Ketalization of glycerol to solketal in supercritical acetone

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ABSTRACT

In the last few years, the increasing production of biodiesel has led to an overproduction of glycerol, the main byproduct of this industry. This paper reports on the ketalization of glycerol in supercritical acetone to give solketal (4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane), an oxygenated compound useful as chemical and fuel additive for gasoline, diesel and biodiesel. The application of supercritical fluids (SCFs) in the chemical synthesis was explored to carry out reactions to obtain the above cyclic ketal. The experimental results reveal a drastic change in the reaction behavior when the critical condition of acetone is reached ($T = 508\,K$). Below 508 K the reaction rate of solketal production is very low, but above this temperature a rapid increase in the reaction rate is observed. Finally, the reaction rate is stabilized at 533 K and higher temperatures due to the conversion of glycerol to acrolein and polymeric products as side reactions.

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1. Introduction

Glycerol, a renewable raw material, is a product strongly established in many industrial processes. It is obtained as a by-product when vegetable oils and fats are hydrolyzed or esterified to yield fatty acid, metal salts, or other esters. The increasing biodiesel production has brought about concern regarding an oversupply of glycerol to the market. Therefore, the development of new uses and chemicals from glycerol is needed.

Glycerol cannot be added directly to fuel due to its decomposition and polymerization that would lead to engine problems at high temperature. Glycerol must be modified to derivatives compatible with gasoline, diesel and biodiesel before it is added to the fuel. Compounds like ketals and ethers have a potential for being used as additives in fuels and biofuels [1–4]. Some of the most promising compounds are etherified glycerol obtained by using isobutylene, giving new oxygenated compounds that decrease the viscosity and cloud point in biodiesel. These compounds have been shown to be effective for reducing particulate matter emissions in diesel and biodiesel fuels [2].

An interesting alternative is the solketal (4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane) [5], a ketal produced from glycerol and acetone, used as a solvent and plasticizer or as suspension agent in pharmaceutical preparations. In the conventional processes, solketal is produced by using acid catalysts (hydrochloric acid, sulphuric acid, phosphorus pentoxide, p-toluensulfonic acid) in solvents like chloroform, ether or oil [6–8]. The application of the supercriti-

cal fluids (SCF) technology allows the synthesis of solketal from glycerol without catalysts.

In the last few years, we have focused our attention on the development of organic compounds derived from oleochemical materials such as glycerol and fatty acids. In the present work, we describe the reaction between acetone and glycerol that produces the corresponding cyclic ketal (solketal). The use of acetone as a supercritical fluid (SCAc) is not common but has been studied in a few areas like degradation of polymers [9] and dehydration of carbohydrates [10].

In conventional processes, solketal is produced using acid agents as catalysts (Fig. 1).

At standard conditions (298 K; 0.1 MPa) glycerol is poorly miscible with acetone, a disadvantage for the synthesis of solketal. In our experiments, the reaction was performed under conditions of high pressure and temperature (SCAc) making this reaction possible without acid catalysts.

The present study deals with the use of acetone as a supercritical fluid. The aim of this work was to have a better understanding of the influence of the operating conditions on the reaction pathways. The use of acetone under supercritical conditions allows the use of lower temperatures ($T = 508\,K$) for the reaction than those used with other solvents, like water ($T = 647\,K$). The pyrolysis of glycerol to acrolein and its further polymerization, at high temperatures and pressures, was also investigated as some of the possible competing reactions.

2. Experimental

2.1. Materials and methods

Glycerol (99.5%) (J.T. Baker) and acetone (99+%) (Carlo Erba) were used as reactants. Both reagents were kept anhydrous by

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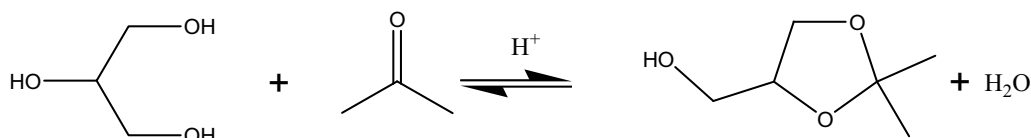*E-mail address:* locateli@unsa.edu.ar (S. Locatelli).

Fig. 1. Synthesis of solketal: scheme of reaction.

the addition of 5A molecular sieves (Aldrich). Solketal (99+%) from Sigma–Aldrich and Cyclohexanol (98%) (Tetrahedron) were used as a gas chromatography (GC) standard. Mesityl oxide and acrolein was synthesized in our laboratory.

The experiments were carried out in a batch reactor. The reactor vessel was made from stainless steel 310, having an internal volume of 20 cm³. To follow the pressure inside the reactor a mechanical gauges ($\pm$0.1 bar) connected to the reactor head with a stainless steel capillary, was used. Temperature was measured with a thermocouple inserted in the reactor wall and connected to a digital thermometer ($\pm$1 °C). Predetermined amounts of reactants (by considering critical volumes) were loaded into the reactor using an acetone/glycerol molar ratio ranging from 2.1 to 10.8. The reactor vessel was immersed in a molten tin-lead bath. The heating time to raise the reactor temperature from near 293 K to the desired reaction temperature was less than 3 min. The temperature (490–550 K) was controlled to within $\pm$ 3 K. The reactor was quenched in a water bath at room temperature after a given reaction time was reached.

To study the influence of water in the synthesis of solketal, experiments were carried out using a 0.14–0.55 water/glycerol molar ratio range, at a constant acetone/glycerol molar ratio of 3.6. We performed phase equilibrium calculations using SPECS V5.24 process simulation software [11] and used the FLASH block with the Soave–Redlich–Kwong equation of state with quadratic mixing rules. Calculations at temperatures and pressures between 520–530 K and 5.5–7.5 MPa, and with water contents up to 0.1 mole fraction, indicate that the system exists as a homogeneous phase.

2.2. Analysis

Reaction products were analyzed with a Shimatzu gas chromatograph equipped with a dual column (Chromosorb 102 and Porapak TYPE P) (2.5 m and 0.5 m, respectively) and thermal conductivity detector. Nitrogen was used as carrier gas. The oven and detector temperature was 468 K. The conversions reported for each point are average values based on three samples for the amount of solketal produced. The uncertainties reported for the conversions are the experimentally determined 95% confidence intervals. IR spectra were measured on Perkin Elmer SPECTRUM GX.

3. Results and discussion

It is well known that under acetone supercritical conditions the miscibility of acetone with glycerol increases substantially, decreasing the resistance to the mass transfer, and consequently favoring the reaction rate. In our case acetone is part of the reaction but it could also have an active role as catalyst when supercritical conditions are reached, acidic property of the alpha hydrogen of the

Table 1
Glycerol conversion and selectivity to solketal.

Time (min)	Acetone/glycerol molar ratio	Conversion (%)	Selectivity (%)
20	2.1	3.6	98 $\pm$ 2
40	2.1	6.2	95 $\pm$ 2
120	2.1	14.4	88 $\pm$ 2
240	2.1	13.5	75 $\pm$ 2
20	3.6	3.5	99 $\pm$ 2
40	3.6	6.1	98 $\pm$ 2
120	3.6	15.5	91 $\pm$ 2
240	3.6	23.0	81 $\pm$ 2
20	10.8	5.1	98 $\pm$ 2
40	10.8	8.4	97 $\pm$ 2
60	10.8	12.5	96 $\pm$ 2
120	10.8	18.5	90 $\pm$ 2
240	10.8	28.2	80 $\pm$ 2

Pressure 8 MPa, temperature 523 K. The selectivity to solketal is calculated as the ratio between moles of solketal produced to moles of glycerol converted.

acetone will increase through the keto-enol tautomerism (Fig. 2). High enol concentration is consistent with rapid and almost complete H-D exchange at the alpha position of acetone in superheated or supercritical water, as reported by several authors [12–14]. Strong acidity of acetone in gas phase at low pressure is also known [15,16], being more acidic than water. This means that above the acetone critical temperature, his acidity will change strongly.

In our system, water concentration is low or absent, however glycerol acts as the media to promote H exchange. Many reactions are catalyzed by protons or hydroxyl ions in near-critical water without the addition of acid or bases, simply because of the high ionic product of water under these conditions [17]. We consider that the same phenomenon occurs with (SCAc). Therefore, SCAc may act simultaneously as a solvent, catalyst, and reagent for a reaction that is typically acid-catalyzed.

Table 1 summarizes the results of conversion of glycerol and the selectivity to solketal as function of reaction time and acetone/glycerol molar ratio.

3.1. The influence of the reaction temperature

When the reaction between acetone and glycerol was studied under subcritical and supercritical conditions, we found a large difference in the reaction rate when temperature was below or above the acetone critical temperature (508 K).

As shown in Fig. 3, up to the acetone critical temperature the reaction rate of solketal production is very low and follows an Arrhenius behavior. However, above 508 K, the reaction rate has a sharp rise up to a temperature of approximately 533 K and begins to stabilize due the competing reactions of glycerol decomposition
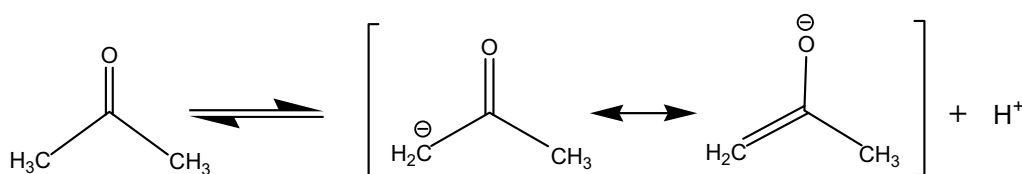

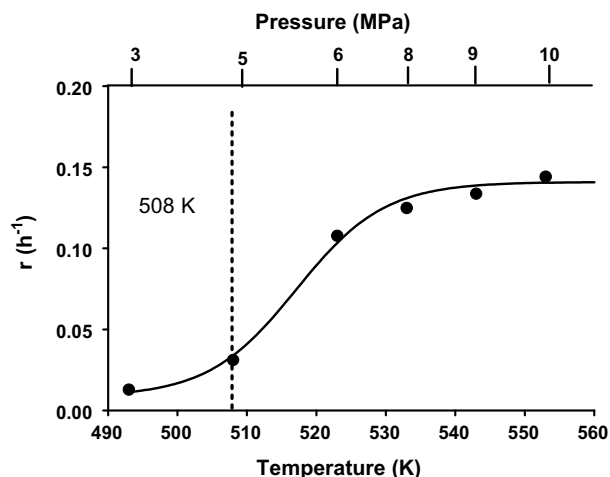Fig. 2. Keto-enol tautomerism of acetone.

Fig. 3. Effect of temperature on the reaction rate of solketal synthesis. Time of reaction: 20 min. Acetone/glycerol molar ratio: 3.6.
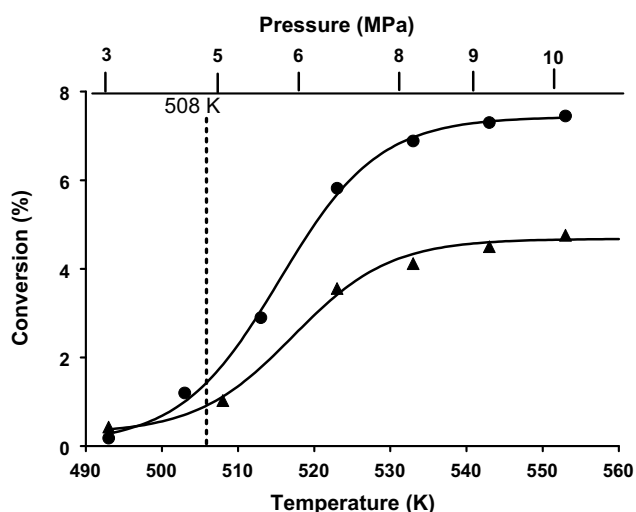

Fig. 4. Effect of reaction temperature on the conversion to solketal. Acetone/glycerol molar ratio: 3.6. Time of reaction: (●) 60 min; (▲) 20 min.

to acrolein and the formation of a low molecular weight polymeric material [18,19].

Fig. 4 shows the glycerol conversion to solketal as function of temperature at two different reaction times. In both experiments, the conversion to solketal was kept below 10% to avoid side reaction. Fig. 4 also shows that as the reaction time changes, the way the

glycerol conversion increases as a function of temperature remains unchanged.

The results of our investigation show a large increase in the reaction rate at temperatures above 508 K, which shows that the catalytic activity derives from the acidic property of the alpha hydrogen of acetone, when the critical state is reached. This behavior has also been reported in the reaction between acetone and alkenes through the alpha hydrogen when the system is above the acetone critical temperature [20].

We consider that the acidity of the alpha hydrogen of acetone also catalyzes the glycerol conversion to acrolein and its further polymerization when higher pressures and temperatures are reached inside the reactor. However, we found by GC analysis that acrolein concentration was practically constant and lower than 0.3% in all our experiments at temperature above 530 K, indicating a fast polymerization to other products. IR spectra of these polymeric product (Acetone/glycerol molar ratio of 2.1, reaction time 2 hs, pressure 8 MPa and 523 K) shows that it is a complex mixture of low molecular weight polyacrolein. Bands at $2930\,cm^{-1}$, $2880\,cm^{-1}$, $1710\,cm^{-1}$ and $1610\,cm^{-1}$, are indicating structure like polyacrolein [21,22]. Under supercritical acetone, up to 550 K, and in the absence of glycerol, ketone condensation products (like mesityl oxide) were lower than 0.1%, as observed by GC analysis. This result indicates that polymerization of acetone thorough condensation reaction can be neglected.

3.2. The influence of the reaction time and acetone/glycerol molar ratio

The synthesis of solketal at different acetone/glycerol molar ratio was studied at 523 K.

Fig. 5(A) shows that the reaction rate does not change significantly when acetone/glycerol molar ratio varies from 2.1 to 10.8. This result shows that the acetone is mainly in the enol form, therefore a large amount of acetone works as a catalyst. Usually, when the reaction is carried out at standard conditions, an excess of alcohol is used to increase the equilibrium conversion. We found that under critical acetone conditions there is no need of an excess of alcohol since the amount of catalyst in the system is large enough, therefore the reaction rate is practically independent of the glycerol concentration.

On the other hand, for long reaction time (>2 h), the solketal production rate decreases rapidly, more noticeable at low acetone/glycerol molar ratio. Fig. 5(B) shows the change in the conversion to solketal as function of reaction time. The conversion to solketal rises to a maximum level and then drops rapidly. The maximum is reached at greater reaction times as the acetone/glycerol ratio increases. After the maximum is reached, the polymeric side product appears in a large amount.
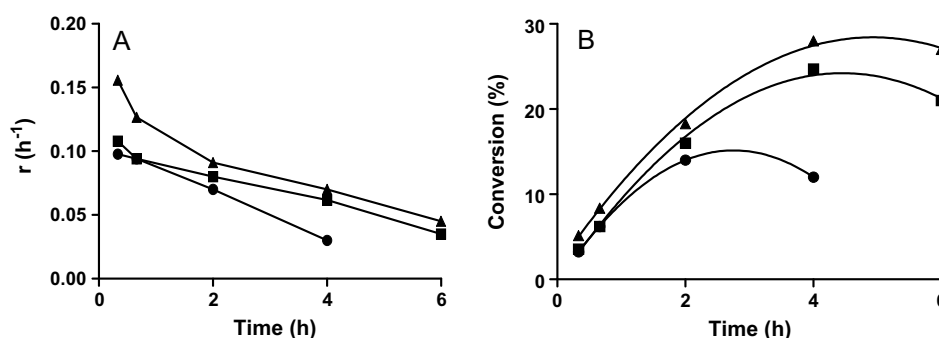

Fig. 5. Influence of the acetone/glycerol molar ratio on: (A) reaction rate of solketal synthesis, and (B) conversion to solketal; over time. Temperature of reaction: 523 K. Acetone/glycerol molar ratio: 10.8 (▲); 3.6 (■) and 2.1 (●). Pressure: 8 MPa.
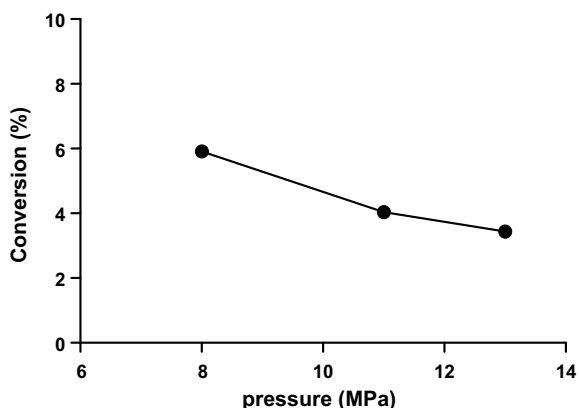
Fig. 6. Effect of system pressure on the conversion to solketal. Temperature: 523 K. Acetone/glycerol molar ratio: 3.6. Time of reaction: 40 min.

3.3. The pressure influence

The effect of pressure was examined in the range of 8–13 MPa, with the system at supercritical conditions (523 K). The glycerol conversion to solketal decreased as pressure increased, as is shown in Fig. 6. We observed that the production of acrolein and polymeric material are significantly enhanced as pressure is increased. The formation of these byproducts is also enhanced if both reaction time and temperature increase, due to the acetone acidity under supercritical conditions. Under acidic conditions acrolein is stable [19], but in our case as stated before, a low concentration of acrolein is indicative that at high pressure and temperature polymerization takes place rapidly.

3.4. Water influence

In the traditional process the equilibrium for the solketal synthesis is unfavorable and water elimination or an excess of alcohol are needed to overcome the chemical equilibrium limitation in the formation of ketals [7,8]. It was expected that the water content in our system would affect the yield negatively, since the presence of water would displace the balance towards the left side of the reaction and would produce the solketal hydrolysis. However, we found that under acetone supercritical conditions, water did not affect significantly the conversion to solketal compared with the effect observed in the conventional processes.
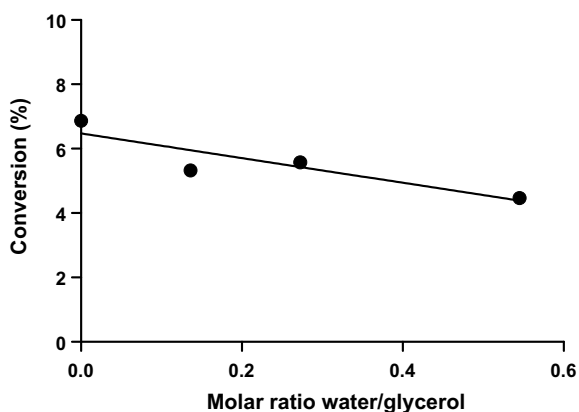

Fig. 7. Effect of water on the conversion to solketal. Time of reaction: 40 min. Acetone/glycerol molar ratio: 3.6. Temperature: 523 K. Pressure 8 MPa.

Fig. 7 shows that, even when the initial water/glycerol molar ratio was high, the observed change in conversion was low. We must point out that for a water/glycerol molar ratio of 0.55, the water produced by the reaction is about 1/10 of the added water.

4. Conclusions

Solketal synthesis in supercritical acetone is possible due to the catalytic effect of the acidic strength of the alpha hydrogen of acetone in gas phase. The solketal yield depends mainly on temperature and pressure. At temperature near and above acetone critical temperature (508 K) the reaction rate rises very fast. Above 540 K, selectivity to solketal decreases rapidly due to the production of acrolein and polymeric materials. Water did not affect significantly the rate of solketal production under SCAc conditions. Our results show that supercritical acetone work as a solvent, reactant and catalyst, making it an interesting alternative for organic synthesis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.supflu.2011.04.012.

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