Teaching green chemistry: from lemons to lemonade bottles

Stewart Tavener, Jeff Hardy, Nick Hart and Andy Goddard from the Clean Technology Centre at the University of York, UK, describe their experiences in trying to design challenging but realistic green chemistry experiments for advanced undergraduate and Masters level chemistry students

Introduction

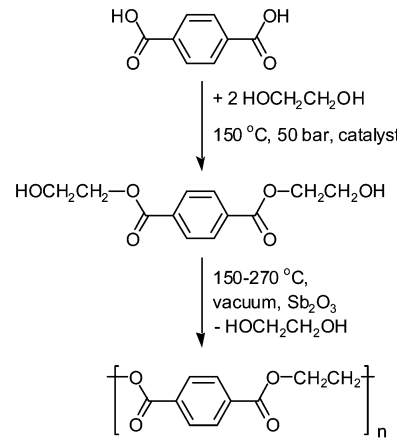
In the spring term of 2000, we started to run green chemistry mini-projects as an optional part of the undergraduate courses at the Department of Chemistry, University of York. The projects were run over a period of six weeks, with a total of six days laboratory time allocated during that period. The projects were intended to cover key areas of green chemistry, including clean synthesis, life cycle analysis, atom efficiency, and the use of renewable feedstocks. An additional aim was to broaden the students' view of chemistry by encouraging them to estimate the total resources required for a particular process. We would like to share some of our experiences from the first year of these projects.

To encourage independent learning, the students were involved in the selection of their own project. Rather than studying a single reaction in isolation and judging its success on the basis of 'percent yield' alone, the students were asked to consider a product and to work backwards. They were each asked to select an everyday product that could be found in a supermarket or high street store, and to think about the chemicals that went into the manufacture of that product. We then met to discuss their suggestions and make a final choice for study.

The suggestions at this stage included a nylon rucksack, plastic drink bottles (PET) and washing-up liquid (detergents and surfactants). We were looking for something that contained enough chemistry to keep five students busy for six days in the laboratory, and any of these suggestions would have fitted the bill. We could have studied the manufacture of nylon polymers and the synthesis of the monomers (including adipic acid) necessary for its production; or we might have investigated the synthesis of non-ionic surfactants and their fate in the environment. Instead, the students voted to investigate all aspects of the manufacture of polyethylene terephthalate fizzy drinks bottles, including the polymerisation itself, and manufacture of the monomers. They were asked to keep track of everything they used during their lab work, measuring volumes of aqueous and organic solvent use, water usage for cooling, and the electricity consumption alongside the familiar % yield calculations. They were also asked to calculate 'mass' and 'atom' efficiencies (see box below for an example), and to consider whether less harmful solvents or renewable feedstocks could be used at any stage.

The chemistry

PET is formed by reaction of ethylene glycol with either terephthalic acid (Scheme 1), or with dimethyl terephthalate via transesterification. These



Scheme 1

Sample measurements and calculations for the conversion of limonene to p-cymene using N-lithioethylenediamine

% Yield
Limonene used = 13.6 g = 0.100 mol
p-cymene produced = 12.7 g = 0.095 mol
∴ yield = 95%

Reagents used

Lithium metal	4.12 g
Ethylene diamine	84.5 g
Limonene	13.6 g
Diethyl ether	35.2 g
water (quenching)	300 g

Total mass of reagents 437 g (not including cooling water)
∴ mass yield = 12.7/437 = 2.9%

Other resources
water (cooling): 32.6 kg electricity: 1 kW hr (approximate)

Table 1 Atom efficiencies

Element	Number in reagents	Number in product	Theoretical efficiency (%)	Actual efficiency[a] (%)
Li	1	0	0	0
N	2	0	0	0
C	12	10	83	79
H	22	14	64	60

[a]Calculated from (yield) × (theoretical efficiency).

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reactions proceed at high pressures and temperatures, which we were unable to replicate safely with equipment available to us in a teaching laboratory environment. These steps are very efficient anyway, particularly if the ethylene glycol produced in the second step can be reused. Instead, attention was turned to the monomers.

The monomers: ethylene glycol and terephthalic acid

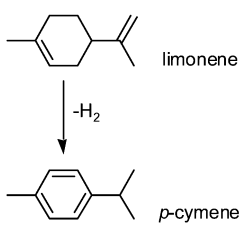
Ethylene glycol is generally produced by catalytic hydration of ethylene oxide, which, in turn, is manufactured by catalytic epoxidation of ethene. Because of the high toxicity of ethylene oxide, and the need for high temperatures and pressures, manufacture of ethylene oxide was not considered a suitable practical for undergraduates. We could have studied a model alkene epoxidation, for example cyclohexene using a supported reagent catalyst, but instead we focused on manufacture of the other half of the PET jigsaw, terephthalic acid.

Terephthalic acid

Terephthalic acid is generally produced *via* oxidation of *p*-xylene in the liquid phase using a Mn or Co salt catalyst at relatively high temperatures (140–200 °C). A co-catalyst or promoter (bromide) is often used, and a co-oxidant such as acetaldehyde is frequently employed to ensure oxidation of both methyl groups. Some attempts were made to recreate these conditions on a lab scale, and to measure the waste produced. This reaction appeared to be a likely candidate for a green study. The students recognised *p*-xylene as a non-renewable feedstock, and wondered if there might be a better route starting with a renewable.

An alternative route to terephthalic acid?

Limonene is a cyclic terpene and is found as a major constituent of citrus peel oils, of which about 50,000 tonnes are produced annually. It is generally considered safe and is sometimes used as a solvent substitute for xylenes. Importantly, it may be converted to p-cymene (Scheme 2), which provides a renewable method of synthesising aromatics. This was investigated further.



Scheme 2

The production of *p*-cymene from limonene was initially achieved by a literature method involving lithium metal in ethylenediamine. Whilst very effective (95% yield), this required stoichiometric amounts of the lithium reagent, and so a catalytic method was sought. Having identified this as a dehydrogenation and aromatisation reaction, the students suggested that some kind of hydrogenation catalyst should, in the absence of additional hydrogen, also be capable of catalysing dehydrogenations. Palladium on charcoal sprang to mind, and this was applied to a liquid phase reaction of limonene. The reaction gave complete conversion of the limonene, but only about 50% selectivity to *p*-cymene [subsequent projects have already seen this figure improve to about 70%]. It is potentially a very green way of preparing an aromatic from a renewable feedstock.

Oxidation of p-cymene

This was a greater challenge. We found that *p*-cymene could be oxidised to terephthalic acid successfully using stoichiometric CrO_3 as an oxidising agent—hardly a green method! The search for a catalytic method, perhaps using a supported reagent oxidation catalyst and air or hydrogen peroxide as the oxidant, would have been the next sensible step. Frustratingly, our allocated lab time had run out and we had to stop here. If a suitable catalytic oxidation method could be found, then limonene really could give a green route from lemons to lemonade bottles.

Outcomes

The decision to give the students free choice over the topic had the advantage that they felt ownership of the project and displayed a genuine enthusiasm for it. However, this left us, the 'learning facilitators' feeling somewhat under-prepared as we didn't know what the students would be doing until a week before laboratory work commenced. In subsequent years we gave the students a list of perhaps four or five projects from which to choose, although this perhaps sacrificed some of the spontaneity and enthusiasm witnessed during that first year. One of the most exciting aspects of running the project was seeing the students discover solutions to problems that we had not thought of ourselves—indeed it was as much of a learning experience for us as it was for them (see box below).

Postscript

The mini-projects have since been superseded by a full MRes postgraduate course in Clean Chemical Technology course. Building upon the experience gained during the mini-projects, a practical experiment was developed for the MRes students, based on examining all steps of transforming limonene to terephthalic acid. The practical is carried out over two days and the students are

A student's perspective

The project was our first experience of carrying out genuine research, as opposed to the following of a pre-defined laboratory script during our university studies. Although it was initially a daunting task to attempt to locate reports on relevant subjects, the guidance given made this a very useful and confidence-building exercise. From knowing nothing about how to research previous work done on a subject, we became confident in using both library and internet resources in order to develop a starting point for the laboratory work.

It was especially exciting to be able to integrate a number of principles forming the basis of green chemistry – namely the use of heterogeneous catalysis in organic synthesis, the development of a process originating from a widely available natural and renewable product (limonene), and working to minimise both the amount of waste produced and the energy used throughout the stages of the reaction.

The exercise was not only beneficial in teaching how to approach novel research, it also taught us important principles in designing a process from a green chemistry prospective. The project was one of the deciding factors in my decision to continue my studies at PhD level in the Department of Green Chemistry at the University of York.

Nick Hart

split into small teams (2–3 students) to examine separate steps in the process. The stages examined in the practical are as follows:

(1) Extraction of limonene from citrus fruit *via* cold pressing, steam distillation and solvent extraction methods.

(2) Transformation of limonene to *p*-cymene *via* catalytic dehydrogenation (both in a batch reactor and in a continuous flow reactor), oxidative dehydrogenation and stoichiometric dehydrogenation (using *N*-lithioethylenediamine).

(3) Oxidation of *p*-cymene to terephthalic acid (to date only stoichiometric CrO_3 has been examined, but other oxidation methods will be examined next time around).

In all steps the students are asked to measure all inputs (including energy) and measure (or estimate) all outputs (including chemicals required in neutralisation *etc*.). The results from all the steps are then pooled in a common table from which the students metadoxically decide upon which route has the lowest environmental impact. The students also are required to comment upon the suitability of each method for scale-up for industrial production. This often results in some excellent discussion.

The practical has been running for two years now, and each year more experimental routes are added. We are currently setting up a suite of clean technology reactors for teaching and other purposes, so in next year's experiment the students will hopefully have the opportunity to examine supercritical CO_2 as a solvent for extracting limonene from citrus fruit peel.

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