Increased in acetins production. Effect of ethanol oxidation on acetins production by transesterification of glycerol with ethyl acetate.

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Introduction

Acetins are raw-material widely utilized in chemical, pharmaceutical and cosmetic industries. Traditionally, acetins are produced by glycerol esterification with excess of acetic acid and/or acetic anhydride but this process has drawbacks as high cost and use of corrosive and toxic reagents.[1]

In previous work, we studied the synthesis of acetins by glycerol transesterification with ethyl acetate catalyzed by acidic resins such as Amberlyst 15 Dry and Amerlyst 16 Wet, fig. 1.

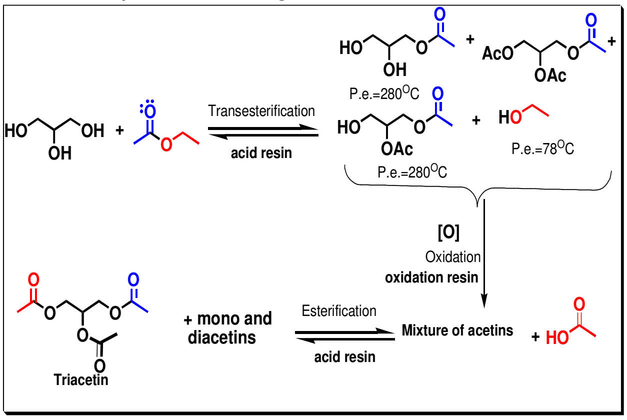

Figure 1: Acetins production acid catalyzed via transesterification of ethyl acetate with glycerol. Ethanol Oxidation to acetic acid improving triacetin production.

This environmentally attractive approach has the advantage of producing ethanol as a byproduct, which can be oxidized to acetic acid, the primary reagent for the synthesis of acetins fig. 1.

We wish report the preliminary studies on the effect of ethanol oxidation, reaction by-product, in acetins synthesis performed by this method.

Results and Discussion

For ethanol oxidation was tested chromium oxidizing resin Amberlyst 26. The conditions were tested with pure glycerol and crude glycerol obtained from the biodiesel process. All analysis were made by MS / GC.

First, the reaction was allowed to reach equilibrium, entry 1. After equilibration resin Amberlyst A 26 was directly added into the reaction flask, entry 2. Table 1.

Tabela 1. Reactions conditions.[a] All reactions 100% of glycerol conversion

Entry	Catalyst	Time (h)	Mono: Di:Tri (%)[a]	Byprotuct (%)
1	Amberlyst® 15	20	9,3 : 77,3 :13,3	-
2	Amberlyst® 15 + Amberlyst® - A26	23	4,2 : 74,3 : 13,2	7,56
3	Amberlyst® 15	20	49,2 : 39,4 : 1,2	10,24
4	Amberlyst® 15 + Amberlyst® - A26	23	41,9 : 45,6 : 0,9	11,58
5	Amberlyst® 15 + Amberlyst® - A26	20	1,2 : 26,4 : 54,0	18,40

The reaction, with Amberlyst A 26, caused a decrease in the concentration of mono and diacetin but triacetin, more valuable acetin, remained stable. Under these conditions it was observed the formation of byproducts due to the oxidation of mono and di acetins. The same reaction profile was observed using crude glycerin, entries 3 and 4.

To prevent acetins oxidation, the ethanol oxidation should occur in a separate reaction vessel. For it was chosen using soxhlet apparatus, where Amberlyst A 26 resin were placed. As can be seen,,entry 5, by using the pure glycerol, a significant reduction in the concentration of mono- and diacetins, and an increase of more than four times the concentration of triacetin, 13.3 to 54%, becoming the main product of reaction. Different by-products were observed in this reaction condition.

Conclusion

The oxidation of ethanol by-product formed in the production of glycerol acetinas by transesterification reaction of glycerol with ethyl acetate, can become an efficient and environmentally way for triacetin production, one of the glycerol derivatives with high commercial valuable.

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