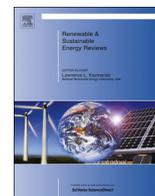




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Catalytic conversion of glycerol for sustainable production of solketal as a fuel additive: A review

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ABSTRACT

The exponential growth of biodiesel industries all around the world has produced a large amount of glycerol as a byproduct, which must be valorized for the sustainability of the biodiesel industry. Ketalization of glycerol with acetone to synthesize solketal—a potential fuel additive is one of the most promising routes for valorization of glycerol. In this article, state-of-the-art of glycerol ketalization is reviewed, focusing on innovative and potential technologies towards sustainable production of solketal. The glycerol ketalization processes developed in both batch and continuous reactors and performance of some typical catalysts are compared. The mechanisms for the acid-catalyzed conversion of glycerol into solketal are presented. The main operation issues related to catalytic conversion of crude glycerol in a continuous-flow process and the direct use of crude glycerol are discussed.

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Contents

1. Introduction	1023
2. Recent progress in the reaction processes	1023
2.1. Historical context	1023
2.2. Improvement in batch process	1024
2.3. Development of continuous processes	1025
3. Catalysis – the important parameter in ketalization reaction	1026
3.1. Influence of catalyst acidity	1026
3.2. Development and performance of transition metal catalysts	1027
4. Reaction models	1027
4.1. Reaction mechanism	1027
4.2. Reaction kinetics	1028
5. Key operation issues of flow reactors and use of crude glycerol as feedstock	1028
6. Conclusions	1029

Abbreviations: pTSA, p-toluenesulfonic acid; Ar-sBA-15, Arenesulfonic acid-functionalized mesostructured silica; PW, Tungsto-phosphoric acid; SiW, Tungsto-silicic acid; PMo, Molybdo-phosphoric acid; SiMo, Molybdo-silicic acid; CMR, Continuous microwave reactor; FM, Fluidic modules; WHSV, Weight hourly space velocity; Pr-SBA-15, Propylsulfonic acid-functionalized mesostructured silica; Ar-SBA-15, Arenesulfonic acid-functionalized mesostructured silica; HAR-SBA-15, Hydrophobised arenasulfonic acid-functionalized mesostructured silica; MPV, Meerwein–Ponndorf–Verley reduction; G, Glycerol; A, Acetone; F, Vacant adsorb sites; S, Solketal; FTIR, Fourier Transformation Infrared Spectroscopy; CTAB, Cetyltrimethyl ammonium bromide; TEOS, Tetraethyl orthosilicate; Zr-TUD-1, Three dimensional mesoporous Zirconium containing catalyst; Hf-TUD-1, Three dimensional mesoporous Hafnium containing catalyst; Sn-MCM-41, Mesoporous tin containing catalyst with mobil composition of matter number 41; Sn-MCM-1, Mesoporous tin containing catalyst with mobil composition of matter number 1; A/G, Acetone to glycerol molar ratio; Pr-SO₃H-SiO₂, Silica bonded-propylsulfonic acid; T-SiO₂, Silica bond-tosic acid; SAC-13, Nafion silica composite

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Acknowledgments.....	1030
References.....	1030

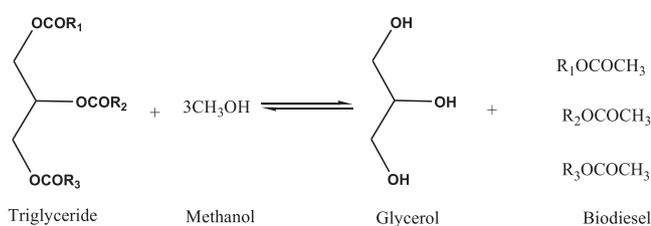
1. Introduction

The depletion of non-renewable fossil fuels and their environmental impacts are among the main factors that have drawn increasing attention towards biofuels, mainly bio-ethanol and biodiesel. Biodiesel is mainly produced by the transesterification of animal fats or vegetable oils (triglyceride) with a mono-alcohol (usually methanol) in presence of alkalis as shown below (Scheme 1) [1–3]. This biodiesel can be used directly or after blending with fossil-based diesel fuel.

In the transesterification process, glycerol is formed as the principal byproduct. It is estimated that 10 wt% amount crude glycerol is generated for each amount of biodiesel produced [4]. With the continued increase in the production of biodiesel, an excessive amount of glycerol is expected to accumulate. It is predicted that by 2020 the global production of glycerol will be 41.9 billion liters [5]. The crude glycerol produced from biodiesel industry contains impurities such as water, inorganic salts (sodium or potassium salts), methanol, fatty acids, and esters etc. [6–8], hence it is commonly treated as the waste stream of biodiesel industry. It is economically viable for the large biodiesel producers to refine this waste stream for the industrial applications, whereas for small biodiesel producers, they are unable to leverage the treatment costs and instead they pay for glycerol removal. Due to the excessive amount generated, the current crude glycerol price is as low as 0.04–0.09 \$/lb [9]. The predicted rapid growth of biodiesel production will further lower the glycerol price once it enters into market [10]. Therefore, new and economical ways of using glycerol must be developed to increase the value of crude glycerol to enhance the sustainability of biodiesel industries.

That being said, glycerol has diverse applications in different fields especially in the pharmaceuticals, food, cosmetics, and polymer industries [11–13]. The versatility of glycerol is mainly due to its physical and chemical properties. The presence of three hydroxyl groups in glycerol makes it completely soluble in water and alcohols whereas insoluble in hydrocarbons. Furthermore, the inter and intramolecular hydrogen bonds due to the presence of hydroxyl groups lead to the high boiling point of glycerol (290 °C) at ambient pressure and high viscosity (1.412 Pa s) at room temperature [14].

On the other hand, catalytic and biological conversion of glycerol offer a tremendous potential to produce value-added chemicals such as propanediols, acrolein, dihydroxyacetone, glyceric acid, tartaric acid, epichlorohydrin, hydrogen, syngas, ethers, esters, etc. [15–21]. Therefore glycerol can be considered as a platform chemical. A selection of these possibilities were reviewed recently [12,22,23]. Production of cyclic acetals and ketals from glycerol with aldehydes and ketones, respectively, is believed to be one of the most promising glycerol applications as fuel/chemical intermediates [24–27].



Scheme 1. Glycerol as byproduct during biodiesel production.

The ketalization reaction between glycerol and acetone is given in Scheme 2, where solketal (2, 2-dimethyl-1, 3-dioxolane-4-methanol or 1,2-isopropylidene-glycerol) is formed as the condensation product over an acid catalyst. Solketal can be used as a fuel additive to reduce the particulate emission and to improve the cold flow properties of liquid transportation fuels [28]. It helps to reduce the gum formation, improves the oxidation stability, and enhances the octane number when added to gasoline [29]. Maksimov et al. reported its use as a versatile solvent and a plasticizer in the polymer industry and a solubilizing and suspending agent in pharmaceutical preparations [30].

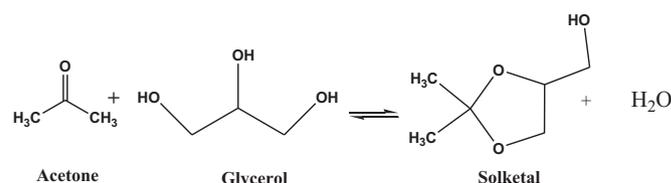
This review paper mainly over-views the state-of-the-art of the sustainable production of solketal by catalytic reaction of glycerol with acetone. Different types of processes and catalysts developed and their performances are compared. Fundamentals of reaction mechanisms for the acid-catalyzed conversion of glycerol into solketal are presented. The main operation issues related to catalytic conversion of crude glycerol in a continuous-flow process and the direct use of crude glycerol are discussed.

The review article aims to (1) introduce various applications of solketal in different industries including polymer, pharmaceutical and cosmetics, food, and fuel industries, (2) highlight some major challenges for industrial production of solketal, and (3) demonstrates promise of some new processes for utilization of crude glycerol as feedstock for the production of solketal.

2. Recent progress in the reaction processes

2.1. Historical context

It is well-known that ketals can be prepared by the reaction of an alcohol with a ketone in presence of an acid catalyst. Based on the public sources of literature, Fischer first prepared the solketal from acetone and glycerol in a batch reactor catalyzed by hydrogen chloride [31]. 25 years later Fischer and Pfahler reported ketalization of glycerol using hydrogen chloride and anhydrous sodium sulfate in a similar process [32]. Later, in 1948, Renoll and Newmann published their work on the synthesis of solketal in a three neck flask with reflux equipped with a sealed mechanical stirrer [33]. The authors chose petroleum ether as the reaction medium and p-toluenesulfonic acid (pTSA) monohydrate as the catalyst to achieve a high yield of solketal (87–90%). After the reaction, the products were separated by distillation under reduced pressure; however the reaction time was very long (21–36 h). These early studies on the synthesis of solketal remained without further advances until the end of the 20th century when massive amount of cheap glycerol was produced from biodiesel industry.



Scheme 2. Ketalization reaction between glycerol and acetone.

Nomenclature

[CpIrCl₂]₂ Pentamethylcyclopentadienyl iridium(III) chloride
k Rate constant

K_c Equilibrium constant for the reaction
r Rate of the reaction
K_w Equilibrium adsorption constant for water
E_a Activation energy

2.2. Improvement in batch process

A Spanish patent was filed in 1981–1982 aiming to utilize a large volume of glycerol [34]. The inventors studied the reaction of glycerol with acetone at the molar ratio of 1:1.1 in a batch reactor over acid catalyst without a water entrainer. In the process, by-product water was removed under reduced pressure (10 Torr) at equilibrium. However, the solketal yield never exceeded 80%, which was the major disadvantage of this process. In addition, a designed apparatus is required to work under reduced pressure to conduct the experiment. A very similar process was reported in literature where the authors heated glycerol with an excess of acetone over pTSA and reported a maximum of 56% solketal yield [35]. The low solketal yield is ascribed to the presence of water in the reaction.

The major issue in the ketalization reaction of glycerol is the formation of by-product water, which creates a thermodynamic and kinetic barrier for high glycerol conversion to solketal. Different processes were developed to overcome this issue.

Mushrush et al. studied the ketalization reaction using toluene as solvent [36]. In their experiment, 4.5 mol (232 g) of acetone was added to 1.1 mol (100 g) of glycerol and 3.0 g of pTSA with 255 g of 5 Å molecular sieves in a two neck round-bottomed flask (2 L), equipped with a mechanical stirrer and a refluxing condenser. The reaction mixture was heated under gentle reflux for 33 h using a heating mantle. The acidic reaction mixture was then neutralized with 3.0 g of sodium acetate and distilled to give solketal at a yield of 88%.

Garcia et al. studied the reaction with acetone-to-glycerol molar ratio (A/G) of 3 over pTSA monohydrate [37]. The mixture was heated to reflux for 16 h. During the process wet acetone was distilled off and dry acetone was simultaneously introduced to the reactor to maintain the liquid concentration. The yield of solketal was about 90% and no purification was required after solvent removal. Considering the fact that pTSA monohydrate is soluble in the reactants, the process can be classified as homogeneous catalysis, which causes a difficulty for catalyst recovery—typical drawback of reaction systems employing homogeneous catalysts. In fact, the use of homogeneous acid catalysts for chemical reaction processes has many serious shortcomings in addition to catalyst recovery, such as corrosion of the reactor, and the environmental and economic concerns over the effluent disposal. Hence, it is of significance to explore heterogeneous acid catalysts for the glycerol ketalization process. Deutsch et al. reported the use of Amberlyst-36 (an arenesulfonic acid polymer)—a heterogeneous acid catalyst in a batch reactor with organic solvent (dichloromethane) [24]. The authors conducted the experiment in the presence of the solid catalyst in a 100 mL flask equipped with a refluxing condenser. A Dean-Stark trap was used to remove the formed water continuously. The maximum yield of solketal was 88% (w.r.t. glycerol) (reaction conditions: 0.1 mol glycerol, 0.15 mol acetone, 17.5 mol dichloromethane, 0.5 g Amberlyst-36, 8 h reaction time at room temperature).

It is well known that the ketalization reaction has a very low equilibrium constant [37]. Therefore, to get high conversions of glycerol it is necessary to shift the equilibrium towards the formation of solketal. This could be achieved by either feeding excess amount of acetone or by removing the water generated during the

reaction continuously. Removing water produced from solketal synthesis is an effective way to break the thermodynamic barriers. To remove the water from the reaction mixture, entrainers have been used in different processes [39]. Benzene is not a preferable entrainer for this process as acetone is removed by distillation before benzene. Other entrainers for this process can be petroleum ethers and chloroform [39]. However, the efficiency of these entrainers is not great either because their boiling points are still higher than acetone. Acetone co-distillation creates the problem of low efficiency in azeotropic water removal. This phenomenon was evident from its very long reaction time when using petroleum ether as entrainer [16]. The use of phosphorous pentoxide and sodium sulfate as catalysts as well as desiccants for the removal of water generated from the system has also been reported [39], but high consumption of the catalysts in this case increased the operation costs. More recently, molecular sieves were used for this purpose [40]. All these processes are not economical on an industrial scale.

The above problems could be addressed more effectively by using excess acetone, which not only acts as a reactant but acts as an entrainer for the system. The excess acetone could be distilled off and reused in the same or other processes. Roldan et al. modified the batch reactor to a membrane batch reactor to remove the water from the reaction system [41]. The authors conducted the experiment by refluxing a mixture of glycerol, anhydrous acetone and heterogeneous acid catalyst, Montmorillonite K-10 (total weight 1 g) in a three-neck flask (250 mL) equipped with a reflux condenser, a septum cap and a zeolite membrane fixed in the central mouth (Fig. 1). The membrane allowed permeation of small sized water vapor instead of pervaporation. A maximum solketal yield of 82% was achieved by the authors using a very high A/G (20:1) for 2 h of reaction. As expected, a negligible effect of the catalyst on the solketal yield was observed in this work.

Recently, Vicente et al. attempted to remove water continuously from the reaction system by carrying out the reaction in a two-step batch mode operation [42]. In the first step, the reaction mixture (glycerol, acetone and a heterogeneous catalyst) was stirred under reflux at 70 °C in a 100 mL flask and in the second

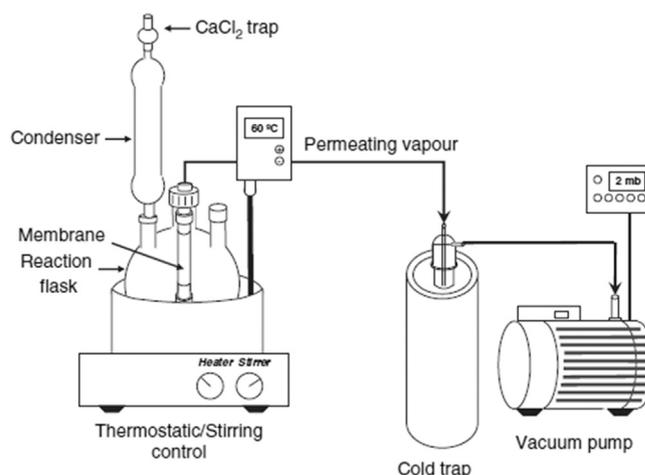


Fig. 1. Membrane reactor for synthesis of solketal (adopted with copyright permission [40]).

step, the water produced along with the excess amount of acetone was removed by vaporization under vacuum at 70 °C and fresh acetone was added to maintain the liquid level to start a new cycle. After three consecutive cycles (each cycle has two steps), a maximum solketal yield of 90% was achieved under the following reaction conditions; 70 °C, 5 wt% (w.r.t. glycerol) loading of Ar-SBA-15 catalyst, and 30 min for each step.

To search for an effective heterogeneous catalyst for the ketalization process, Ferreira et al. studied the reaction in a stirred batch reactor over a series of silica-induced heteropolyacid catalysts, i.e., tungsto-phosphoric acid (PW), tungsto-silicic acid (SiW), molybdo-phosphoric acid (PMo), and molybdo-silicic acid (SiMo) [43]. The reported catalytic activities for the catalysts are in the order of: SiMo < PMo < SiWS < PWS, mainly owing to the increase in acidity [43]. The authors reported glycerol conversion of more than 97% with a very high selectivity of 99% towards solketal at the reaction conditions: 70 °C, A/G of 12:1, catalyst (PW) loading of 0.2 g, and 2–3 h. The high yield of solketal in this work was attributed to the strong acidity of the catalyst that promoted the reaction kinetics and to the high A/G (12:1). Good catalytic stability was also observed, as the catalyst lost its activity by ~15% after four consecutive batch runs using the same catalyst.

Glycerol is poorly miscible with acetone in normal conditions (25 °C and 1 atm) (only 5 wt% of glycerol is soluble in acetone), which is the major disadvantage for the synthesis of solketal. Royon et al. proposed to use the supercritical acetone with better solubility for glycerol to synthesize solketal without using any catalyst [44]. The authors carried out the experiment at 508 K and 48 bar in a batch reactor, where acetone was at its supercritical state. However, a maximum of 28% glycerol conversion with a selectivity of 80% towards solketal was observed after 4 h reaction at the A/G of > 10. The low glycerol conversion and solketal yield might be due to the lack of active acid sites in acetone at supercritical condition. Hence, the result was not very encouraging. Since ketalization is an exothermic process [25], temperature is another important factor that affects the equilibrium conversion. To seek highly active catalysts at low temperature is another strategy to enhance the economy of the solketal production. Menezes et al. reported the highest ever solketal yield obtained in a batch reactor (95%) at ambient conditions [45], over 10 mol% of stannous chloride (SnCl₂) (w.r.t. glycerol) by reacting 6 M ratio of A/G for 0.5–2 h in presence of methyl cyanide (CH₃CN) solvent. Table 1 presents a summary of the performance of various catalysts for ketalization in batch reactors. From the Table, irrespective of the catalysts, a usual long reaction time was observed (0.5–33 h) for the solketal yield in the range of (82–96%). However, all the batch processes described above have common limitations in terms of the difficulty in scaling up for production of solketal on a large scale. Thus, the advances in glycerol ketalization with continuous-flow processes are discussed in the following section.

2.3. Development of continuous processes

As discussed earlier, the majority of the studies on synthesis of solketal were operated in batch reactors although using heterogeneous catalysts such as Zeolites, Amberlysts, montmorillonite, silica induced heteropolyacids, nafion, etc. [41–43,30] However, a batch process has various limitations of which the main ones are a long time of reaction (usually exceeding 2 h) hence relatively lower efficiency, and the difficulty in process scale-up [46]. Production of solketal in a continuous-flow reactor using heterogeneous catalysts is thus much more advantageous because the continuous-flow process enables better heat and mass transfer efficiency, and easy scaling-up of the process from laboratory to industrial scale as well as more environmental and economical benefits [47–50]. The continuous operation of the process also offers constant quality of the end product.

The use of a continuous microwave reactor (CMR) for the synthesis of solketal was reported [51]. In this CMR process, a solution of acetone, glycerol and pTSA as a homogeneous catalyst was mixed and pumped into the reaction coil (inside the microwave cavity) to react at a desired temperature (process similar to Fig. 3). The authors reported a maximum 84% yield of solketal at A/G of 13.5, in the presence of pTSA under the reaction conditions of 132 °C, 1175 kPa, 1.2 min residence time and of 20 mL/min feeding rate. However, the system was restricted only to homogeneous catalysts. Moreover, this technique would not be appropriate for conducting the reaction at a low temperature or for reactants that are not compatible with microwave energy.

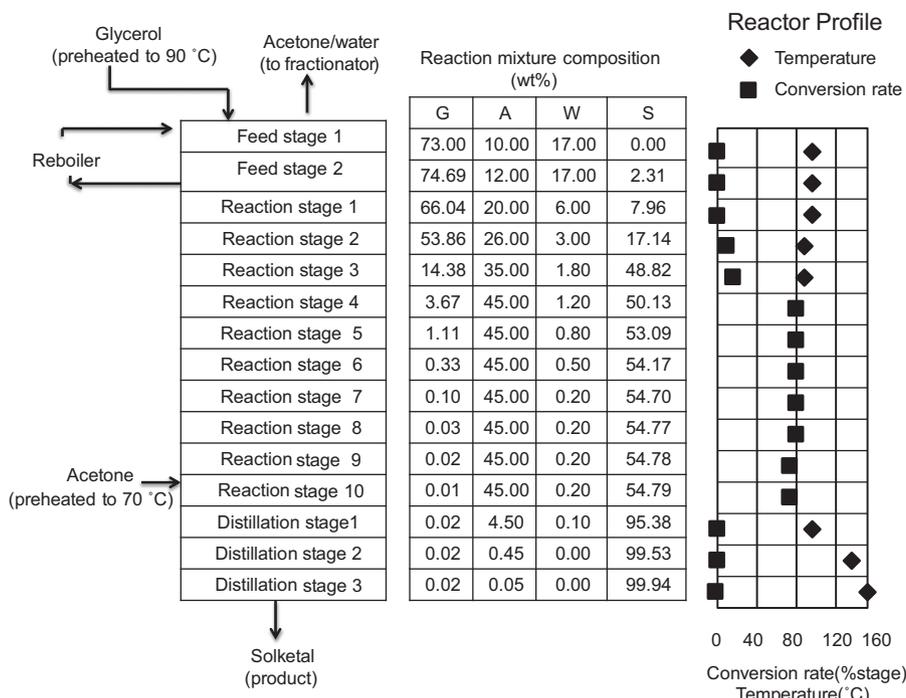
Clarkson et al. used a multi-tray reactive distillation column with deep reaction stages containing catalyst (Amberlyst DPT-1) in suspension for the synthesis of solketal [52], as illustrated in Scheme 3. In their process, glycerol was preheated at 90 °C before feeding into the reaction column. An extra amount of acetone was added in the reaction stage to drive the reaction towards the production of solketal and the process has a long reaction time (more than 4 h). With this, the process is actually a semi-continuous process (continuous operation with respect to acetone, but batch mode for glycerol). The process was found to be difficult to operate at a lower temperature due to the high viscosity of glycerol. A continuous glass flow reactor (Fig. 2) made of several glass fluidic modules and connected in series has been reported by Monbaliu et al. [53]. In their work, the total volume of the reactor is 72 mL and the first two fluidic modules (FM01 and FM02) were used for feeding, preheating and premixing of the reactants. Glycerol (feed 1) was preheated (on FM01) and reacted with acetone in all other modules (FM03–FM09) for the solketal product. Acetone (feed 2) and sulfuric acid (feed 3) were premixed and preheated in the fluidic module FM02. The main challenges of this reactor system include: a high residence time of the reactants, unsuitable for using heterogeneous catalysts,

Table 1
Performance of various catalysts for glycerol ketalization in batch reactors.

Experimental conditions ^a			Catalyst	Glycerol conversion (%)	Solketal selectivity (%)	Solketal yield (%)	Ref.
Temperature (°C)	A/G ratio ^b	Reaction time (h)					
Refluxed	4	33	pTSA		98	88	35
Refluxed	3	16	pTSA		–	90	36
38–40	1.5	8	Amberlyst 36	89	99	88	24
Refluxed	20	2	Montmorillonite K10	83	99	82	24
70	6	> 2.5	Ar-SBA 15	91	99	90	42
70	12	2–3	PW	99	97	96	43
235	11	4	–	28	80	22	44
Ambient	6	0.5	SnCl ₂	97	98	96	45

^a Reaction pressure is not available.

^b Acetone-to-glycerol mole ratio; Ar-SBA-15: Arenesulfonic acid functionalized mesostructured silica; PW: Tungstophosphoric acid; pTSA: p-Toluenesulfonic acid.



Scheme 3. Schematic diagram of a multi-tray reaction column for glycerol ketalization adopted from Clarkson et al. [51].

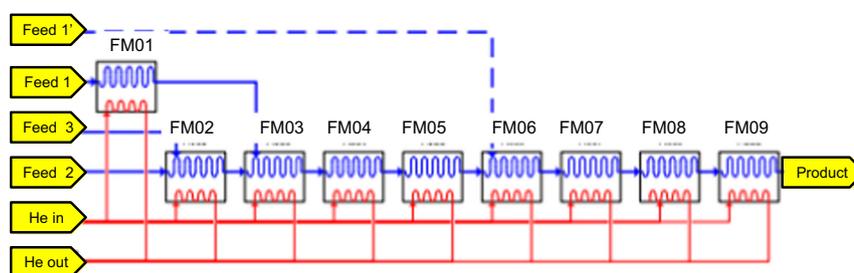


Fig. 2. Schematic diagram of a continuous glass flow reactor developed by Monbaliu et al. [52] (used with copyright permission).

difficulty in conducting the reaction at low temperature, and separation issues for the final product after neutralization, etc.

Maksimov et al. reported a continuous reactor for the preparation of high-octane oxygenate fuel components from plant-derived polyols, however no description of the reactor was given in the literature [30]. Recently, Nanda et al. have developed a continuous-flow reactor based on the concept of “Novel Process Windows” with respect to temperature, pressure and/or reactant concentration to enhance the intrinsic kinetics of the reaction for an optimum yield [54–57]. The reactor is a continuous down-flow tubular reactor (Inconel 316 tubing, 9.55 mm OD, 6.34 mm ID and 600 mm length) heated with a tube furnace. A similar flow process diagram is given in Fig. 3. The feed, a homogeneous solution of reactants (acetone and glycerol) with the solvent (ethanol) mixed at a selected molar ratio, was pumped into the reactor using a HPLC pump at a specific flow rate. The reactor was maintained at a desired temperature and pressure. In each run, a pre-determined amount of catalyst was preloaded into the catalytic bed, where the catalyst particles were supported on a porous Inconel metal disc (pore size: 100 μm) and some quartz wool. The amount of catalyst in each run was determined by the selected weight hourly space velocity (WHSV). This flow reactor can operate in a wide range of temperature and pressure using different heterogeneous catalysts. Amberlyst-36 wet was used to optimize the process, and the optimum process conditions are: 25 $^{\circ}\text{C}$, 500 psi, A/G of 4, WHSV of 2 h^{-1} , under which a very high yield of solketal (94 \pm 2 wt%) was

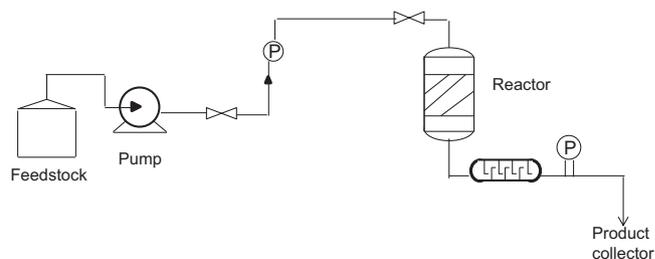


Fig. 3. Process scheme of continuous-flow reactor reported in literature [51,54].

obtained [58]. A summary of the performance of various catalysts for glycerol ketalization in flow reactors is given in Table 2. From the table, it is clear that high solketal yields (84–94%) are feasible in the range of 0.02–0.5 h reaction time in a continuous reactor. Therefore, development of continuous-flow processes is promising for production of solketal on a large scale.

3. Catalysis – the important parameter in ketalization reaction

3.1. Influence of catalyst acidity

As discussed later, the ketalization reaction proceeds via an acid catalyzed mechanism, hence catalysts with stronger acidity

Table 2
Performance of various catalysts for glycerol ketalization in continuous reactors.

Experimental conditions				Catalyst	Glycerol conversion (%)	Solketal selectivity (%)	Solketal yield (%)	Ref.
T (°C)	P (psi)	A/G ratio ^a	Reaction time (h)					
132	170	13.5:1	0.02	pTSA	–	–	84	51
40	600	6:1	0.25	H-β zeolite	87	98	84	54
40	600	6:1	0.25	Amberlyst 36 wet	91	97	88	54
40	600	6:1	0.25	Amberlyst 35	90	97	86	54
40	600	6:1	0.25	ZrSO ₄	79	97	77	54
25	500	4:1	0.5	Amberlyst 36 wet	97	97	94	54

pTSA: p-Toluenesulfonic acid;

^a Acetone-to-glycerol mole ratio.

Table 3
Influence of catalyst acidity on solketal yield.

Active phase	Reaction conditions (°C, A/G, T _r)	Acidity (meq/g)	BET (m ² /g)	Pore size (nm)	Yield (%)	Ref.
H-β Zeolite	40, 6:1, 0.25	5.7	480	2	84	54
Amberlyst-36 wet	40, 6:1, 0.25	5.6	33	24	88	54
Amberlyst 35	40, 6:1, 0.25	5.4	35	16.8	86	54
ZrSO ₄	40, 6:1, 0.25	–	–	–	77	54
Polymax	40, 6:1, 0.25	–	–	–	60	54
Montmorillonite K10	40, 6:1, 0.25	4.6	264	5.5	68	54
Amberlyst 36	38–40, 1.5:1, 8	5.4	19	20	88	24
Pr-SBA-15	70, 6:1, 0.5	0.94	721	8	79	42
Ar-SBA-15	70, 6:1, 0.5	1.06	712	9	83	42
HAr-SBA-15	70, 6:1, 0.5	1.04	533	8	80	42
Amberlyst 15	70, 6:1, 0.5	4.8	53	30	85	42
Pr-SO ₃ H-SiO ₂	70, 6:1, 0.5	1.04	301	2–20	77	42
T-SiO ₂	70, 6:1, 0.5	0.78	279	2–20	73	42
SAC-13	70, 6:1, 0.5	0.12	> 200	> 10	74	42

Pr-SBA-15: Propylsulfonic acid-functionalized mesostructured silica; Ar-SBA-15: Arenesulfonic acid-functionalized mesostructured silica; HAr-SBA-15: Hydrophobised arenesulfonic acid-functionalized mesostructured silica; SAC-13: Nafion silica composite; T-SiO₂: Silica bonded tosic acid; Pr-SO₃H-SiO₂: Silica bonded propylsulfonic acid.

(relatively more number of acid sites per unit mass) might lead to higher glycerol conversion. The influence of catalyst acidity on the solketal yield is shown in Table 3. It is clear that the catalyst acidity is a crucial parameter influencing the catalytic performance. Vicente et al. compared the performance of a series of catalysts with different acidities (ranging from 0.12 to 4.8 meq/g) for ketalization of glycerol: propylsulfonic acid-functionalized mesostructured silica (Pr-SBA-15), arenesulfonic acid-functionalized mesostructured silica (Ar-SBA-15), hydrophobised arenesulfonic acid-functionalized mesostructured silica (HAr-SBA-15), Amberlyst-15, silica bonded-propylsulfonic acid (Pr-SO₃H-SiO₂), silica bonded-tosic acid (T-SiO₂), and Nafion silica composite (SAC-13) [42]. They obtained a solketal yield of 74% for SAC-13 catalyst (acid strength 0.12 meq/g) and 85% for Amberlyst-15 (acidity 4.8 meq/g). Thus, a catalyst with a stronger acidity would likely perform better in the ketalization of glycerol with acetone. On the other hand, the results as shown in the table imply that surface area and the pore volume/size of a catalyst have negligible influence on the catalytic activity for the ketalization of glycerol. A recent study by Nanda et al. also revealed similar results in a continuous flow reactor [54]. The authors observed that the activity of catalysts was in the order of Amberlyst wet > H-beta zeolite > Amberlyst dry > zirconium sulfate > montmorillonite > Polymax, which follows the same order of the catalytic acidity (Table 3). Similar correlation between the catalyst acidity and the product yield has

been reported by Ferreira et al. in ketalization of glycerol by acetone [43].

3.2. Development and performance of transition metal catalysts

Transition metal catalysts have demonstrated good catalytic performance in glycerol ketalization [59]. In fact, iridium catalyzed ketalization reactions are promising and have been well studied among other transition metal catalysts [60–64]. The most active catalyst for the ketalization reaction was [CpIrCl₂]₂ (Cp= pentamethylcyclopentadienyl) [59], with a glycerol conversion of 87% and 98% selectivity towards solketal in a batch reactor (other experimental conditions were: 40 °C, [Ir]=3.0 × 10⁻³ M, [glycerol]/[Ir]=500, and 1 h reaction time). Li's group specifically studied the performance of mesoporous substituted silicates [65], in which the metal atoms were incorporated in the silicate framework. The authors reported that the Zr-TUD-1 and Hf-TUD-1 were prepared by a one-pot sol-gel procedure, where triethanolamine was used as chelating and template agent and zirconium propoxide and hafnium chloride as the metal precursors. Another catalyst Sn-MCM-41 was prepared by hydrothermal synthesis in a procedure similar to that of Li et al. [65], using cetyltrimethylammonium bromide (CTAB) as the template in a gel formed from a solution of tetraethyl orthosilicate (TEOS), SnCl₄ · 5H₂O and tetraammonium silicate [66]. The conversion of glycerol reached around 64%, 65% and 62% for Zr-TUD-1, Hf-TUD-1 and Sn-MCM-1 catalysts, respectively, with almost 100% selectivity towards solketal in a batch reactor under the experimental conditions of: 80 °C, 6 h reaction time, and A/G of 2:1.

4. Reaction models

Establishing reaction paths for any process and for ketalization in particular is very crucial in the design of a catalyst. In addition, establishing the reaction rate equations helps in designing the reactor as well. The reaction mechanism and the kinetic models developed for the glycerol ketalization process are discussed below.

4.1. Reaction mechanism

As discussed previously, the relative acidity of the catalysts has significant effects on the glycerol conversion and the product yield. It is thus of significance to discuss the reaction mechanism for the glycerol ketalization reaction catalyzed by acid catalysts. The condensation reaction of glycerol with acetone leads to the formation of both five membered and six membered rings (ketals) [67]. However the six membered ring ketal is less favorable because one of the methyl groups in the final product is in axial position of the chair conformation (Fig. 4) [30,68]. So the resulting product has a ratio of 99:1 for five membered ring (4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane, or solketal) to six membered ring (5-hydroxy-2,

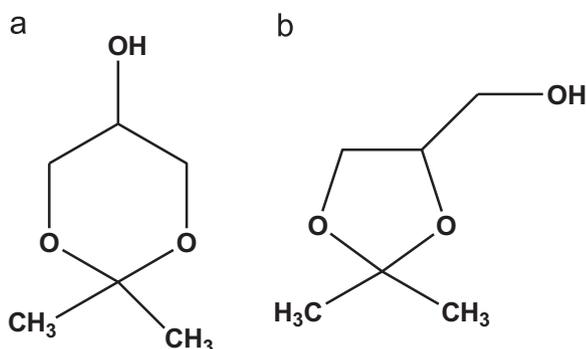


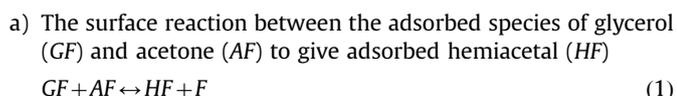
Fig. 4. The cyclic acetals from the reaction between glycerol and acetone: 5-hydroxy-2,2-dimethyl-1,3-dioxane (a) solketal i.e. 4-hydroxymethyl-2,2-dimethyl-1,3-dioxane (b).

2-dimethyl-1,3-dioxane). For the ketalization reaction catalyzed by Brønsted acids, the five membered ring solketal is dominantly formed through a mechanism involving a short-lived carbenium ion as an intermediate [65,69]. Li and co-workers proposed a similar mechanism for the ketalization reaction over Lewis acid catalysts [65]. According to this mechanism, the Lewis acid metal sites play a role similar to the MPV reduction (Meerwein–Ponndorf–Verley) or Oppenauer oxidation reactions, by coordinating and activating the carbonyl group of the acetone. Then the carbon atom of the carbonyl group is attacked by the primary alcoholic group of glycerol accompanied by the formation of a bond between the carbonyl oxygen atom and the secondary carbon atom of glycerol followed by dehydration to form the five membered ring solketal. The detail mechanism is displayed in Scheme 4.

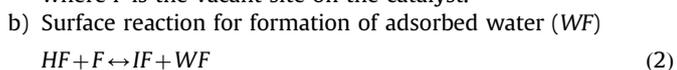
Nanda et al. have also used a reaction framework (Scheme 5) for the ketalization reaction proceeding via acidic catalytic mechanism involving 3 steps [38]. The first step involves the surface reaction between the adsorbed acetone and glycerol over the catalyst surface to form the hemi-acetal. The next step is the removal of water leading to the formation of a carbocation on the carbonyl carbon atom, and the last step is the removal of the proton to form solketal.

4.2. Reaction kinetics

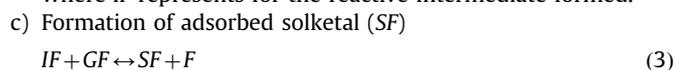
The general reaction rate for the ketalization reaction has been expressed in form of Langmuir–Hinshelwood model with surface reaction as the rate determining step [38]. The key reaction steps of this model are given as follows:



where F is the vacant site on the catalyst.



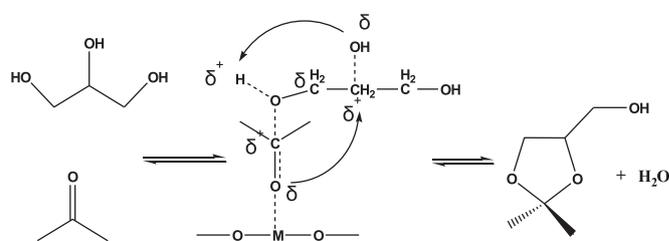
where IF represents for the reactive intermediate formed.



The simplified rate expression for the reaction is given as [38]:

$$r = k \frac{[G][A] - [S][W]/K_c[G]}{\left\{1 + K_w[W]\right\}^2} \quad (4)$$

where K_w is the equilibrium constant for water adsorption on the catalyst surface. According to the above kinetic model three



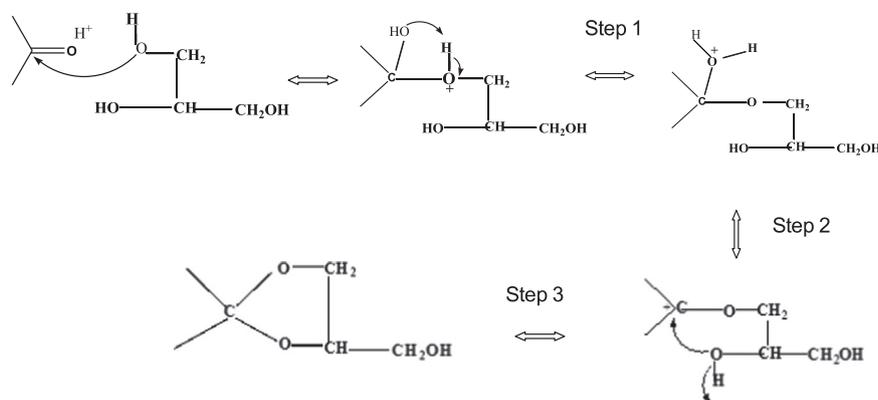
Scheme 4. Mechanism proposed by Li et al. [64] for the reaction of acetone and glycerol over Lewis acid catalyst (M is the metal atom).

parameters (kinetic constant; k and water adsorption constant; K_w and ketalization equilibrium constant; K_c) are to be estimated at each temperature to find the rate of the reaction. The estimated values of these parameters are given in Table 4. Based on the variation of kinetic constant with temperature, the activation energy (E_a) of the reaction has been reported to be $55.6 \pm 3.1 \text{ kJ mol}^{-1}$. [38]

5. Key operation issues of flow reactors and use of crude glycerol as feedstock

As discussed earlier, the ketalization reaction proceeds via an acid catalyzed mechanism, which means catalysts with stronger acidity might lead to higher glycerol conversion. However, catalysts with strong acidity would enhance fouling. Nevertheless, since the reaction is exothermic and carried out at a low temperature (usually below 80°C), the deactivation of catalyst due to fouling can be avoided. Nanda et al. investigated the catalytic deactivation process of different heterogeneous acid catalysts such as H-beta zeolite, Amberlyst-35 dry and Amberlyst-36 wet in a continuous-flow reactor and observed a slight reduction in the activities of these catalysts after 24 h on-stream as compared to that of the fresh catalyst [54]. To better understand these phenomena, they measured the textural properties and acidity of the spent catalyst (Amberlyst-36 wet) after 24 h on-stream and compared to the results of the fresh catalyst. The slight reduction in the activity of the spent catalyst was attributed to the loss of active acid sites during the reaction, not due to fouling. In order to regain the initial activity of the catalyst, the spent catalyst was regenerated and the regenerated catalyst demonstrated almost the same activity ($> 93\%$ yield) as that of the fresh catalyst [70]. However, after a long time (days or months) operation of a continuous-flow reactor using heterogeneous catalysts, reactor clogging might occur, caused by fine particles of disintegrated catalysts [54]. This problem can be effectively alleviated by diluting the catalyst with glass beads and/or by decreasing the catalytic bed height.

The price of glycerol depends on the technical grade. The refined pure glycerol is currently expensive, costing around US\$ 500–600 per ton [70]. Crude glycerol is available for only US\$ 40–90 per ton [9]. Thus, use of crude glycerol for the production of value-added products is crucial for achieving a sustainable and economical production of solketal. However, as mentioned earlier, crude glycerol contains impurities including water, potassium or sodium salts, esters, fatty acids and alcohols. Therefore, the direct use of crude glycerol as feedstock may cause problems such as deactivation of catalyst (by poisoning the active sites by the impurities) or plugging of reactor (due to deposition of high boiling organic compounds or inorganic salts). To facilitate the use of crude glycerol, da Silva and Mota investigated the effect of impurities on the production of solketal in a batch reactor [71]. They added impurities such as 10% water, 15% NaCl and 1% methanol (assuming that these are the common impurities present in crude glycerol) to pure glycerol and conducted the ketalization experiment in presence of heterogeneous catalysts such as Amberlyst-15 and H-beta zeolite. They observed significant



Scheme 5. Mechanism used by Nanda et al. [37] for the reaction of acetone and glycerol over acid catalyst.

Table 4
Kinetic model parameters at different temperatures.

Temperature (K)	K_C	k (L mol ⁻¹ min ⁻¹)	K_W
298	2.66	0.11	2.65
303	1.82	0.16	1.50
308	1.51	0.24	1.09
313	1.30	0.33	0.73
323	0.98	0.63	0.34

K_C : Equilibrium constant for the reaction; k : Kinetic constant; K_W : Equilibrium constant for water adsorption on the catalyst surface

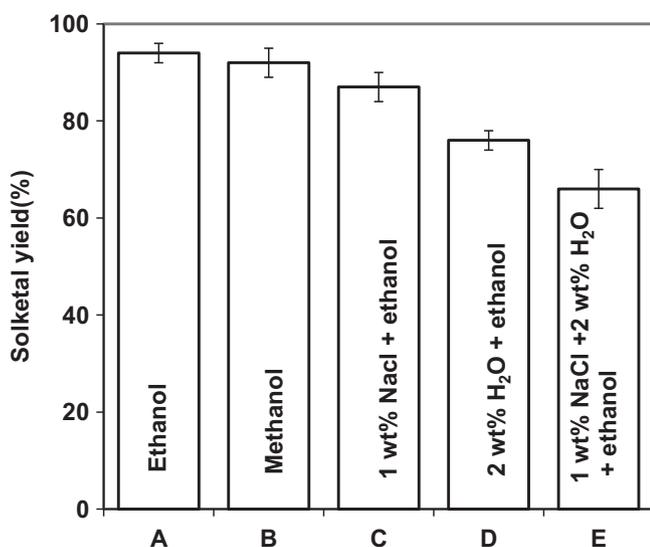


Fig. 5. Deactivation of catalyst by impurities in the glycerol feed.

reduction in glycerol conversion (from 95% to 47% for Amberlyst-15 and from 90% to 50% using H-beta zeolite) while switching the feed from pure glycerol to the impurities-added glycerol. A similar result has also been observed by Nanda et al. in a continuous-flow reactor (Fig. 5) [58].

Nanda et al. moved one step further and developed a modified continuous-flow reactor consisting of guard reactors allowing online removal of impurities in the glycerol feedstock and online regeneration of deactivated catalysts (Fig. 6) [70]. Using crude glycerol and the modified continuous-flow reactor, a significant yield of solketal (~78%) was obtained after 1 h on-stream. Moreover, the authors have carried out an on-line regeneration of the deactivated catalysts in the guard reactor and ketalization experiment simultaneously using purified crude glycerol ($\approx 96\%$ purity) as the feedstock and found that the

catalyst (Amberlyst-36 wet) could be successfully regenerated for four consecutive cycles (96 h) with acceptable reduction in the solketal yield (from 92% to 81%) [70]. For the regeneration of the catalyst (Amberlyst-36 wet) in the guard reactor, a 0.5 M sulfuric acid solution was used to pass through the guard reactor, followed by washing the regenerated catalysts with methanol solution and drying the bed with nitrogen for 5 h.

6. Conclusions

This review paper over-views the state-of-the art of the sustainable production of solketal by catalytic reaction of glycerol with acetone. Different types of processes and catalysts developed and their performances are compared. Fundamentals of reaction mechanisms and kinetics for the acid-catalyzed conversion of glycerol into solketal are presented. The main operation issues related to catalytic conversion of crude glycerol in a continuous-flow process and the direct use of crude glycerol are discussed. Some key conclusions are summarized below:

- (1) Conversion of glycerol to solketal can proceed either using a homogeneous or heterogeneous catalyst; nevertheless the use of heterogeneous catalysts is preferred, as there are many shortcomings for using homogeneous catalysts, e.g., difficulty in catalyst recovery, corrosion to the reaction systems, and the environmental and economical concerns over the effluent disposal. Hence, it is of significance to explore heterogeneous acid catalysts for the glycerol ketalization process.
- (2) The ketalization reaction has a very low equilibrium constant. In order to reach high conversions of glycerol it is necessary to shift the equilibrium towards the formation of solketal, by either feeding excess amount of acetone or by removing the water generated during the reaction continuously.
- (3) All the batch processes have common limitation in terms of the difficulty in scaling up for production of solketal on a large scale. Compared with operation in a batch reactor, a continuous-flow process results a similar product yield with relatively shorter reaction time. Therefore, development of continuous-flow processes is promising for production of solketal from glycerol on a large scale.
- (4) The best yields of solketal were achieved by catalysts like Amberlyst-15, Amberlyst-35, Amberlyst-36, Ar-SBA-15, Zeolites, and SnCl₂. The preferred reaction conditions are: catalysts with higher acidity, higher A/G, and lower temperature ($< 70^\circ\text{C}$). Using Amberlyst-36 wet catalyst, a very high yield of solketal ($94 \pm 2\%$) was obtained at 25°C , 500 psi, A/G of 4, and WHSV of 2 h^{-1} .

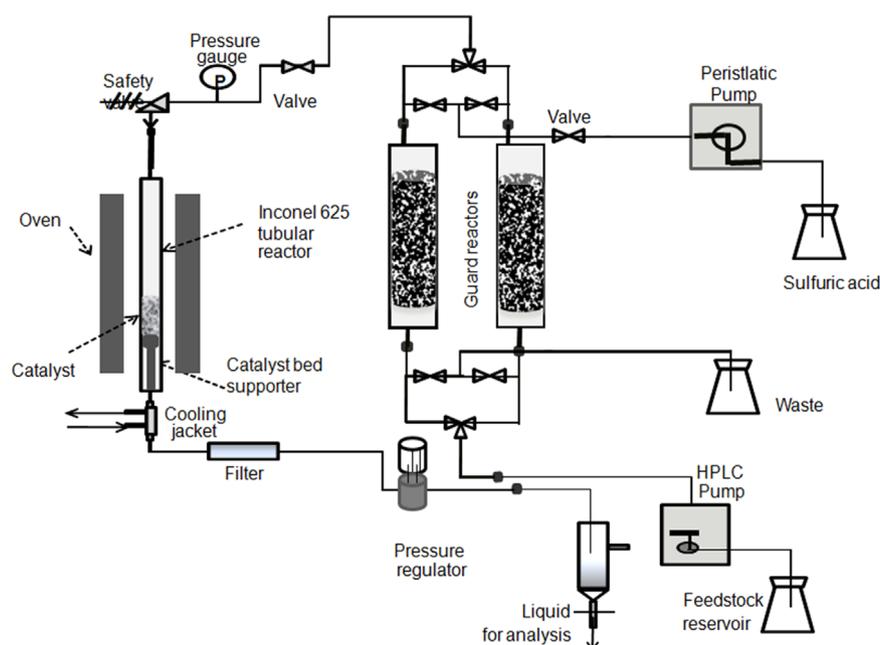


Fig. 6. Novel flow-reactor consisting of guard reactors allowing online removal of impurities in the glycerol feedstock and online regeneration of deactivated catalysts.

- (5) The ketalization reaction proceeds via acidic catalytic mechanism, hence catalysts with strong acidity might lead to high glycerol conversion.
- (6) Heterogeneous catalysts for glycerol ketalization in a continuous-flow reactor can be deactivated, attributed to the loss of active acidic sites during the reaction, not due to fouling. For a long time (days or months) operation, however, the reactor clogging might occur, caused by fine particles of disintegrated catalysts.
- (7) Direct use of crude glycerol as feedstock may cause problems such as deactivation of catalyst (by poisoning the active sites by the impurities) or plugging of reactor (due to deposition of high boiling organic compounds or inorganic salts).
- (8) The review article introduces various applications of solketal in different industries including polymer, pharmaceutical and cosmetics, food, and fuel industries, and highlights some major challenges for industrial production of solketal. In addition, this review article demonstrates the promise of new processes for utilization of crude glycerol as feedstock for the production of solketal.

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Glossary

- Biodiesel: vegetable oil/or animal fat based diesel having long chain alkyl esters;
 Ketalization: reaction between a ketone and excess of alcohol to form a ketal;
 Valorization: route to enhance the value of the raw material;
 Solketal: a compound formed by the reaction between acetone and glycerol;
 Transesterification: an organic process of exchanging the alkyl group between an alcohol and an ester;
 Crude glycerol: impure glycerol formed during the production of biodiesel;
 Entrainer: reagent which can carry water into the vapor phase;
 Pervaporation: a process used to separated a mixture of liquids by partial vaporization through a membrane;
 Homogeneous catalyst: catalyst that exists in the same phase as the reactants in the reaction;
 Heterogeneous catalyst: catalyst that exists in a different phase from the reactants in the reaction.