Catalytic Reactor

Instruction Manual

CEU

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1 Introduction

This manual contains instructions for the correct use and maintenance of the CEU manufactured by Armfield Limited.

The information contained in this manual is intended for the user who is required to read it carefully and to ensure that he has fully understood it before operating the machine.

The user manual must be available for ready consultation at all times.

If the manual is lost or damaged contact the manufacturer for a replacement copy.

 WARNING - The manufacturer is not liable for consequences resulting from an improper use of the machine due to the user's failure to read this manual or incomplete reading of it.

The manual is an integral part of each piece of equipment and consequently must be kept throughout the entire service life of the machine and accompany it at all times, even if transferred to another user.

This manual contains instructions required for the safety, receiving, installation, storage, correct operation and maintenance of the CEU.

 WARNING - Armfield Limited reserves the right to modify the specifications referred to in this manual or the characteristics of each machine. Some of the illustrations in this manual may include parts that are slightly different to those mounted on your machine.

 WARNING - All practical work areas and laboratories should be covered by local regulations which must be followed at all times

2 EC Conformity

Each machine is accompanied by an EC Declaration of Conformity signed by the representative of Armfield Limited.

The declaration of conformity states the model and serial number.

The equipment has been constructed in compliance with the essential health and safety requirements laid down in the following applicable directives:

2006/95/EC The Low Voltage Directive

2004/108/EC The Electromagnetic Compatibility Directive

2006/42/EC The Machinery Directive

The following harmonised standards were also consulted for the design and construction of the equipment:

BS EN 61010-1:2010	Safety requirements for electrical equipment for measurement, control, and laboratory use
BS EN 61000-6-1:2007	Electromagnetic compatibility (EMC). Generic standards. Immunity for residential, commercial and light-industrial environments
BS EN 61000-6-3:2001	Electromagnetic compatibility (EMC). Generic standards. Emission standard for residential, commercial and light-industrial environments

 WARNING - This declaration is only valid if the Equipment is installed, used and maintained in compliance with the above mentioned directives and instructions and with the instructions and equipment described in this manual.

Table of Contents

3 Disclaimer

This document and all the information contained within it are proprietary to Armfield Limited. This document must not be used for any purpose other than that for which it is supplied and its contents must not be reproduced, modified, adapted, published, translated or disclosed to any third party, in whole or in part, without the prior written permission of Armfield Limited.

Should you have any queries or comments, please contact the Armfield Customer Support helpdesk (Monday to Thursday: 0830 - 1730 and Friday: 0830 - 1300 UK time). Contact details are as follows:

United Kingdom	**International**
(0) 1425 478781 (calls charged at local rate)	+44 (0) 1425 478781 (international rates apply)
Email: support@armfield.co.uk	
Fax: +44 (0) 1425 470916	

4 Copyright and trademarks

5 Symbols


General warning indicating the potential risk of personal injury


Danger warning


Caution: Explosion Risk


Electrical hazard


Cold Burn hazard


High Voltage hazard


Caution: Flammable


Rotating parts hazard


Caution: Biohazard


Caution: corrosive material


Do not remove safety guards from rotating parts


Do not repair or oil machine whilst in motion


This symbol draws your attention to the information


Wear protective gloves


Wear eye protection


Wear ear protection


Wear safety shoes


Wear breathing protection

6 Safety

6.1 Failure to comply with safety standards

 Failure to comply with the safety standards described in this manual and those relating to common sense can cause danger to people and the environment and damage the Equipment.

Specifically, such non-observance can cause:

- inability of machine and/or plant to perform key functions;
- damage to the machine and /or plant ;
- electrical, mechanical and/or chemical danger to persons;
- environmental danger due to leakage of hazardous substances.

Failure to observe and comply with these safety standards will invalidate the warranty.

Keep these instructions and all related documents together, ensure that they are legible and easily accessible to all employees.

 Do not remove any safety equipment before operating the Equipment or during its operation. Make sure that there is no evident danger before powering up the Equipment. The system must be inspected regularly to check for damage and to ensure that all safety devices are in good working order.

 The Equipment contains moving parts. Do not insert limbs or materials other than the processing material while the Equipment is functioning. In the event of malfunction, danger or lack of appropriate safety systems, shut down the Equipment immediately and inform the qualified personnel.

6.2 Start up, operation and maintenance

The customer is required to verify the suitability of the Equipment for his specific needs, to provide the necessary processing data for a correct selection of the Equipment type and the accessories needed to guarantee the safety of the Equipment. If the user notices that any accessories he considers useful or essential are missing in the order confirmation, it is the customer’s responsibility to contact the manufacturer and request that the accessory or accessories be applied to the Equipment.

 While the Equipment is being used the safety devices provided must be present and correctly installed. Do not carry out any operation on the safety devices while the Equipment is operating.

6.3 Intended conditions of use

The Equipment is designed to give students an appreciation of the design and operating characteristics of packed bed chemical and biochemical catalysis.

 The Equipment must always observe the operating limitations for which it was constructed and those stated in the order confirmation: observe the temperature, pressure, capacity, viscosity and speed limits. Unless otherwise stated in the order, the Equipment must not be used in environments subject to the formation of potentially explosive atmospheres.

6.4 Safety guidelines relating to maintenance, inspection and assembly work

 The user must ensure that all maintenance, inspection and assembly operations related to the Equipment are carried out by qualified technicians.

Technicians must carefully read this instruction manual before acting on the Equipment. Only authorised and trained personnel are permitted to work on the Equipment.

6.5 Arbitrary production and transformation of spare parts

 Changes or modifications to the machine, within the limits that do not go beyond extraordinary maintenance, are only permitted if agreed on beforehand with the manufacturer.

Only original spare parts or parts specifically declared as compatible by Armfield Limited must be used for regular maintenance operations.

These parts have been designed specifically for the system. There is no guarantee that non-original parts can withstand the loads, and function correctly and safely.

The use of non-original parts voids the warranty.

6.6 Noise

The A-weighted sound power level emitted by the machine does not exceed 85dB(A).

This value is guaranteed if the Equipment is installed correctly, that is, in stable conditions with appropriate fastenings and measured at a distance of 1 metre from the Equipment.

6.7 Chemical Safety

 The unit is designed to use clean water (deionised or demineralised to avoid scale build up due to impurities) during normal operation, but cleaning should be carried out regularly as described in the maintenance section of this manual which may involve the use of detergents/chemicals. In addition, under certain conditions causing algal growth, it may be necessary to use disinfectants or biocides to avoid the possibility of water-borne infections as described above.

6.8 Control of Hazardous Substances

 The Control of Substances Hazardous to Health Regulations

The COSHH regulations impose a duty on employers to protect employees and others from substances used at work which may be hazardous to health.

COSHH covers substances that are hazardous to health. Substances can take many forms and include:

- chemicals
- products containing chemicals
- fumes
- dusts
- vapours
- mists
- nanotechnology
- gases and asphyxiating gases and
- biological agents (germs). If the packaging has any of the hazard symbols then it is classed as a hazardous substance.
- germs that cause diseases such as leptospirosis or legionnaires disease and germs used in laboratories.

The regulations require you to make an assessment of all operations which are liable to expose any person to these hazards. You are also required to introduce suitable procedures for handling these substances and keep appropriate records.

Since the equipment supplied by Armfield Limited may involve the use of substances which can be hazardous (for example, cleaning fluids used for maintenance or chemicals used for particular demonstrations) it is essential that the responsible person in authority implements the COSHH regulations or local equivalent.

Safety data sheets

The regulations also ensure that the relevant Health and Safety Data Sheets must be available for all hazardous substances used in the laboratory.

Products you use may be 'dangerous for supply'. If so, they will have a label that has one or more hazard symbols. These products include common substances in everyday use such as paint, bleach, solvent or fillers. When a product is 'dangerous for supply', by law, the supplier must provide you with a safety data sheet.

Note: medicines, pesticides and cosmetic products have different legislation and don't have a safety data sheet. Ask the supplier how the product can be used safely.

Any person using a hazardous substance must be informed of the following:

- Physical data about the substance.
- Any hazard from fire or explosion.
- Any hazard to health.
- Appropriate First Aid treatment.
- Any hazard from reaction with other substances.
- How to clean/dispose of spillage.
- Appropriate protective measures.
- Appropriate storage and handling.

Although these regulations may not be applicable in your country, it is strongly recommended that a similar approach is adopted for the protection of the users operating the equipment. Local regulations must also be considered.

More information can be found on http://www.hse.gov.uk/coshh/index.htm

 Any such chemicals used must be stored, handled, prepared and used in accordance with the manufacturer's instructions and with all applicable local regulations. Protective clothing (e.g. gloves, eye protection) should be worn when appropriate, and users should be supplied with any relevant safety information (e.g. the correct procedure in the event of contact with skin or eyes, the correct procedure in the event of a spill, etc.).

6.9 Water Borne Hazards

 The equipment described in this instruction manual involves the use of water/fluid, which under certain conditions can create a health hazard due to infection by harmful micro-organisms.

For example, the microscopic bacterium called Legionella pneumophila will feed on any scale, rust, algae or sludge in water and will breed rapidly if the temperature of water is between 20 and 45°C. Any water containing this bacterium which is sprayed or splashed creating air-borne droplets can produce a form of pneumonia called Legionnaires Disease which is potentially fatal.

Legionella is not the only harmful micro-organism which can infect water, but it serves as a useful example of the need for cleanliness.

Under the COSHH regulations, the following precautions must be observed:

- Any water/fluid contained within the product must not be allowed to stagnate, i.e. the water must be changed regularly.
- Any rust, sludge, scale or algae on which micro-organisms can feed must be removed regularly, i.e. the equipment must be cleaned regularly.
- Where practicable the water/fluid should be maintained at a temperature below 20°C or the water should be disinfected. In the CEU this may not be practicable so the equipment should be drained after use and filled with fresh water for each run. Note that other hazards may exist in the handling of biocides if these are used to disinfect the water.
- After use the water system should be filled and run with water containing a mild disinfectant such as ‘Milton’ to kill any micro-organisms or algal growth then flushed with clean water and left empty.
- A scheme should be prepared for preventing or controlling the risk incorporating all of the actions listed above.

Further details on preventing infection are contained in the publication “The Control of Legionellosis including Legionnaires Disease” - Health and Safety Series booklet HS (G) 70.

6.10 Hot/Cold Surfaces

 This unit contains components that operate with a maximum temperature of 50°C and minimum temperature of ambient.

Do not touch any surfaces close to ‘Hot Surfaces’ warning labels, any of the interconnecting tubing or components whilst the equipment is in use or returning to a safe temperature.

6.11 Hot/Cold Liquids

 This unit is designed to operate with a maximum liquid temperature of 50°C and minimum liquid temperature of ambient.

There is also a potential risk of scalding from hot liquids or vapours (e.g. steam).

Before disconnecting any of the pipes or tubing:

- Stop the liquid pump.
- Leave time for the equipment to return to room temperature.
- Check that the temperature of the Equipment and liquid is at a safe level

Do not touch any surfaces close to 'Hot Surfaces' warning labels, any of the interconnecting tubing or components whilst the equipment is in use or returning to a safe temperature.

6.12 Leakage of hazardous fluids

 If the Equipment is used to pump/operate with hazardous liquids (toxic, corrosive, flammable, etc.), the volumes of fluid that leak through the seals must be collected and disposed of without endangering human health or the environment and in accordance to local legislation.

6.13 Protective clothing

Wear appropriate protective clothing to protect body parts.

 Safety gloves

Wear suitable gloves to protect your hands from various types of possible hazards: mechanical, electrical, chemical and high/low temperatures.

 Clothing

Wear appropriate clothing to protect your body from chemical hazards.

 Footware

Wear safety footwear to protect your feet from falling objects.


Eye Protection

Wear suitable eye protection to protect your eyes from various types of possible hazards: mechanical debris, chemicals and hot water/steam.


Ear Protection

Wear suitable ear protection to protect your ears from excessive noise.


Breathing Protection

Wear suitable breathing protection to protect your respiratory system from fumes.

6.14 Machine maintenance


Do not disassemble the Equipment before emptying the contents/fluids (if applicable). Even if the tubes are all empty, some liquid could remain in the unit. The fluid(s) can be hazardous to human health and the environment, and can be very hot/cold.


All maintenance work must be carried out with the machine isolated from the power supply.


Before beginning maintenance on the Equipment remember to isolate the power supply. All the devices must be secured against automatic or accidental restart. (Where possible turn the main switch to OFF and remove the key). In particular situations where you need to run the Equipment while servicing at least 2 persons must be present so that in the event of danger one person will be able to disconnect the power supply or raise the alarm. Once maintenance has been completed remember to restore the safety devices and check that they are in good working order.


To give increased operator protection, the unit incorporates a Residual Current Device (RCD), alternatively called an Earth Leakage Circuit Breaker, as an integral part of this equipment. If through misuse or accident the equipment becomes electrically compromised, the RCD will switch off the electrical supply and reduce the severity of any electric shock received by an operator to a level which, under normal circumstances, will not cause injury to that person.


At least once each month, check that the RCD is operating correctly by pressing the TEST button. The circuit breaker MUST trip when the button is pressed. Failure to trip

means that the operator is not protected and the equipment must be checked and repaired by a competent electrician before it is used.

7 General Overview

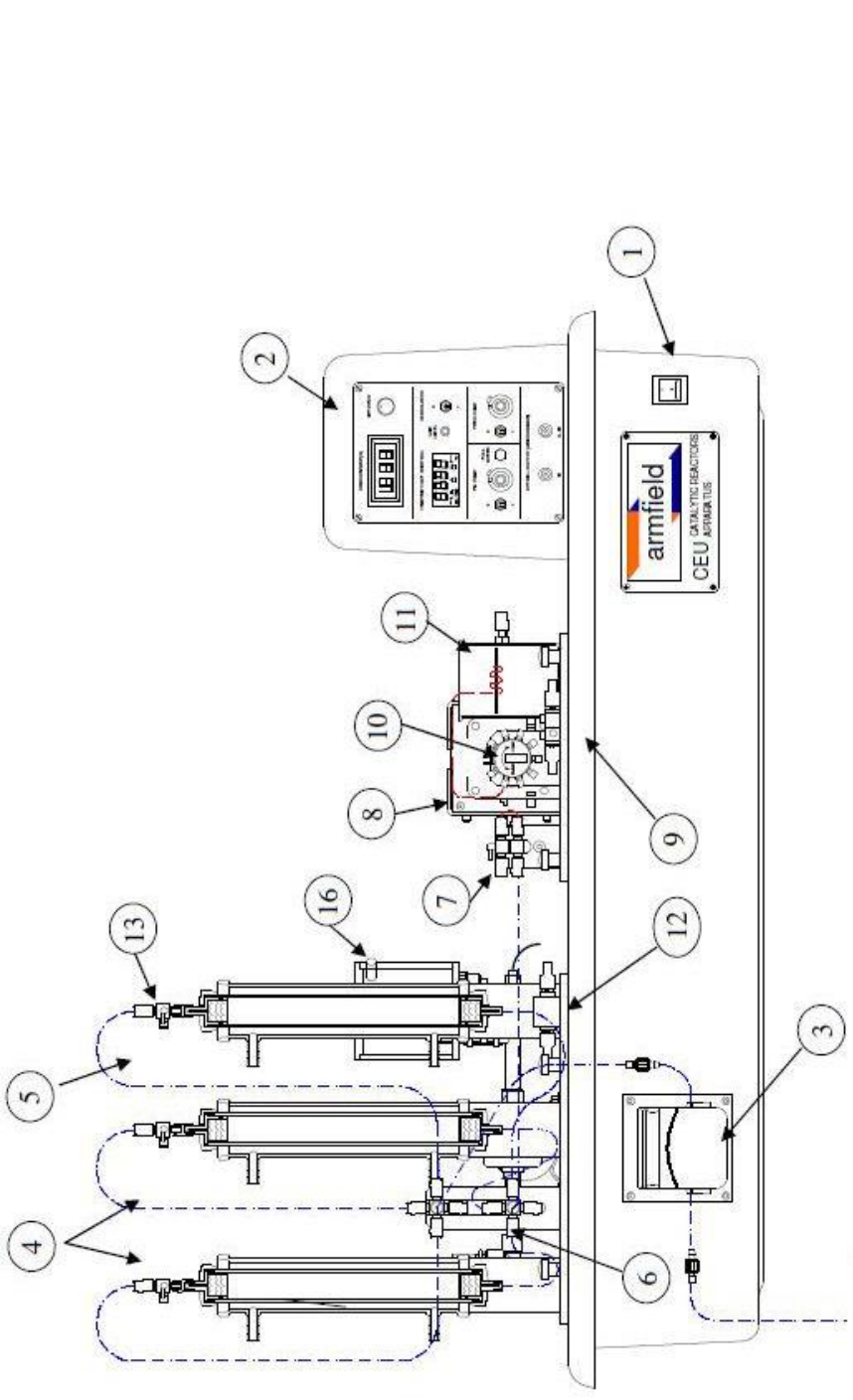
The Armfield CEU catalytic reactor demonstrates the principles of packed bed catalysis. In such a system the catalyst is immobilised on porous spherical particles (support matrix) that are retained within the reactor. Feed material is pumped into the reactor where it mixes with the immobilised catalyst which leads to product formation. The product, which is soluble, passes out of the bottom of the reactors. An advantage of this type of reactor compared to alternative designs such as the stirred tank and tubular reactor is that the need for an additional stage to separate the catalyst from the product is removed. With this design re-use of what is often an expensive catalyst is simple. Additionally this approach lends itself to continuous operation.

The unit is fitted with two reactor columns as standard which are used to demonstrate chemical catalysis. A third column, which is available as an option, uses a biological, enzymic catalyst. All columns use the sucrose inversion reaction, splitting sucrose to form glucose and fructose.

CEU can be used to examine steady state and unsteady state reactor performance, to compare chemical and biological catalysis (requires CEU-5 option), to characterise the flow in a packed bed, to determine the relative effects of rate of diffusion and reaction rate (Thiele modulus), and to demonstrate the principles of flow injection analysis (requires CEU-3 option).

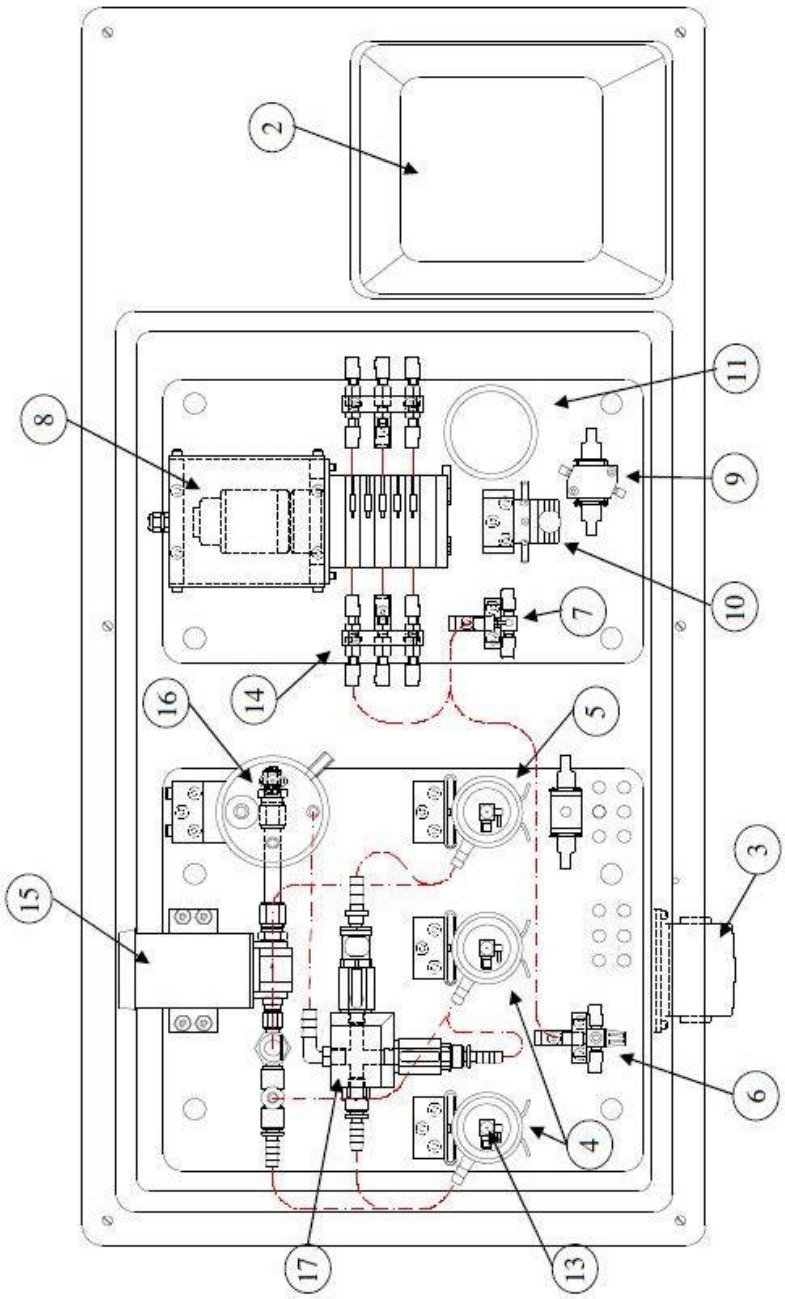
All measurements required to demonstrate the different aspects of packed bed catalysis can be made with the CEU unit. The unit can be operated in a stand-alone fashion or in conjunction with a PC – connected via an optional interface device (IFD5) and supplied with Armfield's CEU software. The software allows experimental data logging and also takes the student through each of the exercises defined in the Laboratory Teaching Exercises.

8 Equipment Diagrams



1	On/off switch	**2**	Control console	**3**	Feed pump	**4**	Chemical reactors	**5**	Biological reactor*	**6**	Reactor input/output selector valves
7	T-piece/3-way valve**	**8**	FIA pump**	**9**	Optical flow cell**	**10**	FIA valve**	**11**	Beaker/holding tube**	**12**	Batch optical cell**
13	Bleed valve	**16**	HWC tank		* Option CEU-5, ** Option CEU-3						

Figure 1: Front view of CEU with CEU-3 and CEU-5 options



2	Control console	**3**	Feed pump	**4**	Chemical reactors	**5**	Biological reactor	**6**	Reactor input/output selector valve	**7**	T-piece/3-way valve**
8	FIA pump**	**9**	Optical flow cell**	**10**	FIA valve**	**11**	Beaker/holding tube**	**12**	Batch optical cell**	**13**	Bleed valve
14	Tubing couplings**	**15**	HWC pump	**16**	HWC tank	**17**	HWC distribution block				

Figure 2: Plan View of CEU with CEU-3 and CEU-5 options

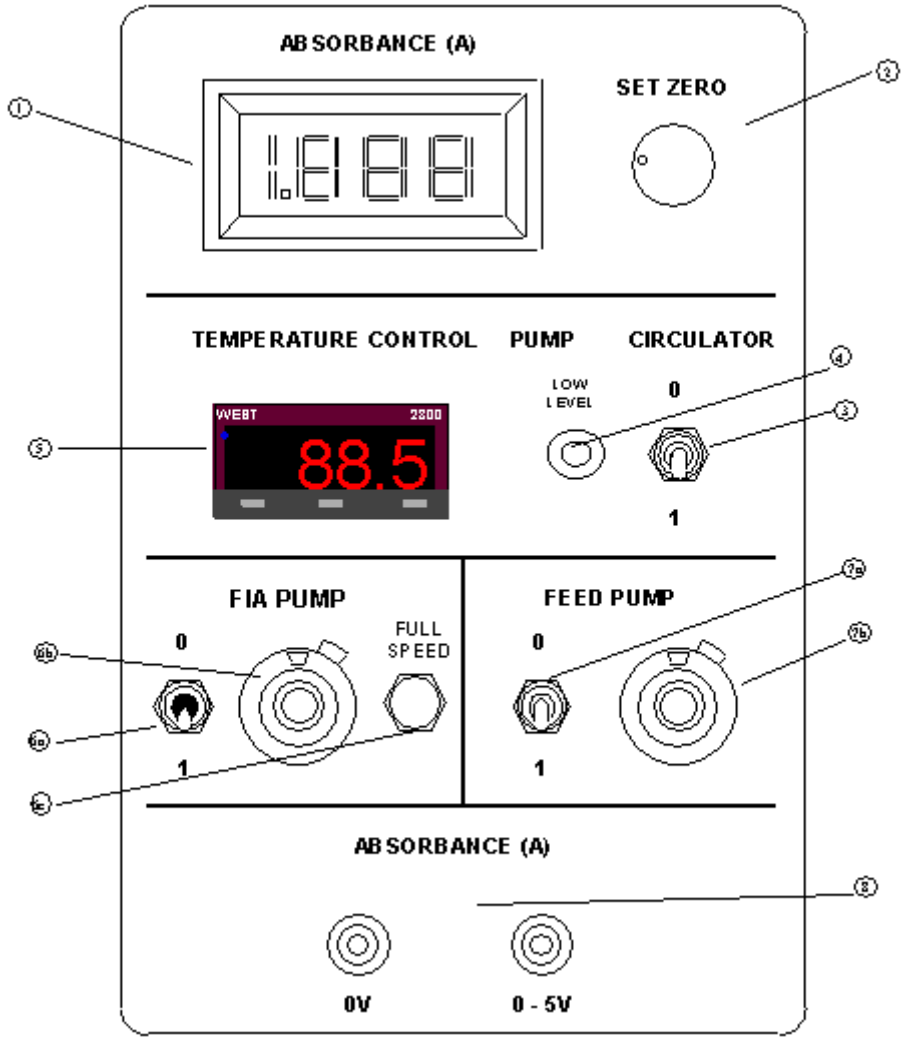


Figure 3: Control panel

1	Absorbance digital meter	2	Absorbance zero
3	HWC heater on/off switch	4	HWC pump on/off switch
5	Temperature controller	6a	FIA pump on/off switch
6b	FIA pump speed control	6c	FIA pump full speed button
7a	Feed pump on/off switch	7b	Feed pump speed control
8	Absorbance output for data logger		

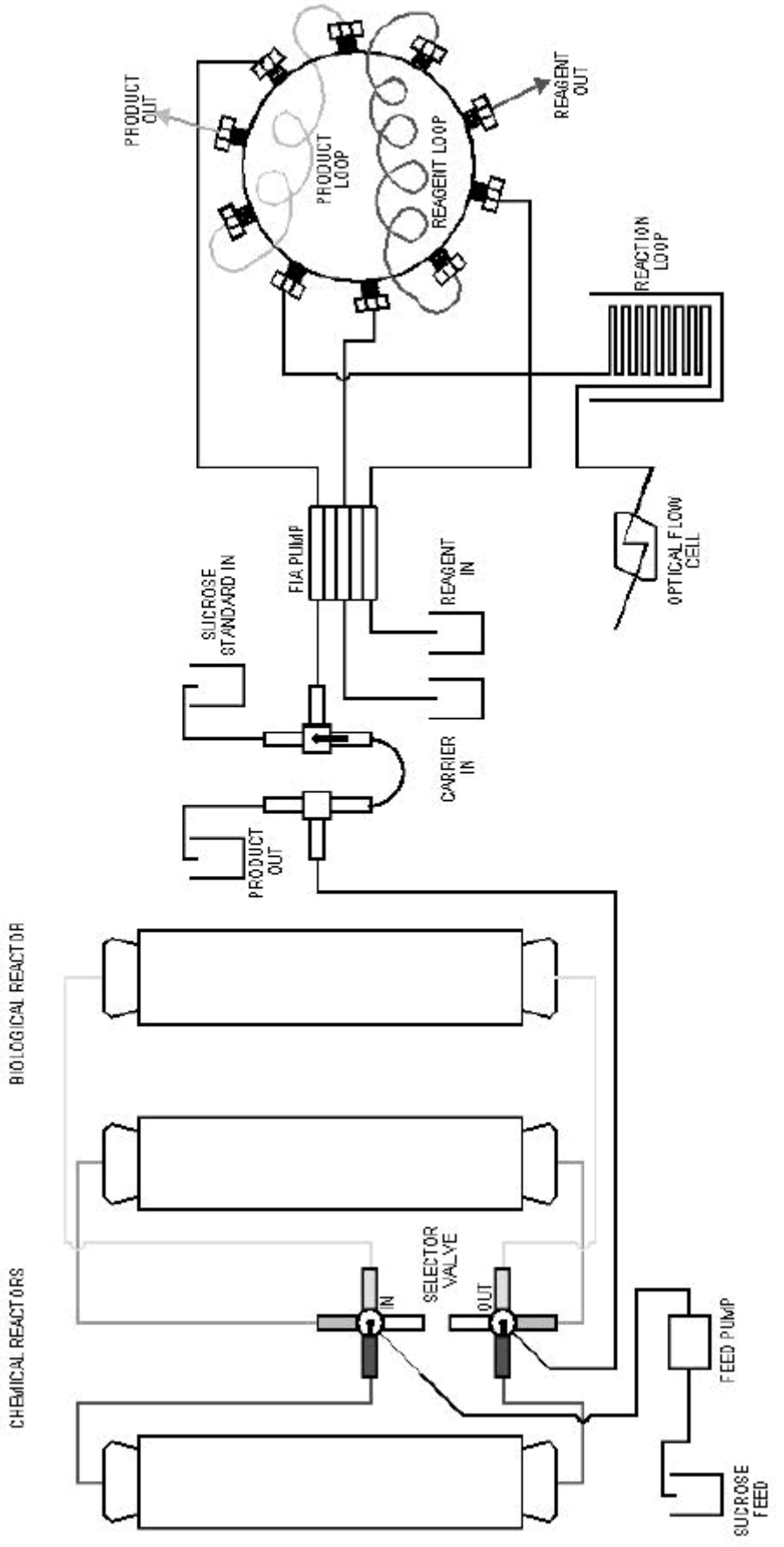


Figure 4: Process flow schematic for CEU showing optional biological reactor (CEU-5) and optional FIA system (CEU-3). The feed pump delivers sucrose to one of the reactors (defined by positioning of selector switches). The output

from the reactor feeds to a T-piece with most material then passing to the 'product out' vessel. Some of the material is drawn through the 3-way valve and through the FIA peristaltic pump. Note: the 3-way valve can be re-positioned so that glucose standards are drawn in place of process material in order to calibrate the optical analysis system. When the FIA valve is in the load position reagent and product fill their respective loops and only the carrier liquid is pumped through to the optical flow cell. Note: reagent passing out of the FIA is collected in the 'reagent out' container and can be re-used in future experiments. When the FIA valve is switched to injection position the contents of the loops are carried through to the reaction loop where they mix and dye formation takes place at constant temperature. This then passes to the optical flow cell where the absorbance is measured and hence the glucose concentration, and from that the degree of conversion, can be determined.

9 Description

Where necessary, refer to the drawings in Equipment Diagrams section 8.

9.1 Overview

The CEU uses the Armfield common plinth. The unit consists of:

- Control console
- Two packed bed chemical reactor columns with water jackets
- A packed bed biological reactor column with water jacket – available as an option
- Feed pump
- Hot water circulation system
- Optical sensor
- Flow injection analysis (FIA) – available as an option

9.2 Control console

There is a control console for controlling and displaying the operating temperature of the reactor columns and operating the hot water circulation system, adjusting Feed and FIA pump settings, displaying the optical absorbance. Sockets are also provided for relaying optical absorbance data to a chart recorder. On the side of the console there is a port for connection to a PC via an optional IFD5 computer interface.

9.3 Packed bed reactor columns

CEU is supplied with two reactor columns as standard to examine packed bed chemical catalysis. Having two columns enables the performance of two different particle size support matrices to be determined without the need to re-pack the column during experimentation. A third column, available as an option (CEU-3), uses an immobilised biological catalyst: the enzyme invertase. All the reactor columns have a glass jacket through which water is circulated in order to maintain the desired reaction temperature.

9.4 Feed pump

A 4 roller peristaltic pump, situated on the front of the console, is used to supply sucrose solution to the reactor columns. On/off switch and pump speed are controlled from the console.

9.5 Hot water circulation system

This is used to control the temperature in each of the reactor columns. A pump situated behind the reactor columns pumps water in a loop from the reactor columns, through the cartridge heater, into the water tank where the temperature is measured by a thermocouple, and back to the reactor columns. The thermocouple inputs to a PID temperature controller situated in the console which acts on the cartridge heater in order to control to the desired reaction temperature.

9.6 Optical sensor

Conversion of sucrose is determined by measuring the glucose concentration. This is achieved using an optical assay. A reagent is added to the product and a dye is formed. The concentration of this dye is directly proportional to the glucose concentration in the product sample. The dye absorbs light at a wavelength of 510 nm. The transmitter diode of the optical sensor emits light at this wavelength. The receiver measures the amount of light that passes through the sample. Thus the light absorbance, and therefore the glucose concentration, can be determined.

Glucose concentration is determined manually by adding reagent to the product sample in a glass tube which is then placed in the flow path of the optical sensor. As an option (CEU-3) this process may be automated using flow injection analysis. With CEU-3 the assay mixture is pumped through the optical flow cell where the absorbance is measured.

9.7 Flow injection analysis (FIA)

A three channel peristaltic pump used in conjunction with a 2-position, 10-way valve drives the FIA system. On/off and speed control of the FIA pump is situated on the console. Valve position is switched manually. The FIA system mixes defined quantities of product and reagent and transports them to an optical flow cell where the optical absorbance is measured. Thus the product concentration may be measured on-line.

9.8 Description of process

See Figure 4 for a process flow schematic including both the optional 3rd reactor column and the FIA system. The hot water circulation (HWC) system is removed for clarity. The peristaltic feed pump delivers a sucrose solution to the reactor input selector valve which is positioned to direct flow to the inlet (top) of the desired reactor column. The feed pump uses soft walled tubing whereas most of the other plumbing is hard walled. The two types of tubing are joined together using connectors situated on the inlet and outlet sides of the feed pump. The feed is pumped through the column where the catalysed reaction occurs. Temperature in the column is set via the controller mounted in the console and is controlled via the hot water circulation system which feeds the jacket of each of the reactor columns.

Product leaving the reactor column is fed to the reactor output selector valve. For CEU units without the optional FIA system, the product is collected in a beaker and samples are taken at intervals for product (glucose) concentration measurement. This is achieved by mixing a defined quantity of product with a defined quantity of reagent in a glass tube which is then

placed in the batch optical sensor housing where changes in absorbance are measured. Prior to the experiment the optical sensor is calibrated with glucose standards so that absorbance values can be converted to glucose concentrations.

For CEU units with the FIA system the product stream passes, via a 3-way valve and T-piece, to the FIA peristaltic pump. The 3-way valve allows the user to select either a glucose calibration solution or a reactor product stream as the input the FIA system. The valve is marked with ‘load’ and ‘charge’ to indicate the appropriate position of the valve handle during use. Be aware that 3-way valves follow a different convention to normal valves and the valve is open when the handle is at 90° to the valve body.

The T-piece allows most of the reactor product stream to pass to waste whilst a sample is drawn off for analysis by the FIA pump. This pump uses 3 channels which enables the product, reagent and carrier liquid streams to be pumped to the FIA 10-port valve using a single pump. The FIA pump, like the feed pump, is a peristaltic type and uses soft-walled tubing. The remainder of the CEU uses hard-walled tubing. Hard and soft walled tubing are joined together using 2-way connectors; three of which are situated either side of the FIA pump. The three streams, product, reagent and carrier liquid are pumped to the FIA valve where the product and reagent are mixed in a defined ratio before being transported to a reaction coil held at constant temperature (the reaction coil should be placed in a beaker of water at room temperature). From there the mixture passes to the flow cell where the optical absorbance is measured.

10 Installation

10.1 Advisory

Before operating the equipment, it must be unpacked, assembled and installed as described in the steps that follow. Safe use of the equipment depends on following the correct installation procedure.

10.2 Electrical Supply

Electrical Supply for version CEU-A
Ensure that all the miniature circuit breakers (1-5) are in the off (down) position. Connect the mains electrical supply to the unit.

The equipment requires connection to a single phase, fused electrical supply. The standard electrical supply for this equipment is 220/240V, 50Hz. Check that the voltage and frequency of the electrical supply agree with the label attached to the supply cable on the equipment. Connection should be made as follows:

GREEN/YELLOW	-	EARTH
BROWN	-	LIVE (HOT)
BLUE	-	NEUTRAL
Fuse rating	-	13 AMP

Electrical Supply for version CEU-B
Ensure that all the miniature circuit breakers (1-5) are in the off (down) position. Connect the mains electrical supply to the unit.

The equipment requires connection to a single phase, fused electrical supply. The standard electrical supply for this equipment is 120V, 60Hz. Check that the voltage and frequency of the electrical supply agree with the label attached to the supply cable on the equipment. Connection should be made as follows:

GREEN/YELLOW	-	EARTH
BROWN	-	LIVE (HOT)
BLUE	-	NEUTRAL
Fuse rating	-	15 AMP

Electrical Supply for version CEU-G
Ensure that all the miniature circuit breakers (1-5) are in the off (down) position. Connect the mains electrical supply to the unit.

The equipment requires connection to a single phase, fused electrical supply. The standard electrical supply for this equipment is 220-240V, 60Hz. Check that the voltage and frequency

of the electrical supply agree with the label attached to the supply cable on the equipment. Connection should be made as follows:

GREEN/YELLOW	-	EARTH
BROWN	-	LIVE (HOT)
BLUE	-	NEUTRAL
Fuse rating	-	13 AMP

10.3 Connection to Services

See diagrams below.

The following connections must be made to make the unit operable:

10.3.1 Temperature Sensor (type k thermocouple)

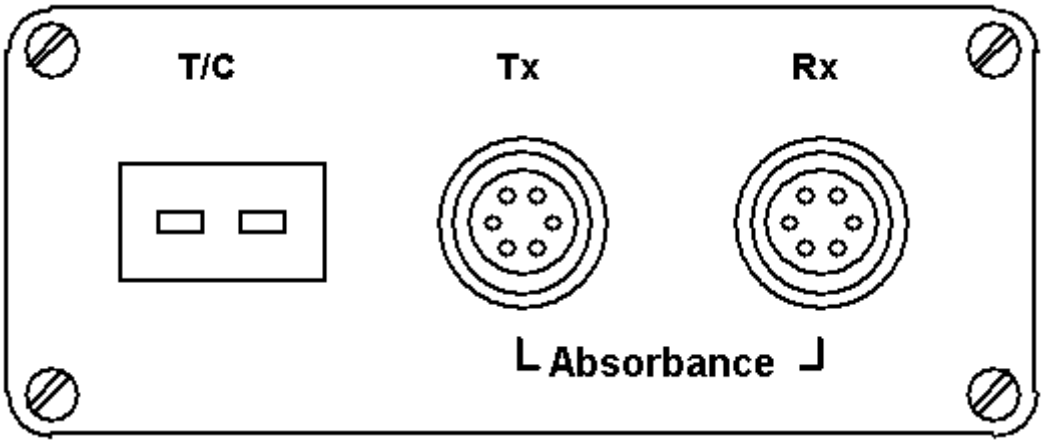
Ensure that the thermocouple is plugged into socket T/C on the side of the console.

10.3.2 Absorbance Meter

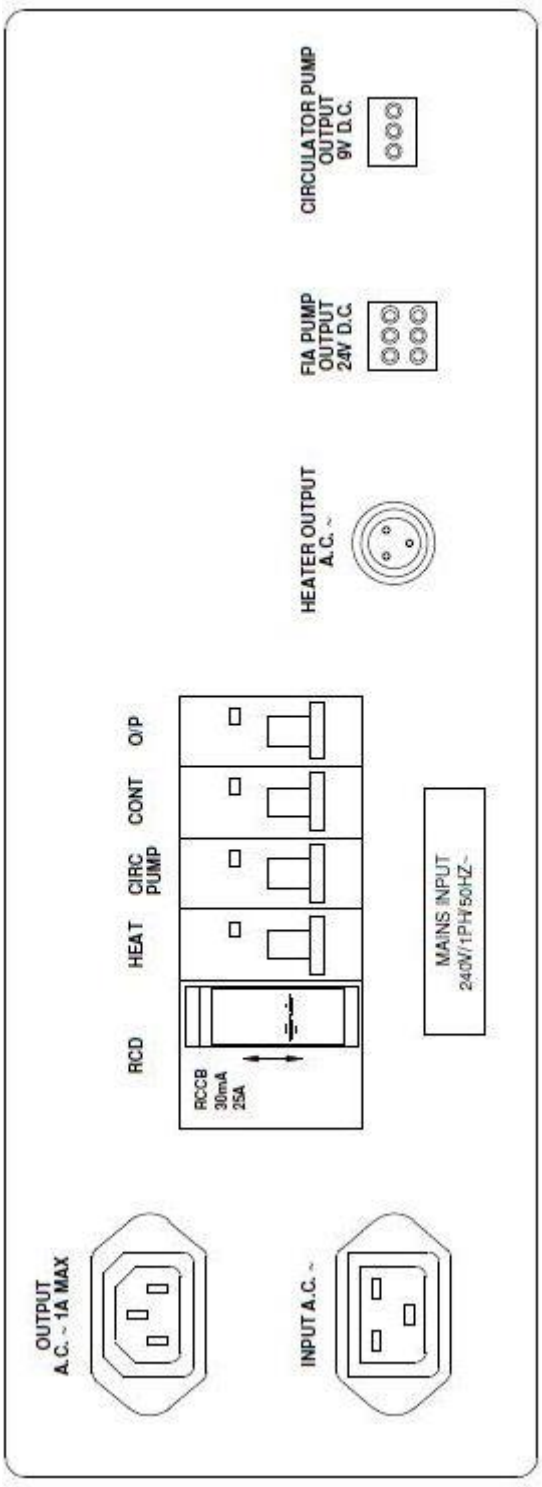
Ensure that the absorbance meter transmitter plug (Tx) and receiver plug (Rx) are fitted to the appropriate sockets located on the side of the control console.

10.3.3 Connections to hot water circulation (HWC) pump, heater and FIA pump

Ensure that the leads from the HWC pump, the heater and the FIA pump (if fitted) are connected to the appropriate sockets on the back of the plinth.



Sensor panel: T/C, thermocouple; Tx, optical sensor transmitter; Rx, optical sensor receiver



Rear panel

Input A.C. - Mains input to the unit RCD - Residual current device

Heat - Supply to HWC heater Circ Pump - Supply to HWC pump

Cont - Supply to control console, sensors and peristaltic pumps

O/P - Supply to OUTPUT socket

10.4 Installing the Software supplied with CEU

Please refer to the software installation instructions supplied on the Armsoft CD ROM or data stick.

10.5 Installing the Equipment

CEU Catalytic Reactor is supplied fully assembled. The matrices used in the chemical and biological reactors must be prepared before experimentation – see Operation section.

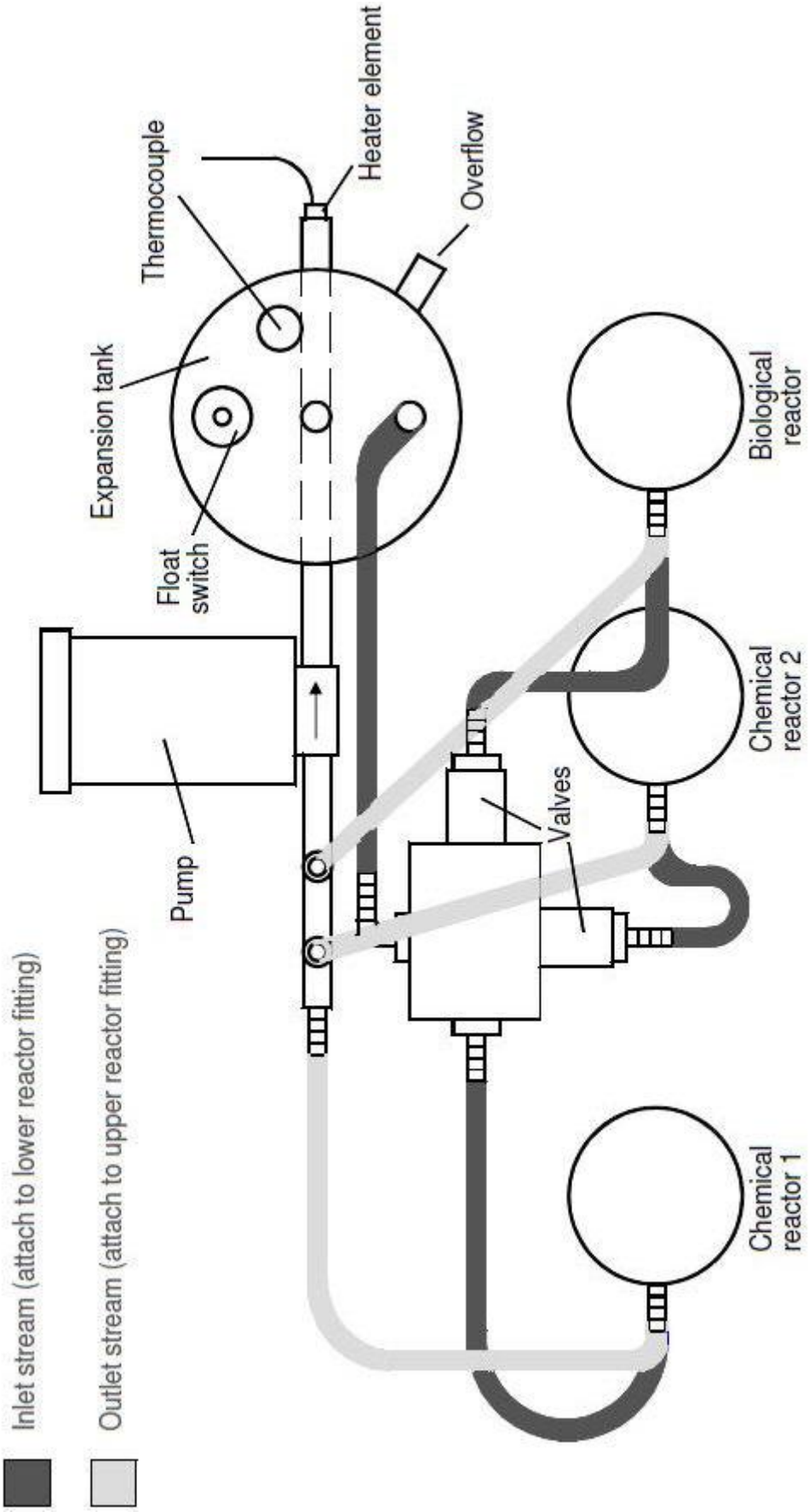
Note: The end fittings at the top and bottom of each glass column section are designed to fit tightly to ensure a reliable seal. If problems are experienced when replacing the end fittings then any interference can be reduced by chilling the fitting in a refrigerator and warming the glass column in hot water before inserting the fitting into the column.

10.6 Commissioning

1. Ensure that the mains on/off switch (1) on the front of the unit is in the OFF position.
2. Ensure that the switches for HWC pump and heater, and the feed and FIA pump are in the OFF (up) position
3. Ensure that the mains electrical supply is connected and switched on.

   Turn ON (up) the RCD (1) and check its operation by pressing the TEST button. The RCD must trip when the button is pressed. If it does not trip or it trips before pressing the TEST button then it must be examined by a competent electrician before the equipment may be used.
4. Ensure that the miniature circuit breakers are in the ON (up) position.
5. Set the mains on/off switch (A) on the front of the unit to the ON position. Observe that the two digital panel meters are illuminated.
6. The HWC system is drained of water before dispatch. Adjust the controller set point to a value a few degrees below the displayed temperature. This ensures that the heater is not turned on before the system is primed. Fill the HWC tank with deionised water. This will cause the float to rise which in turn provides power to the HWC pump. Turn ON the HWC pump in order to prime the system. It may be necessary to adjust valves located on the distribution block (see Equipment Diagrams section 8) in order to fully prime the system. Replenish the HWC tank with deionised water as required – there should always be water in the HWC tank.
7. Once the HWC circuit is fully primed, adjust the controller set point temperature to 50°C (see Operation section). Turn ON the HWC pump. The temperature, as displayed on the controller, should rise and level off at the set point. Turn OFF the heater and the HWC pump.
8. Turn off the mains ON/OFF switch on the front of the unit. Turn off (down) all the miniature circuit breakers. Disconnect the mains supply.

9. Preparation of the matrices for the reactor columns is described in the Operation section.



Hot water circulation (HWC) system which is used to control reactor temperature

10.7 Electrical Wiring Diagram

Please see the following wiring diagrams attached at the rear of this manual. If you are viewing this manual electronically please see accompanying pdf.

Wiring Diagram CDM28481E

11 Operation

Where necessary, refer to the drawings in Equipment Diagrams section 8.

11.1 Operating the Software to operate CEU

Please refer to the software operating instructions supplied on the Armsoft CD ROM or data stick.

11.2 Operating the Equipment

Note: The end fittings at the top and bottom of each glass column section are designed to fit tightly to ensure a reliable seal. If problems are experienced when replacing the end fittings then any interference can be reduced by chilling the fitting in a refrigerator and warming the glass column in hot water before inserting the fitting into the column.

11.2.1 Preparation of matrices for the chemical reactors

Matrices of two different average particle sizes are used. Both use the strong cationic resin Amberlite IR 120. The four sieves required (included) to obtain the desired particle size fraction are 1.00mm, 0.71mm, 0.355mm and 0.250mm. The resin is filtered through each of the filters in the order given. The cut between 1.00mm and 0.71mm is used for one column and the cut between 0.355mm and 0.250mm is used for the other column.

2-3kg of Amberlite IR 120 yields sufficient material of the two cut sizes to fill the chemical reactors. Resin is placed in the sieve and is gently agitated by hand whilst running tap water through it. This procedure should be repeated several times (at least 3 times). The holes in the sieve will eventually become blocked and may be cleaned using a metal brush. Care must be taken when performing this procedure, for example, when filtering with the 0.71mm sieve the sieve may become blocked with larger particles thus preventing the smaller particles from being washed through and hence the resulting size distribution will not be as expected. Therefore repeated washings are essential. In addition, if there are facilities to determine the particle size distribution, for example by using a Coulter Counter, then these should be used to confirm particle distribution results.

The two collected fractions should be allowed to settle and excess water can then be removed by pipette. The top end caps of the two chemical reactors should then be unscrewed and the appropriate resin cut poured in. The resin should come within 2cm of the top of the column, the remaining space being taken by water. Replace the reactor end caps. Some air should be introduced to prevent column breakage through pressure during heating – see later.

If the end caps prove difficult to remove then place the columns in a refrigerator for a few hours and then try again. Once apart lightly lubricate the O ring seals of the end caps with silicone grease before refitting.

Reactor activation – The matrices must be acidified prior to experimentation. This is achieved by passing 500ml of 2 M hydrochloric acid (HCl – see ‘Preparation of materials’ below) through the column using the feed pump set to 10ml min^{-1}. (see ‘Feed pump operation and calibration’ section 11.2.4). Remaining acid in the reactors is washed out with deionised water: with the feed pump set to 10ml min^{-1} feed 500ml of deionised water through each reactor.

Note: for the protection of the columns and ancillaries only deionised water should be used to flush the reactors. Deionised water should also be used for the preparation of materials such as sucrose feed solution, HCl solution etc. Use of deionised water prevents deactivation of the chemical matrices through ion-exchange. Chemical reactor reactivation will be required approximately once a semester depending on amount of use.

11.2.2 Preparation of matrices for the biological reactor (Option CEU-5)

This procedure immobilises the enzyme within alginate beads that are retained within the reactor. The advantage of this is that the enzyme can be easily re-used without the need of a recovery operation and also the immobilisation procedure improves the stability, and therefore the longevity, of the enzyme. The life of invertase in solution at 5ºC is approximately 1 week whereas when it is immobilised it can be stored for 2-3 weeks.

Sucrose inversion, like most enzymic reactions, follows Michaelis-Menton (M-M) kinetics and the reaction rate can be written as:

$$-r_{suc} = -r_{max}\frac{[S]}{K_M + [S]} \quad (M-M)$$

where r_{max} is the maximum reaction rate, [*S*] is the substrate (sucrose) concentration and K_M is the M-M constant. If in equation (M-M) the substrate concentration is kept at a level well above the M-M constant ([*S*] > K_M), then the enzyme is saturated with substrate and the reaction proceeds at the constant and maximum rate ($-r_{suc} = -r_{max}$) i.e. with zero order kinetics. Hence catalytic activity is linearly dependent on the amount of enzyme used.

The activity of an enzyme is usually measured in units (U) per mass unit of that enzyme. A unit (U) is the mass of enzyme capable of catalysing 1 μmol/min of reagent in the optimal temperature and pH conditions. A unit (U) of invertase (β-Fructosidase, 270 000 a.m.u.) is therefore capable of hydrolysing 1 μmol of sucrose per minute at 55°C and pH 4.6. Invertase has an activity of 300 U/mg. For a reactor feed of approx. 10cm³/min of a 7.6 g/dm³ sucrose solution, that is for a feed of 76mg of sucrose per minute, which corresponds to 222 μmol of sucrose per minute you will need 222/300=0.741mg of invertase for a complete conversion. Therefore it should be sufficient to add approx. 1mg of invertase to the sodium alginate solution. In fact 200mg of invertase must be added to the sodium alginate solution. This is mainly because the substrate concentration is of the same order of magnitude as K_M (K_M is normally between 2 mM and 5 mM). There is also a contribution from losses: not all the sodium alginate is retained within the calcium alginate particles, not all the calcium alginate particles are packed in the reactor and not all the immobilised enzyme inside the calcium alginate particles is fully accessible or active to catalyse the sucrose inversion reaction. In addition some loss of activity is due to biodegradation.

Dissolve 0.5g of invertase (Fluka 57629) in 300ml of deionised water. This will require gentle agitation. Then dissolve in the invertase solution 15g of sodium alginate (Aldrich 180947-100G) gently agitate for an hour. Once dissolved the next stage is to form the beads inside of which the enzyme is trapped.

Fit the spare feed tubing into the feed pump. Position the outlet tubing 20cm above a beaker containing 500ml of 0.2 M calcium chloride solution. Set the pump to a flow rate that gives slow discreet drips. Drip the sodium alginate/invertase solution into the calcium chloride solution. Exchange between sodium and calcium ions results in precipitation of the alginate in the form of beads inside of which the invertase enzyme is trapped. The alginate beads should be kept in the calcium chloride solution for 1 day. Then remove the beads and wash them with distilled water.

Allow the alginate beads to settle and remove excess water using a pipette. Remove the top end cap of the biologic reactor and pour in the alginate beads. These should fill almost to the top leaving a 2cm gap which should be filled with liquid. Remaining calcium chloride in the reactor is then washed out with deionised water. With the feed pump set to 10ml min^{-1} feed 500ml of deionised water through the reactor.

The reactor should be stored at refrigeration temperatures (< 5ºC) when not in use. Activity will be retained for approximately 2 weeks. After this time a fresh batch of beads will be required using the above procedure.

The steady state conversion of the biological reactor depends on the amount of invertase used, which can vary from 300mg to 1500mg.

11.2.3 Hot water circulation system

See diagram in Commissioning section 10.6.

The working temperature for the two chemical reactors is 70ºC. This is sufficiently high to obtain good conversion and for the reaction control to be of diffusional nature. It is also sufficiently low to avoid significant bubble formation in the reactor due to degassing of the feed solution.

The biological reactor uses the enzyme invertase which works most efficiently at 55ºC. It may be denatured at 70ºC therefore it is essential that the valve which allows flow of hot water to the reactor jacket of the biological column is closed when high temperatures are used.

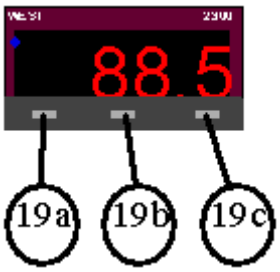
11.2.4 Feed pump operation and calibration

See Figure 1 and 3 in the Equipment Diagrams section 8. The feed pump is turned on and off using switch 7a and the pump speed is adjusted using the pot (7b).

Set the input and output selector valves (6) to one of the packed chemical columns. Place the input pipe of the feed pump into a beaker of deionised water. Set the feed pump to 10% and turn on the pump. Measure the flow rate at 10% intervals up to a maximum flow rate of 20ml min^{-1}. Plot the data. Repeat for the second chemical reactor and for the biological reactor. Care should be taken to prevent any air from entering the columns since this will drastically affect column performance.

11.2.5 Controller operation

The PID controller controls the reactor process temperature. In normal operation there are three parameters which may be accessed by pressing the scroll key (19a); these are: process value (PROC), set point (SP) and alarm value (AL). If left for a short period the display will automatically revert to the process value. By pressing the scroll key the required display is reached and after 1.5 seconds the value of that parameter is displayed. The process value simply indicates the current temperature in the reactor vessel (T1). The set-point (SP) temperature is the desired operating temperature (normally 60ºC). This value is set by pressing the scroll key (19a) until SP is displayed and once the set point value is shown this may be adjusted using the up (19c) and down (19b) keys.



To the right of the display are three indicators. In normal operation the green indicator is off if the process variable is less than the set-point, flashes if the process variable is greater than the set-point, and is lit continually if the process variable is equal to the set-point.

Other parameters of the controller are factory set and should not require adjustment. Should there be a need to adjust these values then they can be accessed by entering the Control Setup mode by pressing the up and down keys simultaneously for 3 seconds. Factory set values are given below:

SP	0.1
Pb	1.5
rSEt	1.50
rATE	0.08
biAS	25
AL	95.0
FiLt	2
OFFS	0.0
Ct	16
SPL	OFF
AEn	Enab

The PID settings are factory tuned for accurate temperature control. Should the user wish to re-tune the controller then this can be done manually or automatically – refer to the enclosed manual for operating instructions.

11.2.6 Pipework and connections

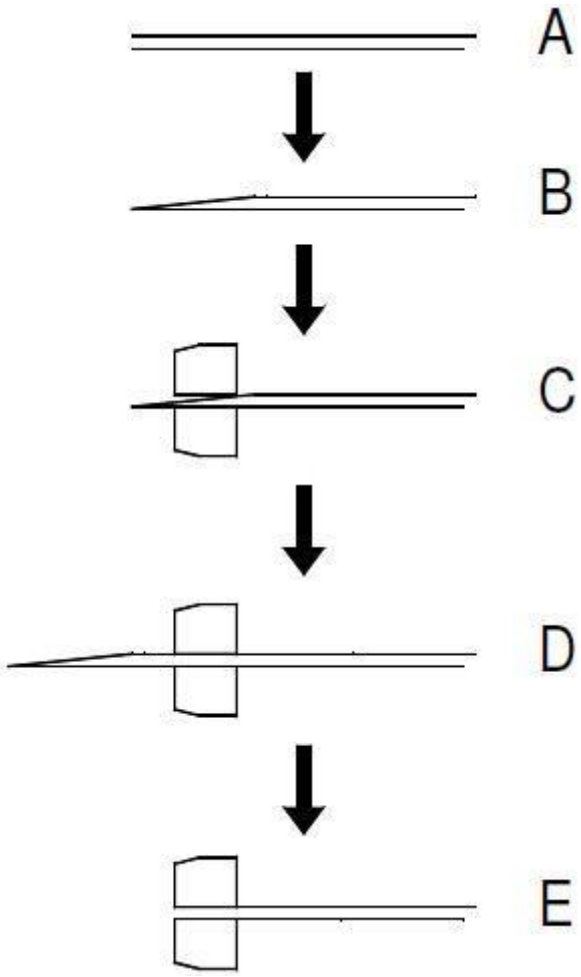
Process pipework

CEU pipework is mainly hard walled teflon tubing (1.6mm o.d., 0.8mm i.d.). However for peristaltic pumps soft walled tubing is used. Two basic types of connectors are used: the peristaltic feed pump soft walled tubing is connected to hard walled tubing using gripper fittings. This allows simple disconnection as required. The optional FIA valve, optical flow cell and holding tube use the same gripper fittings. The remainder of the pipework uses connectors with rubber O rings. Care must be taken not to over-tighten these fittings when

using soft-walled tubing (FIA peristaltic pump tubing only) as this will lead to strangling of the tube which may impair flow.

The CEU is supplied with all pipework and connections in place however there may be an instance when the user wishes to alter the arrangement. Gripper fittings are only attached to hard walled tubing. The tolerance between the tubing outer diameter (o.d.) and the bore of the gripper fitting is very close so that a good seal is formed. For this reason a special technique is required for fitting the grippers (see below).

Hard walled tubing normally has a flat ending (A). Due to the tightness of fit between the tubing and the gripper fitting it is not possible to simply push the tubing through the hole. Instead the tubing must first be chamfered using a sharp knife (B). This can then be partially inserted through the gripper (C). Using a pair of pliers the tubing can then be pulled through the gripper until unchamfered pipe appears (D). Using a sharp knife and a sawing action in order not to crush the tubing it is cut off flush to the gripper (E).



Method for attaching gripper fittings (only used with hard walled tubing)

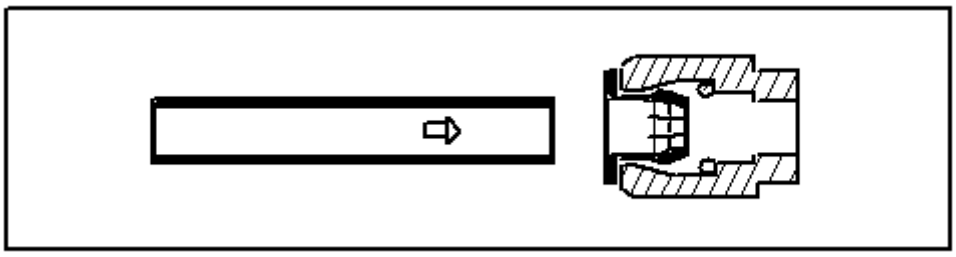
HWC pipework

Hot water circulation pipework for the chemical reactors is designed for permanent attachment. The biological reactor must be stored at 4ºC when not in use and hence quick release fittings are used. Plugs are also provided to contain water within the reactor jacket. The method for disconnecting the quick release fittings is described below.

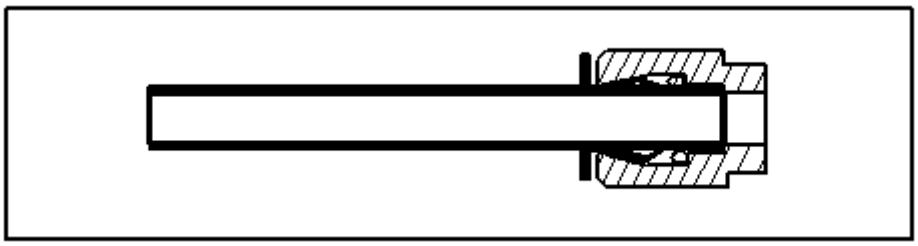
11.2.7 Use of quick release fittings

Quick release fittings are used on the equipment for convenience when changing the configuration or removing items for cleaning. The diagrams below show the simple operation of these fittings:

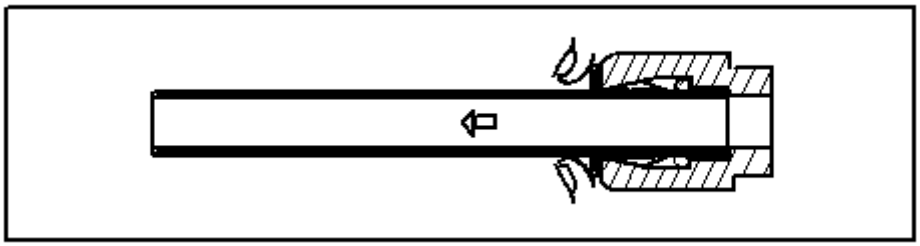
To connect to a quick release fitting
Align the parallel section of the rigid tube with the loose collet on the quick release fitting and push firmly until the tube stops.



An 'O' ring inside the fitting provides a leak-proof seal between the tube and the fitting. The collet grips the tube and prevents it from being pulled out from the fitting.



To disconnect from a quick release fitting
Push the loose collet against the body of the quick release fitting while pulling the tube firmly. The tube will slide out from the fitting. The tube/fitting can be assembled and disassembled repeatedly without damage.

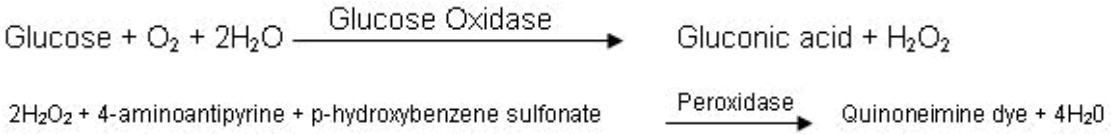


11.2.8 Glucose measurement using the batch optical cell

The reaction that takes place in the columns is the hydrolysis of sucrose to form fructose and glucose. Thus the performance of the columns can be determined by monitoring the glucose concentration. This is achieved using a manual optical assay. As an option continuous performance monitoring may be achieved by flow injection analysis (option CEU-3).

A defined quantity of the product stream is added to a defined quantity of the assay reagent. This results in a colour change which absorbs light at 510 nm. Thus by using an optical

sensor the amount of dye formation and thus the glucose concentration may be determined. The reactions that take place to form the dye are as follows:



A sample tube containing the reagent alone is placed in the optical sensor and the absorbance value is adjusted to zero using switch 2 (Figure 3). 20 μl of sample are added to 1ml of reagent within the sample tube. This is mixed rapidly by inversion and placed within the optical cell. Absorbance values are recorded at 5 s time intervals. Data should be obtained for glucose standards of 1, 2, 3 and 4 g L^{-1} glucose concentration. When plotted this data should yield a straight line from which the gradient is calculated. A plot of the gradient versus the glucose standard concentrations yields a calibration curve from which unknown glucose concentrations may be determined. The assay should yield many data points between 0 and 1.99 (the limit of the sensor) so that a statistically meaningful gradient can be determined. If there are few points due to the absorbance reading climbing too rapidly then samples can be diluted prior to the assay procedure. Note dilutions must be allowed for when prior to plotting gradient data versus standard glucose concentration, i.e. if a ½ dilution is performed for a particular sample then the data obtained should be multiplied by a factor of 2.

Note: the optical sensor is pre-calibrated so that it is possible to zero the absorbance using water or assay reagent. The upper range of the sensor is adjusted so that the most concentrated glucose standard gives a maximum absorbance near the upper range of the sensor (1.6 – 2.0 absorbance). If there is a need to adjust the set-point then this can be achieved by adjusting VR7 located inside the control console - See PCB layout diagram in the control console.

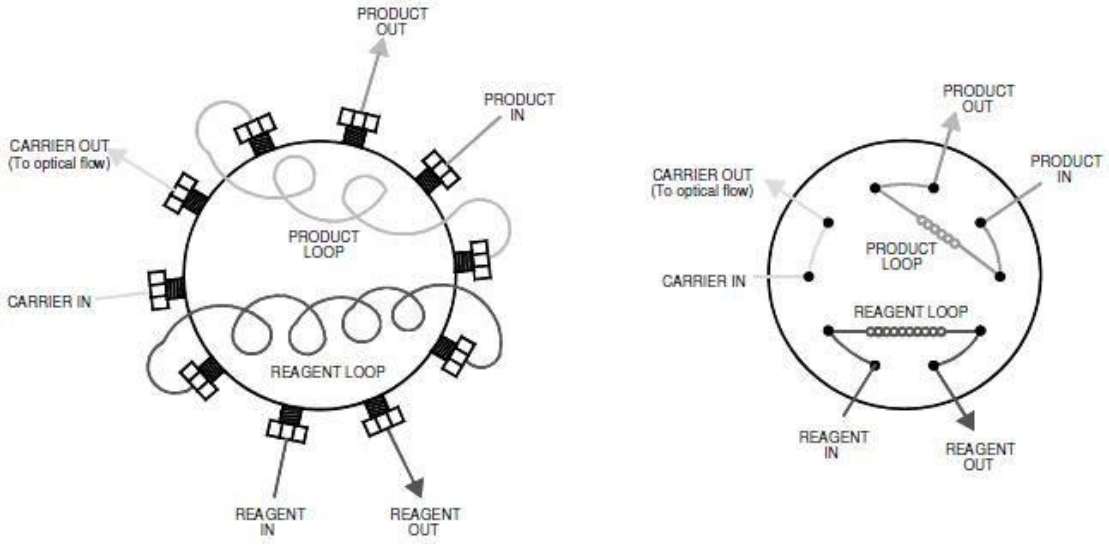
11.2.9 Flow injection analysis (FIA) – option CEU-3

The manual technique described above may be automated using the flow injection analysis technique. Option CEU-3 provides the option to use FIA with the CEU reactors. Note that the CEU-3 replaces the use of the batch optical cell on the CEU reactor unit.

FIA has the added advantage of consuming low quantities of the assay reagent. The system consists of a 3-channel peristaltic pump, a two position 10 port valve, a holding section and an optical flow cell. FIA allows a sample of the product stream to be mixed with the assay reagent in a defined ratio. This mixture is pumped through a holding tube which gives sufficient residence time for dye formation to occur prior to passing the mixture through an optical flow cell where the absorbance is measured.

FIA peristaltic pump – This uses 3 channels in order to pump the assay reagent, the product and the carrier liquid which in this case is deionised water. The speed of the peristaltic pump is set to give optimal residence time in the reaction system such that the degree of dye formation takes place to the desired extent. The user needs to 'tune' the system in order to optimise performance. This is done using 1 and 4g L^{-1} glucose standard. The aim is to determine a FIA pump speed which gives a high absorbance value (1-2 absorbance units, A) using 4g L^{-1} glucose standard and a significant lower value for the 1g L^{-1}glucose standard. This means that full use is made of the optical sensor range and therefore the system will be sensitive at low glucose concentrations. An initial FIA pump setting of 15-40% is recommended depending on ambient temperature. Lower ambient temperature results in slower dye formation since this is an enzymic reaction. This reaction rate can be increased by submerging the reaction coil in a water bath controlled to 20-30°C.

FIA valve (see below) – The valve, which has 10 ports, has two positions. In one position alternate adjacent ports are linked together inside the valve so that there are 5 pairs of linked ports.



FIA valve. Left: external view of valve showing the ten ports with inlet and outlet streams and product and reagent loops. Right: diagrammatic representation showing inlet and outlet streams and product and reagent loops and also the alternate internal valve linkages when the valve is set in the load position.

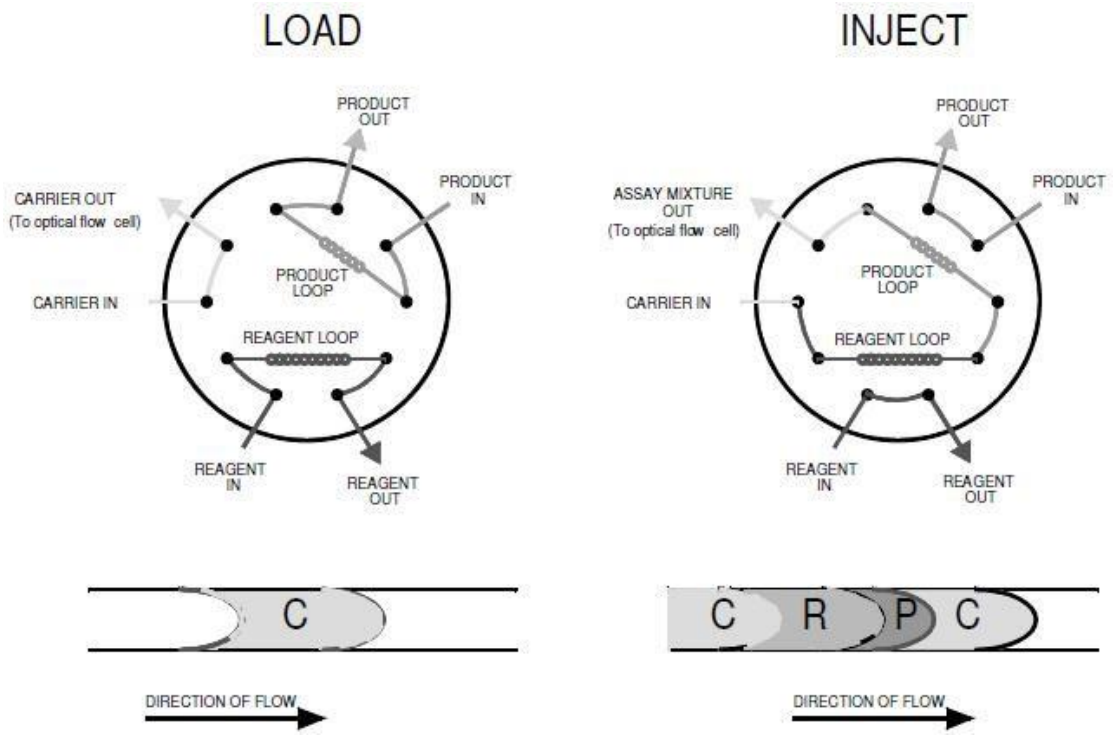
Changing the position of the valve links the alternative port pairs together (see below). The function of the valve is to mix the reagent and the product in a defined volume ratio. This is achieved by using reagent and product loops of defined lengths (52cm and 13cm respectively).

When the valve is in the load position (see below left) the reagent and product loops are filled. Product that passes out of the valve is led to a waste container. Reagent that passes out of the valve is collected in a suitable container for re-use in the next practical session. Carrier liquid (water) out passes through the optical flow cell.

When the valve is switched to the injection position (see below right) the carrier liquid picks up the reagent and product contained in the two loops and passes it to the holding coil (the holding coil is immersed in a beaker of water to maintain a constant temperature) where reaction between product and reagent occurs and a colour change results. This is then pumped to the optical flow cell where the optical absorbance is measured.

Be aware that 3-way valves follow a different convention to normal valves and the valve is open when the handle is at 90° to the valve body.

Between injection of consecutive samples the valve must be kept in the load position for sufficient time for the loops to be filled (approximately 40s when the FIA pump is set to 40%). When the samples are different, i.e. not replicates, then 2 minutes should be allowed between injections to prevent sample to sample contamination (FIA pump set to 40%). These times can be reduced by using the maximum speed button for the FIA pump. This button should only be used when the valve is in the load position since if it is used in the injection position the reaction time in the reaction loop will be reduced.

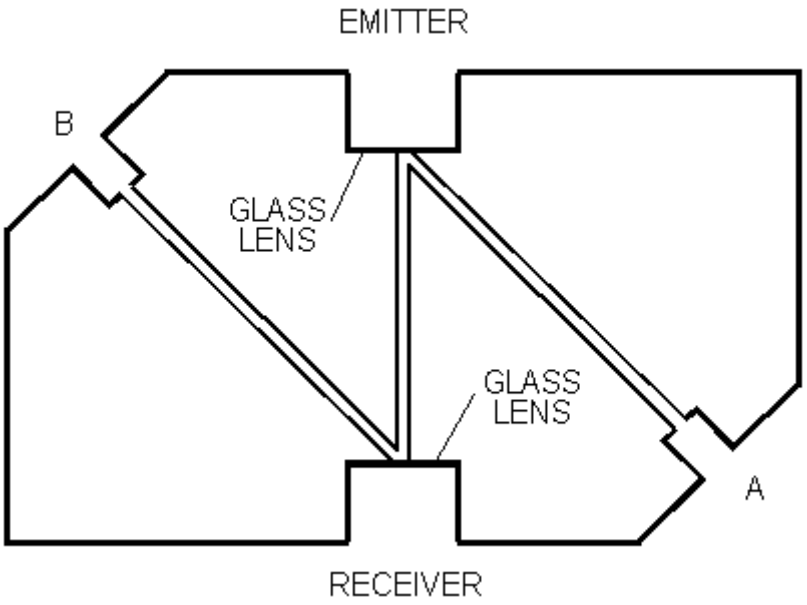


Showing the two positions of the FIA valve and contents of the stream flowing to the optical sensor for each position. Left: valve in load position – Carrier liquid enters and leaves the valve and passes to the optical sensor, product and reagent loops are filled. Right: valve in injection position – Carrier picks up contents of product and reagent loops which pass on to the optical sensor.

Transport and reaction system – This is composed entirely of 0.8mm internal diameter Teflon tubing. The reaction system consists of 1m of tubing wrapped around a metal mesh. The looping of the tubing in the mesh promotes axial dispersion which promotes mixing of the reagent and product samples thus improving the sensitivity of the assay. The reaction system is submerged in a beaker of water in order to maintain constant temperature. This is important since the reaction rate is temperature sensitive.

Optical flow cell – This consists of a stainless steel block through which is drilled a flow path as shown below. Material is pumped into the cell at A and exits at B. The 'Z' shaped design of the cell gives a straight path through which light may be shone in order to determine the optical absorbance.

Occasionally air bubbles will enter the flow cell. This event is highlighted by a large increase in the optical absorbance. It may be necessary to use the FIA pump maximum speed button in order to remove the air bubble from the flow cell. Persistent air bubbles may be removed by introducing a large air bubble.



Optical flow cell used with the FIA system. Assay sample from the FIA valve is pumped into the flow cell via a connection at A. It follows the Z-shaped path before leaving at B. Light at 510 nm produced by the emitter passes through the assay sample and transmitted light is monitored by the receiver. This is converted into an optical absorbance value which is displayed on the control console.

Note: the optical sensor is pre-calibrated so that it is possible to zero the absorbance using water or assay reagent. The upper range of the sensor is adjusted so that the most concentrated glucose standard gives a maximum absorbance near the upper range of the sensor (1.6 – 2.0 absorbance). If there is a need to adjust the set-point then this can be achieved by adjusting VR7 located inside the control console - See PCB layout diagram in the control console.

11.2.10 Overall Process

Having reviewed the components of the CEU it is worthwhile considering the process as a whole. See Figure 4.

The feed pump delivers the feed (sucrose) to the upper of the two selector valves. The valve should be set so that the feed is delivered to the required reactor column. The feed passes into the top of the column and the reaction occurs inside breaking down sucrose to form glucose and fructose. The product stream exits the bottom of the column and passes to the lower of the two selector valves. This valve must select the same reactor column as the feed selector valve. The product stream is pumped through to the T piece. With the CEU without the FIA system the product is then collected in a suitable vessel. Samples are taken manually at intervals in order to determine glucose concentrations. Where the FIA system is fitted some of the product stream is drawn into the FIA peristaltic pump before being delivered to the FIA 10-port valve. This pump also delivers the reagent and the carrier liquid (deionised water) to the FIA valve. The valve is placed in the Load position in order to prime the loops and then switched to Injection position in order to pass the mixture through the reaction coil and then to the optical sensor where the optical absorbance is measured.

11.2.11 Gas bubbles

Reactor Columns

Bubbles should not be allowed to enter the reactor columns since this will have a dramatic effect on performance. Care should be taken not to pump any air into the columns. Bleed valves are provided on the top of the columns to assist. In addition the feed sucrose solution should be de-gassed. This may be achieved by bubbling nitrogen or helium gas through the

solutions or by applying a vacuum or by heating to 70ºC and then storing in a sealed container.

It is inevitable that some bubbles will enter the column. These can be displaced by removing the column from its bracket and inverting. Deionised water should be fed to the column and the column gently shaken until all the air bubbles are seen to leave. The column can then be righted and returned to its brackets.

Flow Injection Analysis
The FIA analysis system is susceptible to air bubbles in the pipework. These lead to unexpectedly high optical absorbance measurements and they can lodge in the optical sensor affecting future readings. In order to reduce the incidence of these it is best to de-gas the standard glucose solutions and the supply of deionised water used as the carrier liquid. This can be done either by applying a vacuum or by heating to above 70ºC. The de-gassed solutions should be stored in a sealed container with little air space so that re-dissolving of gas does not occur. De-gassing should be performed immediately prior to experimentation in order to minimise problems. The FIA assay solution should also be degassed although heating cannot be used; vacuum or bubbling with nitrogen or helium should be used.

The CEU is fitted with a bubble trap which removes air bubbles before they reach the optical sensor. The bubble trap should be mounted so that the pipe connections are from the bottom and the small holes from which the air bubbles escape are uppermost. There is approximately 1m of Teflon tubing attached to the outlet of the optical sensor in order to provide backpressure to the bubble trap which helps to force air bubbles through the PTFE membrane inside. The PTFE membrane is rated to withstand 2 bar pressure so it is unlikely that it will ever be damaged. However, should it be damaged or should its performance reduce due to fouling with time then undo the central screw and replace with a new membrane (supplied).

Occasionally a bubble will pass through the bubble trap and reach the optical cell where it may become trapped. If this does occur then it can often be dislodged by introducing a larger air bubble. This is achieved by disconnecting the pipe attached to the bubble trap which leads to the optical cell. Introduce a bubble by blowing on this pipe and then reattach. This usually dislodges the trapped bubble first time but if not then repeat.

11.2.12 Preparation and Source of Materials

Deionised water
All water used directly or in buffers should be from a deionised and filtered source. When using the biological reactor it is not strictly necessary to buffer the deionised water but this will give more accurate results. De-gas before use.

Sucrose feed solution for chemical reactors
This solution contains 7.6 g L^{-1} sucrose. De-gas before use.

Sucrose feed solution for the biological reactor
This solution contains 7.6 g L^{-1} sucrose. Method for making 5 L of sucrose solution: dissolve 38g of sucrose in 4 L of deionised water. The pH should be adjusted to 4.6 by addition of dilute acetic acid since this is the ideal value for invertase activity. **NEVER** feed this solution to the chemical reactors. The sucrose feed solution should be prepared shortly before experimentation. De-gas before use.

Note: enzymes are very sensitive to pH. A pH value of 4.6 is optimum for invertase and in fact the activity halves at pH 7.0.

Glucose reagent
The Trinder assay is used to measure the glucose concentration. The reagent uses enzymes and must be stored at 4ºC when not being used in order to prolong its shelf-life. The reagent is available from Roche Diagnostics Ltd (known as Glucose GOD-PAP reagent cat no. 1448676). Alternative suppliers for this reagent are: Pointe Scientific Inc. (reagent known as Liquid Glucose (oxidase) reagent set, product code G7519-500) – www.pointescientific.com; Spinreact, Glucose GOG-PAP (product code 1001190) www.spinreact.com. Note: reagent that exits the FIA valve via the Reagent Out port should be collected for use in the next experiment. This will be slightly diluted compared to original but this is unimportant since the glucose standard calibration routine is repeated each time (see below).

Invertase
This is available in solid form from most biochemical suppliers, for example Fluka – 57629 or Sigma Aldrich – www.sigma-aldrich.com (Product code I 4504). Preparation of immobilised invertase is discussed earlier.

Cationic resin
The resin used is Amberlite IR120 and is available from most chemical suppliers. 2-3kg of dry resin is required in order to make sufficient resin of the correct particle size to fill the columns. Preparation and activation are discussed earlier. Amberlite IR120 is available from VWR International (VWR.com), product code 1.15131.0500.

Calcium chloride solution
A 0.2 M calcium chloride solution is used to form the alginate beads. $CaCl_2$ is available from most chemical suppliers.

Hydrochloric acid solution
The chemical reactors are activated using 2 M hydrochloric acid. Available from most chemical suppliers.

Glucose standards
Before each experiment the enzyme assay reagent should be calibrated using glucose standards. Glucose standards of 1, 2, 3 and 4 g L^{-1} of glucose in deionised water are required. Glucose is available from most chemical suppliers.

11.2.13 Invertase Immobilization

Reactants

- Alginic acid, sodium salt from Aldrich ref. 180947
- Invertase from baker's yeast (S. cerevisiae) from Fluka ref. 57629
- 500ml of calcium chloride solution 0.2M

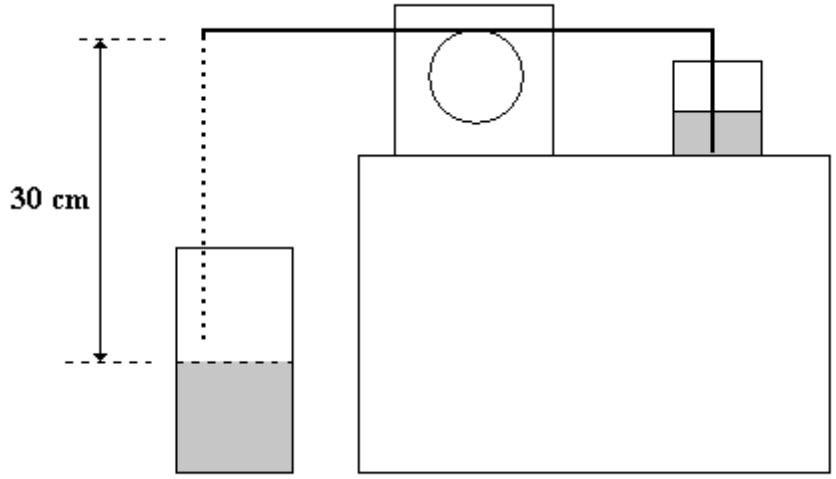
Material

- Magnetic stirrer
- Peristaltic pump
- Glassware

Method
Weigh 3g of alginic acid and 1.5g of Invertase.

With s proper magnetic stirrer dissolve the Invertase in 300ml of distilled water. Then dissolve the alginic acid noticing that as the viscosity increases the stirring power should be adjusted. At the end a light yellowish viscous and homogenous solution should be obtained.

Place the peristaltic pump in a higher level and the 1000ml beaker containing the 500ml 0.2M solution of $CaCl_2$. Start pumping with a proper flow that allows drop formation at the outlet of the peristaltic tube. These drops must fall from ca. 30cm high before reaching the $CaCl_2$ solution (see below):



Sketch of experimental set up

Leave the alginate spheres in the $CaCl_2$ solution for one day and wash them with distilled water before filling the column.

11.2.14 Calibration of the Optical Sensor

Manual calibration (without the FIA option)
Before experimentation begins the optical measurement system must be calibrated so that optical absorbance measurements can be converted to glucose concentration data. This is achieved by performing the assay procedure described above using the glucose standards in place of reactor product. Note the optical sensor should be set to zero using a sample bottle containing the assay reagent or deionised water. Zeroing is achieved using switch 2 (see Figure 3 in Equipment Diagrams section 8). The measurement procedure is described in 'Glucose measurement using the batch optical cell' section 11.2.8.

Calibration with the FIA system
The FIA valve should be set to the load position. There are 3 streams that input to the FIA pump: carrier (deionised water), assay reagent and the sample stream. The tube for the carrier should be placed in a suitable beaker containing deionised water. The tube for the assay reagent should be placed in the reagent bottle. The sample stream can receive material from either the reactors or from an external source depending on the positioning of the 3-way valve. (Note that the 3-way valve follows a different convention to many other valves, and the valve will be open when the handle is at 90° to the body of the valve)

Starting with the highest concentration glucose standard (4 g L^{-1}), place the external source tube into the standard bottle and ensure that the 3-way valve is correctly positioned so that the standard is being drawn into the FIA pump. Set the FIA pump to required speed (see 'Flow injection analysis (FIA)' section 11.2.9) and turn on. Press the Max speed button for the FIA pump so that the loops on the FIA valve are filled rapidly. With the valve set in the Load position the carrier (deionised water) will pass through the optical sensor and out to drain. Once this occurs adjust the optical absorbance to 0.000 using the knob 2 (see Figure 3 in Equipment Diagrams section 8). Release the Max speed button and switch the FIA valve to the injection position. The peak for the sample should appear after approx 20s. After the peak appears the FIA valve should be switched back to Load position. To prevent one sample interfering with another 40 s should pass before the valve is again switched to the Inject position. This time period can be much reduced by using the Max speed button when loading. Note the time periods suggested are only appropriate when the FIA pump is set to 40%, changing the pump speed will affect times. When switching to a standard of a different glucose concentration a longer loading period should be used (approx 2 min at 40% pump speed).

Note: contamination of one sample to another is due to flow in the tubes being essentially laminar and not plug flow.

Note: After the peak corresponding to the reaction of glucose passes through the optical flow cell the absorbance tends to show negative values particularly for low glucose concentrations. This is because the buffer solution and the transport medium have different reactive indexes.

At least two values that agree well should be recorded for each standard. The procedure should be repeated for the other standards. A graph should be plotted of glucose concentration vs optical absorbance peak and from this graph the glucose concentration of reactor samples can be determined.

12 Equipment Specifications

12.1 Overall Dimensions

- Internal reactor diameter – 2.5 10^{-2}m
- Internal reactor length – 0.25m
- Average volumetric diameter of the larger diameter resin (protonic form) – 8.8 x 10^{-4}m and bed porosity – 0.52
- Average volumetric diameter of the smaller diameter resin (protonic form) – 3.1 x 10^{-4}m and bed porosity – 0.59
- Average volumetric diameter of calcium alginate – 3.1 x 10^{-4}m and porosity of biological reactor bed – 0.36
- Activation energy for sucrose inversion reaction with Amberlite 120 particles (diam 0.715mm) – 66.67 kJ mol^{-1}.

12.2 Environmental Conditions

This equipment has been designed for operation in the following environmental conditions. Operation outside of these conditions may result reduced performance, damage to the equipment or hazard to the operator.

a. Indoor use;

b. Altitude up to 2000 m;

c. Temperature 5 °C to 40 °C;

d. Maximum relative humidity 80 % for temperatures up to 31 °C, decreasing linearly to 50 % relative humidity at 40 °C;

e. Mains supply voltage fluctuations up to ±10% of the nominal voltage;

f. Transient over-voltages typically present on the MAINS supply;

   Note: The normal level of transient over-voltages is impulse withstand (over-voltage) category II of IEC 60364-4-443;

g. Pollution degree 2.

   Normally only nonconductive pollution occurs.

   Temporary conductivity caused by condensation is to be expected.

   Typical of an office or laboratory environment.

13 Routine Maintenance

13.1 Responsibility

To preserve the life and efficient operation of the equipment it is important that the equipment is properly maintained. Regular maintenance of the equipment is the responsibility of the end user and must be performed by qualified personnel who understand the operation of the equipment.

13.2 General

In addition to regular maintenance the following notes should be observed:

1. The unit should be disconnected from the electrical supply when not in use.

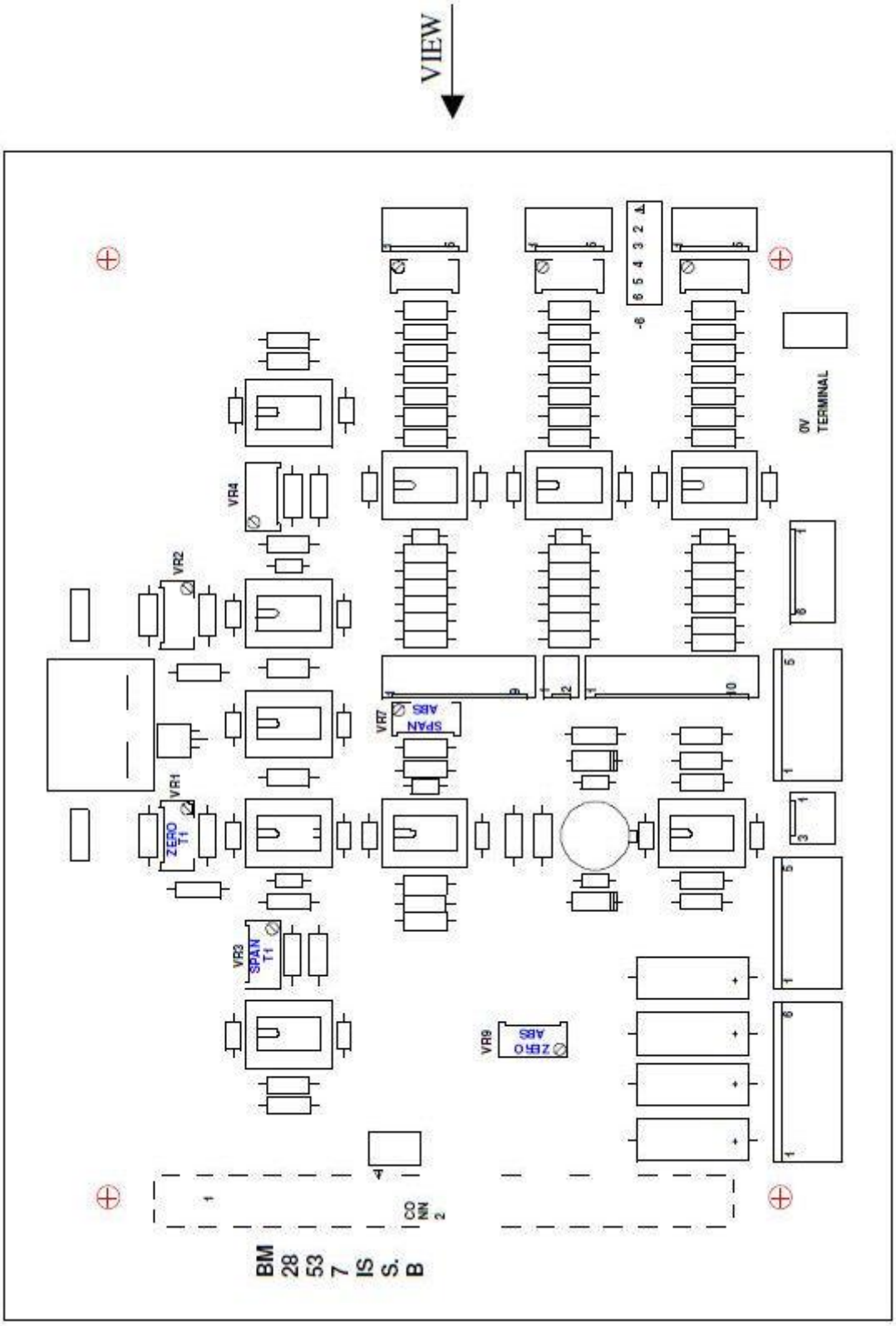
2. The thermocouple and optical sensor conditioning circuits are located on a PCB inside the electrical console. The PCB is attached to the right wall of the console. These circuits are calibrated before dispatch and should not require re-calibration. However, should re-calibration become necessary then the appropriate zero and span potentiometers can be located using PCB layout see section 13.3. It should be possible to do this with the PCB in-situ but if this proves difficult then it can be removed by undoing the screws on the outside of the console.

   This exercise should only be carried out by a competent electrician since live electrical components within the console are exposed when the lid is removed.

   A type K thermocouple simulator should be connected to T/C and the zero and span potentiometers adjusted to calibrate the circuit. If such a simulator is not available then the type K thermocouple can be used with crushed ice and boiling water as the 0 and 100ºC reference points.

3. Test the RCCB by pressing the TEST button at least once a month. If the switch does not trip when the TEST button is pressed then the equipment must not be used and it should be checked by a competent electrician.

13.3 PCB layout



Layout of PCB showing variable resistors (VR) for SPAN and ZERO adjustment of absorbance (ABS) and temperature (T1)

14 Laboratory Teaching Exercises

14.1 Index to Exercises

Exercise A - Study of Sucrose Inversion (section 15)

Exercise B - Examination of Unsteady State Kinetics (section 16)

Exercise C - Effect of Flow Rate, Temperature and Feed Concentration on Conversion (section 17)

Exercise D - Tracer Studies to Characterise Fluid Flow in the Reactor (section 18)

14.2 Nomenclature

Name	Symbol	Unit
Thiele's modulus	Φ	-
Kinetic constant	k	s^{-1}
Particle radius	r_o	m
Effective diffusivity	D_e	$m^2\ s^{-1}$
Effectiveness factor	η	-
Peclet number	Pe	-
Residence time distribution	E(t)	-
Average residence time	τ	s
Average particle diameter	d_p	m
Reactor length	L	m
Reynolds number	Re	-
Particle porosity	ε	-
Conversion of sucrose	x_{suc}	-
Sucrose concentration	C_{sac}	$kg\ m^{-3}$
Time	t	s
Reactor volume	$V_{reactor}$	m^3
Volumetric flow rate	Q	$m^3\ s^{-1}$

15 Exercise A - Study of Sucrose Inversion

Overview

The aim of this practical exercise is to study the sucrose inversion reaction. This reaction, a hydrolysis which has fructose and glucose as products, will take place in a fixed bed catalytic reactor. Two catalysts are proposed: a strong cationic exchange resin and an immobilised enzyme, invertase, the activity of which is specific to the catalysis of this reaction. The reactors' steady state conversion is followed either manually or by an automated analytical technique known as FIA (Flow Injection Analysis). Further objectives of this practical work are the familiarisation of the student with specific problems associated to catalytic and enzymatic reactions, as well as contact with the FIA analytical technique.

Theory

The hydrolysis reaction of sucrose (+):

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \Leftrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \qquad (1)$$

is a first order reaction. The sucrose has a specific optical rotation power of +66.5°, while the equimolar mixture of fructose (-) and glucose (+) has a specific optical rotation power of -22.2°. The reaction of hydrolysis of sucrose is therefore also called sucrose inversion, since the specific optical rotation power is inverted. Glucose and fructose are stereo-isomers.

The sucrose inversion reaction is acid catalysed. Homogeneous catalysis in an aqueous solution of sucrose would ultimately require the separation of the products of the reaction from the acid catalyst. A more practical way of conducting this reaction is by "immobilisation" of the catalyst. A cationic exchange resin in the protonated form is in fact no more than an immobilised acid, where the anion is covalently bonded to the 3-D structure of the resin and the cation H+ is ionically bonded to this group.

Sucrose inversion is a reaction with very high activation energy, approx. 15950 cal/mol (66.67 kJ/mol) for Amberlite IR 120 particles with an average diameter of 0.715mm (i). This reaction is therefore very sensitive to temperature. The reaction is controlled by the transport kinetics (diffusional control), i.e. by the diffusion of sucrose inside the particle and of the products towards the outside. This is easy to verify by using progressively smaller resin diameters. Gilliand et al. (1971) presented results for sucrose inversion catalysed by the cationic exchange resin Dowex 50W-X8, at 50°C, as summarised in Table 1:

$d_p\,(mm)$	$k/k_{0.04}$	$\phi = r_p\sqrt{k/D_e}$	η
0.04	1.0	0.57	0.98
0.27	0.568	3.90	0.55
0.55	0.335	7.80	0.332
0.77	0.252	10.9	0.224

Table 1 - Kinetic data relative to the inversion of sucrose catalysed by Dowex 50W-X8 resin [2]

The efficiency factor (η), defined as the ratio between the rate of the reaction with diffusional control and the rate of the reaction for the conditions at the surface of the catalyst, is a function of Thiele's modulus (ϕ):

$$\emptyset = r_o \left(\frac{k}{D_e}\right)^{1/2} \qquad (2)$$

where r_o is the radius of the catalyst particle, k is the kinetic constant and D_e is the effective diffusivity. For catalysts with spherical symmetry and first order kinetics, η is given by:

$$\eta = \frac{3}{\phi}\left[\frac{1}{tanh\phi} - \frac{1}{\phi}\right] \qquad (3)$$

The dependence of the efficiency factor (η) as a function of Thiele's modulus (ϕ) is shown graphically in Figure A1. The diffusional control region is situated at high values of ϕ, where $\eta \approx 3/\phi$. The chemical control region is situated at small values of ϕ with $\eta \approx 1$.

If the apparent kinetic constant is known for two catalyst particle sizes it is possible to obtain the efficiency factor and Thiele's modulus:

$$\frac{\eta_1}{\eta_2} = \frac{k_1^{apparent}}{k_2^{apparent}} \qquad (4)$$

and, from the definition of Thiele's modulus (Eq. 2) arises:

$$\frac{\phi_1}{\phi_2} = \frac{r_{01}}{r_{02}} \qquad (5)$$

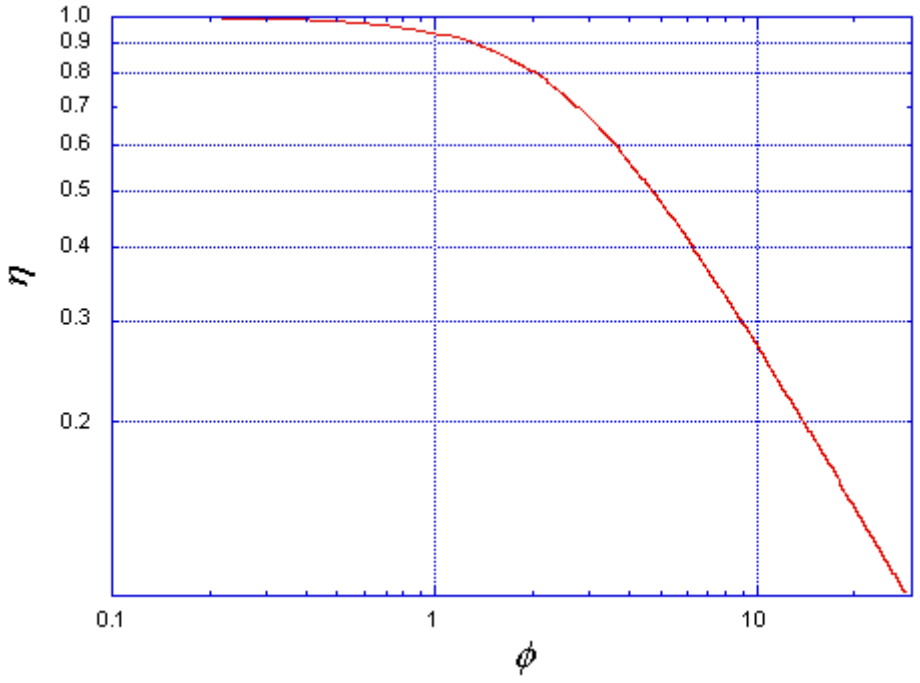


Figure A1 - Efficiency factor as a function of Thiele's modulus for a spherical catalyst.

Combining equations (3) and (5) into equation (4) and rearranging:

$$\frac{\eta_1}{\eta_2} = \frac{k_1^{apparent}}{k_2^{apparent}} = \frac{\frac{3}{\phi_1}\left[\frac{1}{tanh\phi_1} - \frac{1}{\phi_1}\right]}{\frac{3}{\phi_2}\left[\frac{1}{tanh\phi_2} - \frac{1}{\phi_2}\right]} = \frac{r_{02}}{r_{01}} \frac{\frac{1}{tanh\phi_1} - \frac{1}{\phi_1}}{\frac{1}{tanh\left(\phi_1 \frac{r_{02}}{r_{01}}\right)} - \frac{1}{\phi_1 \frac{r_{02}}{r_{01}}}} \qquad (6)$$

This equation may now be solved in order to obtain Φ_1. From this value it is possible to obtain Φ_2 (Eq. 5), η_1 (Eq.3) and η_2 (Eq.4).

The apparent activation energy can be obtained from Arrhenius law:

$$k^{apparent} = k_o^{apparent} e^{-E^{apparent}/\Re T} \qquad (7)$$

where $k_o^{apparent}$ is an apparent frequency factor and $E^{apparent}$ is the apparent activation energy, when the apparent kinetic constants are known for at least two temperatures, preferably three. The latter is called apparent activation energy because it also includes the activation energy corresponding to mass transport.

Quantitative analysis of resin behaviour with two different particle sizes

The kinetic constant for sucrose inversion catalysed by a cationic exchange resin Amberlite IR120 was determined by Reed and Dranoff (1964) at 70°C for particles with average diameters of 0.715 and 0.505mm. These authors determined values of k=0.168 min^{-1} and k=0.226 min^{-1} for the two particle sizes respectively. The obtained kinetic constants were based on the reactor's total volume.

For a flow with a Reynolds number < 1000, the Peclet number of a fixed bed particle varies between 0.3 and 1 for liquids. By taking the intermediate value, Pe=0.6, for the Peclet number of the particle and using a column working length of 19cm and a particle diameter of 0.505mm then the following can be obtained:

$$Pe = 0.6\ \frac{L}{d_p} = 0.6\ \frac{0.19}{5.05\ x\ 10^{-4}} = 225.7 \qquad (8)$$

where d_p is the average diameter of the particles and L is the column length. Chung and Wen (1968) suggested another expression for the calculation of the Peclet number, valid for packed columns with non-porous inert particles:

$$Pe = \frac{0.2+0.011Re^{0.48}}{\varepsilon}\ \frac{L}{d_p} = \frac{0.2+0.011\left(\frac{pud_p}{\mu}\right)^{0.48}}{\varepsilon}\ \frac{L}{d_p} \qquad (9)$$

For a flow of approximately 10 $cm^3 min^{-1}$, and taking the specific density and viscosity of the solution as approximately that of water at 20ºC it can be shown that:

$$Pe = \frac{0.2 + 0.011\left(\frac{1.00\ x\ 10^3 x\ \frac{1.67\ x\ 10^{-7}}{\pi(1.25\ x\ 10^{-2})^2}\ x\ 5.05\ x\ 10^{-4}}{1.0\ x\ 10^{-3}}\right)^{0.48}}{0.55} \frac{0.19}{5.05\ x\ 10^{-4}} = 132.7$$

(10)

where ε is the bed porosity, u is the superficial velocity, ρ is the specific density and μ is the viscosity of the solution. The porosity of the bed and the specific density of the resin were measured using a measuring cylinder. The values obtained were ε = 0.52 and ρ =1.27 g/cm^3 (in the resin's literature the value of the specific density is ρ =1.28 g/cm^3).

For total segregation or for first order reactions, if the residence time distribution E(t) is known, it is possible to obtain the conversion of sucrose inversion at steady state from the following expression (iv):

$$x_{sac} = 1 - \int_o^\infty \frac{C_{sac}(t)}{C_{sac_o\ [batch}}\ E(t)dt \qquad (11)$$

and, substituting the ratio $C_{Sac}(t)\ /\ C_{Sac_o}$ for a first order reaction gives:

$$x_{Sac} = \int_o^\infty \left(1 - e^{-kt}\right)E(t)\mathrm{d}t \qquad (12)$$

where *k*, the reaction kinetic constant, is related to the total volume of the reactor.

The residence time distribution for a semi-infinite reactor has the following analytical solution (iv):

$$E(t) = \frac{\sqrt{\tau Pe}}{2\sqrt{\pi t^3}} e^{-\frac{Pe(\tau - t)^2}{4\tau \times t}} \qquad (13)$$

where τ, the average residence time, is related to the total volume of the reactor. For relatively high Peclet numbers the boundary conditions have little influence on steady state conversion.

Finally, combining eq. (13) and eq. (12) gives:

$$x_{Sac} = \int_o^\infty \left(1 - e^{-kt}\right)\frac{\sqrt{\tau Pe}}{2\sqrt{\pi t^3}} e^{-\frac{Pe(\tau - t)^2}{4\tau \times t}} \mathrm{d}t \qquad (14)$$

which may be solved easily.

For a plug flow reactor (Pe=8), the previous equation is simply (i):

$$x_{Sac} = 1 - e^{-k\tau} \tag{15}$$

For a reactor working length of 19cm and a feed flow of 10cm^{3}min^{-1}, the residence time based on the total volume of the reactor is:

$$\tau = \frac{V_{reactor}}{Q} = \frac{0.19 \times \pi \times 1.25 \times 10^{-2}}{10 \times 10^{-6}} = 9.33 \text{ min} \tag{16}$$

Steady state conversion at a temperature of 70°C can then be calculated for catalyst particles with an average diameter of 0.505mm and assuming that eq. (9) is a good estimate for the Peclet number:

$$x_{Sac} = \int_o^\infty \left(1 - e^{-0.226t}\right) \frac{\sqrt{9.33 \times 132.7}}{2\sqrt{\pi t^3}} e^{-\frac{132.7(9.33-t)^2}{4 \times 9.33 \times t}} \, dt = 0.875 = 87.5\% \tag{17}$$

Alternatively, for plug flow:

$$x_{Sac} = 1 - e^{-0.226 \times 9.33} = 0.879 = 87.9\% \tag{18}$$

Steady state conversion for particles with a diameter of 0.715mm can be obtained through the same procedure. For these particles the Peclet number estimated by Eq. (9) is Pe=99.3. Assuming the same porosity the conversion of steady state at 70°C is:

$$x_{Sac} = \int_o^\infty \left(1 - e^{-0.168t}\right) \frac{\sqrt{9.33 \times 99.3}}{2\sqrt{\pi t^3}} e^{-\frac{99.3(9.33-t)^2}{4 \times 9.33 \times t}} \, dt = 0.787 = 78.7\% \tag{19}$$

and again for plug flow:

$$x_{Sac} = 1 - e^{-0.168 \times 9.33} = 0.791 = 79.1\% \tag{20}$$

The performance of the reactor with the smaller catalyst particles is clearly better. The efficiency factor relative to the two particle sizes can now be obtained, as well as the respective Thiele's modulus. The particles of average diameter of 0.715mm will now be called (1) and the ones of average diameter of 0.505mm will be called (2). Solving equation (6) in order to Φ_1 and for plug flow with axial dispersion gives:

$$\frac{\eta_1}{\eta_2} = \frac{k_1^{apparent}}{k_2^{apparent}} = \frac{0.168}{0.226} = \frac{r_{o_2}}{r_{o_1}} \frac{\frac{1}{\tanh\phi_1} - \frac{1}{\phi_1}}{\frac{1}{\tanh\left(\phi_1 \frac{r_{o_2}}{r_{o_1}}\right)} - \frac{1}{\phi_1 \frac{r_{o_2}}{r_{o_1}}}} = \frac{0.505}{0.715} \frac{\frac{1}{\tanh\phi_1} - \frac{1}{\phi_1}}{\frac{1}{\tanh\left(\phi_1 \frac{0.505}{0.715}\right)} - \frac{1}{\phi_1 \frac{0.505}{0.715}}} \tag{21}$$

Using Newton's method, $\Phi_1 = 9.34$. Φ_2 can now be obtained from equation (5):

$$\phi_2 = \phi_1 \frac{r_{o_2}}{r_{o_1}} = 9.34 \frac{0.505}{0.715} = 6.60 \tag{22}$$

η_1 is obtained from equation (3):

$$\eta_1 = \frac{3}{\phi_1}\left[\frac{1}{\tanh(\phi_1)} - \frac{1}{\phi_1}\right] = \frac{3}{9.34}\left[\frac{1}{\tanh(9.34)} - \frac{1}{9.34}\right] = 0.287 \tag{23}$$

and η_2 is obtained from equation (4):

$$\eta_2 = \eta_1 \frac{k_2^{apparent}}{k_1^{apparent}} = 0.287 \frac{0.226}{0.168} = 0.386 \tag{24}$$

As expected, the efficiency factor of the smaller particles is higher but this is still low (38.6%). It would be desirable to increase the efficiency of the mass transport in those particles. For a given reaction temperature, this can be achieved by reducing the particle size and/or modifying the pore size distribution. The reduction of the particle size corresponds to an increase in the pressure drop in the column. This can become unacceptable if the pressure drop is above a maximum value. This has led to the appearance in the market of new macro-reticulated resins which are more rigid and have wider pores and a higher catalytic efficiency. At the same time, the widening of the pore diameters results in a reduction of the specific internal area and therefore to a lower concentration of active centres. The pore size and the pore size distribution have therefore to be optimised in order to optimise catalytic reactor performance.

Procedure

Begin by familiarising yourself with the experimental set-up. Explanation of the workings of the reactor and product analysis is given in the Operation section.

Verify the position of the directional process valves – direct to the reactor to be used. Close the HWC valves to the reactor(s) not being used. The reactor on the left side of the unit always receives circulating water. In order to prevent pressure build up in this reactor as the HW temperature rises it is necessary to ensure that there is an air bubble at the top of the column (see 'Preparation of matrices for the chemical reactors' section 11.2.1). The reactor to be used does not need this since the entrance and exit valves are open and the third, biological reactor, if fitted, may also be protected by closing its own HWC valve.

Ensure that there is sufficient volume of solutions, that they are made to the correct concentrations and that they are degassed as required.

Ensure that there are no air bubbles within the reactors – see 'Gas bubbles' section 11.2.11.

Turn on the power to the unit.

Set the controller to the desired temperature (70ºC for chemical reactors, 55ºC for the biological reactor).

Set the feed pump to give a flow rate of 10ml min^{-1} (~50%) and the FIA pump to the required speed (see 'Flow injection analysis (FIA)' section 9.7). Steady-state operation will be reached after approximately 1.5 times the column's volume has passed through. Assuming a volume of 100ml (in fact it will be less due to the volume taken up by the packing) and the flow rate above is used, then steady state will be reached after approximately 15 minutes.

Set the FIA valve to the load position and turn on the FIA pump. This will direct deionised water through the optical sensor. Set the optical absorbance reading to zero using switch 2 on the control console (see Figure 3 in Equipment Diagrams section 8).

It is necessary to determine the optical absorbance for each of the glucose standards so that a standard curve may be generated. Direct the 3-way valve so that material is taken from the standard rather than from the reactors and follow the procedure in 'Glucose measurement using the batch optical cell' section 11.2.8 or 'Flow injection analysis (FIA)' section 11.2.9. Once complete a standard curve of glucose concentration vs gradient (batch optical cell) or vs peak optical absorbance (FIA flow cell) may be constructed. From this graph unknown glucose concentrations may be determined. Remember with the FIA system it is best to use the maximum speed button between samples to speed up loading. In addition when switching between different glucose concentration standards it is important to load for a longer period in order to prevent contamination from the preceding sample.

In order to save time it is best to start the first reactor whilst performing the calibration procedure. Turn on the HWC system and allow the system to reach the set-point temperature then turn on the feed pump. Steady state will be reached after approximately 15 minutes. At this time break off from the calibration procedure and take 3 concordant measurements of the reactor product stream. Stop the feed pump and switch the set-up to the next reactor, valve positioning, temperature set-point etc. Begin pumping feed to the new reactor and then complete the calibration procedure. After 15 minutes take 3 concordant measurements of the reactor product stream.

At the end of the experiment it is important to flush the reactors with de-gassed distilled water in order to reduced microbial growth within them. This is achieved by replacing the glucose feed with deionised water and pumping this through the reactors at 100% pump speed for 5 minutes.

Determine the steady state conversion for each of the reactors, and for the chemical reactors determine the corresponding kinetic constants, efficiency factors and Thiele's modulus. Compare the performance of the three reactors.

Perform a sensitivity analysis to determine the significance of the various experimental errors. For example: to what extent does a 1ºC error in the temperature affect the kinetic constant. To determine this you will need to know the activation energy of the reaction.

References

i. Reed, E. and J. Dranoff; "Ion Exchange Resin Catalysis of Sucrose Inversion in Fixed Beds", I&EC Fundamentals, **3**, pg.304-307 (1964).

ii. Gilliland, E., H. Bixler and J. O'Connell; "Catalysis of Sucrose Inversion in Ion-Exchange Resins"; Ind. Eng. Chem. Fundam., **10**, pg.185-191 (1971).

iii. Chung, S.F. and C.Y. Wen, "Longitudinal Dispersion of Liquid Flowing Through Fixed and Fludized Beds", AIChE Journal, **14**, 857 (1968).

iv. Rodrigues, A. E.; "Theory of Residence Time Distribution"; in *Multiphase Chemical Reactors Vol. I Fundamentals*, Editors: A. E. Rogrigues, J. M. Calo and N. H. Sweed, Nato Advanced Study Institute Series, nº51, Sijthoff Noordhoff, 225-284 (1981).

v. Froment, G. and K. Bischoff, "Chemical Reactor Analysis and Design", John Wiley & Sons, N.Y. (1990), pg.165.

16 Exercise B - Examination of Unsteady State Kinetics

Theory

To examine the unsteady state kinetics of the reactors it is necessary to collect samples as a function of time after starting up the reactor. For a pure plug flow reactor, starting with the reactor washed, the final conversion is attained after a period of time equal to τ, the space time. When the reactors flow pattern is axially dispersed plug flow, the reactor response is more complex. The mass balance for a first order reaction can be written as follows:

$$D_{ax}\frac{\partial^2 C}{\partial z^2} = u\frac{\partial C}{\partial z} + \varepsilon_t\frac{\partial C}{\partial t} + k^{app}C \qquad (1)$$

where D_{ax} is the axial dispersion, C is the sucrose concentration, u is the interstitial velocity, z is the reactors axial coordinate, ε_t is the accessible porosity, t is time and k^{app} is the apparent reaction rate coefficient. The dimensionless form of equation (1) can be written as:

$$\frac{1}{Pe}\frac{\partial^2 C^*}{\partial z^{*2}} = \frac{\partial C^*}{\partial z^*} + \frac{\partial C^*}{\partial \theta} + k'C^* \qquad (2)$$

where

$$Pe = \frac{uL}{D_{ax}}, \quad C^* = \frac{C}{C_o}, \quad z^* = \frac{z}{L}, \quad \theta = \frac{t}{\tau}, \quad \tau = \frac{\varepsilon_t V}{Q}, \quad k'^{app} = \frac{Lk^{app}}{u}$$

and C_o is the feed sucrose concentration, L is the reactor length and Q is the feed flow rate. The unknown parameters of this model are: Pe, τ and k'^{app}.

Equation (2) can be solved numerically, using a numerical package like PDECOL, for obtaining the concentration history as a function of Peclet number, space time and apparent reaction rate.

Procedure

Wash the reactor with distilled water while it heats up until the steady state temperature is reached. Then, start feeding the reactor with a 7.6 g/dm^3 sucrose solution at 10cm^3/min. Collect samples of ≈5cm^3 each 30s and analyse their concentration. Simulate the reactors' unsteady state response using equation (2) and the apparent rate coefficient (k^{app}) obtained from steady state experiments, the space time (τ) and Peclet number (Pe) from the flow pattern characterisation experiment.

References

1. Froment, G. and K. Bischoff, "Chemical Reactor Analysis and Design", John Wiley & Sons, N.Y. (1990).

17 Exercise C - Effect of Flow Rate, Temperature and Feed Concentration on Conversion

Theory

The conversion of a reactor, conducting an irreversible reaction, depends mainly on the temperature, residence time and flow pattern and is almost independent of the feed concentration. The temperature directly affects the reaction kinetic constant, usually in an exponential way (Arrhenius law). The flow rate directly affects the residence time, which also affects the conversion. The way the conversion is affected by the residence time depends on the reaction kinetic equation and on the flow pattern.

In the present case, the reaction can be considered a first order irreversible reaction:

$$\underset{(Sucrose,\ 342\ a.m.u.)}{C_{12}H_{22}O_{11}} + \underset{}{H_2O} \rightarrow \underset{(Glucose,\ 180\ a.m.u.)}{C_6H_{12}O_6} + \underset{(Frutose,\ 180\ a.m.u.)}{C_6H_{12}O_6} \quad (1)$$

This reaction takes place in a packed bed reactor where the flow pattern can be approximated by an axially dispersed plug flow model. The reaction rate of sucrose can be written as:

$$-r_{Suc} = k^{app} C_{Suc} \quad (2)$$

where k^{app} is the apparent reaction rate coefficient for the packed bed (s^{-1}) and C_{suc} is the sucrose molar concentration (mol/m^3_{bed}). The ratio between the apparent reaction rate and the measured reaction rate if the reaction takes place at the catalyst surface (K^{real}) is known as the effectiveness factor:

$$\eta = \frac{k^{app}}{k^{real}} \quad (3)$$

which is always smaller or equal to one. Indeed, the apparent reaction rate coefficient has to be smaller or equal to the surface reaction rate because in a porous catalyst the reactants do not have instantaneous access to the entire catalyst internal surface.

For an axially dispersed plug flow reactor the conversion can be obtained from:

$$x_{Suc} = \int_0^{\infty} \left(1 - e^{-k^{app} t}\right) \frac{\sqrt{\tau Pe}}{2\sqrt{\pi t^3}} e^{-\frac{Pe(\tau - t)^2}{4\tau \times t}} \, dt \quad (4)$$

where Pe is the Peclet number, t is the time and τ is the residence time based on the total reactor volume:

$$\tau = V_{rector} / Q \quad (5)$$

where *Q* is the volumetric flow rate. The Peclet number can be obtained using available correlations. The one we propose was developed by Chung and Wen (i) for packed beds with non-porous spherical particles:

$$Pe = \frac{0.2 + 0.011\,\mathrm{Re}^{0.48}}{\varepsilon}\frac{L}{d_p} = \frac{0.2 + 0.011\left(\frac{\rho u d_p}{\mu}\right)^{0.48}}{\varepsilon}\frac{L}{d_p} = \frac{0.2 + 0.011\left(\frac{\rho d_p}{\mu}\frac{Q}{d_r}\right)^{0.48}}{\varepsilon}\frac{L}{d_p} \quad (6)$$

where Re is the Reynolds number, ε is the bed porosity, *L* is the reactor length, d_p is the particle diameter, d_r is the reactor's internal diameter, μ is the reactant's solution viscosity, ρ is the reactant's solution density, *u* is the surface velocity.

Equation (4) shows the reactor's conversion dependency on the residence time and on the apparent reaction rate. The conversion dependency on the feed flow rate, *Q*, can be obtained by combining equations (4), (5) and (6). The dependency of conversion on the temperature is mainly due to the apparent reaction rate:

$$k^{app} = k_o^{app} e^{-E^{app}/\Re T} \quad (7)$$

where k_o^{app} is the pre-exponential term, E^{app} is the reaction's apparent activation energy, $\Re$ is the ideal gas constant and *T* is the absolute temperature. The apparent activation energy considers both the reaction and mass transport activation energies.

Procedure

Considering the basic case of the reactors packed with ion exchange resin when fed with 10cm³/min flowrate and operate at 70°C. Two experiments can be performed, keeping the temperature constant: for 5 and 20cm³/min. Then, for 10cm³/min feed flowrate, the temperature can be changed to 30°C and 50°C. Finally, the feed concentration can be changed from 7.6g/dm³ sucrose to 3.8g/dm³.

References

1. Chung, S.F. and C.Y. Wen, "Longitudinal Dispersion of Liquid Flowing Through Fixed and Fludized Beds", AIChE Journal, **14**, 857 (1968).

18 Exercise D - Tracer Studies to Characterise Fluid Flow in the Reactor

Theory

To characterise the flow pattern of a reactor a tracer technique can be used. The most convenient experiment is to make a step perturbation using a glucose solution. Glucose does not react (the reactant is sucrose) and there is only slight absorption. Also it can be detected readily using the glucose optical assay. Several samples can be collected from the reactor's output and analysed later.

The response of an axially dispersed plug flow reactor can be obtained from (i):

$$F(t) = \frac{C}{C_o} = \int_o^t E(t)\mathrm{d}t = \int_o^t \frac{\sqrt{\tau Pe}}{2\sqrt{\pi t^3}}\, e^{-\frac{Pe(\tau - t)^2}{4\tau \times t}}\, \mathrm{d}t \qquad (1)$$

where *F(t)* is the so called *F* curve of Danckwerts, *C* is the output concentration, C_o is the glucose feed concentration, *E(t)* is the residence time distribution, *Pe* is the Peclet number, τ is the space time and *t* is the time coordinate.

By fitting this equation to the experimental values, minimizing the sum of the square of the residues, using e.g. Excel ("solver" tool), it is possible to obtain simultaneously the *Pe* number that indicates the dispersion of the flow, and space time, τ. These two numbers allow characterisation of the macro mixture flow pattern.

The value for Peclet obtained can be compared with the one obtained by the correlation by Chung and Wen (ii), see above, and the space time obtained by this procedure can be compared with the space time definition:

$$\tau = \frac{V_{avail}}{Q} \qquad (2)$$

where V_{avail} is the available volume in the reactor, the bed porosity plus the accessible particle porosity, and *Q* is the feed flow rate. However the available volume is not known *a priori*.

Procedure

Wash the reactor with distilled water for some time and then start introducing a 4g/dm^3 glucose solution at a feed flow rate of about 10cm^3/min. Collect small sample from this time on, a sample of ≈ 5cm^3 each 30s. These samples can be analysed after using the glucose optical assay.

References

1. Rodrigues, A. E.; "Theory of Residence Time Distribution"; in *Multiphase Chemical Reactors Vol. I Fundamentals* edit by A. E. Rodrigues, J. M. Calo and N. H. Sweed, Nato Advanced Study Intitute Series, nº51, Sijthoff Noordhoff, 225-284 (1981).

2. Chung, S.F. and C.Y. Wen, "Longitudinal Dispersion of Liquid Flowing Through Fixed and Fludized Beds", AIChE Journal, 14, 857 (1968).

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