Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Synthesis of indene in liquid-phase by one-pot process using orthogonal tandem catalysis

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SI.1. Calculations of sustainability parameters

To the best of our knowledge, one of the most employed indexes for evaluating the sustainability of a process where the desirable product is obtained from a chemical reaction is the atom economy (AE) (1):

$$AE = \frac{MW\ of\ desired\ product}{MW\ of\ all\ reactants}.100$$

where *MW* is molecular weight.

In the case under study in this work, the desired product is indene (MW=116.18 g/mol), and the only byproduct is water (MW=18.016 g/mol), while the reactants are 1-indanone (MW=132.18 g/mol) and H_2 (MW= 2.02 g/mol). Therefore, the AE factor may be calculated as follows:

$$AE = \frac{MW\ of\ indene}{MW\ of\ all\ reactants}.100 = \frac{116.18\ g/mol}{(132.18 + 2.02)\ g/mol}.100 = 86.7\%$$

The value obtained for the AE is relatively high for the production of fine chemicals (1), so it is possible to say that our process seems very attractive from the point of view of sustainability (2). It is widely known that catalytic reactions such as hydrogenations (the same as isomerizations and additions) are chemical reactions with the highest atom economy for synthetic methods, much higher than the processes based on no reaction or on a wrong reaction (see the atom economy triangle in Fig. S.1 (3)(2)), as the process based on the recovery of indene from coal tar.

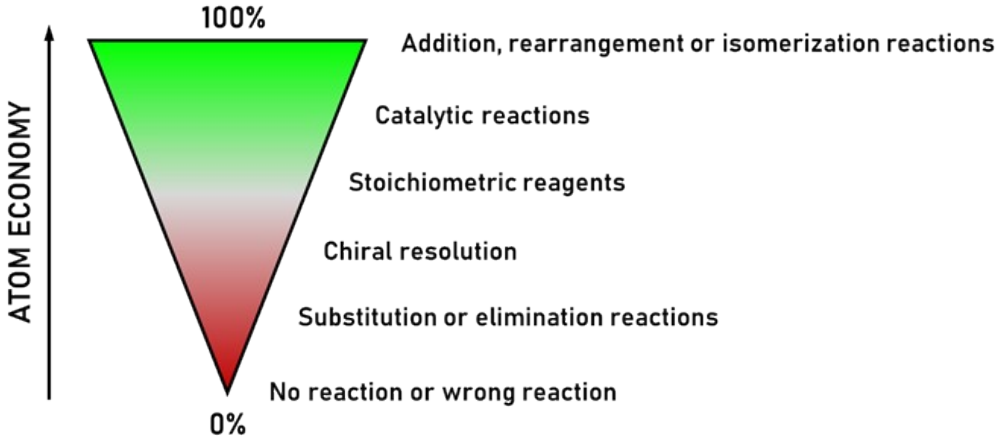

Fig. S1. Atom economy (AE) triangle (2).

It is worth mentioning that the traditional process of indene production based on coal tar involving fossil-derived raw materials is not based on a chemical reaction, but in unit operations including complex separation steps. Therefore, it is not possible to calculate an *AE* for this process, so the direct comparison with our proposal is not possible.

Nevertheless it is possible to estimate the AE of the process for producing indene from the coupling of benzene and propylene (4). In this case, the desired product is indene (MW=116.18 g/mol), while the reactants are benzene (MW=78.12 g/mol) and propylene (MW= 42.08 g/mol). Thus, the AE factor of this process may be calculated as follows:

$$AE = \frac{MW\ of\ indene}{MW\ of\ all\ reactants}.100 = \frac{116.18\ g/mol}{(78.12 + 42.08)\ g/mol}.100 = 96.7\%$$

This indicates that this process seems very attractive from the point of view of the atom utilization from reactants, though it is based on the use of toxic and carcinogenic benzene. Thus, to perform a more complete analysis, it is necessary to include the calculations of other sustainability parameters.

Another widely employed index for measuring the sustainability of a process is the *E-factor* (5) that is defined as:

$$E - factor = \frac{Total\ mass\ of\ waste}{Mass\ of\ desired\ product}$$

The *E-factor* takes into account waste byproducts, leftover reactants, solvent losses, spent catalysts and anything else that can be regarded as a waste (water is always excluded). In the case of the one-pot process for indene production proposed in this work, from the catalytic activity results it is possible to estimate the amounts of undesirable byproducts at the end of the process (unreacted ONE and NOL, and the ANE produced by ENE hydrogenation). Thus, the E factor may be obtained considering these byproducts as the reaction waste and dividing the amount obtained by the mass of ENE produced. Cyclohexane solvent is not considered as a waste since it can be easily separated from the reaction mixture, taking advantage of its low boiling point, and reuse in subsequent batch processes. Similarly, spent catalysts may be initially excluded from this calculation since their recovery and reutilization would be possible. Therefore, considering a unitary molar base for the species and excluding the spent catalysts, H_2 and solvent losses:

$$E - factor = \frac{n_{ONE} \cdot MW_{ONE} + n_{NOL} \cdot MW_{NOL} + n_{ANE} \cdot MW_{ANE}}{n_{ENE} \cdot MW_{ENE}}$$

$$E - factor = \frac{0.052\ mol \cdot 132.16\frac{g}{mol} + 0.07 \cdot 134.18\frac{g}{mol} + 0.07 \cdot 118.18\frac{g}{mol}}{0.79 \cdot 116.16\frac{g}{mol}} = 0.27$$

In the case that the spent catalysts are included, this value increases up to:

$$E - factor = \frac{n_{ONE} \cdot MW_{ONE} + n_{NOL} \cdot MW_{NOL} + n_{ANE} \cdot MW_{ANE} + W_{HZSM-5} + W_{Cu/SiO2}}{n_{ENE} \cdot MW_{ENE}}$$

$$E-factor=\frac{0.052\ mol\cdot 132.16\frac{g}{mol}+0.07\cdot 134.18\frac{g}{mol}+0.07\cdot 118.18\frac{g}{mol}+20\ g+\ 40\ g}{0.79\cdot 116.16\frac{g}{mol}}=0.92$$

Where 20 g and 40 g are the weight of HZSM-5 and Cu/SiO_2, respectively, needed for converting 1 mol of ONE with a similar n^0_{ONE}/W_C ratio that in our process.

This means that, even in the case of including the spent catalysts as waste, the *E-factor* of our proposal is still considerably low for the production of a valuable fine chemical. It is worth mentioning that most of the fine chemicals are produced in processes with an *E-factor* between 5 and 50 (6).

In order to evaluate the sustainability of our proposal in comparison with the other reported processes, the *E-factor* of them should also be estimated. However, for the process based on the recovery of indene from coal tar carried out in an oil refinery, it is very difficult to perform the calculation because of the scarce information available in the patents (7–10). Besides, many of the patents use as raw material an indene-rich stream (50-93%) coming from coal tar that then it is purified by different unit operations.

On the other hand, for the process in liquid-phase based on the coupling of benzene with propylene (4), the E factor can be calculated by considering a unitary molar base for the species and excluding the spent catalyst, solvent losses and other byproducts (25 mol%) not specified in the work:

$$E-factor=\frac{n_{PP}\cdot MW_{PP}+n_{STY}\cdot MW_{STY}+n_{MSTY}\cdot MW_{MSTY}}{n_{ENE}\cdot MW_{ENE}}$$

$$E-factor=\frac{0.25\ mol\cdot 42.08\frac{g}{mol}+0.15\cdot 104.15\frac{g}{mol}+0.15\cdot 118.18\frac{g}{mol}}{0.20\cdot 116.16\frac{g}{mol}}=1.89$$

Where PP is propylene, STY is styrene and MSTY is methylstyrene. It is worth noticing that the 25 mol% of other byproducts can not be considered in the estimation at the light that these products were not specified by the authors. However, in case of considering them, the *E-factor* of this process would be even higher. In other words, even without considering the spent catalyst and the non-specified byproducts, this value is twice of the *E-factor* of our proposal even when the spent catalysts are considered as waste.

Finally, it is important to mention that several authors have emphasized that mass-based metrics such as atom economy and E-factor need to be supplemented by other metrics, in particular life cycle assessment (LCA), which measure the environmental impact of waste and, in order to assess sustainability, by metrics which measure economic viability (11). LCA is a methodology for assessing environmental impacts associated with all the stages of the life

cycle of a commercial product, process, or service (12). In this case, an LCA study for the process we proposed would involve a thorough inventory of the energy and materials that are required across the industry value chain of the process, and calculates the corresponding emissions to the environment. Thus, LCA evaluates cumulative potential environmental impacts and its main aim would be to document and improve the overall environmental profile of the process (13). Although a strong development and harmonization of LCA has occurred since 1990 (resulting in international standards and several guidelines), its results are often criticized. Without a formal set of requirements and guidelines, an LCA can be completed based on a practitioner's views and believed methodologies. Nevertheless, an LCA completed by 10 different parties could yield 10 different results, so the susceptibility of particular LCAs to practitioner bias is quite high (14). These problems can be more serious when totally different processes (continuous vs. batch), carried out at very dissimilar conditions (gas phase at high temperature vs. liquid phase at low temperature) and using completely different raw materials (coal tar vs. 1-indanone), are compared.

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