Article

Valorization of Solketal Synthesis from Sustainable Biodiesel Derived Glycerol Using Response Surface Methodology

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Abstract: Biodiesel production has gained considerable importance over the last few decades due to the increase in fossil fuel prices as well as toxic emissions of oxygen and nitrogen. The production of biodiesel via catalytic transesterification produces crude glycerol as a co-product along with biodiesel, amounting to 10% of the total biodiesel produced. Glycerol has a low value in its impure form, and the purification of glycerol requires sophisticated technologies and is an expensive process. The conversion of crude glycerol into value-added chemicals such as solketal is the best way to improve the sustainability of biodiesel synthesis using the transesterification reaction. Therefore, the conversion of crude glycerol into the solketal was investigated in a batch reactor simulation model developed by the Aspen Plus V11.0. The non-random two liquid theory (NRTL) method was used as a thermodynamic property package to study the effect of four input ketalization parameters. The model was validated with the findings of previous experimental studies of solketal synthesis using sulfuric acid as a catalyst. The influence of the following operating parameters was investigated: reaction time of 10,000 to 60,000 s, reaction temperature of 303 to 323 K, acetone to glycerol molar ratio of 2:1 to 10:1, and catalyst concentration of 0.005 to 0.03 wt %. The optimum solketal yield of 81.36% was obtained at the optimized conditions of 313 K, 9:1, 0.03 wt %, and 40,000 s. The effect of each input parameter on the ketalization process and interaction between input and output parameters was investigated by using the response surface methodology (RSM) optimizer. The relationship between independent and response variables developed by RSM fit most of the simulation data, which showed the accuracy of the model. A second-order differential equation fit the simulation data well and showed an R^2 value of 0.99. According to the findings of RSM, the influence of catalyst amount, acetone to glycerol molar ratio, and reaction time were more significant on solketal yield. The effect of temperature on the performance of the reaction was not found to be significant because of the exothermic nature of the process. The findings of this study showed that biodiesel-derived glycerol can be effectively utilized to produce solketal, which can be used for a wider range of applications such as a fuel additive. However, further work is required to enhance the solketal yield by developing new heterogeneous catalysts so that the industrial implementation of its production can be made possible.

Keywords: renewable energy; biodiesel production; solketal; optimization; simulation; modeling and kinetics

1. Introduction

The energy demand of the world is extensively increasing due to its exponential economic and population growth. Therefore, more attention has been given to implement the use of renewable energy sources such as biofuels [1,2]. Biofuels are environment friendly, biodegradable, and non-toxic in nature. Their handling and restoration is easier as compared to conventional petroleum diesel. They are widely used as airways, railways, and as heating oils in generators as well as public transport vehicles. Biofuels normally consist of biogas, biodiesel, biomethane, and biohythane [3,4]. Biodiesel is one of the cheapest energy sources that can fully replace the use of fossil fuels due to its excellent combustion and flow properties [5]. It has good lubrication properties and causes less carbon dioxide (CO_2) emissions in comparison with conventional diesel [6,7]. Biodiesel is most commonly synthesized via conventional catalytic transesterification in which triglycerides react with three moles of short-chain alcohols i.e., methanol or ethanol, resulting in the production of biodiesel and crude glycerol [8]. One complete transesterification run produces glycerol amounting to 10% of biodiesel produced in a single batch [9]. The produced glycerol from the transesterification is highly impure. It contains methanol and unreacted fatty acids as major impurities apart from the traces of calcium, magnesium, phosphorus, and sulfur [10].

Impure glycerol has very limited applications due to the deficiency of purification facilities to purify it including vacuum distillation, ion exchange, adsorption treatment with activated carbons, and membrane separation [11]. The overproduction of low-value glycerol also affects the economy of biodiesel in the market. Therefore, the conversion of crude glycerol into more value-added chemicals seems to be the best option to create a new market for glycerol and enhance the sustainability of biodiesel synthesis as well [12–14]. In this way, the demand for glycerol will be increased, minimizing the pollution caused by the crude glycerol produced from the transesterification [15,16]. Glycerol can be upgraded to oxygenated fuel additives using various processes including etherification, esterification, and ketalization [2,15]. Among the various products obtained, solketal synthesized through the ketalization process can be used as a viscosity and flash point improver in biodiesel as well as conventional fuel. The addition of solketal in gasoline causes a significant increase in cetane number. Apart from this, solketal is also used as a solvent in pharmaceutical and paint industries [17,18]. The solketal production from glycerol has been investigated in the past few years using various solid acid as well as liquid catalysts [19–21].

Marnoto et al. [22] investigated the kinetics and thermodynamics of the ketalization of glycerol using sulfuric acid as a homogenous catalyst. The reaction took place in a three-neck bottle flask equipped with a heater, temperature controller, cooler, and a magnetic stirrer. The reaction conditions were varied as the reaction time of (14,400–43,200 s) and acetone to glycerol molar ratio (2:1–7:1) at the constant boiling temperature. The highest glycerol conversion (>80%) was reported at the optimized reaction conditions of 335 K, 36,000 s, and 6.9:1 molar ratio. The change in entropy and enthalpy were found to be 280.02 J/mol. K and 95.948 J/mol, respectively. Dmitriev et al. [1] reported the synthesis of solketal using sulfuric acid as a homogeneous catalyst. The rates of the direct and reverse transformation were shown to be described by the first-order kinetics. The activation energy for the ketalization reaction was found to be 87110 J/mol. Royon et al. [23] reported the conversion of glycerol using supercritical acetone to produce solketal (4-hydroxymethyl-2,2-dimethyl-1,3–dioxolane). The experimental findings revealed a drastic change in the reaction behavior at the critical temperature of acetone (508 K). Below 508 K, the reaction rate was very low. However, the increase in temperature significantly increased the reaction rate of acetalization. Dmitrieva et al. [24] proposed various processes to covert crude glycerol into solketal. A catalytic process was recommended for selective decomposition of solketal to glycerol to obtain highly purified glycerol of the concentration up to 99.8 wt %.

Esteban et al. [25] studied the synthesis of solketal from acetone and glycerol in the absence of solvents. A heterogeneous catalytic method was used using the resin of Lewatit GF101 as a catalyst after the selection from a few other sulfonic ion exchange resins. A series of kinetic runs were conducted varying the reaction temperature (303–313 K),

acetone to glycerol molar ratio (3–12), and catalyst concentration (0.5–1.0 wt %). The activation energies for forward and reverse reaction were found as 124.0 ± 12.9 kJ/mol and 127.3 ± 12.6 kJ/mol, respectively. Rossa et al. [26] used zeolite HBEA (SAR-19) as a catalyst to investigate the solketal synthesis via the fractional experimental design method. The conversion and kinetic parameters were determined varying the temperature in the range of 303–353 K giving the forward and reverse reaction activation energy of 44.77 kJ/mol and 41.40 kJ/mol, respectively. The glycerol conversion in the range of 70−76% was obtained using the same catalyst for five reactions without pre-and post-treatment.

The optimization study using tools such as response surface methodology optimizer helps to investigate the influence of every reaction parameter on the reaction output variable. Few optimization studies have been conducted for experimental findings of the ketalization process. Mortaza et al. [27] investigated the interaction of input and output ketalization parameters using RSM. The R^2 value for the predicted and actual solketal yield was determined to be 0.99, which showed the significant model fitness. Shirani et al. [28] investigated the synthesis of solketal using purolite (RD206) as a heterogeneous acid catalyst and optimized its yield. The predicted yield for the chosen model for this study was found to be 100%, whereas the experimental yield was found to be 95%. The reported literature indicates that solketal synthesis has been widely discussed in the past under the influence of various solvents. However, the experimental investigation offers a lower range of operating parameters to study and optimize the ketalization process as presented in the discussed literature.

Moreover, not much attention has been given to the simulation-based study of the ketalization process to maximize the solketal yield. In addition, only a narrow range of parameters affecting the solketal yield has been considered for the experimental investigations. However, a broad of range of the operating parameters are needed to be investigated to obtain higher solketal yield. Therefore, this study focused on the synthesis of solketal from crude glycerol using Aspen plus simulator, which shows the significance of the present study. The simulation model was validated, and findings were compared with the previous experimental studies available on solketal synthesis. To the best of our knowledge, the ketalization process has not been optimized by using statistical and mathematical tools for the simulation study of ketalization parameters. In this study, the interaction of input and output parameters was also studied and optimized using a response surface methodology optimizer. The optimization is necessary to investigate the effect of each input parameter to find the most significant parameters that can lead to a higher solketal yield. It is hypothesized that solketal synthesis from crude glycerol can help to minimize the pollution caused by crude glycerol as well as can produce 99.9% pure solketal, which can be effectively used as a fuel additive in addition to other useful laboratory purposes. The findings of the present ketalization study were found to be significantly compared with the published literature.

2. Materials and Methods

2.1. Simulation Study of Solketal Synthesis on Aspen Plus

The simulation study of solketal synthesis using crude glycerol produced from the transesterification reaction along with the biodiesel was done using Aspen Plus process simulator V11.0. The ketalization reaction for the reaction between glycerol and acetone is expressed in Figure 1.
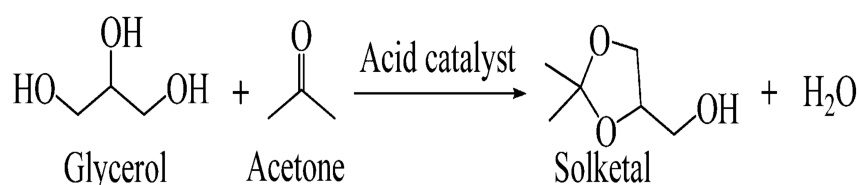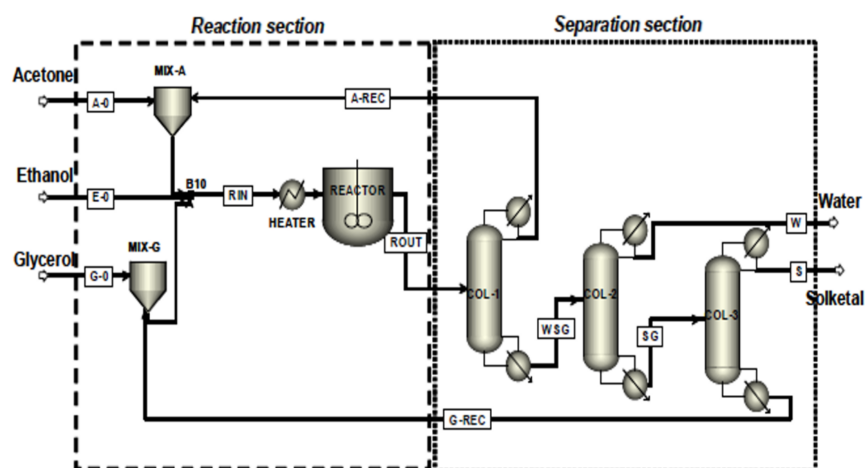

Figure 1. Ketalization of glycerol for solketal production.

Figure 1 shows that one mole of glycerol reacts with one mole of acetone to produce one mole of solketal and water. The industrial catalyzation process involves a series of unit operations including mixers, reactor, separators, and distillation columns [29], as presented in Figure 2.

Figure 2. Synthesis of solketal via industrial ketalization process. Reproduced with the permission from [30], Springer, 2015.

The industrial process involves a large number of unit operations, which increases the overall cost of the production of solketal. In this study, a simple batch reactor model was developed and simulated to maximize the overall solketal yield from the ketalization process. Five components were added to the Aspen Plus components list. Acetone and glycerol were introduced as the reactants, while solketal and water were formed. Sulfuric acid was introduced as a homogeneous catalyst. For trial simulation, the input data such as rate constant and activation energy values were taken from the previous studies. The input data taken from the literature are presented in Table 1. The purpose of each component and its formula is given in Table 2.

In the process, glycerol, acetone (solvent), and H_2SO_4 (catalyst) were mixed in the mixer to ensure the homogeneity of the reaction mixture. It is assumed that there is no pressure drop across the mixer. The mixed reactants were introduced into the heater to increase the temperature of the mixture before introducing into the batch reactor. The operating temperature of the batch reactor was kept at 303 K. It is also necessary to increase the temperature of the reactants in the inlet stream to the reactor to 303 K from 298 K. The following reaction parameters were varied: acetone to glycerol molar ratio (2 to 10), reaction temperature (303–323 K), catalyst concentration (0.005–0.03 wt %), and reaction time (10,000–60,000 s). The reaction parameters affecting the solketal yield were also optimized. The best operating parameters were found, giving maximum solketal yield. The batch feed and discharge time is set at 1 s because the inlet specifications are in terms of flow rates per second. The valid phases in the reactor were liquid and biphasic for an acetone to glycerol molar ratio less than 5. However, for a higher molar ratio, it is liquid only, because the reaction is homogeneous in nature and operating at a temperature lower than the boiling point of the reactants. The Aspen Plus process flow diagram developed for ketalization reaction is shown in Figure 3.

Table 1. Referenced input parameters for Aspen Plus simulation taken from the literature.

Parameter	Value
Temperature (K)	303
Pressure (atm)	1
Time (sec)	60,000
Glycerol: Acetone molar ratio	1:5
Catalyst weight (g)	0.0126
Activation energy for forward reaction (kJ/mol)	87,110
Rate constant for forward reaction ($L^{2/}$ mol^2.s)	0.0411
Activation energy for reverse reaction (kJ/mol)	101,670
Rate constant for reverse reaction (L^2/mol^2.s)	0.053

Table 2. Components list for simulation on Aspen Plus simulator.

Component	Formula	Purpose in the Process
Acetone	C_3H_6O	Solvent
Glycerol	$C_3H_8O_3$	Reactant
Water	H_2O	Co-product
Solketal	$C_6H_{12}O_3$	Main product
Sulfuric acid	H_2SO_4	Catalyst
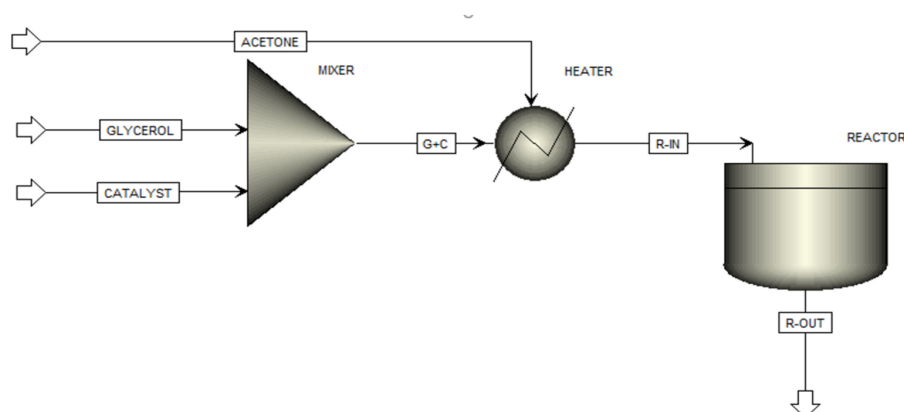
Figure 3. The simulation model developed for the ketalization of glycerol.

2.2. Optimization of Solketal Yield Using Response Surface Methodology (RSM)

Central composite design (CCD) and response surface methodology (RSM) optimizer was used to design and optimize the operating parameters of solketal synthesis [31]. This was done using design expert (V12.0) software. The effect of the acetone to glycerol molar ratio, catalyst loading, reaction time, and reaction temperature was studied on solketal yield. The solketal yield was the target response (output) variable. The model correlations were obtained for all significant input variables to optimize their values. The relation between input and output variables by coded and uncoded model equation was obtained. The effect of each input parameter alone was investigated on solketal yield using one factor at a time (OFAT), because the investigation of solketal yield by varying the two input parameters at a time is not a good decision for experimental and simulation studies, as it increases the overall number of runs. Therefore, the method is used due to the limited number of simulation runs. Different model equations were fitted for the simulation study

of solketal synthesis to minimize the error such as first-order, second-order, and third-order polynomials [32]. Thus, complying with an empirical model that presents the relation between responses determined under the influence of input parameters of the simulation, as shown in Equation (1) [33].

$$Y = \beta_o + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} X_i X_j + \sum_{i=1}^{4} \beta_{iii} X_i^3 \tag{1}$$

where Y expresses the solketal yield, β_o is the intercept, β_i is the linear coefficient, β_{ii} is the the squared effect, β_{ij} is the interaction parameter, X_i is the ith independent parameter, and X_j is the jth independent parameter. This equation was fitted for the Aspen Plus simulation model developed to carry out the ketalization process. The number of simulation runs were calculated using the CCD design and were found to be 41. The input parameters range and values for the simulation runs are shown in Tables 3 and 4, respectively.

Table 3. Input parameters and their ranges of the investigation.

	Parameter	Minimum	Maximum
A	Temperature (K)	303.0	333.0
B	Acetone to glycerol molar ratio	1.0	10.0
C	Catalyst loading (wt %)	0.005	0.03
D	Reaction time (sec)	10,000.0	60,000.0

Table 4. Input parameter values for each simulation run using CCD design.

Run	Factor 1 Temperature (K)	Factor 2 Glycerol/Acetone Molar Ratio	Factor 3 Catalyst Loading (wt %)	Factor 4 Time (sec)
1	309.15	1	0.03	60,000
2	317.25	10	0.0195	39,255.5
3	303.0	7.75	0.01175	60,000
4	316.95	4.67	0.02	10,000
5	333	10	0.005	60,000
6	316.89	4.42	0.005	41,000
7	317.25	10	0.0195	39,225.9
8	303	1	0.011	60,000
9	303	1	0.011	22,750
10	316.89	4.42	0.005	41,000
11	333	10	0.03	10,000
12	305.1	1.18	0.03	23,500
13	303	10	0.005	10,000
14	332.25	1	0.0125	60,000
15	333	6.76	0.01375	27,979.6
16	331.35	1	0.03	24,750
17	333	1	0.005	10,000
18	333	6.76	0.01375	27,979.6
19	330.9	7.43	0.03	60,000
20	303	7.75	0.003	23,500

Table 4. *Cont.*

| Run	Factor 1 Temperature (K)	Factor 2 Glycerol/Acetone Molar ratio	Factor 3 Catalyst Loading (wt %)	Factor 4 Time (sec)
21	320.7	3.97	0.02175	44,000
22	316.95	4.67	0.02	10,000
23	318.6	10	0.005	28,223.6
24	318	5.5	0.0175	35,000
25	318	5.5	0.0175	35,000
26	318	5.5	0.0175	35,000
27	325.95	1	0.01212	32,500
28	325.95	1	0.01212	32,500
29	318	5.5	0.0175	35,000
30	303	10	0.03	60,000
31	333	10	0.025	37,250
32	318.6	10	0.005	28,223.6
33	318	5.5	0.0175	35,000
34	318	5.5	0.0175	35,000
35	321.3	5.45	0.005	10,501.8
36	333	5.095	0.025	10,000
37	320.55	7.3	0.01212	60,000
38	303.0	6.47	0.01016	30,052.4
39	313.95	6.085	0.03	60,000
40	333	5.095	0.005	50,705.3
41	303	3.88	0.02187	44,250

3. Results and Discussions

3.1. Simulation Study of Solketal Synthesis

3.1.1. Effect of Acetone to Glycerol Molar Ratio on Solketal Yield

The acetone to glycerol molar ratio plays a significant role in the ketalization process. The ketalization reaction of glycerol and acetone is reversible in nature [34]. Therefore, the acetone to glycerol molar ratio is the important input parameter that can help shift the reaction toward the product side as guided by Le chatelier's principle. A higher acetone to glycerol molar ratio causes a significant enhancement in the yield of solketal [35]. To study the influence on solketal yield, the acetone to glycerol molar ratio was varied between 2 and 10 to achieve the maximum solketal yield. Figure 4 presents that the solketal yield increased as the ketalization reaction was taken place at the higher acetone to glycerol molar ratios.

This occurred due to the better agitation of reactants and catalyst at the enhanced acetone to glycerol molar ratios. The viscosity of the reaction mixture decreases and the rate of mass transfer increases, causing a significant increase in the reaction rate, which eventually resulted in enhanced solketal yield. The increase in solketal yield was observed until the acetone to glycerol molar ratio of 9. The maximum solketal yield of 78.10% was achieved at the optimized conditions of acetone to glycerol molar ratio of 9, the reaction time of 40,000 s, catalyst concentration of 0.03 wt %, and reaction temperature of 313 K. The increase in the acetone to glycerol molar ratio beyond 9 did not cause any improvement in solketal yield. In fact, the decrease in solketal yield was observed beyond the acetone to glycerol molar ratio of 9. This might occur due to the establishment of equilibrium of the ketalization process. Moreover, an extensive increase in the acetone to glycerol molar ratio caused the active sites on the catalyst surface to decrease due to their blockage with acetone on the surface of the catalyst, increasing the total volume of the reaction mixture [36,37]. In addition, a higher acetone to glycerol molar ratio increases the acetone concentration in the reaction mixture, resulting in difficult product separation. However, an increase in solketal yield was only observed until the acetone to glycerol molar ratio of 9.
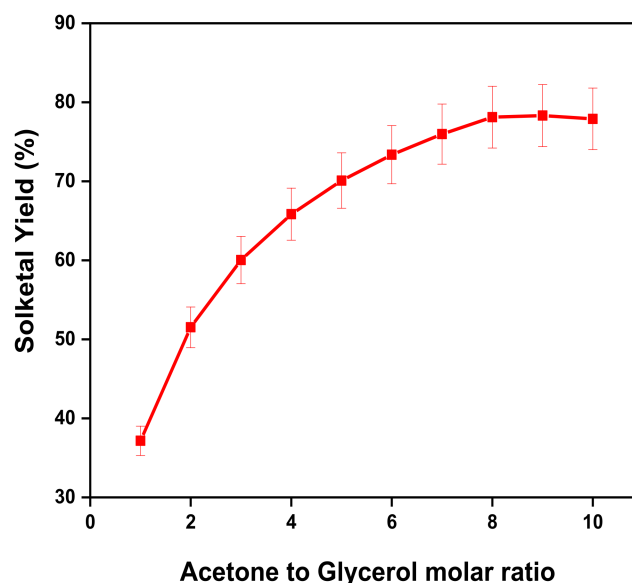
Figure 4. Influence of acetone to glycerol molar ratio on solketal yield.

Marnoto et al. [22] investigated the conversion of pure glycerol into solketal by varying the reaction conditions such as the reaction time (14,400–43,200 s) and acetone to glycerol molar ratio (2:1–7:1) at the constant boiling temperature. The highest glycerol conversion of 75% was found at the optimized reaction conditions of 335 K, 36,000 s, and 6.9:1 acetone to glycerol molar ratio. In another study, Silva et al. [37] investigated the conversion of glycerol into solketal by using tin silicotungstate catalyst. The maximum glycerol conversion of 99% was achieved at the glycerol to acetone molar ratio of 16:1, keeping the other parameters as the reaction temperature of 120 min and reaction temperature of 298 K. Although the overall conversion was higher in this study, the glycerol to acetone was also kept higher. This leads to a higher cost of the reactants. On the other hand, the present simulation study of ketalization of glycerol showed higher solketal yield as compared to the previous study. This shows the use of sulfuric acid to obtain higher solketal yields. In addition, from an economic point of view, the large increase in acetone to glycerol molar ratio would only increase the cost of product separation from the unreacted reactants such as removal of an excessive quantity of acetone. Therefore, the acetone to glycerol molar ratio of 9 is the best decision to achieve maximum solketal yield using sulfuric acid for the conversion of crude glycerol.

3.1.2. Influence of Reaction Temperature on Solketal Yield

The reaction temperature is considered as one of the most significant input parameters that can influence the solketal yield during the ketalization process of glycerol. The production of solketal reaction is exothermic in nature due to which the reaction takes place at low temperatures (303–313 K) [38]. The increase in temperature from 25 to 40 °C can cause the solketal yield to increase because of the reaction directed toward the products side. This is due to the increase in solubility of acetone in glycerol at elevated temperatures typically up to 313 K [14]. In this study, the ketalization temperature effect on solketal yield was investigated between 313 and 323 K, keeping all other operating parameters at constant values. The influence of reaction temperature on solketal yield is presented in Figure 5.
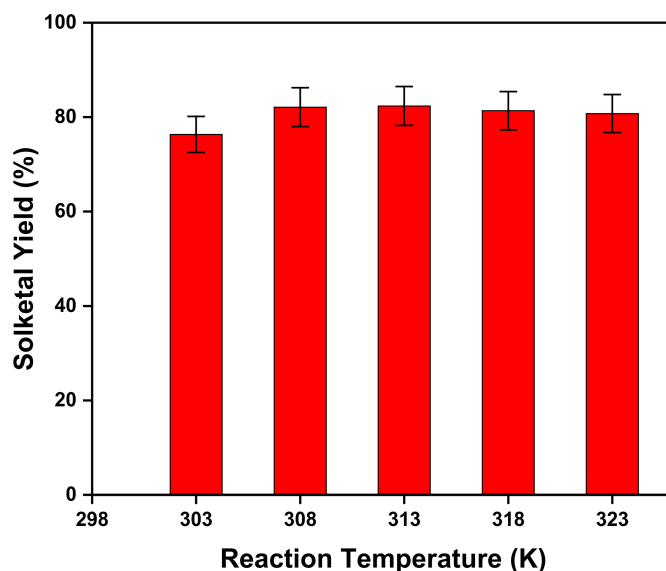
Figure 5. Influence of reaction temperature on the ketalization reaction of glycerol.

It can be seen from Figure 5 that the solketal yield at 303 K was found to be 76.33%. A notable increase in solketal yield was observed at 313 K (82.33%). The increase in reaction temperature beyond 313 K decreased the solketal yield. This occurred due to the low boiling point of acetone [24,39]. The increased reaction temperature decreases the concentration of acetone due to the evaporation of acetone in the reaction mixture due to the extensive evaporation of acetone taking place at elevated temperatures, which in turn decreases the solketal yield [40]. The significant difference in formation energy of the compound, which is strongly influenced by the reaction temperature, also affected the solketal yield [41]. Goncalves et al. [3] produced the solketal using crude glycerol in the presence of acidic carbon-based catalyst. The catalyst has consisted of glycerin and sulfuric acid. The acidity of the catalyst was increased by increasing the concentration of sulfuric acid from 2:1 to 3:1. A maximum solketal yield of 80% was obtained using an acidic catalyst. Nanda et al. [42] investigated the production of solketal using the flow reactor in the presence of Amberlyst-36 as a heterogeneous catalyst. The maximum solketal yield of 94% was achieved at the optimum conditions of acetone to glycerol molar ratio of 4 and reaction temperature of 298 K. In comparison, the present study showed a higher solketal yield by using sulfuric acid, which is far cheaper than heterogeneous acidic catalysts consisting of sulfuric acid and glycerol. From the findings of this study, it can be concluded that the room temperature is the most appropriate reaction temperature for the synthesis of solketal, because the extensive temperature increase will only increase the overall cost of production without enhancing the performance of ketalization process.

3.1.3. Effect of Catalyst Loading on Solketal Concentration

The purpose of adding a catalyst in the ketalization process is to maximize the solketal yield with the minimum associated reaction time. Overall, the increase in catalyst loading increases the number of active sites, causing a significant increase in the catalyst activity and resulting in a higher solketal yield [17,43]. The concentration of H_2SO_4 was varied in the range of 0.005 to 0.040 wt %. The effect of catalyst loading on solketal yield is presented in Figure 6.
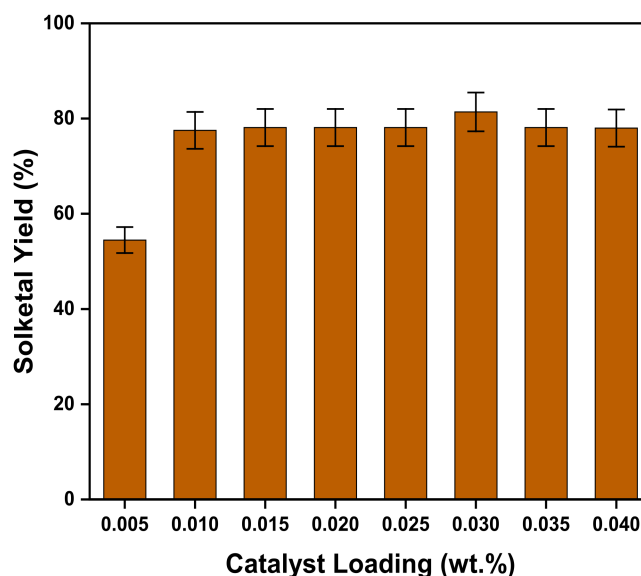
Figure 6. Influence of catalyst loading on solketal yield.

As expected, the conversion of glycerol was significantly increased with the increase in catalyst concentration. The higher catalyst active sites provide sufficient active surface area to the reactants, including glycerol and acetone, to react in maximum proportion, and this eventually resulted in the enhanced solketal yields. For instance, the solketal yield of 54.47% was observed at the catalyst loading of 0.005 wt %. However, it was increased to 81.38% as the catalyst concentration was increased from 0.005 to 0.03 wt %. However, a further increase in the glycerol conversion was not observed. In fact, the increase in catalyst amount decreased the solketal concentration [11,44]. This might happen due to the increased viscosity of the reaction mixture that decreased the rate of agitation of reactants, catalyst, and products [45]. This causes the reaction to slow down. In addition, the catalyst concentration beyond 0.03 wt % caused the reaction mixture to contaminate, which requires a significant amount of energy to separate the catalyst. The removal of an extra amount of catalyst is not easy and results in the lower recovery of pure solketal, which also leads to lesser solketal yields.

Therefore, the concentration of catalyst is not kept higher than 0.03 wt %, as it makes the process expensive and results in the decrease in performance of the ketalization process. Vannucci et al. [46] investigated the production of solketal by using an acidic catalyst consisting of zirconium oxide and H_2SO_4. The optimum solketal yield of 80% was observed at the acetalization conditions of reaction temperature of 40 °C, acetone to glycerol molar ratio of 6, and S/Zr catalyst ratio of 0.2. Li et al. [47] produced the solketal by using Zr-MO-KIT-6 as a catalyst and obtained the overall solketal yield of 85% at the overall reaction temperature of 50 °C, the reaction time of 2 h, and an acetone to glycerol molar ratio of 2. However, a relatively higher solketal yield was obtained in this study. However, the operating conditions were also kept higher, which did not cause much increase in the solketal yield. The solketal yield in the present study utilizing the homogeneous catalyst gave higher solketal yield (81.38%) as compared to the studies of ketalization processes conducted by Vannucci et al. and Li et al. Therefore, the findings of the present study showed the great potential of crude glycerol to be used for solketal synthesis.

3.1.4. Reaction Time Effect on Ketalization Process

The ketalization reaction time plays a very significant role to maximize the conversion of glycerol. When the ketalization reaction starts, glycerol and solvent (acetone) are not completely miscible, and hence, the reaction is slower in nature [26]. However, the solubility of glycerol and acetone increases with the increase in the reaction time that leads to an

increase in the overall yield of solketal. The same findings were observed in the study with the time variance between 10,000 and 60,000 s. The influence of reaction time on solketal yield is presented in Figure 7.
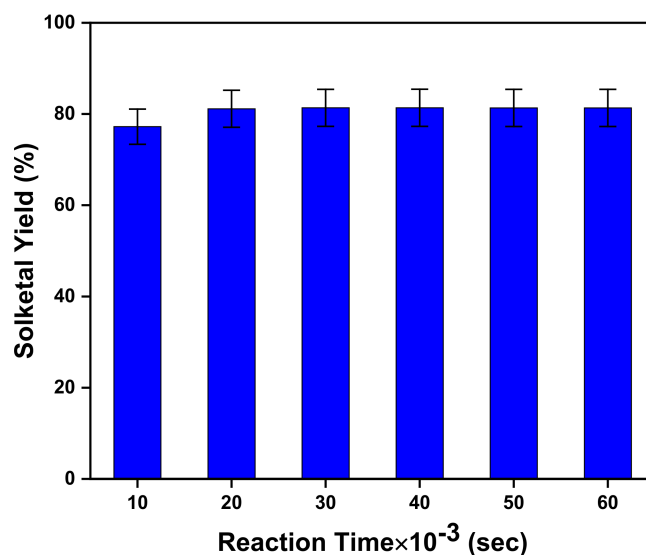

Figure 7. Effect of reaction time on solketal yield.

The increase in solketal yield was observed with the increase in the reaction time, as shown in Figure 7. The reaction rate started increasing after the start of the reaction due to an increased solubility of reactants, which also caused the increase in concentration of solketal in the reaction mixture. The optimum solketal yield of 81.36% was achieved with the ketalization time of 40,000 s. The further increase in reaction time did not increase the concentration of solketal. This might occur due to the equilibrium establishment between reactants and products. At that time, the input energy was occupied by the reactants to achieve the equilibrium of ketalization giving maximum reaction performance. The decrease in glycerol conversion was observed after 40,000 s. This might be explained by the fact that a further increase in reaction time has caused the hydrolysis of the reactants and products, resulting in the overall decreasing concentration of solketal in the reaction mixture [48]. In addition, the products started converting back into the reactants after the equilibrium, resulting in the decrease in solketal yield.

Marnoto et al. [22] observed the influence of reaction time on the solketal yield. The reaction conditions were varied, such as the reaction time (14,400–43,200 s) and acetone to glycerol molar ratio (2:1–7:1), at the constant boiling temperature. The highest glycerol conversion (75%) was reported at the optimized reaction conditions of 335 K, 36,000 s, and 6.9:1 molar ratio. Roldan et al. [49] reported the production of solketal using montmorillonite clay as a heterogeneous catalyst. The maximum solketal yield of 82% was obtained at an acetone to glycerol molar ratio of 20:1 and reaction time of 2 h. In comparison to the previous studies, the present study showed a comparable solketal yield at the lower operating conditions, which shows the significance of the present study. Therefore, the use of crude glycerol for the production of fuel additive solketal in the present study proved to be the prominent way of reducing the pollution.

3.2. Optimization of Solketal Synthesis Using Response Surface Methodology

The response surface methodology results showed that glycerol acetalization for solketal production could be presented by a quadratic polynomial model. The general equation of the model also includes the cubic and even higher order terms. However, such terms were not included due to their non-significant interaction. Moreover, the presence of cubic and higher-order terms decreased the confidence level and hence were eliminated.

The appropriate model fitted for solketal yield based on coded factors is presented in Equation (2).

$$\text{Solketal Yield} = 78.68 + 1.94A + 15.93B + 8.83C + 6.38D + 4.11AB - 6.89A - 5.26AD + 7.85BC + 8.32BD - 8.02CD - 17.19A^2 - 17.19B^2 - 101.2C^2 \tag{2}$$

The developed model equation for the optimization using response surface methodology exhibited a minimum error between the actual and predicted solketal yield. In Equation (2), *A, B, C,* and *D* are the input variables indicating reaction temperature, acetone to glycerol molar ratio, catalyst loading, and reaction time, respectively. There were 41 simulation runs conducted to optimize the ketalization process. The predicted and actual yield for each run is shown in Table 5.

Table 5 shows that analysis of variance (ANOVA) showed the confidence level of 99.5% for predicted and actual simulation yield. This shows the significance of the chosen model. The significant effect of each operating variable was evaluated by the F-test and p-value. The lower value of p and greater value of F exhibits the suitability of the correspondence model. Tables 6 and 7 indicate the sequential model and ANOVA results found in the present simulation study.

Table 5. Predicted and actual solketal yield for each simulation run.

Run	Actual Yield (%)	Predicted Yield (%)
1	41.74	38.80
2	84.49	84.53
3	81.34	81.04
4	72.87	72.16
5	81.39	81.73
6	64.24	63.68
7	84.49	84.53
8	42.76	44.92
9	38.66	35.53
10	64.24	63.68
11	81.39	81.42
12	46.41	50.45
13	8.14	9.40
14	37.34	37.07
15	75.40	75.16
16	37.50	36.00
17	36.83	38.06
18	75.40	75.16
19	77.42	78.42
20	84.16	82.64
21	68.83	72.32
22	72.87	72.16
23	51.85	51.85
24	78.68	78.68
25	78.68	78.68
26	78.68	78.68
27	45.34	45.34
28	45.34	45.34
29	78.68	78.68
30	96.44	96.44

Table 5. *Cont.*

Run	Actual Yield (%)	Predicted Yield (%)
31	83.75	83.75
32	51.85	51.85
33	78.68	78.68
34	78.68	78.68
35	52.02	52.02
36	74.63	74.63
37	88.97	88.97
38	56.33	56.33
39	85.42	85.42
40	70.20	70.20
41	69.98	69.98

Table 6. The sequential model sum for solketal synthesis using crude glycerol.

Source	Sum of Squares	df	Mean Square	F-Value	*p*-Value	
Mean vs. total	1.78×10^5	1	1.78×10^5			
Block vs. mean	830.11	1	830.11			
Linear vs. block	7143.22	4	1785.81	8.91	<0.001	
2FI vs. linear	3832.58	6	637.25	5.78	0.0005	
Quadratic vs. 2FI	3132.58	4	783.15	312.58	<0.001	Suggested
Residual	4.00×10^{-8}	11	3.64×10^{-9}			
Total	1.93×10^5	41	4708.91			

It can be seen from Table 6 that the F and *p* values have been found as 312.58 and <0.0001 for the appropriate reduced quadratic fit for the simulation model of the ketalization process. In addition, each input parameter's p-value was <0.0001, which is less than 0.05 (criterion for significance). Some of the interaction and higher-order parameters such as D^2, *ABC*, *ACD*, and *BCD* decreased the value of adjusted R^2, showing the inaccuracy of the model. Therefore, such terms were not included to get higher accuracy. Table 8 shows the comparison of different models and their accuracies tested in the optimization study.

The comparison of accuracy of the chosen regression models presented in Table 8 proved the suitability of the quadratic model with a confidence level of 99.3%. The lack of fit F and p values for the model were observed to be 3.42 and 0.054 (not significant), as shown in Table 7. For a significant model, F values should be lower, and the p-value should be greater than 0.05 according to the statistical analysis rules. The same observation was reported in this study. Therefore, the model has fit the maximum simulation runs for the ketalization of glycerol with 0.7% inaccuracy. The value of R^2 is determined to check the reliability and accuracy of the fitted model. A graphical representation of the predicted and simulated yield of solketal yield is presented in Figure 8, which exhibited a high correlation and reasonable agreement between predicted and actual results. The good estimation of solketal yield from the chosen model has represented a good similarity between actual and predicted simulation results.

Table 7. ANOVA optimization for the acetalization of glycerol for solketal yield.

Source	Sum of Squares	df	Mean Square	F-Value	p-Value	
Block	830.11	1	830.11			
Model	1499.32	14	1007.09	401.98	<0.0001	Significant
A—Reaction Temperature	67.23	1	67.23	26.83	<0.0001	
B—Glycerine to Acetone molar ratio	4407.64	1	4407.64	1759.28	<0.0001	
C—Catalyst Loading	1385.84	1	1385.84	553.15	<0.0001	
D—Reaction Time	637.16	1	637.16	254.32	<0.0001	
AB	177.22	1	177.22	70.74	<0.0001	
AC	439.84	1	439.84	175.56	<0.0001	
AD	257.38	1	257.38	102.73	<0.0001	
BC	590.59	1	590.59	235.73	<0.0001	
BD	567.14	1	567.14	226.37	<0.0001	
CD	557.99	1	557.99	222.72	<0.0001	
A^2	266.03	1	266.03	106.18	<0.0001	
B^2	1516.79	1	1516.79	605.42	<0.0001	
C^2	178.56	1	178.56	71.27	<0.0001	
Residual	62.63	25	2.51			
Lack of fit	62.63	14	4.47	3.42	0.054	Non-significant
Pure error	4.00×10^{-8}	11	3.64×10^{-9}			
Cor total	14,992.07	40				

Table 8. Comparison of accuracy of chosen regression models.

Source	Sequential p-Value	Lack of Fit p-Value	Adjusted R^2	Predicted R^2
Linear	<0.0001	<0.0001	0.4478	0.2312
2FI	0.0005	<0.0001	0.6966	0.3374
Quadratic (Suggested)	<0.0001	<0.0001	0.993	0.9772
Cubic	<0.0001		1.00	

From Figure 8, the predicted and actual solketal yield shows the confidence level of 99.5%, proving the significance of the model. Residuals plots present the level of deviation between predicted and actual values. If the simulation values errors are random, residuals follow a random distribution. Therefore, it is important to analyze the residuals whether they are randomly distributed or not before explaining the interaction of parameters. Therefore, the residuals were normalized and divided with an estimate of standard deviation and presented as studentized residuals, as shown in Figure 9.
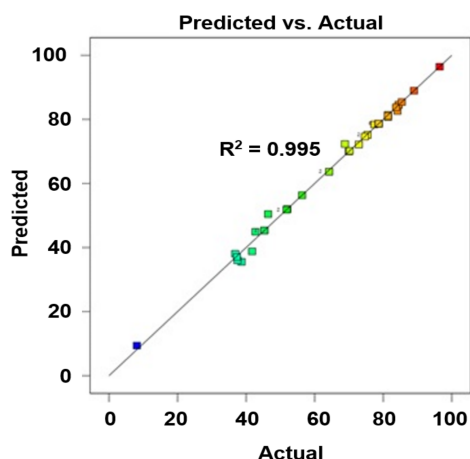
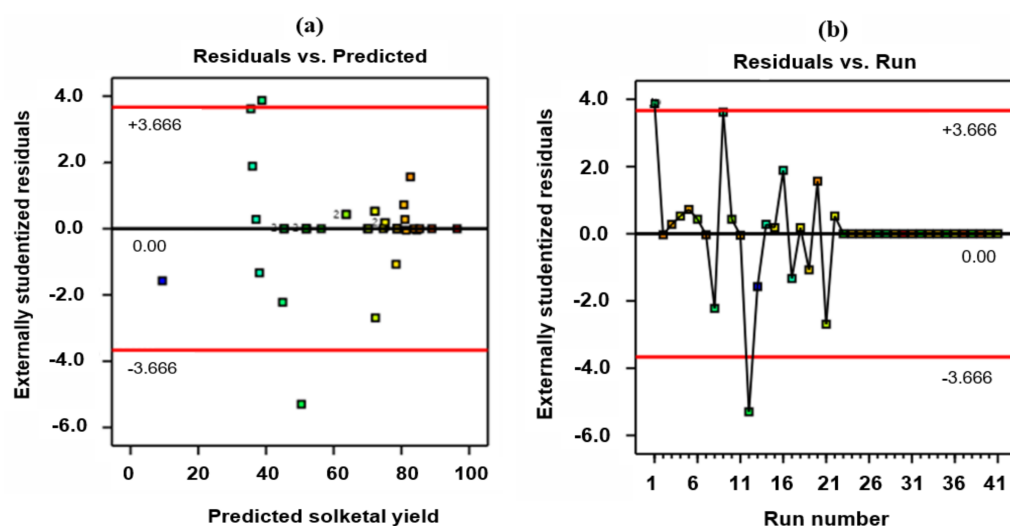**Figure 8.** Predicted versus actual solketal yield.

Figure 9. Residual plots: (**a**) plot of the standardized residuals vs. predicted solketal yield, (**b**) outlier t plot.

It can be seen from Figure 9a that the data points are randomly scattered in the plot. This shows that original observations are not related to adequate response values. This proves that the chosen regression model presents an adequate description of the ketalization of glycerol to produce solketal. Figure 9b shows the outlier t plot for all the simulation runs. It can be noted that outlier t shows the extent to which simulation values can deviate from the predicted values. It can be seen from Figure 9b that most of the Studentized residual values lie within the range of $\pm$ 3.666 interval. Only runs 2 and 12 do not lie within the range. This confirms the good approximation of the fitted model to the response surface.

3.2.1. Influence of Various Reaction Parameters on Solketal Yield

Three-dimensional (3D) surface plots obtained for solketal yield at the center point of CCD are shown in Figure 10a–c. Figure 10a expresses the influence of reaction temperature and glycerol to acetone molar ratio on solketal yield at the catalyst loading of 0.03 wt % and the reaction time of 40,000 s. The increase in acetone to glycerol molar ratio and ketalization reaction temperature increased the solketal concentration. The findings reported in this study indicated that the highest conversion of glycerol can be obtained at the optimized conditions of reaction temperature and acetone to glycerol molar ratio. However, the

increase in solketal yield was observed until the specified acetone to glycerol molar ratio and reaction temperature. The higher acetone to glycerol molar ratio leads to a decrease in the glycerol conversion, making the product separation difficult. Therefore, the optimum solketal yield was observed at the moderate values of acetone to glycerol molar ratio (9) and reaction temperature of (313 K).
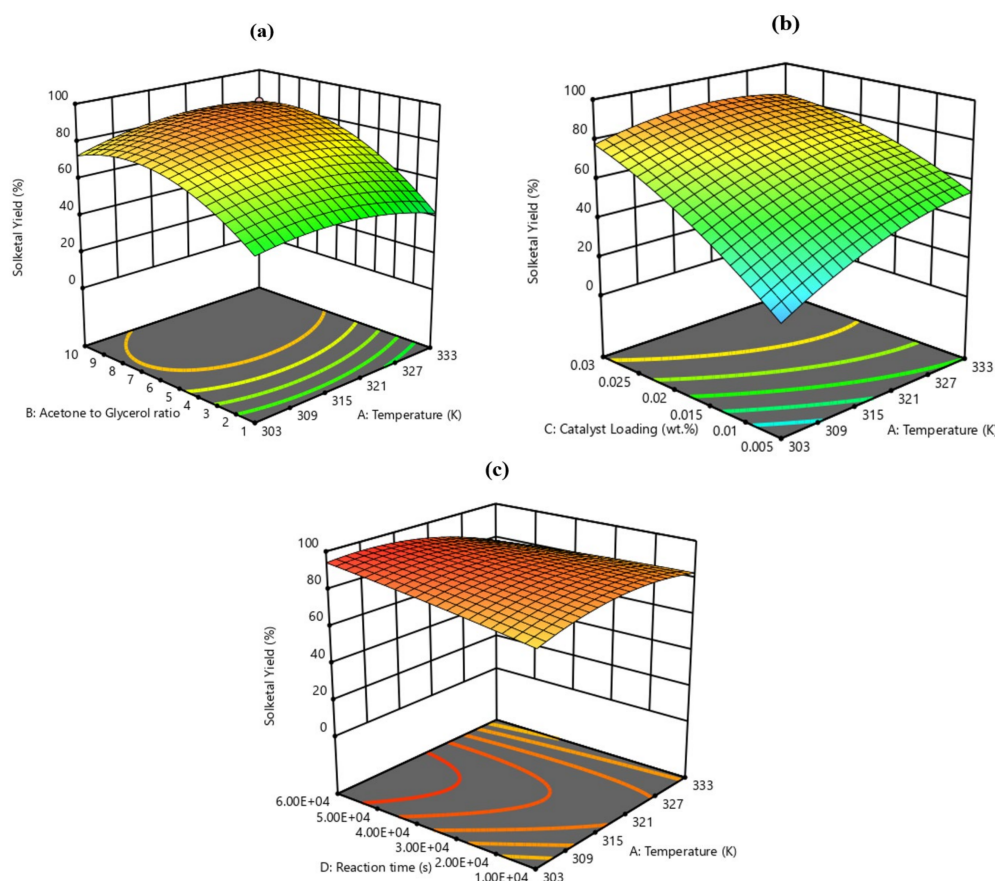

Figure 10. Surface plots for solketal synthesis for the interaction of reaction temperature with (**a**) acetone to glycerol molar ratio (**b**) catalyst loading (**c**) reaction time.

In Figure 10b, 3D plots for the ketalization of crude glycerol under the combined influence of reaction temperature and catalyst concentration are shown, keeping the constant values of reaction time (40,000 s) and acetone to glycerol molar ratio of 9:1. The rate of ketalization of glycerol was slowly influenced by an increase in reaction temperature at the specified amount of H_2SO_4. At the lower temperature, the increasing amount of catalyst concentration would lead to enhancing the synthesis of solketal. Figure 10c expresses the influence of ketalization temperature and time on solketal yield at the catalyst loading of 0.04 wt % and acetone to glycerol molar ratio of 9. At the lower reaction temperature, a significant improvement in solketal yield was noticed at a higher ketalization time. Therefore, a lower reaction temperature (313 K) was more favourable at the optimized reaction time of 40,000 s.

3.2.2. Influence of Interaction Parameters on Solketal Yield

Due to the notable effect of interaction of parameters on solketal yield, the investigation of the influence of a single input variable is not an appropriate way. Therefore, the influence of interaction of operating parameters was reported using statistical approaches. The dependence of solketal yield upon the variance of reaction temperature, time, glycerol to acetone molar ratio, and catalyst loading is presented in Figure 11a–c. Each 3D plot showed

the influence of the interaction of two input parameters keeping the third parameter at a constant value. Three-dimensional (3D) plots showed that the effect of the interaction of all input parameters was considerable on the performance of acetalization of glycerol. However, the effect of reaction temperature was not significant as compared to other input parameters. It was also observed from the interaction effect of variables, increase in reaction temperature (>30 °C), acetone to glycerol molar ratio (>3), catalyst loading (>0.004 wt %), and reaction time (>10,000 s) considerably increased the solketal yield (>75%). The optimum solketal yield was reported at the moderate values of all input variables.
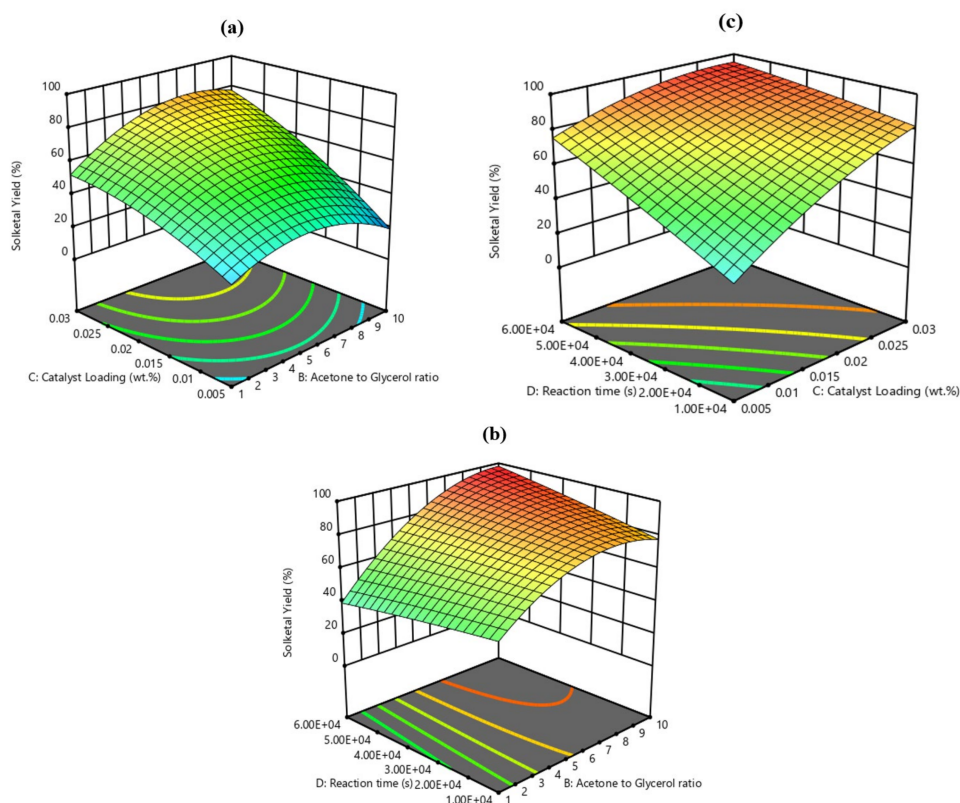
Figure 11. Surface plots of solketal yield for the interaction (**a**) catalyst loading vs. Acetone to glycerol molar ratio (**b**) catalyst loading vs. reaction time (**c**) reaction time vs. acetone to glycerol molar ratio.

The simulation of the batch model using Aspen Plus requires necessary input parameters such as the kinetic data of the reactions taking place in the process. This helps to validate the developed model as well as help to investigate the effect of further input parameters on response variables to optimize the process. Therefore, the necessary input parameters in this study were taken from the previous study of Dmitriev et al. [1]. The simulation results were compared with the previous study done using H_2SO_4 to further investigate the effect of input parameters to optimize the solketal yield. The optimum input and output parameters suggested by ANOVA and 3D plots are acetone to glycerol molar ratio of 8, the reaction time of 10,000 s, reaction temperature of 308 K, and catalyst concentration of 0.03 wt % and gave an optimum yield of 82.108%. Table 9 indicates the comparison of results obtained in this study with the study of Dmitriev et al. [24]. The results of this study were comparable to the previous study, which shows the accuracy of the developed simulation model.

Table 9. Effect of catalyst concentration on solketal concentration in simulation model with study Dmitriev et al. Reproduced with the permission from [24], Springer, 2018.

	Concentration of Solketal (mol/L)					
	Cat. Loading 0.001 wt %		0.006 wt %		0.03 wt %	
Time (min)	[24]	This Study	[24]	This Study	[24]	This Study
0	0	0	0	0	0	0
100	1.75	1.75	1.70	1.70	1.67	1.55
200	1.76	1.75	1.75	1.75	1.73	1.70
300	1.76	1.75	1.75	1.75	1.75	1.75
400	1.76	1.75	1.75	1.75	1.75	1.75
500	1.76	1.75	1.75	1.75	1.77	1.75

3.3. Kinetic and Thermodynamic Modeling of Ketalization Process

3.3.1. Kinetic Modeling for Equilibrium Constant

The kinetic parameters for the production of solketal that took in the batch reactor in a relatively lower temperature range of 303–323 K were determined. Kinetic modeling was performed to obtain the parameters such as activation energy and rate constant for the simulation of the ketalization process conducted on Aspen Plus in this investigation. The operating temperature of ketalization reaction was kept moderate as it is exothermic in nature, which is thermodynamically not favorable at higher operating temperatures. In this series of simulation runs, a high initial molar ratio of acetone to glycerol was employed as it can significantly enhance the yield of solketal [50,51]. To ensure the equilibrium of the reaction, all the experiments were allowed to take place for enough time while monitoring the concentrations of glycerol and solketal vs. time until there was no change observed in the results (equilibrium was established). The equilibrium rate constant was determined using the kinetic equations of forward and reverse reactions of the ketalization process. The power Law Approach is one of the simplest and most commonly used approaches. It characterizes the course of the reaction by temperature-dependent rate constant k(T) and component concentration or partial pressures, respectively. The rate constant k(T) is typically determined using the Arrhenius Equation. Considering the formation of carbonium ions as the rate-determining step in the reaction, the rate equation can be expressed as in Equation (3). The rate equation based on the overall rate constants is expressed as in Equation (4).

$$r = k_1.C_{cat}.C_{Gly}.C_{Ac} - k_2.C_{cat}.C_{sk}.C_w \tag{3}$$

$$r = K_1.C_{Gly}.C_{Ac} - K_2.C_{sk}.C_w \tag{4}$$

The equilibrium constant (K_c) for the liquid phase ketalization reaction was determined using the concentrations of the reactants and products found at the optimized operating conditions. The equilibrium constant was determined by the formula expressed in Equation (5).

$$K_c = \frac{C_{sk}.C_w}{C_{Gly}.C_{Ac}} \tag{5}$$

In Equations (3)–(5), C_{Gly}, C_{Ac}, C_{sk}, *and* C_w are the concentrations of glycerol, acetone, solketal, and water, respectively. Overall, the increase in the reaction temperature gradually decreases the equilibrium constant, ensuring the exothermic nature of the reaction [52]. The equilibrium constant at the optimized reaction conditions was found to be 0.714. The activation energy and Arrhenius constant for forward and backward reactions were deter-

mined using the Arrhenius plot. The Arrhenius equation for activation energy calculation is expressed in Equation (6).

$$K = A. \, e^{\frac{-E_a}{RT}} \tag{6}$$

In Equation (6), E_a is the activation energy, and A is the Arrhenius constant. The simplified form of Arrhenius is shown in Equation (7).

$$\ln K = \frac{-E_a}{RT} + \ln A \tag{7}$$

The plot between *ln K* and *1/T* gives the values of Arrhenius parameters as expressed in Figure 12.
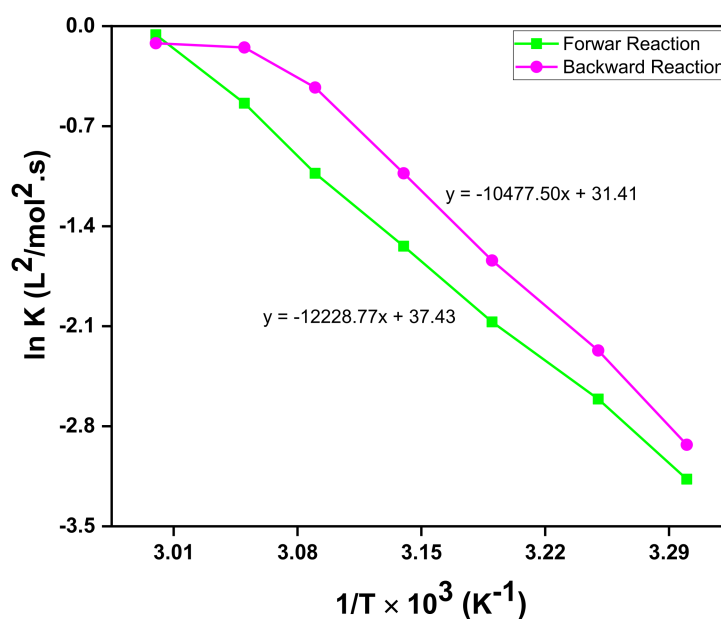

Figure 12. Plot between *ln K* and *1/T* for forward and backward reactions.

From Figure 12, the Arrhenius parameters found for forward and backward reactions are presented in Table 10.

Table 10. Activation energy of forward and reverse reactions.

Forward Reaction	Slope = $-E_a/R$ = $-10,477.50$ E_a = 87,110 J/mol Intercept = ln(A) = 31.41 $A = 4.36 \times 10^{13}$
Reverse Reaction	Slope = $-E_a/R$ = $-12,228.77$ E_a = 101,670 J/mol Intercept = ln(A) = 37.42914815 $A = 1.8 \times 10^{16}$

3.3.2. Thermodynamic Modeling of Ketalization Process

Thermodynamic modeling was performed to obtain the parameters such as entropy, enthalpy, and Gibbs free energy for the simulation of ketalization process conducted on Aspen Plus in this investigation. The thermodynamic properties of the acetalization process such as entropy, enthalpy, and Gibbs free energy can be determined by plotting the simulation findings of *ln K_c* vs. *1/T* (K^{-1}). The plot between *ln K_c* and *1/T* (K^{-1}) is

linear, and the equation of the straight line gives the thermodynamic parameters is shown in Equation (8).

$$\Delta G = \Delta H - T \cdot \Delta S \tag{8}$$

The simplified form of Equation (8) is used to calculate the thermodynamic parameters, as expressed in Equation (9).

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (9) \tag{9}$$

The plot between $\ln K_c$ and *1/T* for calculating the thermodynamic parameters is expressed in Figure 13.
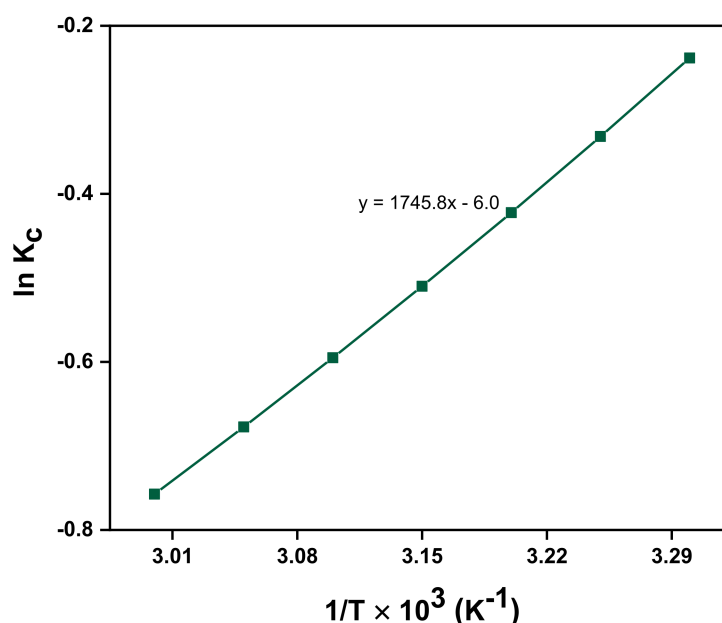

Figure 13. Plot between $\ln K_c$ and *1/T*.

From Figure 13, the thermodynamic parameters including ΔH, ΔS, and ΔG were found to be -14.5 kJ/mol, -49.884 J/mol. K, and 862.63 J/mol.

4. Conclusions

In this study, biodiesel-derived glycerol was used to investigate the production of solketal using the Aspen Plus simulation model. The developed model was validated with the previous experimental studies before further investigating the broad range of parameters. The solketal yield was maximized by varying these parameters. The maximum solketal yield of 81.36% was obtained at the best ketalization conditions of 313 K, 9, 0.03 wt %, and 40,000 s. The solketal yield was reported to be higher in comparison to previous studies of ketalization. The effect of each input parameter on solketal yield was found using a response surface methodology optimizer. The optimum input and output parameters suggested by ANOVA and 3D plots are an acetone to glycerol molar ratio of 8, a reaction time of 10,000 sec, a reaction temperature of 308 K, and a catalyst concentration of 0.03 wt %, giving an optimum yield of 82.108%. However, the effect of acetone to glycerol molar ratio and catalyst loading was found to be significant in comparison to other parameters, including reaction time and temperature. The kinetic and thermodynamic parameters were determined using the simulation data of the ketalization process. The findings of this study showed that biodiesel-derived glycerol can be effectively utilized to produce solketal, which can be used for a wider range of applications such as a fuel additive. This study used sulfuric acid, which is a homogeneous catalyst. However, although it can give

higher solketal yields, further research work is required to enhance the solketal yield by developing new heterogeneous catalysts especially from the wastes and clays i.e., kaolin, which will lead to cheaper availability of solketal. This will open new doors for the research and will implement solketal synthesis possible on an industrial scale.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Abbreviation	Description
NRTL	Non-random two liquid theory
RSM	Response surface methodology
CCD	Central composite design
ANOVA	Analysis of variance

Nomenclature

Variable	Description	Unit
E_a	Activation energy	kJ/mol
T	Temperature	K
k	Rate constant	$L^2.mol^2/s$
K	Overall rate constant	$L^2.mol^2/s$
C	Concentration	mol/L
R	General gas constant (8.314)	$Pa.m^3/g.K$
K_c	Equilibrium constant	–
ΔG	Gibbs free energy	J/mol.K
ΔH	Heat of reaction	kJ/mol
ΔS	Entropy	J/mol
A	Arrhenius factor	–

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