AIDIC
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FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Glycerol valorization via acetylation reaction performed in batch reactor and reactive distillation

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Highlights

- low-cost by-product for high-value chemicals production
- reactive distillation for glycerol valorization
- homogeneous and heterogeneous catalysis

1. Introduction

In recent years, Reactive Distillation (RD) has fascinated an extended piece of chemical industry in the field of reversible reactions limited by adverse equilibrium conditions. Removal of this restriction by continuous subtraction of one product from the reactive mixture, represents the major advantages of this worthy unit operation. In particular in the massive evolution of biodiesel, glycerol valorization represents a relevant example: a low-cost by-product for high-value chemicals production. The promising chemical transformation performed consists on the production of triacetin (TA), diacetin (DA) and monoacetin (MA) by consecutive acetylation reactions of glycerol. At the current, TA and DA are mainly exploited as fuel additive to improve cetane number and viscosity properties of biodiesel. On the contrary MA is not suitable as a diesel component due to its relatively high water solubility[1]. Despite the MA is the first product of the three consecutive reactions, its presence can be limited to the earliest reaction time operating in suitable conditions (i.e. by removing the produced water or methanol). Considering that the recovery by distillation of singular MA, DA and TA is complicated due to the practically undistinguishable boiling points, this work tries to ehnance the selectivity toward the desired products during the acetylation. Sulfuric acid and Amberlyst-36 Dry were used as liquid and solid acid catalyst respectively. It must be specified that the production of TA from glycerine is a process that already exists but its performance could be further improved to treat big amount of glycerine in the most environmental friendly way. The actual triacetin industrial production involves in series reactors and a subsequent distillation; acetic anhydride is used as raw starting material together with acetic acid in order to enhance triacetin final yield[2].

2. Methods

Glycerol esterification reactions were performed varying different operating conditions (substrates/catalyst and reagents ratio, type of catalyst and temperature). In Fig.1 the equipment configuration is reported. For homogeneous catalysis the catalyst was introduced from the top of the equipment, while for the and heterogeneous one the catalyst was charged in the column (reaction zone). In both systems, acetic acid was charged into the boiler, whereas glycerol was regularly

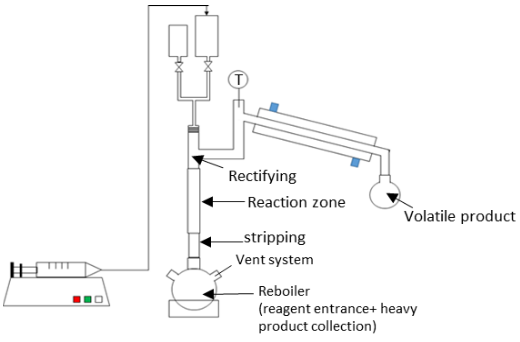

Figure 1. reactive distillation laboratory apparatus

dropped down from the upper part of the apparatus into the column using a syringe pump. Different operating conditions were explored (temperature, substrate/catalyst and molar reagents ratios (R=acetylating agent/glycerol)) for any configurations to find the optimal one. Reaction products were evaluated by GC/TCD analysis.

3. Results and discussion

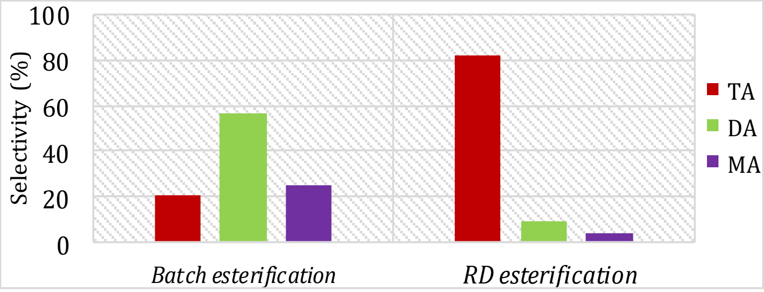

Figure 3. comparison between batch and RD esterification

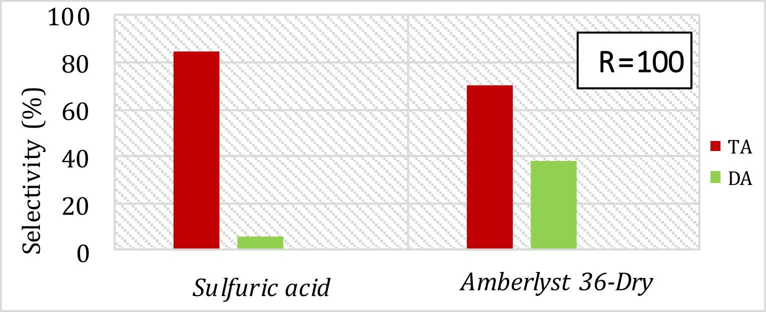

Figure 2. Homogeneous and heterogeneous selectivity results

In Fig.2 the comparison of the results performing homogeneous esterification reaction in batch equipment and in reactive distillation apparatus are reported. Using the same operating conditions the selectivity toward TA is four times higher for RD esterification than the batch one. Therefore a positive contribution on the reaction performance are provided by subtracting volatile compounds (i.e. water and methanol) from the reaction media, moving the reaction equilibrium to the products. MA selectivity is lower than 5% in the case of reactive distillation apparatus and this improvement becomes a key issue in an hypothetical industrial application. Moreover, an heterogeneous catalysis was exploited using Amberlyst-36 Dry as acid solid catalyst (Fig.3). No MA was detected both for homogeneous and heterogeneous reaction, but the performance of sulfuric acid were greater than the Amberlyst one, even if a total glycerol conversion was observed for both the two tests. On the other hand, Amberlyst-36 Dry is safer to handle and it offers many industrial and laboratory advantages in terms of products and catalyst recovery, corrosion concerns and less separation/purification costs.

4. Conclusions

Acetylation by RD apparatus can be used alone to achieve a total conversion and a significant increment of TA selectivity. Homogeneous acid catalysis gives better results respect heterogeneous catalysis by Amberlyst 36 samples.

References

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Keywords
Reactive Distillation; Glycerol; Triacetin; Catalysis.