, respectively. The activation energy of 15.3 kJ/mol and 26.8 kJ/mol were obtained for Ea<sub>4</sub> and Ea<sub>5</sub>, respectively. It appears that the model predicted the experimental data well at high conversion (above 80 min) and showed relatively poor prediction below 80 min.

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## Notation

A	= pre exponential factor, mol L <sup>-1</sup> men-1
Ac	= acetone, mol L <sup>-1</sup>
Ea	= activation energy, J mol <sup>-1</sup>
G	= glycerol, mol L <sup>-1</sup>
H	= hemi acetal, mol L <sup>-1</sup>
k	= reaction rate constant, L mol <sup>-1</sup> L <sup>-1</sup>
R	= gas constant, 8.314 J mol <sup>-1</sup> K
S	= solketal, mol L <sup>-1</sup>
T	= temperature, K
*	= catalyst surface active side

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