



Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive



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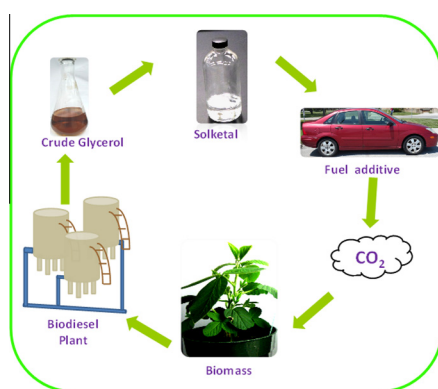
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HIGHLIGHTS

- Thermodynamics and kinetics of glycerol ketalization were studied for the first time.
- External mass transfer resistance was completely eliminated above 400 rpm.
- Moisture content demonstrated an adverse effect on the yield of solketal.
- Kinetics of the reaction was modeled by Langmuir–Hinshelwood rate expression.
- The activation energy for the reaction was determined to be 55.6 kJ mol^{-1} .

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 5 August 2013

Received in revised form 13 September 2013

Accepted 19 September 2013

Available online 2 October 2013

Keywords:

Adsorption

Batch reactor

Glycerol

Ion exchange resin

Kinetics

ABSTRACT

Glycerol is a byproduct of biodiesel industry and can be converted into high value-added applications. The heterogeneous ketalization of glycerol with acetone was conducted over a solid acid catalyst of Amberlyst-35 in a batch reactor. The thermodynamics and kinetics of the ketalization reaction for the synthesis of solketal were investigated. The reaction equilibrium constants were determined experimentally in the temperature range of 293–323 K, with which the following standard molar properties (at 298 K) were obtained: $\Delta H^0 = -30.1 \pm 1.6 \text{ kJ mol}^{-1}$, $\Delta G^0 = -2.1 \pm 0.1 \text{ kJ mol}^{-1}$, $\Delta S^0 = -0.1 \pm 0.01 \text{ kJ mol}^{-1} \text{ K}^{-1}$. Effects of various experimental conditions (stirring speed, catalyst addition amount, pressure, temperature, moisture content and the feed composition) on the reaction kinetics (glycerol conversion and solketal yield vs. time) were also investigated in this work. A two-parameter kinetic law based on a Langmuir–Hinshelwood rate expression was used. The activation energy of the overall ketalization reaction was determined to be $55.6 \pm 3.1 \text{ kJ mol}^{-1}$. The obtained solketal could be synthesized from renewable resources like bioglycerol and biomass derived acetone, and seem to be a good candidate for different applications such as fuel additive and in pharmaceutical industries. The work is an important step for further development of a technology for the continuous synthesis and separation of solketal from glycerol and acetone.

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1. Introduction

Glycerol (propane-1,2,3-triol) is the simplest trihydric alcohol, commercially known as glycerin. It is well known for its versatile applications in diverse fields such as the food, pharmaceutical, polymer and fuel industries [1].

Glycerol is produced at a large amount as a byproduct or waste stream from biodiesel production via transesterification reactions. The biodiesel production generates approximately 10% of glycerol by volume [2]. Due to the increased concerns over the environment and energy security associated with petroleum-based transportation fuels, the interest in producing bio-fuels (bio-ethanol and biodiesel) has been intensified worldwide in last decade. The production of biodiesel has increased exponentially all over the world. Hence a large amount of glycerol is expected to be generated from the biodiesel industry. It is predicted that by 2020 the global production of glycerol will be 41.9 billion liters [3]. The large scale producers are able to refine this waste stream for the industrial applications whereas small scale producers are unable to justify refining costs and instead pay a fee for glycerol removal. The current crude glycerol price is as low as 10 cents/lb [4]. The predicted generation of huge amount of glycerol will further lower the glycerol price once it enters the market. Therefore proper utilization of glycerol is required in different value-added applications for the sustainability of the biodiesel industry.

The presence of three hydroxyl groups in glycerol makes it unsuitable to be used as a direct fuel component due to its low heating value. Various processes have been investigated for conversion of glycerol into fuel components. Condensation of glycerol with aldehydes and ketones to cyclic acetals and ketals, respectively, is often considered one of the most promising glycerol applications for fuels/chemical intermediates [5–8]. The ketalization reaction between glycerol and acetone is given in Fig. 1, where solketal (2,2-dimethyl-1,3-dioxolane-4-methanol) is formed as the condensation product in the presence of an acid catalyst. Solketal can be used as a fuel additive to reduce the particulate emission and to improve the cold flow properties of liquid transportation fuels [9]. It helps reduce the gum formation, improves the oxidation stability, and enhances the octane number when added to gasoline [10]. Maksimov et al. [11] reported its use as a versatile solvent and a plasticizer in the polymer industry and a solubilizing and suspending agent in pharmaceutical preparations.

Traditionally ketalization of glycerol is carried out via a homogeneous catalytic process using mineral acids like H_2SO_4 , HCl, HF, and *p*-toluenesulphonic acid, etc. [12,13]. These processes have serious shortcomings such as corrosion and catalyst separation from the product stream, hence raising environmental and economic concerns for the effluent disposal. Most of these problems could be addressed by using heterogeneous catalysts. Studies of ketalization of glycerol using solid acid catalysts like Amberlyst-15 [14], Amberlyst-36 [5], Montmorillonite K-10 [15], Zeolite [11,14], silica supported heteropoly acids [16], and mesoporous silicates containing arylsulfonate groups [17] were reported. Among these catalysts, Amberlyst has demonstrated its potential for the synthesis of solketal. Deutsch et al. [5] investigated the reactivity

of different heterogeneous catalysts for the formation of cyclic ketals by the condensation of glycerol with aldehydes. A high yield of solketal (more than 90% with high selectivity) was reported at a high molar ratio (approx. 6:1) of acetone to glycerol in a batch reactor [17]. However, so far kinetics and thermodynamics of the ketalization reaction of glycerol with acetone over solid acid catalysts have not been reported.

It is of no question that to understand thermodynamics and kinetics of the ketalization reaction is important for further development of the glycerol ketalization technology. Thus, the main objective of this work is to thoroughly investigate thermodynamics and kinetics of the ketalization reaction of glycerol and acetone in a batch reactor over solid acid catalyst of Amberlyst-35. The results of this research would help to suggest a reaction mechanism and a rate equation with experimentally measured kinetic parameters. Furthermore, it will be advantageous for the development of a continuous process for the industrial production of solketal from glycerol.

2. Experimental

2.1. Materials

Glycerol and acetone (both >99 wt.% purity) were procured from Sigma Aldrich and used as received, and commercial grade ethanol was supplied from Commercial Alcohols Inc. Solketal [(S)-(+)-1,2-Isopropylidene-glycerol, 99 wt.%] was also obtained from Sigma Aldrich as a calibration standard for GC analysis. The solid acid catalyst: Amberlyst-35 DRY was obtained from Rohm and Hass Co. (USA) and used as received. The characteristics of the catalyst are given in Table 1.

2.2. Ketalization reaction of glycerol and acetone

The glycerol ketalization reactions were carried out in a 100 mL three-neck glass reactor in a water bath equipped with a magnetic stirrer and a condenser (Fig. 2) in order to condense and reflux all the vapors keeping the reaction volume almost constant. The reaction temperature was precisely controlled for an accuracy of ± 0.03 K with an external thermostat containing an external thermocouple placed inside the reacting mixture. In a typical run, the composition of reaction mixture was 22.83 g of acetone, 18.11 g of glycerol, 9.06 g of ethanol, 0.1811 g of catalyst and the total volume of the mixture was 55 mL. At the beginning of the experiment, known amount of glycerol, ethanol and acetone were charged into the reactor. Amberlyst-35 catalyst was placed in a basket at the top of the condenser and added to the reactor only after the stabilization of temperature of the system (time zero). The use of ethanol as solvent was mainly to improve the solubility of glycerol in acetone and the homogeneity of the solution was observed by the formation of a single phase (naked eye observation), also checked by the GC-FID. The reaction of acetone with ethanol to form

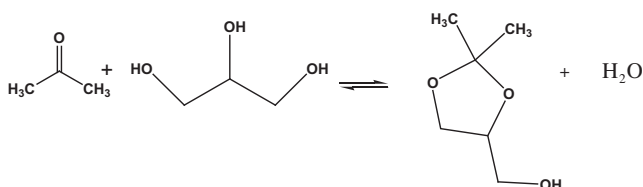


Fig. 1. Ketalization reaction scheme of glycerol and acetone.

Table 1
Characteristics of the solid acid catalyst used.

Catalyst properties	
Acidity (eq/kg) ^a	5
Particle size (μm)	490
Average pore diameter ^b (nm)	30
Max. operating temp ^c ($^{\circ}\text{C}$)	150
Pore volume ^b (mL/g)	0.35
BET surface area ^b (m^2/g)	50

^a Determined by ammonia TPD.

^b Measured by N_2 isothermal adsorption at 77 K.

^c Obtained from the catalyst supplier.



Fig. 2. Batch reactor.

hemiketal/ketal under this experimental condition is highly unfavourable [18,19] and the yields of other undesired products were very small (<2%) [11]. The total mass of the reaction substrate (M) was maintained to be 50 g, unless otherwise specified. A small amount of samples were withdrawn at regular intervals of time for analysis by GC-FID. The reaction was kept at the specific temperature until the equilibrium state was achieved (when the reactants/products concentrations did not vary with time) which was checked by the GC-FID in a regular interval of time.

2.3. Product analysis

The main components in the product mixture were first determined with a gas chromatograph, equipped with a mass selective detector [Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC equipped 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 5×10^{-7} m³/s. The oven temperature was maintained at 120 °C for 2 min and then increased to 200 °C at a ramp rate of 40 °C/min. Injector and detector block temperature were maintained at 300 °C. The components were identified using the NIST 98 MS library with the 2002 update. The concentration of the glycerol and solketal in the products was analyzed with a GC-FID (Shimadzu-2010) under the similar conditions as used for the GC-MS measurement. In a particular run of 70% yield of solketal, a glycerol conversion of 71% was observed and the ratio of yield to conversion was consistent throughout the experiment.

The solketal yield and glycerol conversion were calculated using the following equations:

$$\text{Yield (mol\%)} = \frac{\text{Moles of solketal formed}}{\text{Initial moles of glycerol}} \times 100\% \quad (1)$$

Conversion (mol%)

$$= \frac{\text{Reduction in moles of glycerol in the reaction}}{\text{Initial moles of glycerol}} \times 100\% \quad (2)$$

3. Thermodynamic results

Thermodynamic studies of the glycerol ketalization reaction were carried out in the 100 mL batch reactor in a relatively lower temperature range of 293–323 K, as the reaction is exothermic so thermodynamically unfavourable at higher temperatures [20]. In this series of experiments, a high initial molar ratio of acetone to glycerol (6:1) was used, and the catalyst loading in the batch reactor was fixed at 5 wt.% of the mass of glycerol. To ensure equilibrium of the reaction, all the experiments were kept for an enough long time while monitoring the glycerol conversion and solketal yield vs. time until the measured results did not change (indicator of the reaction equilibrium). The equilibrium compositions at various experimental conditions are listed in Table 2.

The equilibrium constant (K_c) for the liquid phase reaction was calculated using the following equation and the results are presented in Table 2:

$$K_c = \frac{[S][W]}{[A][G]} \quad (3)$$

where [S], [W], [A], and [G] are the molar concentration of solketal, water, acetone, and glycerol, respectively. As shown from Table 2, with increase in the reaction temperature, the equilibrium constant K_c decreases gradually, indicating the exothermicity of the reaction. To achieve a higher equilibrium conversion of glycerol, a lower temperature is preferred. However, as expected the lower the reaction temperature the longer time is required to reach the equilibrium state.

The thermodynamic properties such as entropy and enthalpy can be predicted by plotting the experimental values of $\ln K_c$ vs. $1/T$ (K⁻¹). In a narrow temperature range in the vicinity of room temperature, the plot of $\ln K_c$ vs. $1/T$ would follow a linear correlation as displayed in Fig. 3:

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (4)$$

where ΔS^0 is the standard entropy at 298 K (kJ mol⁻¹ K⁻¹), ΔH^0 is the standard enthalpy at 298 K (kJ mol⁻¹), R is the universal gas constant (J mol⁻¹ K⁻¹) and T is the reaction temperature (K). The linear fitting of experimental data (in Fig. 3) according to above equation gives:

$$\ln K_c = (3615.4/T) - 11.31 \quad (5)$$

By solving Eqs. (4) and (5), we get $\Delta H^0 = -30.1 \pm 1.6$ kJ mol⁻¹ and $\Delta S^0 = -0.1 \pm 0.01$ kJ mol⁻¹ K⁻¹ from the slope and the intercept, respectively. The standard state Gibbs free energy change (ΔG^0) can be related to the standard state enthalpy and entropy changes for the system as:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (6)$$

with the above, ΔG^0 is found to be -2.1 ± 0.1 kJ mol⁻¹, suggesting the reaction can take place at standard state (room temperature). The ΔG^0 value obtained is similar to the result reported in the literature for the synthesis of acetal from butanol and acetaldehyde [21].

4. Kinetic results

Referring to the mechanism proposed for the synthesis of acetal in the presence of a homogeneous catalyst [22] and the mechanism

Table 2
Experimental data of equilibrium composition and equilibrium constants.^a

Temp (K)	I_A	I_G	F_A	F_G	F_S	F_W	K_C	X_E
298	0.6817	0.1145	0.5747	0.0075	0.1070	0.1070	2.6562	0.9345
303	0.694	0.1132	0.5907	0.0099	0.1033	0.1033	1.8247	0.9125
313	0.6823	0.1153	0.5807	0.0137	0.1016	0.1016	1.2975	0.8812
323	0.6827	0.1137	0.5854	0.0164	0.0973	0.0973	0.9861	0.8558

^a I_A = initial mole of acetone; I_G = initial mole of glycerol; F_A = final mole of acetone; F_G = final mole of glycerol; F_S = final mole of solketal; F_W = final mole of water; K_C = equilibrium constant; X_E = equilibrium conversion.

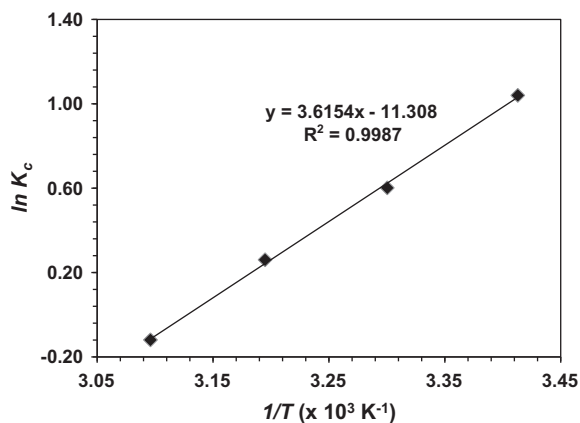


Fig. 3. Plot of $\ln K_C$ vs. $1/T$.

proposed by Maksimov et al. [11] for the synthesis of ketals from plant-derived diols, we proposed a similar mechanism for ketalization of glycerol over a heterogeneous catalyst as illustrated in Fig. 4. The most important steps in the mechanism are:

- (1) Reaction between the adsorbed acetone and glycerol to give the hemi-acetal (Step 1).
- (2) Reaction to form water (Step 2 – considered to be the rate limiting step).
- (3) Reaction to form solketal (Step 3).

In this study, we investigated various experimental conditions (stirring speed, catalyst addition amount, pressure, temperature, moisture content and the reactor feed composition) on the reaction

kinetics (glycerol conversion and solketal yield vs. time) and are summarized in Table 3. The results are presented as follows.

4.1. Mass transfer resistance

To investigate the effects of mass transfer on the reaction kinetics, a wide range of agitation (stirring) speeds (from 400 rpm to 1150 rpm) were tested in the experiments. The solketal yields vs. time under two different stirring speeds (400 and 1100 rpm) are illustrated in Table 3 (entry 1 and 2) and Fig. 5. Clearly, at the same conditions (323 K, acetone to glycerol molar ratio (A/G) of 2, and catalyst loading (W_{cat}) of 1 wt.% of glycerol) both tests under 400 and 1100 rpm led to the same equilibrium yield of solketal (60%) as well as the initial formation rate of solketal (determined from the slope of the trend-line of the solketal yield vs. time at the beginning of the experiment). Thus, no effect of the agitation speed on the reaction rate was observable at >400 rpm. Hence, all further experiments were carried out at 700 rpm to eliminate the external mass transfer resistance. The catalyst used in this study was a macroscopic ion exchange resin (Table 1). In a macroscopic resin, the reactants are able to diffuse into the pores without any resistance. Hence no internal mass transfer resistance was expected [23,24].

4.2. Addition of catalyst

The effects of catalyst addition amount on the reaction kinetics were investigated under the conditions of 313 K and A/G = 2 while with different catalyst addition amount (i.e., W_{cat} = 1 wt.% and 2 wt.% in relation to glycerol). The results are given in Table 3 (entry 6 and 8) and Fig. 6, from which essentially the increase in the catalyst addition amount from 1 wt.% to 2 wt.% does not change the final (equilibrium) yield of solketal (64%) as expected by thermodynamics. Under the same experimental conditions, a two fold

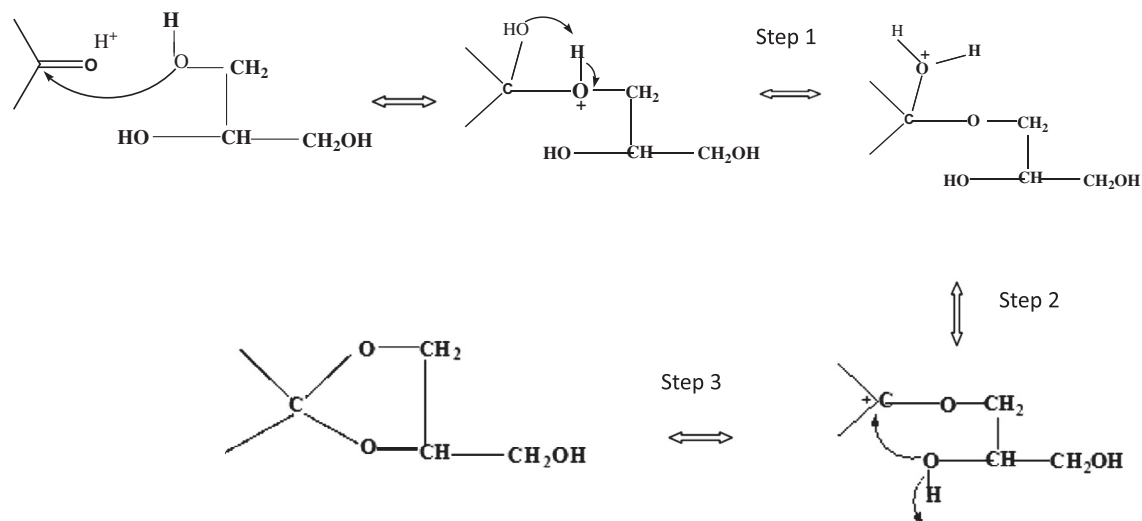


Fig. 4. Scheme of mechanism for ketalization reaction of glycerol and acetone.

Table 3
Summary of the experiments at different conditions.

Entry number	Catalyst loading (wt.% of glycerol)	Stirring speed (rpm)	Temperature (K)	Acetone:glycerol:ethanol (mole)	Solketal yield (%)
1	1	400	323	2:1:1	60
2	1	1100	323	2:1:1	60
3	1	700	298	2:1:1	72
4	1	700	303	2:1:1	70
5	1	700	308	2:1:1	67
6	1	700	313	2:1:1	64
7	1	700	323	2:1:1	60
8	2	700	313	2:1:1	64
9	1	700	298	1.48 :1:1	68
10	1	700	298	2.46 :1:1	74
11	1	700	298	2.04:1:1	72
12 ^a	1	700	298	2:1:1	68
13 ^b	1	High	298	2:1:1	72
14 ^c	1	High	298	2:1:1	72

^a With 3.15 wt.% moisture.

^b Conducted in a pressure reactor at 1 atm.

^c Conducted in a pressure reactor at 54 atm.

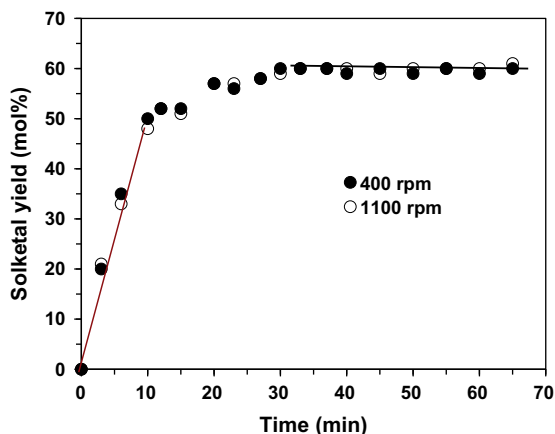


Fig. 5. Effects of reactor stirring speed on the solketal yield (other reaction conditions: 323 K, acetone to glycerol molar ratio (A/G) of 2, catalyst loading (W_{cat}) of 1 wt.% of glycerol).

increase in the mass of catalyst approximately doubled the initial reaction rate for solketal formation, suggesting that the reaction rate can be promoted by increasing the catalyst amount or number of the active sites in the reactor system, as similarly observed in the literature for the synthesis of acetal from butanol and acetaldehyde [20].

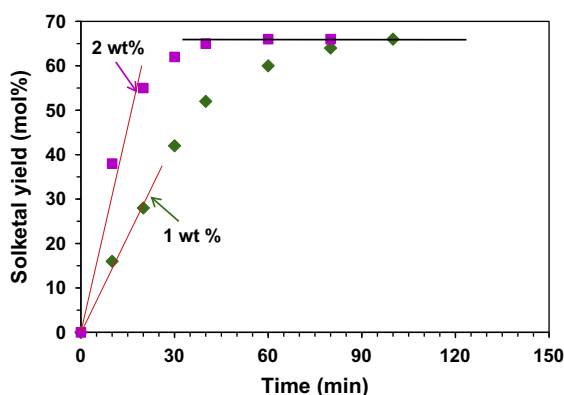


Fig. 6. Effects of the catalyst addition amount on the yield of solketal (other reaction conditions: 313 K and A/G = 2).

4.3. Effect of pressure

The effects of pressure (1–54 atm) on the reaction was tested, and it was found that pressure showed a negligible effect on either the equilibrium product yields or the reaction rate, which is expected for liquid phase reactions (Table 3: entry 13 and 14). In the present study, the reactor pressure for all reported results was fixed at 1 atm, where the maximum number of molecules in gas phase was found to be very small (2.1%) at the maximum operating temperature and the maximum acetone equivalent.

4.4. Effect of temperature

Effects of temperature on ketalization of glycerol were studied at various temperatures ranging from 298 to 323 K under the conditions of A/G = 2 and W_{cat} = 1 wt.% of glycerol, as shown in Table 3 (entry 3–7) and Fig. 7. A higher temperature led to a lower equilibrium product yield, typical of exothermic reactions, as evidenced previously by the thermodynamics results. It is also clear that the initial rate of the ketalization reaction increases with increasing the reaction temperature as expected.

4.5. Initial molar concentration of reactants

According to both reaction thermodynamics and kinetics, the initial molar concentration of a reactant would influence the equilibrium conversion and the reaction rate. In this work, we

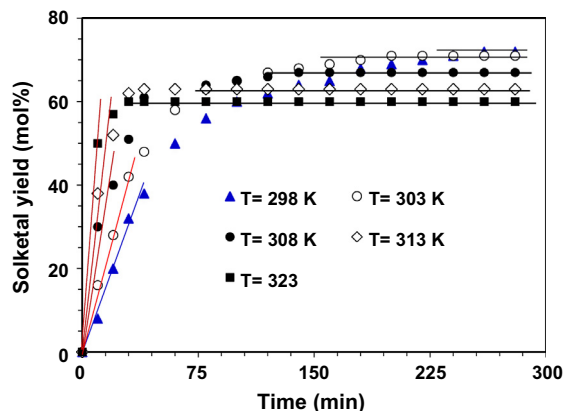


Fig. 7. Influence of temperature on the yield of solketal (other reaction conditions: A/G = 2 and W_{cat} = 1 wt.% of glycerol).

conducted the reaction at 298 K with catalyst loading amount of 1 wt.% of glycerol while varying the initial acetone-to-glycerol molar ratio from A/G = 1.48–2.46. The results are presented in Table 3 (entry 9–11) and Fig. 8. As clearly shown in the figure, the reaction thermodynamics and kinetics are strongly affected by A/G molar ratio: a higher A/G ratio led to a higher reaction rate and larger equilibrium yield of solketal. These results are actually expected, and similar observations were reported by Agirre et al. [6]. We have also examined the effect of initial ethanol concentration on the ketalization reaction at various ethanol–glycerol molar ratios, but the effect was found to be negligible due to the minimal reaction between acetone and ethanol under the present reaction conditions (reaction time, temp, amount of catalyst used, amount of glycerol and acetone used).

4.6. Moisture content

The role of water in the reaction was investigated (Table 3: entry 3 and 12, Fig. 9) by using 3.15 wt.% water in the solution for the ketalization and the yield of solketal (66%) was compared to that of without moisture experiment (72%) under similar reaction conditions (Temperature: 298 K, acetone to glycerol molar ratio (A/G) of 2, catalyst loading (W_{cat}) of 1 wt.% of glycerol). The lower yield of solketal in the later case may be attributed to the adsorption of water on the catalyst surface which inhibits the forward reaction to form solketal [25].

4.7. Kinetic model

The general reaction rate expression for the ketalization of glycerol with acetone could be expressed in the form of Langmuir–Hinshelwood model with surface reaction as the rate determining step [26–28]. The key reaction steps of this model are given as follows:

- (a) The surface reaction between the adsorbed species of glycerol (GF) and acetone (AF) to give adsorbed hemiacetal (HF)



where F is the vacant site on the catalyst.

- (b) Surface reaction for formation of adsorbed water (WF)



where IF represents for the reactive intermediate formed.

- (c) Formation of adsorbed solketal (SF)

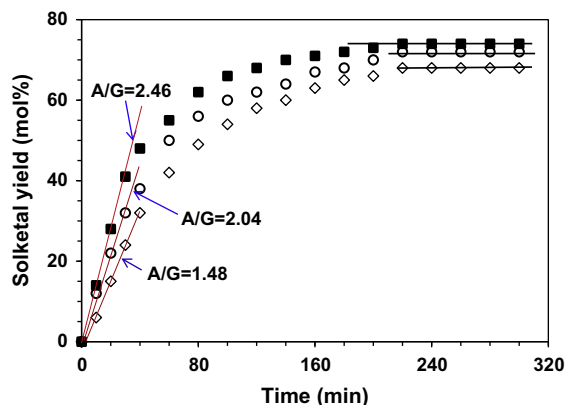
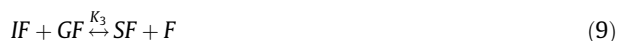


Fig. 8. Effects of initial acetone-to-glycerol (A/G) molar ratio on the yield of solketal (other reaction conditions: 298 K and W_{cat} = 1 wt.% of glycerol).

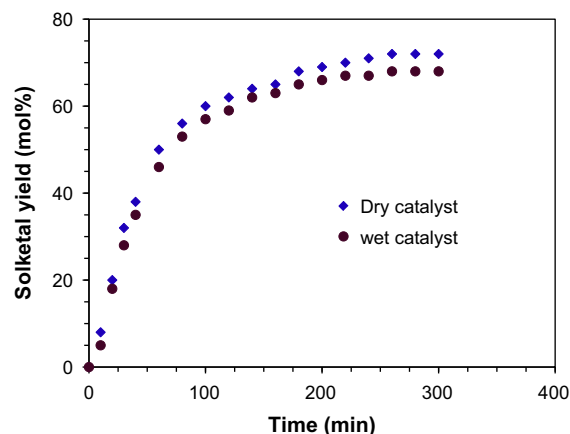


Fig. 9. Effect of moisture content on the yield (other conditions: 298 K, W_{cat} = 1 wt.% of glycerol).

where K_1 , and K_3 are the equilibrium constants in step a and c, respectively. K_2 and K_{-2} are the rate constants for forward and backward reactions, respectively in step b. As reported in the literature, the surface reaction for the formation of adsorbed water (WF) could be the rate determining step [29–31]. So the rate of the reaction (r) can be given as [20,32]

$$r = K_2[HF][F] - K_{-2}[IF][WF] \quad (10)$$

According to Langmuir adsorption isotherm, the adsorption equilibrium for the species i is given as

$$\theta_i = \frac{K_i[i]}{1 + \sum_{j=1}^N K_j[j]} \quad (11)$$

where θ_i the fraction of sites occupied by i and K is the equilibrium adsorption constant. Combining the above equations and assuming that water is the more adsorbed component on the catalyst, the rate of the reaction can be modified as [20,30,31]

$$r = k \frac{[G][A] - [S][W]/K_c[G]}{\{1 + K_w[W]\}^2} \quad (12)$$

where the parameters k , K_w and K_c are the kinetic constant of the overall ketalization reaction, the equilibrium constant for water adsorption on the catalyst surface, and the equilibrium constant for the overall ketalization reaction of glycerol and acetone (Table 2), respectively.

The mass balance in the batch reactor for solketal in the liquid phase at constant temperature can be given as [7]

$$\frac{dn_c}{dt} = W_{cat}r \quad (13)$$

where n_c is the number of moles of solketal, t is the time, W_{cat} is the mass of catalyst and r is the reaction rate with respect to the catalyst mass.

The above equation can be modified using the initial moles ($n_{i,0}$), stoichiometric coefficient of limiting reactant (ν_i) and conversion (X) as [20]

$$\frac{n_{i,0}}{W_{cat}|\nu_i|} \frac{dX}{dt} = r\{[G], [A], [S], [W]\} \quad (14)$$

The theoretical rate of the reaction (Eq. (14)) was fitted to the experimentally measured rates at different temperature and is given in Fig. 10. The values of k and K_w at different temperatures were calculated using non-linear regression method and are given in Table 4.

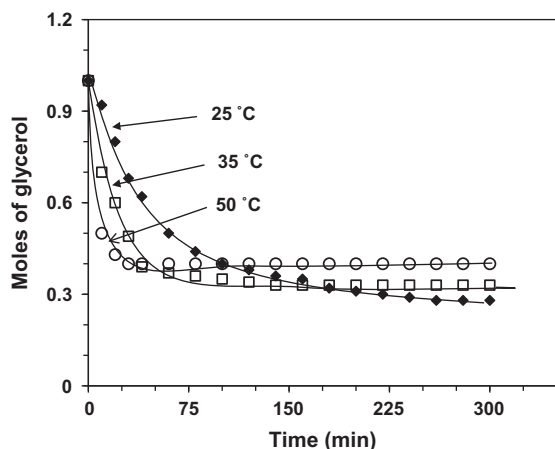


Fig. 10. Experimental and theoretical curves (Other conditions: 313 K, $W_{cat} = 1$ wt.% of glycerol).

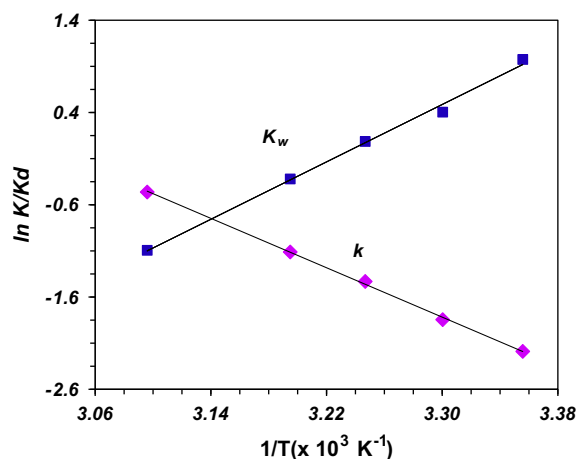


Fig. 11. Plots of kinetic modeling parameters $\ln k$ or $\ln K_d$ vs. $1/T$.

Table 4
Kinetic modeling parameters k and K_w ^a.

Temperature (K)	k (L moles ⁻¹ min ⁻¹)	K_w
298	0.112	2.650
303	0.158	1.498
308	0.239	1.090
313	0.329	0.726
323	0.630	0.335

^a k = kinetic constant; K_w = equilibrium constant for water adsorption on the catalyst surface.

The temperature dependence of k and K_w can be given by the Arrhenius equations:

$$k = k_r \exp\left(-\frac{E_a}{RT}\right) \quad (15)$$

$$K_w = K_a \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (16)$$

where k_r and K_a are the Arrhenius constants for Eqs. (15) and (16), respectively. E_a and ΔH_a are the activation energy of the overall reaction and enthalpy of the water adsorption reaction, respectively. The predicted values of k and K_w are presented as a function of temperature in plots of $\ln k$ or $\ln K_w$ vs. $1/T$ in Fig. 11. From the plots, the values of E_a and ΔH_a were determined to be 55.6 ± 3.1 and -64.7 ± 4.3 kJ mol⁻¹, respectively.

5. Conclusions

Thermodynamic and kinetic studies for the synthesis of solketal in liquid phase were carried out in a well-controlled batch reactor in the presence of an acid catalyst (Amberlyst-35). The thermodynamic equilibrium constant K_c at various temperatures ranging from 293 to 323 K was determined. The reaction is exothermic and the standard enthalpy, entropy and Gibbs free energies at 298 K were found to be -30.1 ± 1.6 kJ mol⁻¹, -0.1 ± 0.01 kJ mol⁻¹ K⁻¹ and -2.1 ± 0.1 kJ mol⁻¹, respectively. The kinetic studies of the same reaction demonstrated that the rate of the reaction increased with increasing temperature, the catalyst addition amount and acetone-to-glycerol (A/G) molar ratio. In this batch study of the liquid phase reaction, pressure showed negligible influence on the reaction thermodynamics and kinetics as expected, and no effect of the agitation speed on the reaction rate was observable at >400 rpm. Langmuir–Hinshelwood model demonstrated to be useful for describing the kinetic mechanism of the ketalization reaction of glycerol with acetone. Based on the Langmuir–Hinshelwood model, the values of the activation energy (E_a) of the overall reaction was determined to be 55.6 ± 3.1 kJ mol⁻¹.

The future study of this project includes the development of a continuous reactor for the synthesis of solketal from both pure and crude glycerol using the thermodynamic and kinetic concepts where the recycle (recovery and reuse) of unreacted reagents could be considered as an added advantage to the system.

Acknowledgements

The authors want to acknowledge the financial support provided by Imperial Oil via University Research Award and the Discovery Grant from NSERC for Dr. Xu. We are also thankful to Professors Yasuo Ohtsuka and Guus Van Rossum from Akita University (Japan) and University of Twente (the Netherlands), respectively, for their invaluable suggestions on some aspects of this research.

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