

The challenge to develop CFC (chlorofluorocarbon) replacements: a problem based learning case study in green chemistry

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Abstract: The value of case studies for teaching both subject specific and transferable skills within chemistry have long been recognised. Coupling this with problem based learning provides a powerful basis for teaching transferable skills within a chemistry context. This problem based learning case study does this via the fascinating story of the industrial challenge to develop CFC (chlorofluorocarbon) replacements on a very short time scale. It provides a vehicle for developing team working, communication, critical thinking, data interpretation and problem solving skills in a 'real life' context. It also introduces students to environmental issues and green chemistry plus the role of the chemical industry in developing solutions to these issues. The, often competing, interplay between chemistry, economics and social and political factors encourages (?) students to make links between different areas of the curriculum and to also appreciate that there are not always single 'correct' answers to scientific problems. Attention is focussed on the discovery and development of the CFC replacement HFA-134a. The paper concludes with a report on the trialling of, and student feedback for, the case study. [*Chem. Educ. Res. Pract.*, 2006, **7** (4), 280-287]

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Introduction

Active learning and open ended problem solving activities in chemistry are becoming ever more popular as their effectiveness in helping to produce more highly skilled and motivated graduates is recognised. This paper describes an active learning approach to introducing some of the principles of green chemistry. A case study proved to be an excellent vehicle for analysing the need for, and development of, CFC replacements. It begins by taking students through the properties and uses of CFCs and, via the seminal work of Molina and Rowland (1974), on the effect of CFCs on the ozone layer. The challenge to develop environmentally acceptable replacements within a technically challenging timescale then unfolds. Not only are the many chemical and environmental aspects explored but also the political and economic ones, which lead to the first ever international agreement on an environmental issue. How the chemical industry turned these challenges into a business success by developing environmentally acceptable alternatives, is a fascinating story. In addition to exploring a wide range of chemistry, the case study is an excellent vehicle for

teaching transferable/key skills in a chemical context e.g. literature searching, oral and written communication, problem solving and team work.

Undoubtedly the hydrofluorocarbons (HFCs) which have replaced CFCs and HCFCs (hydrochlorofluorocarbons) have a lower environmental impact, but are they 'green enough'? Since the HFCs have *relatively* high global warming potentials, the EU has put in place regulations that require their phasing out, beginning at the end of this decade. The USA has taken a different view in the light of HFCs making only a small overall contribution to global warming compared with carbon dioxide, the major greenhouse gas. The Americans suggest that even this small contribution can be controlled by further reducing refrigerant leaks, so that the HFCs, with their many advantages such as non-flammability, need not be abandoned.

This debate raises important general issues concerning green chemistry and technology that go far beyond protecting the ozone layer. Is the EU being driven by the political lobbying of green activists with their own particular agenda, or is it being environmentally responsible by taking a far-sighted perspective? Conversely, is the US Government protecting the interests of big industry, or is it sensibly avoiding being coerced into scientifically dubious policies that could unnecessarily reduce the well-being of its citizens?

Whatever the answers to these questions turn out to be, the UK Higher Education establishments need to produce chemistry graduates who can use their special technical expertise to formulate well reasoned analyses of the issues involved. Problem based learning is an excellent way of developing this competence.

Background

The Higher Education Funding Council for England (hefce) has identified sustainable development as one of its priorities (Dearing, 1995). It encourages higher education institutions to embed the principles of sustainable development in their strategies and to "*develop curricula, pedagogy and extra-curricular activities that enable students to develop the values, skills and knowledge to contribute to sustainable development*". In the context of chemistry curricula, this priority leads to the embedding of the principles of green chemistry into programmes. This will lead undergraduates to recognise the importance of the chemical industry in reducing the environmental impact of chemical-based activities by developing alternative technologies.

In addition, employers continue to emphasise the importance of the development of a wide range of subject specific and transferable skills during university courses (Finer, 1996; Bailey, 1997; Mason, 1998). These skills include, for example, the ability to identify novel problems and plan strategies for their solution, interpretation of chemical information, presentation of scientific arguments as well as the usual range of transferable skills such as communication, group work, information retrieval, time management etc.

Various strategies have been developed within the discipline of chemistry for delivering this range of subject-specific and generic skills. Some of these involve discipline-related activities (Wyeth, 1997), and others are discipline independent (Garratt and Mattinson, 1987). The use of case studies for teaching has a long history in many subject areas, and their value within chemistry has long been recognised (Pontin et al., 1993; Belt and Phipps, 1998; Belt et al., 2002; Summerfield et al., 2003). A case study should involve the learning of chemistry, be active in style, involve a real world context, and develop personal skills.

Problem solving case studies lend themselves very effectively to the teaching of green chemistry. Two examples of this approach have been published previously (Grant et al., 2004; Grant et al., 2005). These publications have prompted us to report details of our case study, which is co-authored by one of the authors of one of the case studies (Grant et al., 2004).

Although the story of the banning of CFCs (Chlorofluorocarbons) because of their adverse environmental effects and the development of environmentally benign replacements is well known to people aged over 30, it may be totally new to current undergraduates. Thus the case study is an excellent vehicle for developing their literature searching and other key skills in a chemical context. Additional strengths include gaining a real understanding of the complex factors involved in the successful development of new products in the chemical industry and the range of chemistry involved, from analytical to organic synthesis to environmental chemistry.

The aims of the case study are to

- introduce students to green chemistry and environmental issues;
- introduce students to the role of the chemical industry in developing solutions to the problem of CFCs in the environment;
- provide a real life context for learning chemistry;
- encourage students to make links between different areas of the curriculum;
- engage students in open ended problem solving;
- help students appreciate that there is not always a single correct answer to scientific problems;
- develop team working, communication, critical thinking, data interpretation and problem solving skills.

Methodology

The students are divided into groups of three to five by the tutor and they work in these groups throughout the case study. We have run this exercise as both 2 x 2 hour and 4 x 1 hour sessions, with tasks being set in between these classroom sessions.

The case study incorporates five phases:

1. *Is there a problem? (1974)*
2. *Evaluating the problem*
3. *Finding replacements*
4. *Synthesising replacements*
5. *Is the problem solved? (2004)*

Each of these will be described in more detail.

1. *Is there a problem? (1974)*

After the aims of the case study have been introduced verbally, with the aid of a handout, the background to CFCs is briefly described. Students are required to search the literature and find out the main properties and uses of CFCs. This information is presented at the next classroom session.

Each student is then given copies of three papers which were printed in *Nature* in the early 1970s (Lovelock, 1971; Lovelock et al., 1973; Molina and Rowland, 1974) and which are crucial to the CFC story. They include the seminal paper by Rowland and Molina. The students must read and critically analyse these papers and decide if CFCs pose an environmental problem (a) at sea level and (b) in the stratosphere. A 200-300 word written summary of the key points and conclusions drawn from these articles must be submitted by each student. This has to be written in an accessible style, which could be used, for example, as a press release.

Following a discussion, the conclusion is reached that CFCs pose no threat at sea level but they certainly do pose an environmental problem in the stratosphere by destroying ozone. The environmental chemistry of this is then explored by considering the chemical reactions involved in the attack on the ozone layer by CFCs.

2. *Evaluating the problem*

A task is set to calculate how many tonnes of CFCs would be required to destroy ALL the ozone in the stratosphere. This requires the student to consider what assumptions have to be made and data needed in order to carry out the calculation. These include: the earth's radius, the height and mass of the atmosphere, the upper and lower heights of the ozone layer (stratosphere) above the earth (15–36 kms), the ozone concentration (10 p.p.m.) there, and finally, how many ozone molecules are destroyed by one chlorine radical (approximately 1,000). CF_2Cl_2 could be used as the CFC molecule. This data yields an approximate result of 13.5 million tonnes of CFCs.

Data is then presented showing CFC production and release from 1931 until 1973. Students then have to predict when the 13.5 million tonnes figure will be reached. Extrapolation of the figures, preferably graphically, shows that this will occur in the early 1980s. It becomes obvious too that CFC production did not continue at the 1970s levels and thus leads nicely into the international agreements of Montreal in 1987 and of Copenhagen in 1992 on limiting the use of, and then banning of, CFCs. Several key points emphasised here include the political pressures reducing dramatically the time scale for developing the replacements, and that the former agreement was the first ever international agreement on an environmental issue.

3. *Finding replacements*

Students should be able to generate the following generally accepted, key requirements for the replacements:

- Thermodynamic properties as close as possible to those of the original CFCs.
- Stability.
- Non-flammability.
- Non-toxicity.
- No significant change in any other properties pertinent to that application, e.g. no change in operating pressure for refrigerators.
- Materials compatibility – e.g. with lubricants in refrigerators.

Other key points are that the replacement should contain no chlorine atoms, and that they are as cheap and easy to make as CFCs.

The students are given essential data on relevant physical and other properties of some CFCs and possible replacements (Table 1), and they have to decide which compounds might be suitable replacements.

Table 1. Physical and other properties of some CFCs and possible replacements.

Material	RMM / gmol^{-1}	Enthalpy of Vaporization / kJmol^{-1}	Bp/ $^{\circ}\text{C}$	Mp/ $^{\circ}\text{C}$
CCl_2F_2 *	121	20.0	-29.8	-155.0
CHClF_2 *	86.5	20.2	-40.8	-160.0
$\text{CF}_3\text{CH}_2\text{F}$ **	102	22.1	-22.2	-108.0
NH_3	17	23.2	-33.4	-77.7
H_2O	18	40.4	100	0
Iso- C_4H_{10}	58	21.0	-11.7	-159.7
CO_2	44	25.1	-78.5	-56.6

*CFCs

** $\text{CF}_3\text{CH}_2\text{F}$ is an HFC (HydroFluoroCarbon) or HFA (HydroFluoroAlkane). It is one of a large group of compounds like CFCs with similar properties, but importantly HFCs do not contain chlorine.

From the data in Table 1 the suitability of any alternatives can be discussed and other factors such as flammability, toxicity and cost compared (Table 2).

Table 2. Features of some CFCs and possible replacements.

Material	Flammable?	Toxicity	Cost in 1970s
CCl_2F_2	No	+	Moderate
CHClF_2	No	+	Moderate
$\text{CF}_3\text{CH}_2\text{F}$	No	Unknown in 1970s	Moderate
NH_3	Yes	+++++	Cheap
H_2O	No	+	Negligible
Iso- C_4H_{10}	Yes	++	Moderate
CO_2	No	+	Cheap

N.B. The more +s the more toxic.

HFCs should come out top as an alternative since they meet the preferred criteria outlined above. The students could also be made aware of HFCs that existed in the early 1970s and whose toxicological properties were already known, e.g. flurane anaesthetics and HFA-152a (CH_3CHF_2). These are generally expensive, but have the right sort of properties.

A broad comparison of the manufacture of CFC-12 and HFC-134a from a thermodynamics point of view, and therefore cost, would be beneficial at this point. There are few commercial chemical-manufacturing methods simpler than those for the current CFCs. When CCl_4 is reacted with HF, it produces CFC-11 (CCl_3F) and CFC-12 along with gaseous hydrogen chloride (HCl). By controlling the temperature and pressure, one can get high yields of the desired CFC. Modifications of these methods can be used to produce CFC-113, -114, and -115. But there are no such simple methods to produce the contemplated replacement discussed here. Similar comments apply to other replacements such as HFA-152a (above) and HFA-125 (CF_3CHF_2).

Taking HFC-134a as an example, there is no evidence to indicate the possibility of developing a single-step process to HFC-134a directly from a chlorocarbon i.e. analogous to existing CFC-12 processes. Instead there are several potential routes, beginning with four different precursors. These potential manufacturing processes have from two to four steps, and each step translates into an entire plant, once commercial manufacturing begins: reactor, feed systems, distillation columns, decanters, dryers, storage tanks, compressors, pumps, and all the other paraphernalia of a chemical plant.

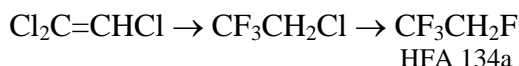
The challenge of developing these replacements within a very short timescale is discussed, as well as the innovations in Research and Development that were necessary in order to achieve this. Examples are the involvement of the chemical engineers who would design the manufacturing plant, in the initial research in the chemistry laboratories, and the unprecedented collaboration of all the CFC manufacturers in setting up the joint ventures: AFEAS (Alternative Fluorocarbons Environmental Acceptability Study) and PAFT (Programme for Alternative Fluorocarbon Toxicity Testing) instead of each carrying out their own environmental and toxicity testing programmes.

The students have to evaluate each of the alternatives given and choose the most appropriate replacement for CFCs. This requires careful consideration of chemical and physical properties to ensure that, as far as possible, they match those of the CFCs which they are to replace. If so, their suitability for the desired applications should be assured. Of course the replacements must be environmentally acceptable, which means that toxicity, ozone depletion potential, global warming potential and atmospheric life time must all be carefully scrutinised.

4. *Synthesising the replacements*

Having established that HFCs or HFAs (Hydrofluoroalkanes) are the likely replacements and that a whole family of these will be required to cover all the uses of CFCs, attention focuses on the 'front runner', HFA 134a (CF₃CH₂F). Each group is required to devise and evaluate synthetic routes for HFA 134a. These are then presented to and discussed with the whole student cohort.

The chosen route will probably be:



The reasons for choosing this route over others is then discussed and comparisons drawn with the simpler synthesis of CFCs. This includes consideration of factors such as the engineering, technological and environmental issues, catalysts used, and costs.

5. *Is the problem solved?*

At this point students view the CFC problem as being 'solved'. Their attention is drawn to the CFCs already in existence and consideration of containment or disposal or reuse are all addressed, as well as the issue of the growing 'fridge mountain' which has been an issue raised in the media (Brown, 2002). In order to address this latter point, each group is given a specific designation, such as Greenpeace, Hotpoint, DuPont or Liverhull Recycling Company and is required to present proposals for dealing with the 'fridge mountain' from their perspective. They have to include proposals as to who bears the responsibility for this problem, and which parties should pay for disposal of old domestic fridges and air conditioning units.

Assessment

The assessment is based on written reports, oral presentations and peer assessment of individual students' contribution to the group work. A proposed assessment scheme is below:

a) Literature search and report	20 %
b) Data interpretation and presentation	30 %
c) Final presentation and debate	30 %
d) Peer evaluation	20 %.

Discussion

The case study has been trialled at several institutions and at the Variety in Chemistry Education conference in Dublin in 2003 (Heaton et al., 2003) and has received very positive feedback from both staff and students. Some fifteen academics participated in the workshop in Dublin and ~ 350 students at the University of Hull and ~ 50 at Liverpool John Moores University. Responses were received from 80 students.

More specifically students were asked to rate in anonymous questionnaires each of the following on a scale of 1 to 5 (where 5 is very highly rated), with the results shown.

"Do you feel that you have developed any of the following skills through studying this case study"?

solving unfamiliar problems	3.8
working with others	4.0
thinking critically	4.0
communicating your ideas	3.9
link between theory and practice	3.7

Most importantly, when asked if they had enjoyed this activity, the students scored it 4.2 out of 5, which is very satisfying for us.

Conclusions

This case study has proved popular with chemistry students and has been successful in its aim of developing an awareness of green chemistry. The importance of developing new products to replace environmentally unacceptable ones and turning what could have been a business disaster into an opportunity and success are important lessons to be learned. It has provided some insight into the wide range of chemistry involved in producing new products in the chemical industry and the range of additional factors, such as economics, engineering and even political ones, which can have a crucial influence on the success of the project. In addition, undergraduate students are provided with an opportunity to develop a range of key skills within a chemistry context and the final part of the case study imparted another important scientific lesson - that there is not always a single 'correct' answer.

Furthermore are HFCs a 'green answer' to the replacement of CFCs or is a new generation of replacements required for them in turn?

Future Plans

We now seek further partners to trial the case study and provide feedback for further refinements. Copies of the resource can be obtained from the authors. Additionally, we need to gain an insight into what and how students have learned from this case study.

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