Continuous synthesis of glycerol acetates in supercritical carbon dioxide using Amberlyst $15^{\ensuremath{\mathbb{R}}}$

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Continuous esterification of glycerol with acetic acid was investigated in supercritical carbon dioxide (scCO₂) using Amberlyst $15^{\text{(8)}}$ as a heterogeneous catalyst. The effect of pressure at (65–300) bar on the substrate conversion and the reaction yield and selectivity was studied. With increasing pressure, the percent of total yield and conversion remain almost unaffected and the selectivity of monoacetin synthesis increases while the selectivity for triacetin stays relatively unchanged. The effect of temperature on the yield, conversion, and the selectivity at (100–150) °C was also investigated. With increasing temperature from 100 to 140 °C, the selectivity for monoacetin decreases while for tri- and diacetin slightly increases. In contrast, with further increase in temperature, from 140 °C to 150 °C, the selectivity of monoacetin synthesis increases while the yield was 41% for the continuous triacetin synthesis in scCO₂. When neat scCO₂ as solvent with no catalyst was used, only monoacetin with 29% conversion was synthesized. The catalyst durability was also studied by monitoring the reaction for 25 h. The results show that the catalyst retains its activity even for 25 h but the selectivity for triacetin synthesis declines from 100% to about 60%.

Introduction

Esters have a wide variety of applications as solvents, as emulsifying and stabilizing compounds, and as raw materials in food, and the cosmetic and pharmaceutical industries.¹ Acetins are mono-, di-, and tri-esters of glycerol acetates. Monoacetin or glycerol monoacetate are used in the manufacture of explosives, in tanning, and as solvents for dyes. Diacetin or glycerol diacetate is used as a plasticizer and softening agent and solvent.² Glycerol triacetate or triacetin is used as a solvent for dissolving or diluting drugs and organic compounds. Also it is used as an antimicrobial and emulsifying agent in cigarette filters.^{3,4} Triacetin is used especially in the pharmaceutical industries as a skin pH controller for treatment of skin disorders and some pathological diseases and is used as a drug delivery compound.^{5,6}

Glycerol acetates have been synthesized *via* esterification of glycerol with acetic acid or acetic anhydride with or without a homogeneous or heterogeneous catalyst using an organic solvent and in batch or continuous processes.⁷⁻⁹ Usually, the produced esters are accompanied with some by-products, which a change in their color and odor so that it makes their purification difficult and costly. As a result, selective synthesis of the esters with high purity has been a great challenge for some researchers.^{10,11}

In recent years, considerable attention has been paid to replacing fossil fuels with bio-diesel, because of its presumed environmental and economic benefits compared to petroleum. Biodiesel is produced by transesterification of vegetable oil where glycerol is the main by-product.^{12,13} It is reported that 1 kg of crude glycerol is formed for every 9 kg of bio-diesel produced.¹⁴ It is therefore a reasonable scientific and technological task to find new or improved methods for the conversion of this huge pile of relatively low price glycerol to valuable products. For example, Suppes et al. have reported dehydration of glycerol via catalytic reactive distillation to produce acetol.¹⁴ Also the synthesis of acrolein from dehydration of glycerol in sub- and supercritical water has been reported.15,16 Indeed, some articles have focused on the esterification of glycerol with fatty acids using a catalyst, especially, heterogeneous catalyst to get the desired esters.¹⁷⁻¹⁹ Mota et al. have done the esterification of glycerol with acetic acid in the presence of different solid acid catalysts in a free solvent medium under reflux.²⁰ According to their report, the esterification achieved 97% conversion at 30 min of reaction time in the presence of Amberlyst 15[®] with selectivity for mono-, di-, and triactin of 31%, 54% and 13%, respectively.

Other researchers have resorted to supercritical carbon dioxide (scCO₂) as a solvent to replace organic ones. Esterification of glycerol with lauric acid over a heterogeneous catalyst has excellent conversion in scCO₂ compared to the use of mesitylene as solvent.¹ Sugi *et al.* have explained that it is mainly due to the decrease in coke formation and removal of the water formed from the catalyst acidic sites by scCO₂. Because scCO₂ is non-flammable, inexpensive, and environmentally safe and it has moderate critical conditions ($t_c = 31.2 \text{ °C}$, $p_c = 73.8 \text{ bar}$), scCO₂ is a preferred solvent.²¹

There are only a few published papers involving continuous acid-catalyst reactions in $scCO_2$. Most researchers have used this system when one or more of the substrates are gaseous, such as in

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hydroformylation,²² hydrogenation,^{23,24,25} and partial oxidation of alcohols.²⁶ The main reason is the greater miscibility of gases in scCO₂ leading to higher reaction rates.

However, investigations have shown that tuning of the pressure of the reactions, when none of the substrates are gases, could change the selectivity and the yield to a high extent. For example, etherification of n-terminal diols in scCO₂, over Amberlyst 15[®] as a solid catalyst, could switch dramatically between monoand bis-ethers, while the pressure was increased from 50 bar to 200 bar.²⁷ Also, Han *et al.* reported esterification of ethylene glycol with propionic acid in scCO₂ in the presence of *p*-toluene sulfonic acid as a catalyst in a batch mode. They showed that with increasing pressure, the yield and selectivity of the diester increased, while those of the monoester decreased. They claimed that the distribution of reactants and products between the vapor and liquid phase at high pressure is the main reason.²⁸

In this work, we have investigated the synthesis of glycerol esters in $scCO_2$ by a continuous esterification of glycerol with acetic acid in the presence of Amberlyst $15^{\mbox{\sc B}}$ as a strong solid-acid catalyst, as shown in Scheme 1. It should be noted that the boiling points of mono-, di-, and triacetin are close to each other. Specially, the boiling points of di- and triacetin are very similar, making their separation by conventional processes very difficult and costly.



Scheme 1 Synthesis of glycerol esters in three reversible steps.

Experimental

As shown in Fig. 1 a continuous flow apparatus was used to carry out the esterification reaction. The details of the system are described elsewhere.²⁹ The catalytic bed reactor. used in most



Fig. 1 The schematic diagram of the setup used for the esterification reaction; 1, molecular sieve trap; 2, liquid pump; 3, check valve; 4, needle valve; 5, air oven; 6, preheating coil; 7, static mixer; 8, T connector; 9, catalytic bed reactor; 10, back pressure regulator.

of our experiments was a 10 mm (i.d.), 316-stainless steel tubing with an internal volume of about 19 mL, containing about 9.5 g of dried catalyst (Amberlyst $15^{\text{(B)}}$), placed in an air oven with a temperature controller (± 1 °C) throughout the experiment.

To be sure that the catalyst is completely dried, a flow of $scCO_2$ at 100 °C was passed over the catalyst for about 1 h.⁸ When the system was set at the desired pressure and temperature, a HPLC pump (PU-980), continuously and at a constant flow rate, pumped a homogenized mixture of liquid glycerol and acetic acid, premixed in the desired molar ratio. Meanwhile another HPLC pump introduced liquid CO₂ into the system at a set flow rate. The two flows met each other in a 1/8 inch (o.d.) tubular mixer, 1.8 m long, filled with glass beads (mesh of 20–40) and then the mixture passed over the catalyst bed. Each sample was collected in a cold trap, at different time intervals and analyzed by GC-FID.

Analytical method

Analysis of the samples was carried out using a GC-FID (Agilent Technologies model 6890 N). The carrier gas was helium and the capillary column of HP-5 (with 30 m length, 0.25 mm i.d., and $0.25 \,\mu$ m of film thickness) was used.

The temperature program was used for the analysis. The GC injection port and the detector temperature were set at 240 and 260 °C, respectively. The initial column temperature was set at 70 °C for 2 min and programmed from 70 °C to 150 °C for 1.5 min at the rate of 45 °C min⁻¹ and from 150 °C to 180 °C at the rate of 8 °C min⁻¹ and from 180 to 240 °C at the rate of 35 °C min⁻¹. The quantification was performed by injecting some standard ester solutions containing an internal standard and integrating their peak areas to establish the calibration curve. Since we could not find commercial monoacetin, it was synthesized *via* a previously reported method.³⁰ The identification of the products in all experiments was carried out by GC-MS (Trio 1000, Fisons Instruments, model 8060).

The yield, conversion, and selectivity for each sample are calculated as follows:

$$Yield = \frac{Total \text{ moles of detected esters}}{Total \text{ moles of glycerol in the feed solution}} \times 100$$
$$Conversion = \frac{Total \text{ moles of detected esters}}{Moles of detected esters and glycerol in exit flow} \times 100$$

Materials

Carbon dioxide with a purity of 99.95% was supplied from ZamZam Co. Ltd (Isfahan, Iran). Acetic acid (purity > 99%) and Amberlyst $15^{\text{(B)}}$ was purchased from Merck. The catalyst capacity²⁶ was calculated as 4.64 meq g⁻¹. Triacetin (glycerol triacetate, purity > 99%) and diacetin (glycerol diacetate, purity = 50% verified by GC analysis) were purchased from Fluka. Absolute ethanol was purchased from Temad Co. (purity > 99%)

Tehran, Iran). Glycerol was purchased from Hopkin & Williams; 1-hexanol was purchased from Riedel-deHaën (purity > 98%).

Results and discussion

The esterification reaction of glycerol with acetic acid proceeds in three consecutive reversible steps as shown in Scheme 1. The effect of pressure, temperature, and molar ratio of acetic acid to glycerol has been investigated for the reaction over Amberlyst 15[®] as a heterogeneous strong acid-catalyst in scCO₂. In addition, we studied the catalyst reusability and the reactor length at two different molar ratio of substrates. The reaction was also performed in scCO₂ in the absence of the catalyst and only the reactor was packed with crushed glass with almost the same grain size as the catalyst. The conversion, yield, and selectivity of the reactions have been reported. All data reported in Fig. 5, 6, and 7 are the equilibrium data, taken after the continuous system has reached a steady state that is about 120 min after the start of the reaction.

Effect of pressure

The effect of pressure on the esterification of glycerol with acetic acid and the formation of tri-, di-, and monoacetin in a continuous flow reactor at (65–300) bar using Amberlyst 15[®] is shown in Fig. 2–4 at different time from the start of the reaction. All the experiments were carried out at 100 °C. The molar ratio of acetic acid to glycerol was equal to 3 and the flow rate of liquid CO_2 (at 0 °C) and substrates was 1.2 mL min⁻¹ and 0.2 mL min⁻¹, respectively.



Fig. 2 Variation of the triacetin selectivity in the continuous esterification of glycerol with acetic acid *versus* time using Amberlyst $15^{(0)}$ (9.5 g) as catalyst at a temperature of 100 °C and acid/glycerol ratio of three at different pressures.

These data show that the effect of pressure on the selectivity of tri- and monoacetin is more significant at the beginning of the reaction, where the selectivity of diacetin has less variation in time at different pressures. The highest variation takes place in the first 60 min. In addition, with increasing the system pressure, a longer time is needed for the esterification reaction to reach equilibrium. Due to higher solubility of the products at the higher pressures, scCO₂ can extract products from the catalyst bed and postpone the equilibration time.²⁸ This phenomena also affects the selectivity of produced esters at different times before the equilibrium is established. The greater solubility of



Fig. 3 Variation of the diacetin selectivity in continuous esterification of glycerol with acetic acid *versus* time using Amberlyst $15^{(0)}$ (9.5 g) as catalyst at a temperature of 100 °C and acid/glycerol ratio of three at different pressures.



Fig. 4 Variation of the monoacetin selectivity in continuous esterification of glycerol with acetic acid *versus* time using Amberlyst $15^{(g)}$ (9.5 g) as catalyst at a temperature of 100 °C and acid/glycerol ratio of three at different pressures.

products in $scCO_2$ at high pressures drives the esterification towards the selective synthesis of triacetin. In addition, dryness of the catalyst at the beginning of the reaction helps the forward reaction proceed to completion and triacetin is formed selectively. As time passes, since the synthesis of one mole triacetin is associated with three moles of water, the catalyst absorbs water and as a result, the reverse reaction to monoacetin lowers the selectivity.

The data reported in Fig. 5 is the equilibrium data shown in Fig. 2–4 and taken after the continuous system has reached to the equilibrium state where the selectivity does not change *versus* time. It seems the esterification reaction was found to be relatively unaffected by changes in the system pressure. As shown in Fig. 5 the total yield was not seen to be very sensitive to change in the system pressure. Moreover, the conversion was about 92% at different pressures. With increasing the pressure, a slight increase in monoacetin formation and a slight decrease in the diacetin formation are observed. Increasing the system pressure increases the scCO₂ density and as a result, the solubility of the monoacetin (*i.e.* more polar) in scCO₂ increases. The produced monoacetin at this condition could be extracted by scCO₂ from the catalyst bed where the esterification takes place.



Fig. 5 The effect of increasing pressure on the conversion, yield, and product selectivity in the continuous esterification of glycerol with acetic acid at a temperature of $100 \,^{\circ}$ C using Amberlyst 15[®] (9.5 g) as catalyst.

Effect of temperature

The effect of temperature on the esterification of glycerol with acetic acid in the range of (100-150) °C at 200 bar, with a molar ratio of acetic acid to glycerol of 3 and a flow rate of liquid CO₂ (at 0 °C) and substrates of 1.2 mL min⁻¹ and 0.2 mL min⁻¹, respectively, in the presence of Amberlyst 15[®], is shown in Fig. 6. The conversion was nearly constant at 91%. But the total yield of the esterification decreased continually with increasing temperature as shown in Fig. 6.



Fig. 6 The effect of increasing temperature on the conversion, yield, and products selectivity in the continuous esterification of glycerol with acetic acid using Amberlyst $15^{\textcircled{}}$ (9.5 g) as catalyst at a pressure of 200 bar.

The decrease in the total yield with raising the system temperature might be due to the reduction of the catalyst activity that is happening *via* lose of the catalyst active sites at high temperatures by desulfonation of the catalyst.³¹ It has been reported that the Amberlyst $15^{\text{(B)}}$ activity at 200 bar and 150 °C in an alkylation reaction in scCO₂, was about 10% lower compared to the untreated one. Morover, at high temperatures scCO₂ density is reduced and as a result the amount of water that could be extracted out of the catalyst bed is diminished. Since the process is reversible and coproduced water would affect the equilibrium the yield of the reaction is lowered at the higher temperatures.

At temperatures above 140 °C, the selectivity for monoacetin formation increases while that for diacetin formation decreases and remains nearly constant for triacetin.

The change in selectivity could be related to the hydrolysis of diacetin to monoacetin as a decrease in the solubility of the produced esters in the presence of the water formed in $scCO_2$ when the system temperature is increased.

Effect of molar ratios of the substrates

In order to investigate the effect of molar ratio of acetic acid to glycerol on the yield and selectivity of the produced esters, the molar ratio was varied from 1.5 to 24 while other variables were kept constant (200 bar and 110 $^{\circ}$ C). The results are shown in Fig. 7.



Fig. 7 The effect of increasing acetic acid to glycerol molar ratio on the conversion, yield and product selectivity in continuous esterification reaction using Amberlyst $15^{\text{(B)}}$ (9.5 g) at 110° C and 200 bar.

Except for the molar ratio of 1.5, the conversion of esterification reaction was 100 percent in all molar ratios studied. On the other hand, the total yield appears to have a maximum at molar ratio of 4.5 and a further increase in acetic acid concentration is accompanied by a decrease in the total reaction yield. The rise in total yield observed when the molar ratio is increased from 1.5 to 4.5 is thought to be related to the role of acetic acid, not only as an excess reactant, forcing the esterification reaction forward, but as a co-solvent in scCO₂. With further increase of the molar ratio, the selectivity for triacetin increases while it significantly decreases for monoacetin and diacetin. Fig. 6 shows that at the molar ratio of 24 the yield reaches a low level. However, the higher acetic acid concentration drives the esterification reaction towards triacetin production with 100% selectivity up to 120 min after the start of the reaction.

More information about the Amberlyst 15[®] performance in this reaction could be found by comparing the yield with the conversion data in all the experiments. The difference between these data could be related to the amount of the fed glycerol that is not taking part in the reaction. It seems that there is an interaction between glycerol and the catalyst active sites causing a decrease in the number of free glycerol molecules for the reaction with the protonated acetic acid over the catalyst surface.¹⁸ Since the catalyst capacity for the adsorption of glycerol and the amount of the catalyst used in all the experiments are more or less the same, the yield is decreased while the molar ratio of the substrates increased.

The influence of the acetic acid concentration on the selectivity of the esters formed shows the esterification equilibrium of the glycerol with acetic acid using Amberlyst $15^{(8)}$ in scCO₂ could be progressed in three consecutive reversible reactions.

Table 1Influence of the reactor length on the conversion, yield, andthe product selectivity of the esterification of glycerol with acetic acid in $scCO_2^a$ using Amberlyst $15^{\ensuremath{\mathbb{R}}}$

Reactor length (cm)	Conversion (%)	Yield (%)	TA (%)	DA (%)	MA (%)
25	100	41	100	0	0
100	100	48	82	19	0

" At 200 bar, 110 °C; the flow rate of $scCO_2$ and reagents was 1.2 and 0.2 mL min⁻¹, respectively; the acid/glycerol ratio was 24.

Therefore, the greater acetic acid concentration as a substrate could promote diacetin to triacetin conversion. Further studies are going on in our research group to increase the yield of the esterification reaction while keeping the high selectivity of triacetin synthesis at 100% for a longer time.

Effect of the reactor length

One of the ways considered to maximize the yield was to increase substrate–catalyst contact time. Table 1 presents the effect of increasing the length of the reactor tube on the yield and the selectivity of products while maintaining the same amount of the catalyst, the volume of the reactor, and the flow rate of $scCO_2$. At a four-fold reactor length, the selectivity of triacetin synthesis was unexpectedly lower while the total yield increased 17% as illustrated in Table 1. It seems that difficulty in removal of water formed in the esterification reaction when a longer reactor is used enhances the reverse hydrolysis reaction of triacetin to diacetin.

Effect of the catalyst and its reusability

Finally, the esterification of glycerol with acetic acid at 200 bar and 110 °C was performed in scCO₂ as solvent with and without the catalyst when the molar ratio of the acid to the alcohol was 24. The results are shown in Table 2. When scCO₂ is used as solvent in the absence of the catalyst, the total yield was 29%, but the selectivity of monoacetin synthesis was 100%. In fact, CO₂ can function in this reaction, in addition to all the factors already mentioned, as a Lewis acid, even a Brønsted acid in high pressures and in the presence of water to catalyze the reaction.³² Alternatively, the reaction under the same conditions in the presence of the catalyst, leads to 100% selective synthesis of triacetin. This confirmed the importance of the catalyst in this esterification reaction. **Table 2** Influence of the catalyst and $scCO_2$ alone on the yield, conversion, and product selectivity of the esterification of glycerol with acetic acid at $scCO_2^a$

Condition	Conversion (%)	Yield (%)	TA (%)	DA (%)	MA (%)
1 ^b	35	29	0	0	100
2 ^c	100	41	100	0	0

^{*a*} At 200 bar, 110 °C; the flow rate of $scCO_2$ and substrates was 1.2 and 0.2 mL min⁻¹, respectively; the acid/glycerol ratio was 24. ^{*b*} The catalyst reactor was loaded with crushed glass or finely crushed ceramic Raschig rings (16/20 mesh). ^{*c*} The catalyst reactor was loaded with dried Amberlyst 15[®].

Table 3 Influence of the catalyst reusability on the yield, conversion, and product selectivity of the esterification of glycerol with acetic acid in $scCO_2^a$

Times catalyst recycled	Conversion (%)	Yield (%)	TA (%)	DA (%)	MA (%)
3 ^b	100	82	27	42	31
3 ^c	100	49	92	8	0

^{*a*} At 200 bar, 110 °C; the flow rate of scCO₂ and reagents was 1.2 and 0.2 mL min⁻¹, respectively. ^{*b*} The acid/glycerol ratio was 6.0 ^{*c*} The acid/glycerol ratio was 24.

We also evaluated the reusability of the catalyst (Amberlyst 15[®]). Since the substrates and products have a good solubility in absolute ethanol, this solvent was used for removal of the unreacted substrates from the catalyst surface using a Soxhlet extraction apparatus. Analysis of the extract by GC-FID and FT-IR spectroscopy confirmed that nearly all of the materials desorbed from the catalyst surface were glycerol. The washed catalyst was subsequently re-used in its dried form to investigate the reusability of the catalyst for the esterification reaction.

Table 3 shows that the recycled catalyst, after three times of usage, has clearly retained its activity in this reaction. However, the selectivity of triacetin synthesis for the molar ratio of 24 was decreased to 91.6%.

Finally as shown in Fig. 8, the catalyst stability was investigated by following the reaction at the optimum reaction condition for 25 h. The results revealed that the catalyst was still active over a long period. Nevertheless, after about 5 hours the system reaches a steady state in which the selectivity for triacetin declines to about 60% while that of diacetin rises to about 40% with no monoacetin among the products. Even at



Fig. 8 Time variation in percent yield and selectivity of tri- and diacetin over a period of 25 h in continuous esterification of glycerol with acetic acid over Amberlyst $15^{\ensuremath{\oplus}}$ in scCO₂, at a pressure of 200 bar, a temperature of 110 °C, and acid/glycerol ratio of 24.

this stage the selectivity for triacetin in the reaction performed in $scCO_2$ is about 4.6 times the reaction under reflux using the same catalyst.³³

Conclusion

The results show that the use of $scCO_2$, the molar ratio of the substrates, and the catalyst play a major role in tailoring the yield and selectivity in the esterification reaction of glycerol with acetic acid. However, the pressure and temperature in the synthesis of the acetins do not have a significant contribution. The continuous flow esterification of glycerol with acetic acid using Amberlyst 15[®] while the molar ratio, pressure, and temperature are 24, 200 bar and 110 °C, respectively, has shown the real advantage of 100% selectivity for triacetin synthesis for about 120 min. However, the selectivity of triacetin was diminished when the reaction is performed for a longer time. Moreover, the results of the catalyst reusability show that, the adsorption of glycerol over the catalyst was due to a physical interaction.

This work has demonstrated that the esterification could be performed without the catalyst at the molar ratio, pressure, and temperature of 24, 200 bar, and 110 °C, respectively, with 100% selectivity of the reaction towards monoacetin synthesis.

In short, the controlling of the yield and selectivity of the produced esters in the continuous esterification reaction of glycerol with acetic acid using Amberlyst $15^{\text{(B)}}$ under scCO₂ was affected by Lewis acidity of CO₂, removal of the formed water from the catalyst surface, the amount of the product solubility in scCO₂, and the adsorption of glycerol by the active sites of the catalyst.

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