Econic: Reactor Commissioning Report

CCUS Innovation 2.0
Key Knowledge Deliverable 1.2

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Key Knowledge Deliverable Cover Sheet

This Key Knowledge Deliverable (KKD) has been produced by Econic Technologies as part of the Department for Energy Security and Net Zero £1bn Net Zero Innovation Portfolio (NZIP) - CCUS Innovation 2.0 programme. The document is reflective of the status of the project at the time of writing. The material presented could have been subject to change as the project matured. These documents should not be considered a full representation of the final project.

There is increasing imperative and demand for fast-moving consumer goods, like household cleaning products, to be made sustainably, and at a competitive price. This project, in partnership with Unilever, will develop sustainable non-ionic surfactants, a component of such cleaning products, based on utilisation of waste CO2. The use of Econic's catalyst and process technology in the production of non-ionic surfactants allows captured waste CO2 to replace up to 40 wt% of traditional fossil fuel-based and palm oil-derived raw materials in a process that can be retrofitted onto existing production plants. The utilisation of waste CO2 as a raw material adds undeniable value to the surfactants industry.

Report 1c: Reactor commissioned & ready for experimentation.
Report 1d: Photos of installation

Report 1a: Design document
Report 1b: HAZID document
Report 1c: Reactor commissioning report
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Report 2a: Samples preparation
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Introduction

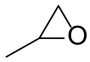
Ethylene Oxide vs Propylene Oxide

Econic's process and technology has to date primarily focused on propylene oxide (PO)-based reactions. As such, a comprehensive understanding of such epoxide reactions in the Econic process has been obtained. Using the knowledge and information acquired from these PO developments, Econic is designing a new reaction system using ethylene oxide (EO), an alternative epoxide for the production of CO2-containing surfactants.

The use of EO, however, creates a far more challenging process, because EO is a flammable gas at room temperature (while PO is a liquid at the same temperature), and hence different handling is required, not only during operation, but also for operator safety.

EO and PO properties are listed in Table 1 below.

Table 1 – Ethylene oxide and propylene oxide chemical properties

	Ethylene oxide	Propylene oxide
Formula	 C2H4O	 C3H6O
Reactive Molecular Mass	44.05 g/mol	58.08 g/mol
Boiling point	10.6 ºC	34.2 ºC
Flash point (closed cup)	-57 ºC	-37 ºC
Flammability limits	2.6-100 %vol	1.7-37 %vol

Ethylene Oxide Hazards

Some of the main challenges regarding EO handling are the following: EO is an extremely flammable gas, and it may react explosively even in the absence of air. The EO cylinders contain gas under pressure and hence, they can explode if heated. In terms of chemical hazards, it is a toxic compound if swallowed or inhaled, and it causes severe skin burns and eye damage. Other potential hazards include respiratory irritation, drowsiness or dizziness, genetic defects, cancer, fertility damage, and damage to organs of the nervous system through prolonged exposure. Figure 1 below shows a summary of the primary hazards that must be considered when using EO. In order to minimise the hazards that come with working with EO, exposure controls must be taken into account, whereby workplace exposure limits of 1 ppm / 1.8 mg/m3 are set for toxicity and a lower explosive limit of 3% is observed.

Figure 1 – Ethylene oxide hazard pictograms

Alkoxylation Reaction Hazards

Alkoxylation polymerisation reactions with PO and EO are typically highly exothermic catalytic reactions, which require control measures to minimise risk and ensure the reaction stays within a safe operating limit. Industrially, the monomers (EO, PO, or a mixture of the two) are fed into the reaction vessel at the rate they are consumed, in order to minimise the inventory of free monomer within the reactor. In the case where the epoxide monomers are fed into the reactor more quickly than they are consumed, a thermal runaway is possible. Such a runaway reaction on an industrial scale leads to uncontrolled heating and pressurisation of the reactor, and temperatures above 250 ºC are readily achievable. Over-pressurisation of the reaction vessel is also likely due to rapid gas generation.

In the case of EO, deflagration, a temperature-induced decomposition of EO in the vapour space, is also possible. Such an event can be initiated by exposure to high temperatures or sparks, and can lead to high rates of energy release as well as over-pressurisation (approximately 10 times higher to starting EO partial pressure), essentially creating a bomb. To ensure that a deflagration event is prevented, additional specific control measures are required, namely introducing an inert gas, like N2 or CO2, to the reactor.

KKD Overview

This report summarises the design, safety, and commissioning of a new reactor system for the production of CO2-based surfactants with control and safe handling of ethylene oxide.

Reactor Design

General Reactor Characteristics

The reactor and control systems have been assembled and commissioned by SciMed UK and Parr Instrument Company US. The system compromises of 2 x 600 mL Parr stirred high pressure autoclave reactors, with independent liquid- and gas-appropriate feeds of solvent, EO, PO, CO_2, and N_2. Each reactor has a dedicated system for the charging of solids/liquids (e.g. catalysts and starters) and for in-line product sampling.

Additional reactor services include vacuum lines for removal of volatiles and vent lines for controlled depressurisation of the reactor. The reactors have the flexibility to operate independently or in series. Extensive use of remotely actuated valves has been incorporated into the design to minimise the potential for exposure of reactor users to hazardous materials. The reactors are located within existing Econic fumehoods. To mitigate against the risks inherent to use of EO, the reactors have rupture discs as well as rupture line containment vessels. Fumehoods are fitted with hazardous gas monitoring systems, which have been integrated into both the lab and Parr Reactor control system's alarm matrices. Suitable fumehood bunding is installed and existing fire suppression systems will be utilised. The reactors will be emptied via bottom valves and will only be disassembled for routine maintenance.

Safety Assessments and Reactor Design Features

As part of the design phase, a HAZID study was completed, chaired by independent risk analysts, establishing required follow-up actions. Amendments were made to the initial reactor design, based on outcomes of the HAZID. To ensure that the system is operated within its safe design window, and with consideration of the deflagration risk posed by EO, calorimetry studies and relief vent sizing calculations have been carried out through a third party (DEKRA) to determine the maximum volume of EO that can be safely used in the reactor. Based on the outcome of these studies, the operating capacity of the reactor systems has been set.

A detailed HAZOP study was conducted, chaired by external risk management consultants, to review the proposed reactor design, planned safety infrastructure (gas detectors, alarm matrices) and consideration of mode of operation. Based on these conversations, a final reactor design was agreed, as well as identification of the safety modifications required within the fumehood and wider laboratory space, and determination of specific actions that should be included in development of standard operating procedures and preventative maintenance plans, all of which will ensure the highest level of safety and consistency when operating the reactor system. In addition to physical safety features, a detailed alarm system has been integrated into the system, which will ensure that should an unsafe situation arise – e.g. high temperature/pressure, fire, etc – the reactor will automatically shut down into a safe mode. A number of interlocks are also present into the control system to ensure that valves can only be opened in a certain sequence.

Laboratory Modifications

Prior to the reactor installation and commissioning, a comprehensive laboratory modification process took place to ensure safe operation and handling of the new reactors. The lab modification actions were determined by the outcomes of the safety assessment, and are divided into the following categories: pipework, electricity, water, gas monitoring, and communication.

Pipework

Each reactor is housed in a separate fumehood, which are further isolated from the other fumehoods in the Econic premises. As such, the fumehoods required separate and CO2/N2 supply lines. The CO2 and N2 cylinders are stored in a cupboard outside of the laboratory, while the EO cylinder is stored in a dedicated gas cabinet in order to further isolate it from the reactors.

Electricity

To ensure that the automated valves built into the reactor are able to default to their safe mode in the event of power loss, incorporation of an unbreakable power supply (UPS) was built into the system. The external battery will provide enough power to allow the reactor to shut down into safe mode, as well as record the final state of the reactor (temperature and pressure), so that it can be safely dealt with once power is restored.

Water

A constant water supply to the reactor is necessary to ensure that in an emergency event the reactor contents can be cooled through a cooling coil built into each reactor. In the case that water is lost to the site and this layer of safety is removed, a dedicated water supply to the reactors was deemed necessary. As such, a water tank was installed in the plant room above the Econic lab space, which is connected to the reactor set up to provide sufficient water to cool both reactors in the event of an emergency and necessary shutdown of the reactors.

Gas Monitoring

In order to protect against build-up of toxic or flammable chemicals due to spills or leaks in the reactor, a comprehensive gas monitoring system has been built into the reactor set up. This system includes flammability detectors in each fumehood, which, when a certain level of chemical is detected, will audibly alarm, shut the reactor system into safe mode, turn the fumehood extraction up, and set off a beacon located in the Econic offices to alert staff of a potentially dangerous environment. EO specific detectors are also located in each fumehood to detect harmful levels of EO outside of the reactor, either from leak in the cylinder cabinet or from the reactor setup. In these cases, detection will result in reactor shut down, increase in fumehood ventilation, audible alarm, and a beacon located in the lab near the reactor fumehoods to alert users of a hazardous environment. Responses to these events from the reactor operators and wider Econic team are built into emergency operating procedures.

In addition, a number of the Econic team are trained in the use of breathing apparatus so that any such situation can be dealt with internally safely and efficiently.

Communication

A series of automated valves have been incorporated into the reactor system to minimise manual user interaction with the reactor. These valves are all in communication with one another, such that they can only open/close in a controlled series. This interlock control provides a layer of safety to the system to avoid the movement of chemicals through the reactor in an incorrect order or to the wrong location.

A comprehensive alarm matrix has been incorporated into the reactor system, whereby when a potentially unsafe situation arises, the system is able to react accordingly to prevent a serious event from occurring. Such situations include high reaction temperature or pressure, loss of gas, loss of power, presence of flammable or harmful chemicals outside of the reactor, loss of heating, insufficient chemical feedstocks, blockages within the system, or fire. In each case, an alarm will alert the user to an issue that can be dealt with by manual intervention. If the situation is not resolved, the system will audibly alarm and shut down into a safe state.

In addition to these automated responses, emergency stop buttons have been installed, such that the user can force the reactors into a safe state.

Reactor Commissioning

Commissioning of the reactor was carried out in three phases: dry commissioning, cold commissioning and wet commissioning. The tests ensure that all features of the reactors and the control system operate correctly, to calibrate the equipment, and to familiarise the operators with the new system.

Dry Commissioning

Dry commissioning was carried out following installation of the reactor by SciMed. The process involved labelling of the main components of the reactor (manual and automated valves), pressure testing of all reactor components, and testing of all actuated valves. Additionally, the alarm matrix, interlock matrix and the E-stop were tested and corrected.

All the peripheral equipment was also tested and calibrated prior to adding any chemicals into the system. The flow rate of all pumps and mass flow controllers were tested, performance of the vacuum pump was confirmed, and the stirrer system testing for straight rotation and correct speed. The use of charge bombs for the loading of chemicals required the development of a protocol for material handling and safe operation. The sample lines were tested, and the minimum required volume was determined. The heat transfer units (Hubers) were tested and both the heating and the cooling rate, specific to Econic processes, were determined.

Cold Commissioning

Cold commissioning involved the introduction of chemicals in the reactors, but without any reactive chemistry being performed. The use of proxy chemicals serves two purposes: 1) it allows for the familiarisation of the users with the new equipment, and in this case the automated and manual valves, and 2) ensures that all of the individual components of the reactor system are communicating correctly with the plc and computer.

Wet Commissioning

The final step for the commissioning plan was wet commissioning, which introduces reactive chemistry to the reactor system. In this case, propylene and ethylene oxide were used in the reactor to repeat reactions that have been carried out previously to ensure that the same polymers could be produced. Initially a standard Econic polyol process with PO was mimicked, with consistent results obtained over four runs on a 150 g scale (4x standard scale). Surfactant molecules prepared previously as part of Work Package 2 were also prepared in the new reactor at two different scales – 150 g and 500 g – with consistent results seen between the sets of experiments. Results are summarised in Table 2.

Table 2 – Summary of samples prepared using the new reactor system

ASample	CO2 wt%	Molecular length, g/mol	Repeat?
1	36.2	900	
2	36.5	900	Repeat of 1
3	35.4	800	
4	35.2	800	Repeat of 3
5	31.2	1500	
6	29.6	1300	Repeat of 5
7	28.4	1200	
8	29.4	1300	Repeat of 6
9	31.7	1600	
10	22.5	900	
11	22.5	1300	
12	31.2	1600	Repeat of 9
13	21.8	900	Repeat of 10

Operating Procedures

In parallel to installation and commissioning of the reactor system, a full list of safety and operational documents have been created and compiled. These documents include risk assessments, emergency operating procedures, instrument calibrations, installation reports, commissioning reports, and reactor material and parts inventories. As understanding and use of the reactor continues, standard operating procedures for the different types of reactions that will be performed on the reactor are also being developed.

Learnings

As so many have, we have encountered and continue to encounter several supply chain issues throughout not only the length of our CCUS2.0 grant, but also in our everyday business operations.

Directly related to our grant deliverables, these supply issues have been observed throughout many aspects our project, from chemicals and consumables in the UK and Europe, to specialised reactor parts sourced from the US, and in sub-contracting external work with companies around the world.

In speaking with suppliers, several reasons behind these delays and shortages were identified and shared, including Brexit, the Covid pandemic and the ongoing war in Ukraine. Perhaps more uniquely, we also saw significant lead times on specific components we require for our new reactor system that were bought in bulk by vaccine manufacturers.

Whilst we made every effort to minimise and mitigate the effect of these delays and shortages on our project progress and more generally in our business, unfortunately where alternative options were limited, supply chains are complicated or where we were not working directly with the suppliers, there is only so much that project management and contingency plans can have an effect. The issues faced are symptomatic of the global economic effects described and were largely out of our control.

Nobody said introducing ground-breaking technology was going to be easy.

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