THE VARIATION OF THE EFFICIENCY FOR THE PHENOXYACETIC ACIDS' ESTER FORMATION WITH THE CATALYST'S TYPE AND USED DOSAGE

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Abstract: *The synthesis of the phenoxyacetic acids' esters is an important intermediary step in obtaining the sulfonamide phenoxyacetic compounds with auxinic type growth stimulating action or with herbicide action, considering the used dosage. The efficiency of this esters formation step depends a lot on the used catalyst type, on the catalysis type (homogeneous or heterogeneous) and on the reaction time. This paper proposes to analyze the conditions for completing the procedure in order to reach efficiencies as high as possible in a short time, conditions acceptable from the reagents necessary's point of view and also regarding the intermediary step number in the ester obtaining process, respectively the technological scheme of this process. There were considered three phenoxyacetic acids, mono and double substituted which were put to react with methanol in order to obtain the esters, in homogeneous catalysis, using concentrated sulphuric acid as catalyst, as well as heterogeneous catalysis, using two solid catalysts with acid sulphonic active groups, in three different doses. The obtained results indicated, for all three general reactions, higher efficiencies for the heterogeneous catalysis, for all catalyst's used dosages, as well as a much simplified technological scheme comparing to the homogeneous catalysis.*

Rezumat: *Sinteza esterilor acizilor fenoxiacetici este o etapă intermediară importantă în obţinerea compuşilor fenoxiacetici sulfonamidaţ i cu acţiune auxinică sau erbicidă, în funcţie de doza aplicată. Randamentul reacţiei de esterificare depinde foarte mult de catalizatorul folosit, de tipul de cataliză (omogenă sau eterogenă) şi de timpul de reacţie. Această lucrare îşi propune să analizeze condiţiile de reacţie necesare pentru a obţine randamente mari într-un timp scurt, atât din punctul de vedere al necesarului de reactivi cât şi din cel al numărului de etape din schema tehnologică a procesului de esterificare. Au fost studiaţi trei acizi fenoxiacetici, mono sau disubstituiţi, care au fost esterificaţi cu metanol în cataliză omogenă, folosind acidul sulfuric drept catalizator, şi în cataliză eterogenă folosind doi catalizatori solizi cu grupări sulfonice acide, în trei doze diferite. Rezultatele obţinute au indicat, pentru toate cele trei reacţii generale, randamente mai mari pentru cataliza eterogenă, pentru toate dozele de catalizatori folosite, la fel ca şi o schemă tehnologică mult simplificată comparativ cu cataliza omogenă.*

The phenoxy acetic derivatives with sulphonamide groups are used as growth stimulators with auxinic action or herbicides, considering the applied dosage. The general scheme for obtaining these derivatives follows the next steps:

- preparation of R-phenoxy acetic acids from the specified phenols, by condensation with mono-chloro acetic acid;
- preparation of ethyl or methyl esters for the obtained esters;
- preparation of the chloro sulphonic derivatives of the esters;

- condensation with ammonia, substituted amines or other aminic compounds.

Because the esters of the R-phenoxy acetic acids are intermediary compounds used in the synthesis of a large number of derivatives, we conducted studies regarding their preparation process, in heterogeneous catalysis using two different catalysts in three doses, comparing to the same processes conducted in homogeneous catalysis.

MATERIAL AND METHOD

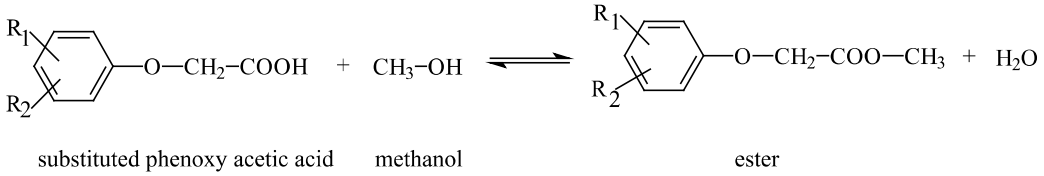
The alcohol used in the process was methanol with 95% volume purity and the considered R-phenoxy acetic acids were: o-chloro-phenoxy acetic acid, o-cresoxy acetic acid and phenyl-1,4-dioxyacetic acid. The catalysts were: sulphuric acid with 98% purity in the homogeneous process, in a ratio of 0.8% moles compared to the organic acid and two ion-changing resins with sulphonic active groups in their molecules: Dowex-50 and Amberlite IR-120, in doses of 3, 5 and 10 g per process in the heterogeneous catalysis.

The process of ester formation for an organic acid with methanol in the presence of a solid macro-porous catalyst takes place in a heterogeneous solid – liquid reaction mixture, with the following steps:

- the diffusion of the acid through the methanol film covering the catalyst particle;
- the diffusion of the acid through the catalyst's pores;
- the absorption of the acid on the resin's active centers and its activation;
- the diffusion of the alcohol through the catalyst's pores;
- the actual chemical reaction;
- the diffusion of the reaction product through the catalyst's pores;
- the diffusion of the reaction product through the methanol film covering the catalyst surface.

The general reaction scheme for obtaining R-phenoxy acetic acids' esters is:

In order to assure a higher efficiency and to increase the reaction's speed, we

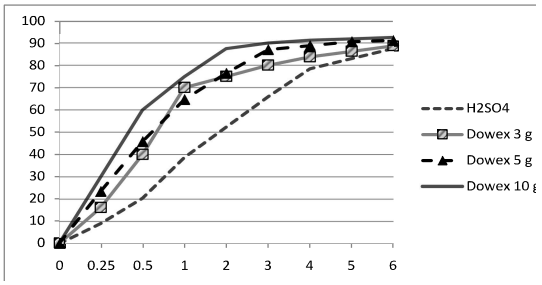


used a molar ratio between the organic acid and the alcohol of 1 : 30. These reaction conditions were the same for all the ester formation processes, regardless the catalysis type.

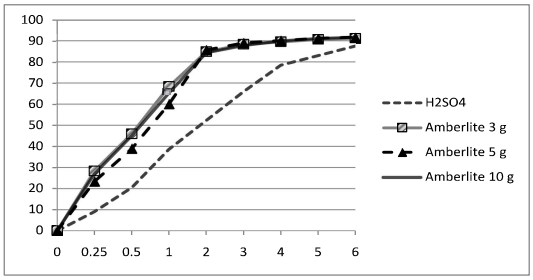
RESULTS AND DISCUSSIONS

Analyzing the data obtained during the kinetic study of the ester formation processes, we observed that the efficiency values for both solid catalysts, after a 6 hours reaction, are quite similar. Still, whilst in the heterogeneous catalysis, after a 3 hour reaction, the efficiency values vary between 85 and 90%, in the homogeneous process, after the same period of time, the efficiency values vary between 50 – 70% (fig. 1 – 3). These differences plead for conducting the ester formation process in heterogeneous catalysis for three hours, when acceptable values for the technique are acquired.

Analyzing the general charts for the ester formation processes in homogeneous and heterogeneous catalysis (fig.4), we observe that in the homogeneous process, there are involve supplementary phases of alkali treatments for removing the reaction mixture's acidity, then a number of washing phases for removing the alkalinity followed by a vacuum distillation.

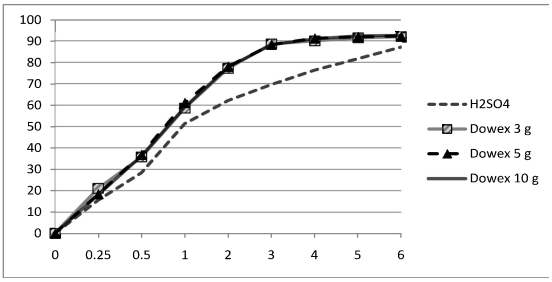


(a)



(b)

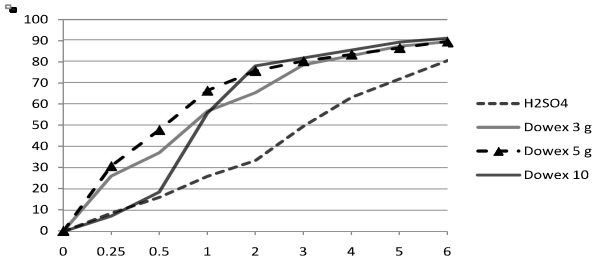
Fig. 1. The variation of the efficiency in time for the ester formation process of the o-chloro phenoxyacetic acid in heterogeneous catalysis using Dowex-50 (a) and Amberlite 150 R (b) comparing to the homogeneous catalysis (H_2SO_4)



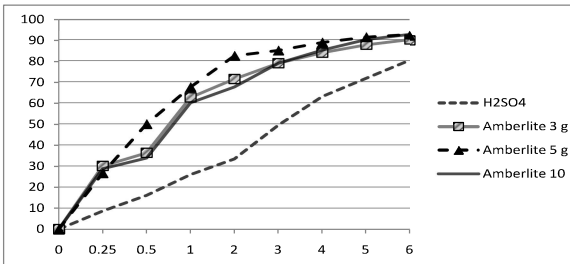
(a)

Fig. 2. The variation of the efficiency in time for the ester formation process of the o-cresoxy phenoxyacetic acid in heterogeneous catalysis using Dowex-50 (a) and Amberlite 150 R (b) comparing to the homogeneous catalysis (H_2SO_4)

Fig. 3. The variation of the efficiency in time for the ester formation process of the phenyl -1,4 – dioxyacetic acid in heterogeneous catalysis using Dowex-50 (a) and Amberlite 150 R (b) comparing to the homogeneous catalysis (H_2SO_4)

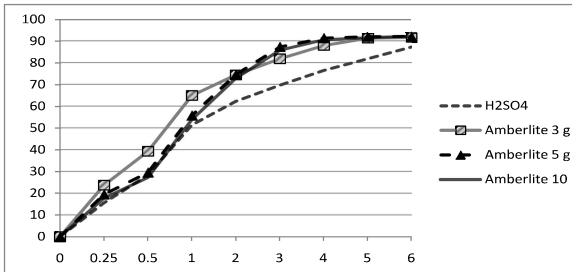


(a)



(b)

This large number of intermediary phases leads to the decrease of the ester formation process's efficiency. For the distilled ester, the efficiency reported to the starting quantity of the organic acid does not exceed 68–70%. In heterogeneous catalysis, the number



b)

of technological phases for the ester separation from the reaction mixture is very small and the whole process offers efficiencies of 84-86% in pure product. Considering all of the above, we recommend the heterogeneous catalysis for the ester formation processes of the R-phenoxy acetic acids, procedure that offers good efficiencies for the technique.

CONCLUSIONS

1. The esters of the R-phenoxy acetic acids are intermediary compounds used in the synthesis of a large number of derivatives with stimulating or herbicidal action.

2. In the heterogeneous catalysis, after a 3 hour reaction, the efficiency values vary between 85 and 90% and in the homogeneous process, after the same period of time, the efficiency values vary between 50 – 70%.

3. In heterogeneous catalysis, the number of technological phases for the ester separation is very small and the process offers efficiencies of 84-86% in distilled ester.

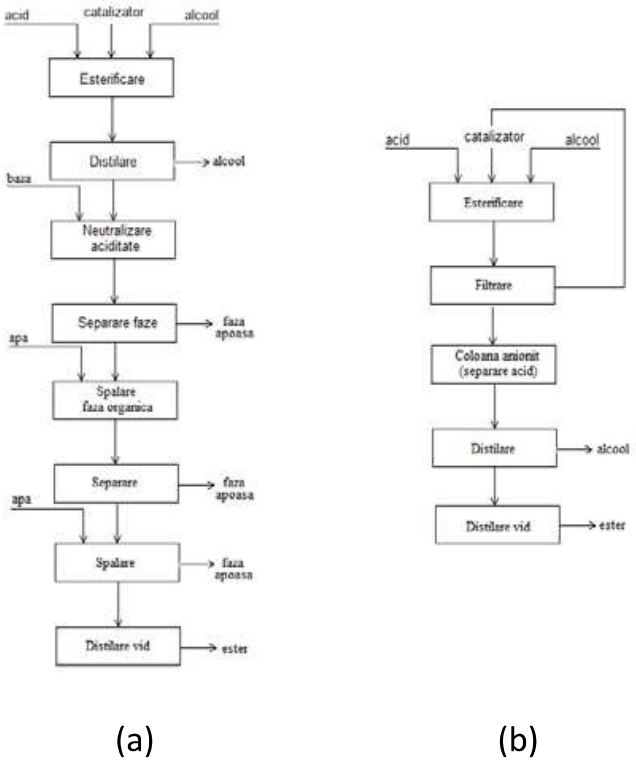


Fig. 4. General technological charts for the ester formation processes' steps in homogeneous (a) and heterogeneous (b) catalysis

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