Letters to the Editor

Comment on “An Ecofriendly Catalytic Route for the Preparation of Perfumery Grade Methyl Anthranilate from Anthranilic Acid and Methanol”

To the Editor:

A recent paper in *Organic Process Research & Development* by G. D. Yadav and M. S. Krishnan (**1998**, *2* (2), 86−95) describes an ecofriendly route to methyl anthranilate using solid acid esterification catalysts. The use of these catalysts is a subject with which I have direct experience, and I have a number of comments on the work.

The authors make a great deal about the ecofriendly nature of their route compared to conventional routes using liquid acid catalysts that produce wastes requiring neutralisation. While I certainly agree with this comparison, there are certain aspects of this paper that lead me to question the ecofriendly claim of the route. From past experience in the use of ion-exchange resins as esterification catalysts, ethers are always formed as byproducts in significant quantities from the alcohol. In the work described by the authors, the preparation of a methyl ester using methanol will result in dimethyl ether being produced. On a commercial plant this would create a serious volatile organic compound (VOC) problem, and hence the overall process is not ecofriendly. The removal of DME is very difficult and hence costly, and even though methanol is relatively inexpensive it is a loss to the process.

I was dismayed to find that the analytical details made no reference to analysis of the reaction product mixture prior to removal of unreacted methanol. Such an analysis of the crude mixture would provide data on conversion and selectivity to the methyl anthranilate and possible byproducts. The workup was simply separation of the catalyst by filtration and then removal of volatiles under vacuum which would easily remove the DME without it being noticed. Perhaps the authors never saw any, but I can assure them that it willhave been produced with different solid acids used toproduce different amounts of ether. Ethers are not produced during esterification when using liquid acid catalysts, and it appears that the authors have erroneously assumed the same for solid acid catalysts. A proper comparison with liquid acid catalysts would have examined selectivity by analysing the reaction mixture.

On reading the paper, I was expecting to find details of whether the overall efficiency of the process was improved compared to that using liquid catalysts, but no mention was made of this. In particular, I was looking for mass balance details and feedstock usage data so that meaningful yield information could be calculated and compared to the conventional route. To claim that any route is ecofriendly, a complete evaluation is required. Even without such a claim, it is important to more fully examine the route than appears to have been the case. To simply compare the nonproduction of acidic wastes is not sufficient evidence of having developed a better process.

The subject of using solid acid esterification catalysts has been around for many years, yet commercially such processes are not as widely used as perhaps they could be. The authors are to be complimented on examining the use of potentially ecofriendly synthetic routes, but other workers should be aware that doing so with only half an eye is self-deceiving, e.g., Lord Nelson.

One final point is the section on the analysis of the methyl anthranilate, where the authors claim the boiling point is 153 °C. This may be a typographical error, because chemical supplier catalogues list the boiling point as 256−258 °C. Incidentally, the melting point of the ester is reported as 25 °C, but in a warm laboratory in India it is perhaps commonly seen as a viscous liquid.

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