A Case Study in Green Chemistry: Developing Replacements for CFCs

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Abstract
Chlorofluorocarbons, CFCs, were developed in the late 1920s for use as safe refrigerant alternatives to sulphur dioxide and ammonia. They were welcomed by industry because of their low toxicity, chemical stability, low flammability, low cost and ease of synthesis. They found wide application as refrigerants, blowing agents, propellants and cleaning agents. Over more than 40 years, applications of CFCs expanded into a wide variety of areas, and grew into a multibillion-dollar industry. Unfortunately, CFCs are not ecologically benign. It became increasingly clear that CFCs were responsible for ozone depletion. In the early 1970s the leading manufacturers of CFCs met to discuss the possible environmental impact of their products.

This case study uses a problem based learning approach to take students through the development of replacements for CFCs from the 1970s to today. They investigate the background to the CFC problem and consider data that leads to the decision to investigate possible replacements. They must select and design replacement molecules (HFCs), devise syntheses and then consider the challenge to develop the replacements in a socio-economic and political framework. They also consider the problems posed by existing CFCs, the 'fridge mountain' and possible disposal and containment alternatives. The case study brings the story up to date with an investigation of the problems now being associated with HFCs and the search for new alternatives.

This activity successfully teaches applied and 'green' chemistry via a real life context. The chemistry encountered is of an applied/industrial nature and is set in a socio-economic context. The influence of political pressures is also brought in when appropriate. Because the activity adopts a problem based approach it is also successful in developing a range of transferable skills, particularly problem solving, teamwork plus verbal and written communication.

Introduction
The Higher Education Funding Council for England (HEFCE) has identified sustainable development as one of its priorites[1]. 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[2-4]. Various strategies have been developed within the discipline of chemistry for delivering this range of subject-specific and generic skills. Case studies have a long history in many subject areas and their value within chemistry has long been recognised [5-8]. Problem solving case studies lend themselves very effectively to the teaching of green chemistry. Two examples of this approach have previously been published elsewhere[9, 10].

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 and the issues of global warming and the ozone hole are certainly still current. Thus the case study is an excellent vehicle for developing their literature searching and other key skills in a chemical context and for giving undergraduates a real understanding of the complex factors involved in successfully developing new products in the chemical industry.

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.

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Methodolgy

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 x1 hour sessions, with tasks being carried out between these classroom sessions.

The case study incorporates five phases:

1. *Is There a Problem*?

Each student is given copies of three papers which were printed in Nature in the early 1970s[11-12] and which are crucial to the CFC story. 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 is submitted. This is written in an accessible style which could be used, for example, as a press release.

Following discussion, the conclusion is reached that CFCs pose no threat at sea level but do pose an environmental problem in the stratosphere by destroying ozone. The environmental chemistry of this is then explored.

2. *Evaluating the Problem*

A task is set to calculate how many tonnes of CFCs would be required to destroy ALL of 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 above the earth, ozone concentration and how many ozone molecules are destroyed by one chlorine radical. 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 shows that this will occur in the early 1980s. It becomes obvious that CFC production did not continue at the 1970s levels and thus leads nicely into the international agreements on limiting the use of and then banning of CFCs.

3. *Finding Replacements*

Students generate the following generally accepted, key requirements for the replacements:

- Thermodynamic properties as close as possible to the original CFCs.
- Stability.
- Non-flammable.
- Non-toxic.
- No significant change in any other properties pertinent to that application - eg no change in operating pressure for refrigerators.
- Materials compatibility - eg with lubricants in refrigerators.
- Cheap and easy to make.
- Contain no chlorine atoms.

Data on relevant physical and other properties of some CFCs and possible replacements are given and students decide which compounds might be suitable replacements.

4. *Synthesising the Replacements*

Having established that HFCs (hydrofluorocarbons) 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 (CF_3CH_2F).

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 consequences of choosing particular routes are discussed and comparisons drawn with the relatively simple synthesis of CFCs– engineering, technology, environment, catalysts, cost etc.

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[13]. In order to address this latter point each group is given a specific designation, such as Greenpeace, Hotpoint, Du Pont 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 students contribution to the group work. A proposed assessment scheme is shown:

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 used in several institutions and has received very positive feedback from both staff and students. Students were asked to rate 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

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.

A copy of the case study with handouts and a tutor's guide is available from the authors.

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.

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