Toward sustainable and eco-efficient novel catalytic distillation process for production of solketal using seepage catalytic packing internal

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Graphical Abstract

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    ✓ Catalytic distillation
    ✓ Sustainable process
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- Sustainable process
 Energy saving
 Eco-efficient catalytic distillation
- ✓ Reduced CO₂ emissions

<image>

Highlights

• The ketalization kinetics using NKC-9 cation resin catalyst was investigated.

- A rigorous model of RD was developed and validated by pilot-scale experiments.
- The effects of key parameters of RD column for SK synthesis were determined.
- The RDWC technology achieves reduction in energy, economics and CO₂ emissions.

ABSTRACT

The initial aim of this paper is to dramatically improve the post-treatment stage of biodiesel production, which converts problematic glycerol to solketal (SK), by introduction of an eco-efficient integrated reactive and dividing wall distillation process. To overcome the chemical equilibrium limitations and the long post-treatment process with the high energy consumption and waste water emission, this study provides the potentially, sustainable and novel reactive distillation (RD) process for cleanly catalytic synthesis of SK, taking into account costs and environmental impact. The ketalization kinetics experiments were carried out to provide a basis for subsequent experiments and simulations. A reliable model was established for further RD technological design and validated by the pilot-scale experiments. Through sensitivity analysis, the effects of multiplex parameters in RD process were determined. The advanced intensification of SK production by reactive dividing wall column (RDWC) achieves reduction in energy, total annual cost (TAC) and CO₂ emissions of 13.9%, 18.2% and 16.4% (as oil resources), respectively, compared to the optimal SK production by RD process. This proposed technology is also compared with the conventional industrial route of ketalization with 18.7% energy saving.

Keywords: Solketal; Ketalization reaction; Catalytic distillation; Sustainable process; Process intensification

1. Introduction

At present, the decrease of oil reserves and global warming issues has prompted countries to develop sustainable sources to substitute fossil fuels aiming to reduce greenhouse gas carbon dioxide (CO_2) emissions. Biodiesel, a long-chain fatty acid methyl ester obtained through transesterification using animal and vegetable oils, is the most promising and viable new energy in the short term^[1]. It has the advantages of environmental friendliness and regenerability that can be used as an alternative source for petrochemical diesel^[2-4]. It is estimated that the transesterification reaction may produce approximately 10 wt% by-product glycerol (G)^[5]. However, glycerol is a low value-added chemical raw material, which market for existing has become increasingly saturated. As the production of biodiesel increases continuously, if improperly use of by-product glycerol, it will not only affect the economic feasibility of biodiesel as a new energy source, but also cause serious environmental pollution, which is incompatible with sustainable development strategy^[6]. The issue of energy utilization has continuously been concerned by the public and recognized as one of important factors for industrial ^[7]. Each year about half investment of the chemical industry is in separation field ^{[8].} As a result, scholars around the world are actively exploring more effective and feasible ways to use the excess substance glycerol ^[9,10]. Currently, a huge number of different methods have been studied for transforming it.

The researches mainly focus on the development of some high value-added products such as 1, 3-propanediol, propylene oxide, cyclic acetal and ketals, etc. ^[11-14].

Solketal (SK) is an important organic synthesis intermediate, which can be used in the synthesis of antihypertensive drugs propranolol, drug carrier and as an inexpensive inducing compound for chiral synthesis ^[15-17]. On the other hand, it can be used as a polyhydroxy protecting group to synthesize high-purity monoglyceride, participated in preparing glycerol phosphate ^[18,19]. The existence of a branched oxygen-rich compound makes it possible to be added into diesel oil, which can effectively enhance the low temperature performance of diesel and reduce its viscosity ^[20], decrease the particulate emission ^[21].

Solketal is generally obtained through the ketalization of glycerol and acetone with catalyst such as strong liquid acid H₂SO₄ and HCl ^[22]. Although the catalytic effect is obvious, the homogeneous process has the disadvantages of corrosion equipment and environmental issues. With the strengthening of people's environmental awareness and the development of green chemistry, more studies have targeted on heterogeneous catalysts such as Amberlyst-36 ^[11], mesoporous amorphous AlPO4 ^[23], Zeolite ^[24] etc., which can overcome the shortcomings of traditional liquid acid catalysts.

The condensation product of glycerol and acetone has both five-membered ring (4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane,solketal) and its isomer six-membered ring (5-hydroxy-2,2-dimethyl-1,3-dioxane) ^[25], however, the solketal is more favorable with selectivity of reaching 98% or more, which are commonly both

considered as final product in industry. The basic properties of this ketalization system are listed in Table 1 and the reaction scheme for ketalization of glycerol with acetone is shown in Scheme1.

After reaction, the catalyst was neutralized, it was recovered by filtration, distillation, 80~83 ° C/1.33 k Pa product was collected to be Solketal (SK). However, low single-pass conversion owing to its thermodynamic limitation results in excessive energy consumption ^[26]. Therefore, the production route has the weakness of cumbersome post-processing, large-scale equipment occupation and low conversion with energy consumption, which result in high cost.

Solketal synthesis is also needed to consistent with the principles of green chemistry and engineering which can be achieved by process intensification (PI)^[7]. By utilizing of RD technology, the product can be separated in real time while the reaction is carried out, thereby not only improving the conversion rate and product yield, but also energy consumption can be saved effectively ^[27,28]. Because of conversion improvement, energy saving and effective CO₂ emissions reduction, RD has advantages in terms of economy, environmental friendliness, sustainability and safety ^[29], which makes it an attractive alternative to conventional procedure.

At present, researches for solketal mainly focuses on catalysts and kinetics by other scholars. Now, several synthetic devices for solketal have also been investigated actively, such as semi-batch reactor ^[22], fixed bed reactor ^[30], microwave assisted ^[31] and membrane reactor ^[32]. But they still have some drawbacks, such as complicated post-processing and the clogging of the reactor with the catalysts, hence raising

environmental and economic concerns. Clarkson et al ^[33] has focused on the study of solketal formation by a continuous reaction column, which computes based on the theoretical model using heterogeneous catalyst. Domínguez-Barroso et al ^[34] has built a continuous flow reactor system in laboratory scale which connected to distillation device for synthesizing solketal in the presence of catalyst Brönsted acid, but none process coupling was involved by them. Al-Saadi et al ^[35] has investigated a novel process for combining solketal synthesis during the triglyceride transesterification to minimize the crude glycerol generation, although the parameters correlation were studied by DoE, this established kinetic model hasn't applied in further research for any integrated process. However, we have not seen any detailed reports about SK's production by RD technology on experimental scale. Therefore, the RD process will be proposed to realize continuous production of SK from Acetone (Ac) and Glycerol (G) using solid acid as catalysts in this paper.

This research focused on the basic study of kinetics with cation resin catalyst NKC-9, green and sustainable process feasibility of RD and RDWC and optimization for SK production. Firstly, the kinetics studies were performed under different conditions catalyzed by NKC-9. Further, based on the data from experiments and thermodynamic method, the possibility of using RD was discussed by simulation through a rigorous RD mathematical model established and validated by the results obtained from pilot-scale experiments, providing theoretical basis for SK's process plant design. And then, the preliminary concept design of RD was systematically studied by using this model to implement optimization of this process. Finally, the

reactive dividing-wall column (RDWC) structure is designed, by contrast, in the aspects of the energy consumption, economic analysis and CO_2 emissions of environmental impact were conducted between the conventional production routes, new RDC and the RDWC ketalization process.

2. Experiments Section

2.1. Materials: Chemicals and Catalyst

Table 2 listed the information of chemicals which was used in this study.

The catalyst used in kinetic experiments and reactive distillation experiments, NKC-9, is purchased from the Chemical Plant of Nankai University, China. The specific catalyst properties are shown in supplementary information Table S1and Fig.

S1.

2.2. Experimental setup and procedure

2.2.1. Kinetics

The kinetics experiments were conducted in a 100 ml three-necked flask made by Tianjin Pengxiang Glass Experimental Apparatus Co., Ltd, sampling needles and thermometer were placed separately on left and right bottle sides (Fig. 1). The system was heated by a constant temperature water bath, temperature control accuracy is ± 1 °C.

The composition of reactant was 36.836 g glycerol, 22.232 g acetone in the presence of 0.737g NKC-9 catalyst, whose volume was 59.74 mL totally. Put the weighed amount of acetone and catalyst into flask and heat to the set temperature while preheating glycerol, then transferring the glycerol into reactor what time was used as the time zero. After certain intervals as 2 min in the first 10 minutes and then

take samples every fifteen minutes until equilibrium, about 0.1 mL liquid samples were taken out for further composition analysis. Several experiments until the equilibrium state were performed in turn to determine kinetic data and study the different influence of parameter changes on the kinetics. Notably, the experiment under the condition of temperature of 343.15K was conducted in autoclave AUTOCHEM100 with temperature and pressure monitored.

2.2.2. Reactive distillation experiments

The experiments of synthesizing solketal studied in this paper were carried out in continuous operation mode. The diagrammatic sketch for the RD column of pilot-scale experiments was depicted in Fig. 2.

The RD column is manufactured of stainless steel, total height of 4 m, 50mm diameter (inner) divided into 4 units, which were recorded as 1-4 sections from bottom to the top, with each one fixing by flange connection. The reactive zone was in the middle about 3m filled with SCPI packing internals. The rectification section and the stripping section were respectively equipped with θ -ring packing (Φ 5*5) for 0.5 m height. The number of theoretical stages per meter (NTSM) is 11-14/m packed with θ -ring packing in nonreactive zone, and 7-9/m for SCPI filled with NKC-9 catalyst in reaction zone ^[36, 37]. The condenser uses circulating cooling water to cool the rising vapor. The reboiler was heated by externally circulated oil bath; the temperature was adjusted by the temperature and flow of the circulating oil. The amount of the rising stream is controlled by the thermal conductive oil. The bottom has a sampling port for timely analysis, which outlet is connected to a product tank to store product. The mass flow of the bottom stream can be obtained by recording the

change of the storage tank quality a fixed time. During the experiment, the mass flow rate of the distillate can be obtained by the weighing the quality of collected distillate in a period of time to calculate the variation. The reflux ratio is adjusted by the electromagnetic controller.

The column was provided with pressure measurement points. Thermocouples were installed in each section to measure the temperature in column, at the same time, the temperature of the kettle and the top reflux liquid is also monitored and recorded. During the reaction, the pressure and temperature change of each section were continuously monitored, which data were displayed on the control panel and transmitted to the computer for recording in real time. In order to prevent heat dissipation and reduce the impact of ambient temperature, the column outside is totally wrapped by insulation mineral wool. The cooled condensate of acetone and water from the top condenser were taken from the column according to the reflux ratio. The produced SK was in the bottom stream and was withdrawn periodically. The temperature and pressure measurement program were set up to automatically record data every 10 minutes. The detailed experimental procedure of RD process was shown in supplementary information SI 1-2.

In order to compare the influence of different fed type on glycerol conversion, for the Exp2 the feed positions of G and Ac are respectively placed at 3.5 m and 0.5 m height metered from the column bottom, which called 3^{rd} section (Feed 1) and 2^{nd} zone (Feed 2) drawn in Fig. 2. For the Exp5, we set G position constant (Feed 1), added Ac from the top of 3^{rd} section (Feed 3), which can make them co-fed.

The study investigated the influence of reflux ratio, operating pressure, feed type and feed molar ratio on the performance of RD process for SK continuously synthesis. *2.3. Analysis*

Chromatography: PE Auto System 690; detector: hydrogen flame ionization detector (FID); column: Agilent 30-m DB-Wax non-polar column, 2.5mm; split ratio: 40:1; carrier gas: nitrogen; carrier gas, air and hydrogen flow rate: 1.00 mL / min, 450 mL / min, 45 mL / min; injector and detector chamber temperature 493.15 K; oven temperature 503.15 K kept 6.0 minutes. The samples were detected repeatedly more than 3 times whose error is less than 0.2% was feasible.

The concentration of water was measured on a Karl Fischer Titration Meter of Trace Moisture Determination (ZDJ-3S), which supplied by Beijing Pioneer Weifeng Technology Development Co., Ltd. A suitable amount of the sample to be tested was taken out using a micro syringe, after examination detection two sets of data with an error of 0.2% were accepted.

$$w = \frac{V \times t}{m} \times 100\% \tag{1}$$

V means the Karl Fischer reagent volume that consumed (mL); t represents the titer of Karl Fischer, mg/mL; m is the mass weight of liquid sample (g).

The acid value was determined by acid-base titration. It is the amount of milligrams of KOH required to neutralize 1 g of sample. The determination was described in supplementary information SI 1-3.

Acid value =56.11×KOH concentration (0.1mol/L) ×KOH volume (mL) ÷sample weight/g, mgKOH/g. (2)

3. Kinetics Experimental Results

A series of experiments were carried out to investigate the impacts of molar ratio, temperature on the glycerol conversion (X_G) of the ketalization reaction. That X_G is defined as the conversion of glycerol and Y_{SK} represents the yield of solketal, computed by Eq. (3) and Eq. (4), respectively.

Glycerol conversion (X_G): X_G(%) =
$$\frac{[Glycerol]_{0}[Glycerol]_{t}}{[Glycerol]_{0}} \times 100\%$$
 (3)

Yield of Solketal (Y_{SK}): Y_{SK} (%) =
$$\frac{[Solketal]_t}{[Glycerol]_0} \times 100\%$$
 (4)

3.1. Effect of speed of agitation

According to the literature ^[38-39], for the resin catalysts such as NKC-9 used in this paper, the particle size of the catalyst is generally controlled as 0.5 to 0.8 mm in the production process to eliminate internal diffusion. The study conducted three sets of comparative experiments under different particle size catalytic conditions to evaluate the effect of internal diffusion as it shown in in SI 1-4 Figure.S2.

In order to eliminate the effect of external diffusion, four comparative experiments were performed under the stirring speed of 200 to 500 rpm. The other conditions were maintained (323 K, the molar ratio of (Ac/G) was 1:1, and the catalyst loading was 2wt% of glycerol).The equilibrium conversion rate and production rate of glycerol were obversed, as it described in Fig. 3, when the stirring speed reaches 400 rpm, the slope of the generated rate curve varies smoothly, and the ultimate equilibrium conversion rate is nearly identical at 67%, indicating that the influence of external diffusion has been eradicated. It is considered that the side-effect of diffusion resistance at speeds > 400 rpm could be negligible. However, continuously increasing the speed will have negative impact on the stability of the

device and the catalyst. In summary, other experiments were performed under the condition of stirring speed of 400 rpm.

3.2. Effect of mole ratio of Ac/G

The effect of different molar ratio of acetone to glycerol (Ac/G) on glycerol conversion was also examined through four experiments. The investigation is performed to obtain appropriate reaction kinetics expressions. Acetone is a polar solvent and the increase of Ac/G will lead to increase in solketal yield and conversion ^[41]. An excess of acetone was selected, because of the cheap price of acetone, it can be used as both a reactant to drive the forward reaction and excess miscible acetone to remove unfavorable by-product water as a stripping agent ^[41].

Comparisons were detected separately which the ratio of the acetone to glycerol were set 1:1, 1:2, 1:4, 1:6. It can be obviously seen from Fig. 4 the conversion rate reached a maximum of 80.4% that close to the literature ^[41] when the ratio of G/Ac achieved at 1:6. The formation rate was relatively fast for the initial 10 minutes, and basically reached equilibrium by 30 minutes, which was consistent with Nanda et al ^[26] and Rossa et al ^[41] reported already. The molar ratio of Ac/G would influence the equilibrium conversion because it will increase the concentration of reactant acetone to promote the forward reaction. As it obviously shown in Fig. 4, under different molar ratio conditions, a higher Ac/G molar ratio will lead to conversion of glycerol increasing, which is consistent with Agirre et al ^[12] described before.

3.3. Effect of reaction temperature

The effects of temperature on glycerol conversion were investigated from 293.15K to 343.15K. The difference rates of change were clearly illustrated in Fig. 5. As temperature higher, the reaction rate was accelerated which can be seen from the gradually steep slope of conversion curve. At the same time, the equilibrium conversion decreased from 62.9% to 59.4% because of the exothermic reactions if the temperature goes up will promote reverse reaction. For reversible reactions, the reaction rate and conversion were impacted directly by temperature because chemical equilibrium will be in the direction of weakening this trend as Le Chatelier's principle referred ^[41].

3.4. Comparison of previous studies

As mentioned above, researchers have reported on ketalization kinetics with acetone and glycerol using diverse catalysts to investigate the reaction conversion and kinetics parameters. As comparison, a detailed literature review is given in Table S2 ^[42-45].

As traditional homogenous catalyst, Suriyaprapadilok et al ^[42] has used PTSA on ketalization, they have studied the conversion of glycerol on different Ac/G molar ratio for over 12hours, obtained the conversion from 60% under the condition of Ac/G of 2:1 to 82.7% of 6:1. Menezes et al ^[43] have investigated typical Lewis acid, such as SnCl₂, SnF₂, Sn (OAc) ₂, they find Sncl₂ own the most excellent catalytic efficiency with the glycerol conversion of 77%, however it will cause some corrosion.

Amberlyst-15 is one of the most promising activators for ketalization, with 95% glycerol conversion and the solketal selectivity of 95%. A reversible kinetic model

was established by Rossa et al ^[41], they have calculated equilibrium constants for a range of 40-80°C and provide the accurate comparison of conversion between the experimental and calculated value, statistical analyze the ways for the kinetics properties improving.

In this work, effect of different conditions (such as particle size, stirring speed, temperature and the feed molar ratio of Ac/G) on kinetics (which reflected on conversion vs. time curve) were also studied, with the glycerol conversion range from 60.4% to 80.4%. The reaction rate constants were determined experimentally in the temperature range of 293-343 K, with the activation energy (Ea) of forward and reverse reaction were obtained, respectively.

It can be concluded from Table S2 that the conversion of glycerol under different conditions are similar with our study; the activation energy has some difference due to the presence of the internal diffusion, the effects of it were shown in SI 1-4, but the value of enthalpy ΔH^0 , difference between forward and reverse activation energy, still on the same order of magnitude. The application of the kinetic data could better match the situation in the practical industrial process.

4. Model Description

4.1. Kinetics

In the simulation, due to the presence of the ketalization, the interactivity between the components is affected by both the thermodynamic equilibrium and the chemical reaction equilibrium. Therefore, it is necessary to add a reaction kinetics equation in the simulation. According to the literature, the reaction is a two-step

reversible reaction, that rate expression for ketalization can be described by Langmuir–Hinshelwood–Hougen–Watson model ^[26,45]. Based on the assumption of the surface reaction of the absorbed water generation process considering as the rate controlled step ^[45,47], the ketalization reaction rate of glycerol and acetone can be expressed by the Eq. (5):

$$r_{SK} = \frac{dc_{Sk}}{dt} = m_{\text{cat}} \frac{k_I [C_G] [C_{Ac}] - k_{-I} [C_{SK}] [C_W]}{(1 + K_W [C_W])^2} \qquad \text{mol}/(L \cdot \min)$$
(5)

Where k_i represents the reaction rate constant of the forward and reverse reactions, K_W means the adsorption equilibrium constant of water.

MATLAB was used to fit each substance concentration in order to determine the apparent rate constant, which was calculated by Levenberg–Marquardt algorithm, above mentioned differential equation (5) was numerical integrated through the method of fourth-order Runge– Kutta ^[48]. The experiments and fitted results are shown in Fig. 6 and Fig. 7. Through established the ode45 function, the reaction rate constants at different temperatures were found in Table 3. The calculation of the rate constants are based on the catalyst per unit mass.

According to the Arrhenius equation:

$$k_i = A_i e^{-Ea_i/RT} \tag{6}$$

The logarithm of the both sides of Eq. (6), a straight line was obtained by drawing fit of $\ln k$ vs. 1/T.

$$\ln K_i = -\frac{E_{a,i}}{RT} + \ln A_i$$

(7)

 $\text{Ln}k_i - \frac{1}{T}$ Graph which was shown in Fig. 7, the slope is equal to $-\frac{\text{Ea,i}}{\text{R}}$, the intercept represents the value of ln A_i.

Calculate activation energy (Ea) based on the slope of the fitted straight line, and compute the pre-exponential factor (A_i) by the straight line intercept. Find the corresponding value of Ea and pre-exponential factor. The conclusion is that the activation energy value of the forward reaction using NKC-9 catalyst was determined as 44.312 kJ/mol and 47.23 kJ/mol for the reverse reaction; the pre-exponential factor was determined as 7.336×10^6 L·(mol·min·gcat)⁻¹ and 1.065×10^7 L·(mol·min·gcat)⁻¹, respectively.

Get the reaction kinetic equation:

$$r_{i} = m_{cat} \left\{ \frac{7.336 \times 10^{6} e^{-44.312 \times \frac{10^{3}}{RT}} C_{Ac} C_{G^{-}} 1.065 \times 10^{7} e^{-47.23 \times \frac{10^{3}}{RT}} C_{SK} C_{H_{2}O}}{(1+1.9603 \times 10^{-7} e^{40.7266 \times \frac{10^{3}}{RT}} C_{W})^{2}} \right\} \qquad \text{mol/(L·min)}$$
(8)

The quantity of catalyst (about 2/3 volume of the catalyst containers in SCPI) was filled in the RD column and it was calculated as 70.67g. The residence time could be controlled by the volume of catalyst filled in the SCPI as 20s on a stage according to the liquid flow behavior of SCPI. The mass of the catalyst is converted into the corresponding pre-exponential factor A^a (A^a represents the pre-exponential factors used in Aspen). Then we obtained the reaction rate equation 9 based on the catalyst quantity and modified the reaction rate expression for reactive distillation simulation in Aspen.

$$r_{i} = \frac{8.64 \times 10^{6} e^{-44.312 \times \frac{10^{3}}{RT}} C_{Ac} C_{G} - 1.254 \times 10^{7} e^{-47.23 \times \frac{10^{3}}{RT}} C_{SK} C_{H_{2}O}}{(1 + 2.309 \times 10^{-7} e^{40.7266 \times \frac{10^{3}}{RT}} C_{W})^{2}} \qquad \text{kmol/(m^{3} \cdot s)} \qquad (9)$$

4.2. Thermodynamic

The accuracy of the Aspen simulation results is highly dependent on the physical data and thermodynamic equations. As mentioned above, there are four compounds of acetone, glycerol, solketal and water. The solution of the reaction system exhibits

strong non-ideality, so it is necessary to find a physical method suitable for it. At present, the description of this strong non-ideal vapor-liquid equilibrium relationship uses NRTL, WILSON and UNIQUAC three physical methods.

Currently, as it referred in the literature, the case of the NRTL equation was successfully used in this system ^[49]. In this simulation, the UNIFAC group contribution method was employed to evaluate the absent parameters, as listed in Table 4. The physical property, such as Antoine equation parameters (vapor pressure) and the enthalpy of vaporization (298.15 K) are provided in Table 5.

4.3. Reactive Distillation Modeling

By establishing a rigorous simulation the effect of all the parameters in RD process can be evaluated systematically. Simultaneously, the validity of the RD model could generally be verified on the basis of the experiments results, which can be useful foundation for the further amplification of the industrial process for SK production.

The RD process involved in this article was based on Aspen V8.4, established by columns unit called Radfrac and equilibrium stage model(EQ model). Because of the interaction among the parameters, the optimization of the RDC is complicated. Therefore, follow the process below to optimize parameters. Basic variables are listed in Table 6 and detail introduced in SI 1-6.

5. Reactive distillation experiment

A total of eight RD experiments were successively conducted to explore the effects of different conditions: feed Ac/G molar ratio, reflux ratio, operating pressure,

feeding type on glycerol conversion and reboiler duty. The experiments operating condition and results are listed in Table 7 and the detail of molar flow rate was in supplementary information SI 1-7.

5.1. Model Validation

The validity of RD model was evaluated by a series of RD experimental work. The experimental results were compared with the simulation to verify the reliability of the established RD mathematics model.

Fig. 8 shows the composition and temperature of different conditions obtained from RD experiments (single points) with the data calculated by simulation used Aspen Plus (filled curves). It can be seen the results in Fig. 8 a favorable consistent between them. It can be observed from the picture that differences put together less than \pm 5% deviation. Some experimental deviations are unavoidable, the main reasons are: (1) the simplified model assumes that the reaction occurs under adiabatic conditions, but in actual operation, there will inevitably be a little heat loss at the junction of the sections. (2) During the experiment, in EQ model it is reckoned to achieve steady-state operation. However, there are some fluctuations in the actual flow conditions and heat transfer conditions in the column. (3) There are experimental errors in the analysis during temperature measurement by thermocouples. (4) The pressure drop was not considered in the simulation, which may cause the experimental temperature is slightly higher than the simulated value as the closer to the bottom. As a result, some deviations between the experimental and simulated

values are still reasonable. In temperature profile (Fig. 8 a.b.d.), the local temperature change is caused by the exothermic reaction.

The experimental data and simulation values agree reasonably well, and the reliability of the RD Radfrac model is verified. Lately, this method will be used to optimize this process. After that, sensitivity analysis was used to analyze the impact of parameters.

5.2. Effect of reflux ratio

As it shown in Table 7 Exp1, Exp2and Exp3 presented the reflux ratio's influence on glycerol conversion and the purity of solketal in bottom stream. While the other experimental conditions remained, it can be seen that as the reflux ratio increases gradually from 1.5 to 5 in Exp1, Exp2and Exp3, the conversion of G firstly rises from 62.4% to 67.5% gradually and then decreases slightly to 65.4%. The results describes that larger reflux ratio have an advantage on conversion, however, excess than a value, slightly decrease.

5.3. Effect of operating pressure

The influence of operating pressure was illustrated between Exp2 and Exp4, with the pressure decreasing from 993 hPa to 775 hPa, the conversion dropped from 67.5% to 55.9%, the mass purity of SK was also reduced from 68.91% to 60.43% after the pressure lowered. It indicates that higher pressure in column would promote reaction to conduct expectedly. However, temperature rises as the pressure increasing, if the temperature is too high, the performance of the catalyst will be reduced and the service life of it will be affected. Therefore, the pressure setting is not suitable for as

high as possible. The trend of the reboiler duty and the conversion of glycerol with the pressure are shown in supplementary information Fig.S3. The optimal operating pressure that can achieve the desired conversion rate without affecting the use of the catalyst is 101.325kPa according to our study, which was described in detail in SI 1-8. *5.4. Effect of feed molar ratio*

The effect of the molar feed ratio can be illustrated by comparing the results of Exp2, Exp6, and Exp7. With Ac/G molar ratio increasing from 2:1 (Exp2) to 3:1(Exp6), the conversion of G (glycerol) changed significantly from 67.5% to 85.9%. The experimental results indicate that the increased molar ratio of Ac/G was beneficial to the reaction to proceed toward the direction in which the forward reaction generates SK. However, the excess acetone will cause the acetone concentration in the column overhead stream to rise which will lead to consume more energy in the later separation.

5.5. Effect of feeding type

The influence of feeding type of glycerol and acetone was investigated by comparing Exp2 with Exp5. The glycerol with acetone is fed separately and contacted in countercurrent mode in Exp2 and co-fed in Exp5. In Exp5, because of delamination after mixing of acetone and glycerol, for Exp5, the feed position of glycerol is unchanged (Feed1), the reactant acetone is fed at the 3rd reaction section, allowing them to be mixed (Fig. 2). When the feed type changed from Exp2 to Exp5, the conversion of glycerol was decreased from 67.5% to 61.7%. The experimental results show that the downward shift of the feed position, that is separate feeding mode,

facilitates the more conversion of G to the target product SK. In order to increase the concentration of the Ac, we have also considered feeding the acetone at a lower point on the stripping stage in the RD column. But the final experimental result is not very ideal, as a result, the conversion rate of glycerol is 59.90% lower than 67.4% before and the concentration of acetone is increased.

6. Reaction distillation process analysis

For the industrial process feasibility and economical, it is desire to increase conversion rate and reduce energy consumption (i.e., reboiler duty), which is limited by only experimental research. Aspen plus, generic software developed by Aspen Tech, USA is used for steady state simulation, process design and optimization. The model analysis, sensitivity analysis, was applied to study the operating parameters of the RDC and to investigate the impact of each variable change on process. Then, the optimal results will provide further guidance for design and construction of the industrial device.

The sensitivity analysis, each parameter changed once, was successively applied for discussing the corresponding effects on conversion of G (X_G), and RD energy consumption per mass g of SK (Q_{SK}) to obtain optimal condition for the SK synthesis by RD technology.

$$X_{G}(\%) = \frac{[Glycerol]_{0}[Glycerol]_{t}}{[Glycerol]_{0}} \times 100\%$$
(10)

$$Q_{SK} = \frac{\text{Reboiler duty}}{\text{mole flow rate of SK in stream}} W/g$$
(11)

6.1. Effect of feed mole ratio

The excess of one reactant can promote the chemical reaction, which requires more attention to the feed molar ratio of Ac/G in the operation. As the price of acetone was cheaper with lower investment, the excess acetone was usually used in industrial production to improve the conversion of glycerol. However, in turn, too much excessive acetone would lead to separation difficulty and huge energy consumption. In this part, Fig. 9 depicts the trend of Ac/G feed mole ratio on glycerol conversion and the reboiler duty when the total feed quality and distillate amount remains constant, raised molar ratio of Ac: G from 1:1 to 6:1.

When the molar ratio is more than 1:1 (the stoichiometric ratio of Ac to G), glycerol conversion enlarges rapidly with the feed ratio increasing. When it is set from 1:1 to 6:1, the conversion rate of G increased from 59.6% to 83.3%. As it can be observed form Table 8, with Ac/G molar ratio reaching 20:1, conversion of G achieved 93.2%. With the molar ratio of Ac/G increasing from 1:1 to 20:1, the energy consumption per unit mass of SK increases from 0.2438w/g to 1.9496w/g. It can be obviously found that although the conversion is significantly increased, due to the relatively less amount of glycerol fed, the quantity of the target product SK obtained was reduced. From the perspective of energy consumption, although the excess of reactants will promote the increase of conversion rate, it will also require larger amount of energy consumption.

Despite the molar feed ratio facilitates the movement of the equilibrium towards the direction of formation, which also greatly added energy consumption. However, when the molar ratio of feed exceeds 3, the slope of the purity of SK varies gradually

slightly; the reboiler duty expands almost linearly. As it reported in research ^[50], energy consumption is one of the key indicators for evaluating equipment's capability. By calculation, when feed ratio reached 3, continue to increase the amount of feed to obtain a unit quality product, the energy consumption gradually increases.

6.2. Effect of reflux ratio

The influence of reflux ratio on RD process includes that it not only influences efficiency of separation and progress of the reversible ketalization, but also affects the energy consumption, thus the operation cost of the RDC. The influence of reflux ratio was investigated in the interval of 0.8-4in this part.

It can be observed from Fig. 10 that as the reflux ratio increases, the trend of the change in G conversion is gradually rising firstly and then slightly down. Simultaneously, the reboiler duty was rapidly increased. This means no improvement in G conversion while operation cost still inflated. The relationship between reflux ratio and the performance of RD process is complex because separate and reactive coupled in one unit.

When the reflux ratio is less than 2.4, that is, the curve appears an inflection point; because of mainly limiting by chemical equilibrium, if the effective separation between water and acetone is enhanced, the forward movement of the reaction is promoted. If the separation in the system is more favorable, the reaction happened more adequately, the conversion rate increases correspondingly. After 2.4 that as the reflux ratio increase, the reaction rate becomes the main factor restricting the

conversion rate. The liquid residence time on the stage decreases with reflux ratio increasing. At this time, further increase of the reflux ratio will reduce the conversion rate due to the decrease of the reaction rate.

The results indicate that when the reflux ratio is large, the impact on increasing for the conversion is not obvious, even decrease, however, the reboiler duty was always increased linearly.

6.3. Number of reaction stages

In RD process, the reaction section stages have effect on the efficiency of the performance of reaction and separation. By appropriately increasing reaction theoretical stages can better combine reaction process and the distillation process to achieve better results. For the purpose of ensure that it has sufficient time to match separation and reaction unit to increase reaction equilibrium conversion, it's necessary to increase the number of theoretical stages reasonably. More stages in reactive section will lead to more glycerol convert into target product solketal. However, when the stages of this section are excess, the investment will be increased unnecessarily.

As it can be seen from the Fig. 11, when the reaction section theoretical stages number was increased from 3 to11, the conversion of glycerol increase rapidly; but too much stages in reaction zone will result in waste if it is no positive effect on reaction conversion. When set 9 stages from 5th stages the feed position of Ac to 14th the position of G, with 9 stages to reaction is enough. Fig. 12 shows the results of the change in the theoretical stages on concentration of reactants and products in column. It can also be observed that excessive stages will bring negative effect, because

reverse reaction between water and solketal may happen, which is adverse for solketal formed.

6.4. Number of rectification stages

When the number of rectification section stages is changed during reactive distillation, the concentrating of the light components will change accordingly, and then the progress of the chemical reaction would be affected. However, more theoretical stages will increase the equipment cost and the operation expense of the reboiler. Therefore, it's very important to select adequate value of rectification section stages.

The number of rectification section was studied in this part varied from one stage to 20stages. The conversion of G and reboiler duty over different rectification sections' number was shown in Fig. 13. As the number of the stages in rectifying section increasing, the conversion of G increases accordingly. This is due to the increase the theoretical stages, which improves the concentration of liquid acetone in the reaction zone, furthermore promotes the equilibrium removes forward. The directional movement helps to improve glycerol conversion and solketal production quantity. When the number is increased to 5, the conversion rate change is no longer obvious.

6.5. Number of stripping stages

In the RD process, the increase of theoretical stages in stripping section can raise the heavy components purity in column, causing separation be promoted and the improvement of conversion rate. Fig. 14 depicts the effect of theoretical stages in stripping section on the glycerol conversion and reboiler duty. When the number of

stripping sections increased from 2 to 10stages, glycerol conversion rate is gradually increasing from 55.8% to 57.5%. Due to the separation efficiency of the stripping section enhancing, promotes the progress of the forward reaction and glycerol conversion will increase. The substances in this system own considerable difference in boiling points (As shown in Table 1) resulting in relatively easy to separate them, so only a few number of theoretical stages demanded for implementing effective separation. When theoretical stages in this section exceed 6, the conversion rate remains almost constant. At this time, if the number of the stripping section is increased, the conversion rate hardly increases, but the reboiler duty increases, the equipment cost goes up.

7. Process intensification by RDWC

Because of non-ideal boiling ranking, the conventional RDC can achieve the task, but since the unconverted lowest boiling point reactants Acetone and highest Glycerol gradually tend to move through the stage for withdrawing the intermediate product and bring consequently separation difficulties. In this research, the novel concept of RDWC is introduced into synthetic process of SK.

Fig. 15 illustrates the equivalent process of RDWC sequence comprising a RD column accompanied with another separation and purification column, which linked mutually through two internal streams, vapor streams (V_2) and liquid streams (L_1), to simulate the internal mass transfer process, specific process are illustrated in SI 1-9. The entire column is divided into four segments, we called reaction zone region I,

product purification section region II, public distillation section and public stripping section.

7.1. Process design

The RDWC is designed with a conventional RDC range as foundation, requiring both feed, product purity, and operating pressure under the same conditions, the design process can be divided into concept design and optimization.

In this paper, the simulation is performed on the Aspen Plus; the Radfrac unit is selected for both columns. There are many variables in RDWC, which are directly interacted to each other. It is difficult to comprehensively analyze all variables. In order to simplify the effects between them, univariate analysis was applied to provide an initial value for optimal analysis.

The optimization process is shown in Fig. 16.

7.2. Process optimization

The optimal design parameters of RDWC were obtained through economic analysis, as calculated by equation in SI 1-10. The objective function annual total cost (TAC) is utilized to select optimal parameters ^[51,52] and TAC based on the economic optimization of global was obtained ^[53]. After maintain product purity requirements by adjusting the two manipulated variables, reflux ratio (RR) and vapor split volume (Vr), the value of other parameters are investigated.

Due to energy integration in the system, where combustion fuel was used, not only improve energy efficiency, but also reduce CO_2 emissions. The rule of Environmental Protection Agency "E9-5711" was applied for CO_2 calculation ^[54].

$$[CO_2] \text{ Emission reduction} = (Q_{Eval}/\text{NHV})^* \alpha^* 44/12$$
(12)

$$Q_{Fuel} = Qs/I$$
(13)

Note: α represents CO₂ emission factor; Qs is energy saving value in the process; Q _{Fuel} is the energy saved from fuel combustion; NHV is the net heating value; η represents the thermal efficiency coefficient.

7.3. Optimization results

7.3.1. Vapor phase distribution ratio

The objective function of the investigation is the purity of SK product and reboiler duty. The vapor split volume (Vr) is an important variable. The vapor distribution ratio and reflux ratio (RR) determine minimum energy consumption of the column. The distillate amount and the side extraction of the column are used to ensure the quality requirements of product SK, the other two degrees of freedom are changed to minimize the energy consumption, effect of the reflux ratio of the main column and the gas phase distribution on reboiler duty is depicted in Fig. 17.

In Fig. 17, reboiler duty monotonically decreases with it value increasing, it is because as the amount of gas entering the region II (Fig. 15) has decreased, the separation ability of the corresponding rectifying section reduced, so the purity of the product solketal decreases. The reaction would be insufficient if the volume of gas phase enters into the region I which came from the stripping section is reduced, it will lead to the amount of solketal decrease. The value for vapor is 100g/hr; RR is 2, whose reboiler duty is lowest.

7.3.2. Liquid phase distribution ratio

Other conditions remained, the liquid distribution flow rate was changed, and the effect on the experimental results was examined. It can be seen from the Fig. 18 that

the liquid phase partition ratio decreases and the purity of solketal decreases. The reason for this trend is that the amount of liquid entering the left reaction section increases(L_1), and the liquid phase load in this area relatively increases, which may cause the products to be taken out of the reaction zone before they are separated; on the other hand, the larger the liquid phase distribution, the better the separation of the light component and the heavy component in the pre-fractionation section, so the lower content of the acetone in the side stream, the excessive return flow of the product solketal hinders the forward reaction would also lead to the decrease of the conversion rate of glycerol and the reduction of solketal purity. As the liquid flow rate increases, the energy required by the reboiler also decreases.

7.3.3. Number of stages

The effects of Nr on TAC is shown on Fig. 19a, it is precisely illustrated that when number of stage in rectifying section is 5, TAC reached a minimum. With the rectification stages increasing, the TAC cost increases first and then decreases, it can be explained that if separation is insufficient, it needs to increase the reflux ratio to meet product requirements, which caused the increase of the premier operation cost and later too many stages may lead to more equipment cost which is waste to some extent.

In Fig. 19b, it is about the impact of the Ns on TAC, which tells us a phenomenon that the trend is decreasing gradually from 5-10 stages. It demonstrated a minimum TAC existing Ns is 7. From Fig. 19c, the change of the number of stages in reaction zone, which is increasing due to the capital cost rising. Meanwhile, when less

than 5 stages, the reaction is not sufficient, it is necessary to increase the residence time or reflux ratio to achieve the corresponding conversion rate, which results larger operation cost with reboiler heat inputting to achieve the purity requirements results more operation cost. When it is fixed at 5, the TAC is lowest.

7.4. Comparison of RD, RDWC and conventional process

Energy consumption saving reduces the amount of steam required for heating in the operation process, that is, reduces the amount of fuel required, and finally makes CO₂ emissions are reduced. Table 9 shows the RDWC calculation of the various kinds of fuel consumption and CO₂ emissions; it proves that the RDWC process has superior CO₂ emission reduction performance, which is conducive to sustainable development.

In RD column, after sufficiently reaction until equilibrium conversion achieving, the bottom stream consist of product solketal and other unreacted glycerol would be added into the distillation column(T_1) for further purification. The reflux ratio, feed position and the theoretical stages number for T_1 were calculated through DSTWU. The RDWC technology combines the reactive distillation column RDC and distillation column (T_1) into the same equipment, with the key advantages of effective energy reduction and lower cost (TAC). In summary, it is not difficult to find that the energy consumption of the RDWC is greatly reduced compared with the RD sequence, in Table 10,which describes the comparison between the continuous RD process and the novel RDWC technology in the aspects of essential parameters and final results.

In economic perspective, by calculating a period of 3 payback years, TAC may dramatically reduce by 18.2%. It can also be seen from Table 10 that RDWC thermodynamic efficiency has improved significantly than that in RD while the energy consumption is dramatically reduced by 13.9%. For environmental impact, it is remarkably that the RDWC process reduced lower CO₂ emissions of 16.4% as oil sources. We have also compared the conventional configuration of reaction with further separation, which the optimal parameters (such as reflux ratio, the number of theoretical stages and the feed position) are optimized by DSTWU in Aspen calculated by short-cut method. The potential RDWC process saved 18.7% energy than traditional ketal production. By above comparison, it could be obviously concluded that the RDWC technology possesses more distinguished properties in terms of economic and environment.

8. Conclusions

In view of the shortcomings of the traditional solketal production, this paper proposes an integrated technology that is conducive to reducing energy consumption and sustainable development to strengthen the catalytic process. In this thesis, the kinetics of the ketalization between acetone and glycerol with NKC-9 catalyzed was investigated. The preliminary simulation was implemented by Aspen Plus software. The contents are summarized as follows: kinetic experiments, reactive distillation experiments and process analysis.

Firstly, the effects of Ac/G molar ratio, temperature were investigated in kinetic experiments in batch reactor, with calculating the kinetic parameters using MATLAB.

In the second part, eight groups of pilot-scale experiments were performed to verify the reliability of RD application for SK production, the effect of several operating parameters was investigated initially. The conclusion is that the conversion of the reactant could be improved by it. Then, the reliability of the established model is verified by comparing the simulation results with the experimental.

Ultimately, sensitivity analysis was performed to systematically explore the effect of multiple parameters on glycerol conversion rate and energy consumption. The optimal results shows the reaction section is 9 theoretical stages, 5 theoretical stages set in rectifying section, 6 stages in stripping sections, pressure 101.325 k Pa, Ac/G molar feed ratio is 2-3(mol: mol), and the reflux ratio is 2.4.

The theoretical model of reactive distillation dividing-wall column (RDWC) was also established by Aspen Plus, by computing energy and TAC as optimized target, the considerably less consumption was obtained. The conclusion is that the RDWC process has obvious superiority of energy consumption saved by 13.9%, the TAC reduced by 18.2% and CO₂ emissions decreased 16.4% compared to RD column. The potential RDWC process was 18.7% energy-efficient than traditional ketal production after optimization, which provides an economical way to produce solketal further.

In future study, several relational experiments to verify the reliability of established RDWC model will be designed scientifically. In next step, the configuration of the column based on the research results would be conducted and then to be applied for SK's industrial-scale and efficient production.

Nomenclature	
G	Glycerol
Ac	Acetone
SK	Solketal
W	Water
RD	Reactive distillation
RDC	Reactive distillation column
RDWC	Reactive dividing wall column
<i>k</i> ₁	Formation constant of products (L/(mol/min/gcat))
<i>k</i> -1	Constant of the reverse reaction (L/(mol/min/gcat))
r	Reaction rate (mol/(L/min))
Ci	Molar concentration (mol/L)
ki	Reactionrateconstant(L/(mol/min/gcat))
m _{cat}	The quantity of catalyst (g)
A_i	Pre-exponential factor
	(L/(mol/min/gcat))
$E_{a, i}$ (kJ/mol)	Activation energy
R	General gas constant (8.314 J/mol/K)
Ns	Stages of stripping section
Nr	Stages of rectifying zone
Nrzn	Stages of reaction zone
nA_C/nG	Molar feed ratio of Ac to G
RR	Reflux ratio
T1	Distillation column for purifying after RDC
T ₂	The stripping column in the equivalent flowsheet for RDWC
N _{T2}	Number of theoretical stages for T ₂
TAC	Total annual cost
Q	Reboiler duty
N _{Ac}	Number of stage for acetone feeding
NG	Number of stage for glycerol feeding
Vr	Vapor split ratio
N _{SK}	Number of stage for solketal
Nvr	Number of stage for internal vapor stream

Credit Author Statement

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Fig. 1. Kinetic experimental device.

1-water bath; 2-three-necked flask; 3-thermograph; 4- Condenser; 5-sample port.



Legend:1-vacuum pump; 2- buffer tank; 3- product tank; 4- reboiler; 5, 6- reactants storage tank; 7- distillate receiver; 8- reflux ratio controller; 9- condenser.

Fig. 2. Schematic diagram for continuous reactive distillation experiments



Fig. 3. Effect of external diffusion on glycerol conversion Conditions: temperature is 323.15 K, catalyst loading is 2 wt%, $Ac/G = 1:1 \pmod{mol}$.



Fig. 4. Influence of reactant Acetone/Glycerol ratio on glycerol conversion. Conditions: 323.15 K, 2 wt % catalyst, Ac/G = 1:1, 2:1, 4:1, 6:1(mol/mol).



Fig. 5. Effect of different temperature on glycerol conversion: temperature of 293.15K, 323.15 K, 343.15K, 2 wt % catalyst, Ac/G molar ratio= 1:1.



(c)

Fig. 6. Comparison between the fitted data (lines) and experimental points in ketalization (a) 293.15K (b) 323.15 K (c) 343.15K for reaction temperature.



Fig. 7. Calculation of the reaction rate constants and the water adsorption equilibrium constant.



(a) Conditions: Reflux ratio 2.5, pressure 993 hPa, Ac/G molar ratio 2:1, separate feeding



(b) Conditions: Pressure 775 hPa, reflux ratio 2.5, Ac/G molar ratio 2:1, separate feeding



(c) Conditions: Feed type of co-fed, reflux ratio 2.5, pressure 993 hPa, Ac/G molar ratio 2:1



(d) Conditions: Ac/G molar ratio 3:1, reflux ratio 2.5, pressure 993 hPa, separate feeding

Fig. 8. Comparison of the mass compositions (left) and temperature profile (right) between experimental (points) and simulated results (continued curves).



Fig. 9. Effect of Ac/G molar ratio on Glycerol conversion and the reboiler duty.



Fig. 10. Effect of reflux ratio on Glycerol conversion and reboiler duty.



Fig. 11. Effect of reactive section theoretical stages on Glycerol conversion and reboiler duty.







(a)

Fig. 12. The influence of the change in the theoretical stages on concentration of column (Nrzn=3,5stages).



Fig. 13. Number of rectifying stages on Glycerol conversion and reboiler duty.



Fig. 14. Number of stripping sections on Glycerol conversion and reboiler duty.



(a)

(b)

Fig. 15. (a) The schematic diagram of reactive dividing-wall column. (b) Detailed flowsheet for RDWC.



Fig. 16. Reactive dividing-wall column optimization process.



Fig. 17. Vapor split ratio and reflux ratio in the RDWC process.



Fig. 18. Liquid split ratio in the RDWC process.



Fig. 19. Relationship between TAC and the variables in the RDWC process.



Scheme 1. Reaction scheme for ketalization of glycerol and acetone.

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Substance Form	Economic	CAS availan	Molecular weight	Th $9C_{101,21}$, D_{2}
	Formula	CAS number	(g/mol)	10 °C (101.5KPa)
Acetone	C_3H_6O	67-64-1	58.08	56.5
Glycerol	$C_3H_8O_3$	56-81-5	92.09	290
Solketal	$C_6H_{12}O_3$	100-79-8	132.16	189
Dioxan	$C_6H_{12}O_3$	4728-12-5	132.16	216.78
H ₂ O	H_2O	7732-18-5	18.01	100

C

 Table 1 Properties of substances in the ketalization reaction.

Table 2 Experimental reagents.

Materials	Company	Concentration
2,2-Dimethyl-3-dioxolane-4-methanol	Shanghai Tikham Industrial Co., Ltd.	>99.5 wt.%
Acetone	Tianjin Lianlong Chemical Co., Ltd.	>99.7 wt.%
	Shanghai China Aladdin Industrial	
Glycerol	Co., Ltd.	>99.5 Wt.%
DMF	Tian In Fuyu Fine Chemical Co., Ltd.	>99.5 wt.%
NWC 0	Tianjin Nankai Hecheng S&T Co.,	≥4.8 %
NKC-9	Ltd.	(mmol/g)
Karl Fischer reagent	Tianjin Concord Co., Ltd.	5mgH ₂ O/ml
	Tianjin Jiangtian Chemical	≥99.7wt%
Ethanol	Technology Co., Ltd.	
Phenolphthalein	Tianjin Bodi Chemical Co., Ltd.	≥99.5wt%
	Tianjin Jiangtian Chemical	
Potassium hydroxide	Technology Co., Ltd.	≥83 Wt%

Table 3 The numeric value of reaction rate constants at different temperatures.

T /V	1/T(1/K)	k_1	k-1	
1/K	1/1 (1/K)	/L·(mol·min·gcat) ⁻¹	/ L·(mol·min·gcat) ⁻¹	
293.15	0.003411	0.9236	1.0583	
323.15	0.003095	1.6784	1.732	
343.15	0.002914	2.1093	3.0413	

Component i	AC	AC	GLY	AC	GLY	Water
Component j	GLY	Water	Water	SK	SK	SK
Aij	-1.8812	6.3981	-0.7318	0	0	0
Aji	-0.6914	0.0544	-1.2515	0	0	0
Bij	1452.5793	8 -1808.991	170.9167	776.3643	115.6255	1345.0123
Bji	375.7571	419.9716	272.6075 •	-394.6647	75.4820	-257.2070
Cij	0.2	0.3	0.3	0.3	0.3	0.3

Table 4. Binary interaction parameters by NRTL model in ketalization system.

Table 5. Antoine equation parameters and enthalpy of vaporization.

ole 5. Antoine equation parameters and enthalpy of vaporization.						
	Antoine ec	luation pa	rameters			
Component	А	В	С	Vaporization enthalpy 298.15 K (KJ/mol)		
ACETONE	21.704	3022.8	-32.52	31.2213		
GLYCEROL	23.387	5574.1	-94.708	89.8224		
WATER	23.385	3949	-40.384	43.8605		
SOLKETAL	23.167	4644.5	-63.778	64.2634		

Note: Antoine equation: log P (kPa) =A-B/(T+C) (T/K)

Parameters	Value
Flow rate of acetone	406.56g/hr
Flow rate of glycerol	322.31g/hr
Column head Pressure	101.3kPa
Number of rectifying stages	10
Number of reaction zone	20
Residence time	20s
Number of stripping stages	10
Reflux ratio	3
Feed Temperature	50°C

Table 6 Preliminary simulation parameters of reactive distillation.

Experiment	Exp1	Exp2	Exp3	Exp4	Exp5	Exp6	Exp7
Reflux ratio	1.5	2.5	5	2.5	2.5	2.5	2.5
Pressure / hPa	993	993	993	775	993	993	993
Feeding mothed	Separate	Separate	Separate	Separate	C - f - l	Separate	Separate
Feeding method	feeding	feeding	feeding	feeding	Co-led	feeding	feeding
Ac: G molar ratio	2:1	2:1	2:1	2:1	2:1	3:1	1:2
Feeding activity	G:Feed1	G:Feed1	G:Feed1	G:Feed1	G:Feed1	G:Feed1	G:Feed1
reeding position	Ac:Feed2	Ac:Feed2	Ac:Feed2	Ac:Feed2	2 Ac:Feed	3 Ac:Feed2	2 Ac:Feed2
Feed Acetone flow rate (kg/h)	0.412	0.430	0.421	0.421	0.417	0.507	0.225
Feed Glycerol flow rate (kg/h)	0.329	0.324	0.340	0.337	0.342	0.279	0.529
Distillate flow rate (kg/h)	0.2989	0.2878	0.2927	0.2916	0.2919	0.3349	0.1131
Bottom flow rate (kg/h)	0.4251	0.4362	0.4303	0.4484	0.4380	0.4101	0.6169
Distillate stream composition (wt%)						
Acetone	91.62	91.84	94.99	98.86	94.31	94.35	96.65
Water	8.38	8.16	5.01	1.14	5.69	5.65	3.35
Bottom stream composition (w	t%)						
Acetone	1.85	0.95	0.50	1.24	1.68	1.66	0.0019
Glycerol	25.63	26.21	18.68	30.86	23.84	8.05	54.22
Water	3.22	3.93	6.51	7.47	5.23	6.12	4.27
Solketal	69.30	68.91	74.31	60.43	69.25	84.17	41.51
Conversion of glycerol %	62.4	67.5	65.4	55.9	61.7	85.9	49.9

 Table 7 Pilot-scale experiments operating condition and results.

Note: The details of materials molar flow rate are shown in the supplementary information.

Ac/G (mol:	X of	Quality of solketal	Reboiler	Energy consumption	
mol)	X _G %	produced (g)	duty/W	per mass W/g	
1:2	54.8(X _{Ac} %)	144.85	71.84	0.496	
1:1	59.61	227.84	55.54	0.244	
2:1	67.57	201.81	59.14	0.293	
3:1	75.21	162.02	68.64	0.424	
6:1	83.30	110.09	79.16	0.719	
20:1	93.22	45.50	88.71	1.950	

Table 8 Ac/G feed ratio on energy consumption per unit mass

Category	Natural gas	Oil resources	Coal resources
CO ₂ Emission $\alpha/kg(C)\cdot kg^{-1}$	on Factor 0.42	0.55	0.69
Qs KW	770.4	770.4	770.4
Q Fuel KW	906.353	906.353	906.353
NHV kJ/kg	48900.00	41500.00	22000.00
η	0.85	0.85	0.85
CO ₂ reduction %	Emission 13.9	16.4	30.9

 Table 9 Computation of CO2 emission reduction.

Table 10 Comparison of RD and RDWC on TAC and reboiler duty.

Parameters	RD		RDW	С	
	RD	T_1	RD	Т	2
Reflux ratio	2.4	1.4		3	
Theoretical stages	16	7	5	1′	7
Reboiler duty of total process (W/g SK)	1.537		1.323		
Save energy (Reboiler duty / W/g $_{SK}$)			-21.4%		
Total annual cost (USD)	1,573,826		1,287,	500	
Save TAC by RDWC			-18.2%		
			Natural	Oil	Coil
Save CO_2 emissions by RDWC (per unit			gas	sources	sources
quantity of SK formed)%			-13.9	-16.4	-30.9

Notes: T_1 represents the distillation column to purify the solketal from bottom stream in RD column. T_2 is the distillation column in the equivalent flowsheet for RDWC to simulate the mass transfer process in it.