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# THE CONTINUOUS MANUFACTURING OF TERPIN

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The continuous or semi-continuous production of terpin from α-pinene by hydration, using 40% sulfuric acid as a catalyst, was studied in a batch laboratory reactor as well as at pilot scale. It was concluded that the mixing intensity affects the distribution of products and that the greatest yields are obtained in a semi-continuous or continuous process.

## 1. Introduction

Terpin is a fine chemical used in the pharmaceutical industries and mainly as an intermediary in the α-terpineol preparation - important raw material in the perfumery industry.

The continuous or semi-continuous production of terpin from α-pinene hydration, using sulfuric acid as a catalyst, was studied from laboratory up to pilot scale in an attempt to optimize the conditions of manufacturing this fine chemical: this reaction involves a complex three-phase system (1,2).

A literature search shows a wide diversity of conditions to carry out the above reaction and in an attempt to optimize the yield, the more important variables were selected and their interation was analysed by using statistical methods from which empirical polynomial mathematical models were derived from a programmed matrix (factorial design) of laboratory experimental results; emulsifing agents were not considered in this study. It was concluded that the optimum acid concentration is about 40% and that the best temperature zone lies between 274 K and 283 K; the ratio of liquid phases is not a critical factor on the reaction yield, as long as the water is an excess reagent as regards α-pinene.

The kinetics of the reaction was also studied at laboratory scale to assess the relative importance of the reaction rate (including by products) and diffusion phenomena. It was concluded that mass transfer plays an important controlling role in the first period of the reaction namely the nucleation and crystal growth of terpin (2,3). The apparent activation energy of formation of terpin, after the above referred step, was determined (25 $KJ.mol^{-1}$), but the reaction presents two different kinds of behaviour, as regards temperature dependence, the limiting temperature being about 283 K (4).

## 2. Results

Figure 1 represents laboratory data obtained in a batch reactor operating isothermically at 283 K. Applying the well known method of Denbigh, the maximum yield is theoretically obtained in a two reactors battery where the first reactor operates continuously and the second batchwise.

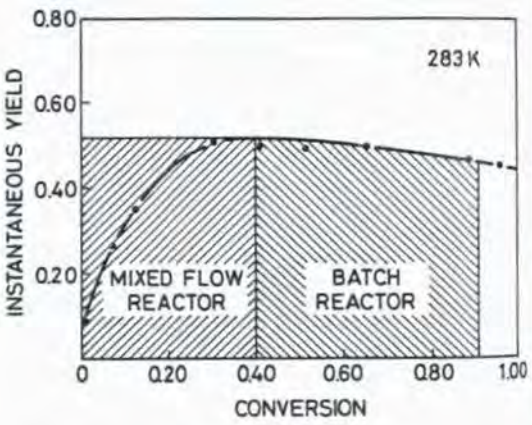


Fig. 1 - Operating conditions corresponding to the maximal global yield

Using the above results, a continuous two stirred reactors pilot plant was designed (4) and built, including the separation of terpin and recycling of the catalyst. The plant can produce continuously or batchwise the desired product.

In order to improve the mixing conditions, the geometry of the pilot reactor was modified by introducing baffles and raising the power number of the agitator. An overall yield of 56% was obtained at pilot scale, an improvement of 11% relative to the laboratory results.

Figure 2 represents the selectivities of the reaction (molar fraction of terpin: molar fraction of by-products) at 283°K in a batch reactor and in a semi-continuous one to which water is continuously added.

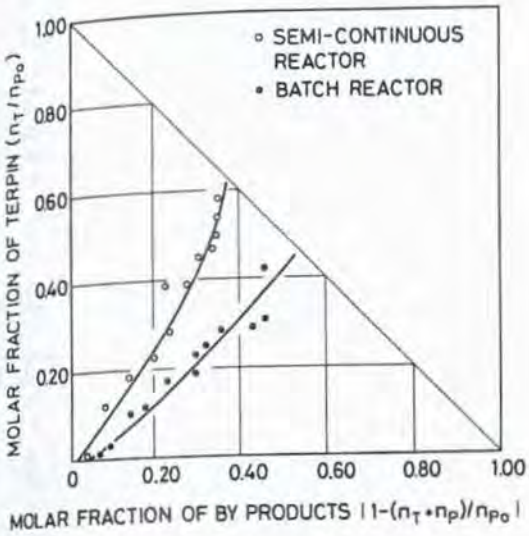


Fig. 2 - Selectivities of the reaction in a semi-continuous and in a batch reactor

As we can see, the selectivity is greater in the semi-continuous reactor, because the acid concentration is kept constant and therefore the by-products formation is decreased.

Also, in this case, after the initial stage of nucleation and crystallization, the instantaneous yield is constant with the conversion as shown in the Figure 3.

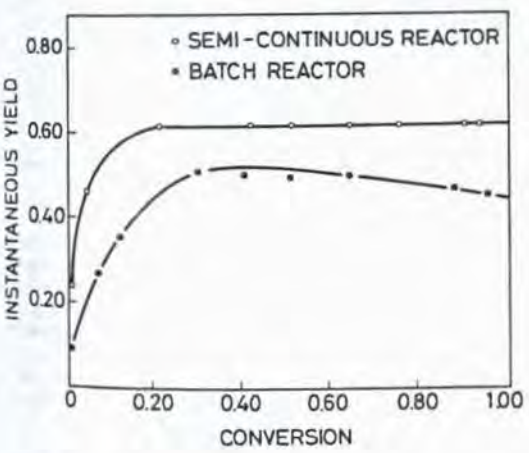


Fig. 3 - Instantaneous yield of terpin formation in a semi-continuous reactor (pilot scale) and in a batch reactor (laboratory scale)

## 3. Conclusions

We can conclude that in terpin manufacturing the greatest yields are obtained in a semi-continuous or continuous process which provides the more favourable distribution of products and that the mixing intensity affects also the yield of terpin by increasing the diffusion rates across the boundaries of the phases.

## Nomenclature

$n_P$ = moles of α-pinene
$n_{P_o}$ = moles of initial α-pinene
$n_T$ = moles of terpin

## References

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