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高階方法工程研習

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摘要

這次到英國羅浮堡大學研習高階方法工程訓練，主要內容以該大學化學工程研究所碩士班高階方法工程課程(Advanced Process Engineering programme)為主，研習的課程包括化學產品設計(Chemical Product Design)、分離與下游加工(Separation and Downstream Processing)、應用工程實習(Applied Engineering Practice)以及應用異相催化(Applied Heterogeneous Catalysis)等內容。同時也與該研究所博士生 Redah Alsabei 共同討論有關流體觸媒裂解工場之研究。

化學產品設計是一門方法學，在面臨市場競爭日益激烈的時代，需要開發新產品或者將現有產品作適度的修正，以保持市場的競爭力。這門課程從瞭解顧客需求(Needs)、提出構想(Ideas)、選擇方案(Selection)、產品製造(Product Manufacture)、經濟議題(Economic Concerns)等，逐步將真正符合市場需要的產品抽絲剝繭而出。顧客的需求永遠無法滿足，甚至當面對的顧客是最終消費者時，他們的需求更是無法明確地被理解，更遑論量化。當深入瞭解消費者產品有關的特殊問題，可有效地評估出產品屬性。當目標產品的規範訂出之後，即可開始提出構想。事實上我們只需要一個好的構想即可，也就是目標產品。不同的生意有著不同的考量，通常在 100 個當中，才能出現一個好構想。構想提出後，要進行初步的篩選，留下幾個最好的方案來作進一步的研發，在進行選擇方案時，會考慮到只以化學和工程的標準來比較新產品，還是另需用”非精確標準”來作比較，此相較於前者，更增添許多複雜性。當進行產品製造的階段，必需考量到智慧財產權的部份，是否申請專利保護，或者保留為商業機密，得視公司發展策略的方向。最後我們仍得考量到有關經濟的議題，有關生產的方式，所需的設備，以及產生的利潤和市場競爭力，到最後整體的投資報酬率，更是考量是否投資的重要因素。

在化學工業製程中，無處不看到分離的程序。分離與下游加工的課程目的在研習以物理或化學原理來分離物質的各種方法理論與實務，以及批次與連續性分離的選擇，包括液-液萃取，結晶化，噴灑乾燥及冷凍乾燥，氣相及液相吸收，離子交換，色層分析法，電泳，超過濾及微過濾法。在煉油廠中的物理分離程序，包括油料經過過濾器將較大雜質去除，蒸餾塔將原油分離成重輕成份，重油裂解後與觸媒經旋風分離器的分離等等。化學的分離例如加氫脫硫將油料中的硫份去

除，除油劑的使用等等。此外，亦可藉由分離的方法進行油料分析。

應用工程實習課程的目的在培養對工程裝置的實務技術，工程製程的操作能力，以及加強結合理論與實驗工作之間的關聯。灌輸重要的安全觀念，例如化學危害與風險評估等。同時也培養數據分析，報告寫作以及簡報技巧的能力。本課程內容包括薄膜與滴狀的冷凝效應，控制閥的特性與現象，以及板式換熱器構造與操作。薄膜與滴狀的冷凝效應，在計算蒸汽的薄膜及滴狀冷凝在一大氣壓下的熱傳導係數。換熱器或加熱爐的熱交換效率與管的熱傳導係數有關，若能避免冷凝薄膜在管表面產生，則能大幅提升換熱效率。

閥在工業製程中使用得相當廣泛，用來控制液體，氣體和粉末的流量。控制閥的固有特性為廠商依照設計，製造出廠時的特性，當依照製程安裝配置在流程中時，受到上下游設備的影響而有安裝特性。此外，依據製程的需要，依閥的用途決定其柱塞的形狀。控制閥通常會有遲滯效應(Hysteresis effect)。以彈簧為例，由虎克定律說明，彈簧的變化量與施力成正比，但事實上，當施力由零逐漸增加與由最大施力逐漸減少，對彈簧的影響應該是不同的。為避免此一現象所產生出來的困擾，多安裝閥定位器(valve positioner)，來使得指令訊號與閥開度能夠一致同步，且能具有再現性。

幾乎所有的製程操作都會有流體間的換熱，最常見的就是管殼式換熱器。不過當流體的黏度大時，容易在換熱表面結垢，影響換熱效率且污染產品，這類的換熱器便不符合需求。板式換熱器便能應付這種狀況，其由許多薄板片所組成，冷熱流體交相川流其中。透過拆解與操作，瞭解板式換熱器的構造與設計原理。

應用異相催化程序課程的目的在探討影響工業觸媒效能的物理及化學因素，著重在觸媒的設計、製造、特性、活性衰減及再生，以及化學動力學與輸送效應在觸媒反應器最佳設計中所扮演的角色。首先介紹催化的背景，歷史和觸媒製程的發展，以及觸媒材料與製備，觸媒試驗與特性，包括組成及結構，表面積與孔隙大小分佈。在吸附與動力學部份，將介紹蘭幕爾(Langmuir)、弗倫德里希(Freundlich)及 BET 等溫線，溫度程控脫附作用，LHHW(Langmuir-Hinshelwood-Hougen- Watson) 及其他動力模式。在觸媒孔洞內的擴散作用，如等溫氣相擴散，表面擴散，液相擴散，有效性因子，選擇性的擬擴散及希爾模組(Thiele modulus)。

此外還將介紹觸媒反應器的設計，包括工業觸媒反應器、薄膜反應器以及微流體裝置，如微反應器、酵素微反應器以及觸媒基體。另外對於觸媒蒸餾與離子交換催化，酵素催化，燃料電池與催化，固體超酸以及以碳為催化基體等之介紹均包含在課程專題中。

流體觸媒裂解(Fluid Catalytic Cracking, 簡稱 FCC)是主要的化學製程之一，工場的產量端賴反應器升舉管內的反應溫度。為達到設備最佳產量，操作溫度應儘量接近升舉管能容忍的最大溫度，同時也應儘量減小在設計溫度範圍內的波動。在介紹的這項研究中，不同的多變數控制組合(multivariable control schemes)以高階比例-積分-微分控制器，將篩選出最佳的操作變數。這項研究的主要目的是研發出一種便於使用者的程序模擬器，其使用以目標為導向的程式環境，可用於瞭解製程動態，操作員訓練，控制結構設計以及控制器調整。

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壹、 研習目的

在煉油廠擔任工程師數年，除了在技術單位接受養成教育，亦參與新建工場試爐與操作，隨後雖轉任工場，但仍是以處理重質油料為主。前後兩個工場，其實是上下游相關，來自常壓蒸餾的重油，硫份常高達數個百分比，加以雜質含量多，無論作為產品或中間進料，均不適宜。然而經過重油加氫脫硫(RDS)之後，產品硫份可低至百分之 0.5 或以下，同時其金屬含量也能降到非常低的比例。加氫脫硫之後的重油，可作為燃料油當成品油售出，亦可作為重油裂解的進料，生產高附加價值產品，以提高原油煉製的利潤。重油裂解的目的在於提高每單位原油所能生產汽油的比例，以及其他相關副產品，例如丙烯，可進一步作為石化產品的原料，都具有相當高的價值。在現在能源短缺逐漸受重視的時代，重油裂解製程獲得高度重視與發展，尤其對於像我國這種高度能源進口國，絕對沒有浪費能源的權力，該怎麼提升能源效率，更是我們自許為朝國際能源公司發展的目標，不能忽略的方向。

此次奉派前往國外進行專題研究，主要以研習高階方法工程課程，內容包含化學產品設計(Chemical Product Design)、分離與下游加工(Separation and Downstream Processing)、應用工程實習(Applied Engineering Practice)以及應用異相催化(Applied Heterogeneous Catalysis)等，與煉油廠製程和設備之設計與操作、保養與維護相關。化學產品設計不限於新產品的設計，也包含現有產品的改良，其精神在於製造出符合市場需求，具有競爭力的產品。由於此為一門方法學，所以也可應用在其他的工作或生活領域。分離與下游加工介紹化學工業中最常見的程序之一，各式以物理或化學原理進行分離的方法之理論與實務。應用工程實習課程的目的在培養對工程裝置的實務技術，工程製程的操作能力，以及加強結合理論與實驗工作之間的關聯。灌輸重要的安全觀念，例如化學危害與風險評估等。應用異相催化程序課程的目的在探討影響工業觸媒效能的物理及化學因素，著重在觸媒的設計、製造、特性、活性衰減及再生，以及化學動力學與輸送效應在觸媒反應器最佳設計中所扮演的角色。

貳、 研習過程

此次的研習主要是前往英國羅浮堡大學化學工程研究所，進行高階方法工程課程的研習。羅浮堡大學在英國教學和研究領域享有盛譽，是所百年學校，在2007年泰晤士報全英大學排名第六，2008年獲選為全英教學品質前三名的學校，獲得過六次女王週年獎(Queen's Anniversary Prize)，只有牛津大學同時保有相同紀錄。該所學校在工程學院方面也非常出色，化學工程在全英排名曾名列第五，2008年研究評量(research assessment)在全英排名第一。此外，學校資源豐富且十分現代化，圖書館藏書60多萬本，電子網路資源方便，學術論文期刊多可從校內及宿舍網路即時查詢。

化學工程研究所碩士班共有三個課程，高階方法工程為其中之一，此次前往研究由於時間經費有限，僅選修部份課程，其中包括化學產品設計(Chemical Product Design)、分離與下游加工(Separation and Downstream Processing)、應用工程實習(Applied Engineering Practice)以及應用異相催化程序(Applied Heterogeneous Catalysis)等內容，將分別介紹如下。

一、化學產品設計

這是一門方法學，目的在介紹一個新的化學產品誕生的流程。化學工業變幻莫測，必需確認顧客是誰，他們的需求是什麼，撰寫產品規範，產品如何產生，如何歸納、過濾以及選定構想，選擇的條件必需考量化學、工程、經濟和風險，以及製造特殊化學產品相當重要的工場操作，智慧財產權，產品和製程的經濟效益，到最後於市場販售。此課程的主要目的是介紹一個標準化的方法(Generalised methodology)，從確認需求、提出解決方案和及其選擇、針對化學產品設計製造程序，並將之投入市場，課程中由教授指定一標的，由同學依照此標準化方法進行化學產品設計。

1. 瞭解顧客需求(Needs)

顧客的需求永遠無法滿足，是產品研發部門腦力激盪的泉源，也是化學產品設計的開端。這些顧客是誰，他們的需求是什麼，都有待確認。當面對的顧客是最終消費者時，他們的需求無法明確理解，更遑論量化。當深入瞭解消費者產品有關的特殊問題，可有效地評估出產品屬性。

需求通常是模糊的，尤其在品質上的要求，通常難以尋求答案。因此需要設定特定的規範，讓產品符合這些要求。而這些規範需要一而再，再而三地修訂更新，修訂時需要鎖定一個目標，這個目標通常會是市場上我們希望取代的產品。要闡述顧客的需求，有三個步驟，依序是訪問顧客，分析他們表達的需求，以及將需求轉譯為產品規範。在這個階段，必需注意勿過早窄化產品定義的空間，通常容易犯的錯誤是，這時候有人馬上指出新產品是什麼，或提出對現有產品改善的方式。請記住此時只是闡述需求，而非解決需求。

以美國明尼蘇達州明尼阿波里斯市聖保羅機場為例，這機場每天超過 700 架次的飛機起降，這也顯示這是一個相當重要的機場。這城市以其酷寒的冬天為惡名。冬天時，光等待起飛，就足以讓白雪滿滿覆蓋在飛機上。機場人員噴灑去冰劑來去除飛機上的白雪，並在使用後隨即棄置，導入地面水收集系統。由於去冰劑具有毒性，當這些廢水送到當地污水處理系統時，造成嚴重污水處理廠沉重的負荷並成為主要的污染源。

我們的任務是尋找一替代性產品，可便於回收並對環境造成較少的損害。全班分成若干小組進行研究，並於課程最後一天作出小組研究簡報，課程後繳交個人研究報告。

在這項研究中，實際上已有相當不錯的產品在使用中，然而我們需要找出一個替代品，既要有好的效果又要污染性低。我們的顧客並不是航空公司，而是機場，實務上，機場乃委託當地工程公司進行處理。所以訪問的對象應該是工程公司直接負責去冰工作的員工。

這個課程有趣之處在於，當課程進行到第三天時，由幾位教授進行角色扮演，角色可以由各研究小組指定，並對其發問問題，以求得訪談的內容。從機師、乘客、機場經理、工程師、工程公司經理、執行去冰工作的人員等等，教授也從善如流，配合回答五花八門的問題。

經過訪談之後，可歸納的最佳產品應包括以下條件：具可噴灑性，低揮發性，不能有異味，對魚無毒性，對人無毒性且容易回收。訪談的內容通常會因為角色地位不同而產生矛盾與重覆，這些都必須在最佳產品的特性清單上去除。例如有人回答他們使用的產品不具揮發性，但另一個人卻回答其臭味讓有些旅客感到不適，這是不可能的，因為產品不可能完全不具揮發性而仍可被聞到，既然有

旅客會對臭味感到不適，他們使用的產品必定具揮發性。另外無論是對魚無毒性，或者是對人無毒性，都是指產品需不具毒性，這在產品特性清單上無需分別列出。

有意義的產品特性包括，產品當然要具有融冰的能力，但也不能忽略另一項建議，最好能在零下 30°C 的溫度下使用，這是二倍低溫於現有乙二醇產品的溶點。另外一點，產品必須方便好用，換句話說，就是易於噴灑。至於無毒性，則可用”非致癌物”替代說明。以上整理後，就是對於新可回收去冰劑產品的需求。在瞭解顧客的產品需求後，需對這些需求進行評量，才能列出這產品的規範。評量顧客產品需求並不像量測電池電力那樣容易，例如好的化妝品可以讓肌膚產生的平滑度，或者冬季毛衣的柔軟性。一個較常見的方式針對某一做法進行分級，例如有 A、B、C 等做法，再對每一做法作 1~10 的評分，其算術式為：

$$\bar{n}_i = \sum_{j=1}^k n_{ij} / k$$

其中 n_i 為 k 個顧客對第 i 項所作個別評估值 n_{ij} 的平均值。

另一種情況是比較性的評估。例如當一個顧客被要求對六塊蛋糕評估其甜度，其可能選定其中一塊作為標準，以此為參考值 n_0 。然後再對其他蛋糕進行評估，例如第一塊為兩倍的甜度，第二塊可能只有一半的甜度等等。需注意的是，沒有零的甜度，而且所有的評估值都是相對的。要計算這些評估值有些複雜，因為每個人的感受是不一致的。欲得出不同顧客的平均值，可以下列計算式來計算該值：

$$n_{ij} = n_{ij}^0 / \left(\prod_{i=1}^l n_{ij}^0 \right)^{1/l}$$

其中 n_{ij}^0 為顧客 j 對產品 i ，在一群 l 產品中的實際評估值。因此對不同 k 個顧客對每一產品的平均評估值所得出的幾何平均值為：

$$\bar{n}_i = \left[\prod_{j=1}^k n_{ij} \right]^{1/k}$$

一旦以上的評估方式被選定，即可提供顧客對潛在產品進行選擇，並以適當的用語供其作評定。例如若產品是羊毛衫則是”柔軟”，若是乳霜則是讓皮膚”潤滑”，

以求得適切的回應。

接下來的步驟包括將需求轉譯為規範，以及更新產品規範請參考講義。

2. 提出構想(Ideas)

當目標產品的規範訂出之後，即可開始提出構想。事實上，我們只需要一個好的構想即可。不同的生意有著不同的考量，有經驗的產品開發人員會建議大約 100 個構想中，只有一個是好的。

構想的來源很多，可以是顧客、競爭者、顧問或是產品開發小組的成員。提出構想的時候應當盡可能地開放而不受限制，可以是瘋狂、漫無邊際的。這些還不夠，還可以利用方法找出額外的化學構想(additional chemical ideas)，像有些民俗療法如果有效，可以找一些天然產品，或者利用合成及分解的方式來尋找出更多的化合物供新產品使用。

一旦搜集出許多構想，就要開始從其中篩選出最佳的構想，通常要從 100 個中選到剩五個。一般來說那些不符合公司策略或並非公司強項的構想都會先被放棄。接著可能會不安地放棄那些看起來是笨主意，但卻也有可能是創新起源的點子。通常到此會僅剩下約二十個構想。

接著再用第二種篩選方式，選出最後五個構想。使用的方式是一種概念式篩選矩陣，通常在這階段會將每一個構想的一般特性加以衡量，如化學認知，工程設備等，再將衡量的結果以加權平均比較，最後的結果將會是強而有力且實際可行，任何人來執行均能成功的構想。

要比較不同的產品構想，必須面對相當廣泛的標準，包括一些非常客觀的問題，例如”兩個吸附劑中，哪一個吸收能力較強?”，”哪一個電池每單位的電力較強?”。若是牽涉到成本問題，也許會選擇雖然活性只有一半的觸媒，但價格卻是原本的十分之一。另外有些則是主觀的標準，例如我們寧可接受較貴一點的產品，只因為”安全”。更複雜的狀況是，當兩個評判的標準有衝突時，必須要有妥協。例如空氣純淨裝置的效能與價格成正比時，該如何選擇?

有很多的策略可用來篩選最佳的產品設計構想，最簡單的方式是在每個標題之下，選擇出最佳的選項，然後在下一步驟中再做方案選定。這樣做的風險是，可能最好的兩個構想出現在同一個標題之下，又或者仍然有相當多的新產品設計有待選擇。另一種較有效的策略是先選定出幾個重要因素作為評量標準，通常包

括：

- (I) 科學成熟性：已熟知的科學知識會較受偏愛；
- (II) 工程便利性：能使用現有設備直接製造出來的較佳；
- (III) 最小風險：要降低不確定性，至少要知道成功的機會在哪；
- (IV) 低成本：要能概略預估構想的相對成本；
- (V) 安全性：要能指出哪項產品本質較為安全；
- (VI) 低環境衝擊：當然要選擇具較低污染的產品。

一旦關鍵因素確定，接下來即附予加權因子，其表示式如下：

$$\sum_{i=1}^n \omega_i = 1$$

其中 ω_i 是屬性 i 的加權因子，全部共有 n 個屬性。接著對這些重要的構想進行分級，最簡單的分級即是從1到10，通常會以標準產品為5，然後將各個構想給於相對級數，因此對每一個構想 j 及每個屬性 i 會有個分數為 S_{ij} ，最後為每個構想計算總分數為：

$$Score(j) = \sum_{i=1}^n \omega_i S_{ij}$$

擁有較高分數的幾個構想，才能進入下個選擇方案的階段。

以上的構想篩選法雖然看似簡單，卻有幾個重點要把握住。首先得慎選標準產品(benchmark)，通常應該是市佔率最高的產品，也有可能是我們推測競爭者即將推出的新產品，也可以是我們希望能製造出，現在市場上最佳的產品。在第一階段的評選時，可以先選擇幾個不同的標準產品，之後，即可確認其中最適合的產品了。其次，評選小組利用這概念式篩選矩陣(concept-screening matrix)所得的分數結果，要與其他方面的專家作比較，例如行銷人員，現有產品的主要使用者。

經過這個階段，工作小組必須對資深管理人員進行簡報和書面報告，並由其決定是否繼續進行這項開發工作。這些資深管理人員所組成的團隊，也許並不具有技術背景，例如法律或行銷人員，如果計畫中包含有較深入的技術層面，他們會需要協助瞭解以作出合理的決定。因此，工作小組必須細心地保持客觀，讓

這些管理人員瞭解潛在的報酬以及風險。通過這關，產品開發再經過選定後，將值得進入製造的階段。

3. 選擇方案(Selection)

現在將選擇幾個最好的方案來作進一步的研發。有些時候只有簡單的一到二個，但大多時候，會選擇五個以下，因為進一步的研發要花費相當多的工作。進行選擇方案的工作時，分別會有兩種情況。其一是只以化學和工程學的標準來比較新產品，例如我們有熱力學的背景，所以能計算化學平衡或反應熱，又或者有動力學的背景，尤其是知道反應速率常數，及其對溫度的變化，同時也瞭解熱量傳遞和質量傳遞。第二種情況是，不僅以技術背景為基礎，還需用”非精確標準(less exact criteria)”來作比較，例如舒適和安全性，相對於前者，複雜許多。這種標準也包括了顧客反應和社會觀點，不同的國家會有不同的標準，也會隨著時間改變。這兩者的差別，舉個簡單的例子，第二種情況用來比較”蘋果和橘子”的差異，也就是說必須依照主觀但又不一致的標準來作選擇，而第一種可能只用來比較”蘋果和蘋果”，也就是在是相同的性質下做比較。

選擇方案中，最簡單的莫過於尋找現有市場產品的新配方產品，因其只牽涉到更換產品成份，例如讓新產品具有較少揮發性及毒性的溶劑。一個非理想溶液在熱力學中可以下式表示：

$$\mu_2 = \mu_2^0 + RT \ln x_2 + \omega x_1^2$$

其中， μ_2 為產品溶質的化學勢； μ_2^0 為標準狀態下之值； ω 是每莫耳能量單位的活性常數； x_1 和 x_2 為產品與溶劑的莫耳比率。其中參數 ω 是選擇替代溶劑的關鍵參數，估計值為：

$$\omega = \underline{V}_2 (\delta_1 - \delta_2)^2$$

其中 \underline{V}_2 為產品溶質的莫耳體積， δ 即為所謂的溶解度係數。為了找出與目前使用有相同性質的溶劑替代品，則可尋找有相同的 δ_1 溶劑，例如氯仿(chloroform)的 δ_1 為9.2，則可找苯(benzene)作為其替代品，因其 δ_1 也是9.2。

選擇方案的目的是在許多好的構想中，挑選出可能是明日之星的產品。使用化學和工程學來做為挑選的工具，其優點是明確而可信任，不過只能用來比較相似的產品。然而在做最終的選擇時，主觀的決定仍無可避免。使用的方法為概

念選擇矩陣(concept selection matrix)，方式和篩選構想時所用的矩陣相同，但程度上有所差異。能存續到這階段的構想都是前景可期的，所以在使用的參數上，也就是加權因子，必須盡可能地精準。有三個重點必須掌握住：

- (I) 要使用獨立標準：例如登山穿的釘鞋必須輕且堅硬，但這都不是獨立標準，因為抓力愈強可能重量愈重，因此最好的獨立標準是高的抓力對重量比。
- (II) 避免重覆：有些標準看似不一，但其實所代表的意涵是相通的。例如在某項議題上，可以確定安全性和民眾反應都是很重要的，但是，民眾的感受卻是建立在到底有多安全的問題上。如果不注意到這個現象，”安全性”這個標準就可能無形中被提升比重。
- (III) 製作一標準清單：列出所有最重要的因素，儘可能將各方意見納入，例如行銷研究人員和可提供重要建議的專家。

到了選擇方案的階段已無可退路，一旦最佳的一到二個構想被選定，隨即投入的成本立即上升，像測試、打模及市調都需開始進行。同時，管理層級也開始嚴格把關，因此必須有能力向小組以外的人提出證明。利用矩陣的方法可仔細審視一直以來所作決定的步驟。

4. 產品製造(Product Manufacture)

產品製造包含了三個部份。首先是智慧財產權，我們必需考慮是否申請專利保護，專利提供特許的執照來銷售產品，可以有較高的利潤讓研發成本快速回收，不過如此必須完全揭露所有的細節，有些時候寧可保留商業機密。其次是尋找遺缺的資訊，用來確認產品能與預期相符，或者是申請專利的條件，通常就是來自化學及物理實驗的結果，因此要有效率地規劃實驗的進行，另外還有就是為這一兩樣可能的產品建立最終的規範。最後就是將產品製造出來，需要化學及化工的背景，包括熱力學，化學反應動力學，輸送現象及單元操作等。

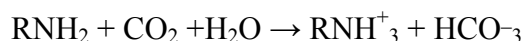
與產品設計有關的智慧財產權可分為專利與商業機密兩種。專利的優點如前所述，受政府保護期間，可賺進高額利潤，但是要與律師打交道，通常讓化學家或工程師頭痛。相對地，商業機密因不受合法保障，容易遭受損害，例如參與機密研發的工程師離職或跳槽到競爭對手公司，同時也將相關經驗或知識帶到新公司，又或者競爭對手公司自行解開機密並註冊專利，此時我們將反而要付費用給對方，如果要繼續使用這機密營運的話。但事實上，專利能保護的範圍有限，

而且防不勝防，有些公司比較實務的作法是，既不申請專利，也不當作商業機密，他們會在一場預估出席率不高的小型技術會議發表，尤其是不會刊出發表的摘要更好，他們會仔細地保留足以作為公證的紀錄，包含商業機密。競爭對手要發現的機會微乎其微，所以秘密仍然是秘密。萬一競爭對手最後仍發現而且準備申請專利，原發明者則可追溯到那場發表會，可使該專利失效且避免付出權利金。到目前為止，已盡可能地搜集各方資訊，包括資料文獻，專家建議以及作了概略的運算，但這些資訊仍有需要再更完整一點，我們需要有足夠的實驗數據來作後盾。茲以下列範例來作說明。

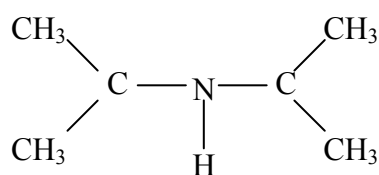
氫氣工場的製程中，甲烷經蒸氣重組後，產生氫氣和二氧化碳，然後再將二氧化碳從產品中分離出。欲使在現有的設備下，將產能去瓶頸，將說明如下。一般使用的方式是用胺液吸收二氧化碳，進行甜化程序，如下列反應式：



反應在氣-液吸收塔以 40-80°C 進行，胺液隨後在 120°C 的高溫及低CO₂分壓下進行再生。在此反應中，每莫耳的CO₂需要兩莫耳的胺液進行吸收。Exxon的化學家Guido Sartori在 1974 年提出下列式子：



如此每莫耳的CO₂只需要一莫耳的胺液吸收。這在效率上將大大提升。式中的胺液使用了一種受阻胺(hindered amine)，例如二異丙基胺(diisopropylamine)：



如果胺受到的阻力太大，則肯定會影響到反應速率，也無法移除CO₂。在此需要的是一種適當的受阻胺，而仍能保有可接受的反應速率。在不曉得何種阻力胺適合的情形下，可列出下列規範：

- (I) 我們需要一種新產品，可使舊有工場的煉量加倍，或者讓新建工場的吸收塔體積能縮小。也就是說需要增加CO₂的吸收效率。
- (II) 反應速率必須至少和原本使用的胺液相當，否則只是用增加的煉量來彌補較差的吸收效率。

(III) 我們只要將舊有工場翻新，所以其他操作條件不能有所改變，也就是吸收溫度仍為 40-80°C，再生溫度 120°C。

(IV) 在現有操作工場中，會添加一種含V⁵⁺的腐蝕抑制劑，新的受阻胺必須要能容忍其存在。

以上所需要進行的實驗如下列所述：

- (1) 建立使用受阻胺的化學反應。
- (2) 依照效能篩選合適的受阻胺。
- (3) 得出反應常數以及優化這項受阻胺的選定。
- (4) 進行溶解度，熱力學穩定性及與V⁵⁺存在時的穩定性試驗。

在作出最終規範之後，開始準備投入大量成本進行製造，而接下來所需要的知識，才是化學工程的開端。

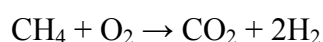
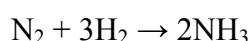
5. 經濟議題(Economic Concerns)

化學產品設計與化學製程設計是不同的，大部份的工業化學描述的是大宗化學品 (commodity chemicals) 的製造，少部份提到特用化學品 (specialty chemicals)，其中的差別可從三個方面來獲得解釋。大宗化學品的產量每年超過 10,000 噸，以連續操作方式進行製造，生產成本愈低所獲的利潤及市場競爭力愈高。而特用化學品的特色是每年少於 10 噸的產量，以現有或原有設備批式生產，首入市場者可享有 70% 的佔有率。

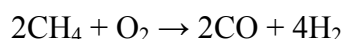
設計一個製程可依照等級評估 (design hierarchy) 的方式來進行，包括四個步驟：批式或連續式的，進料及產品的結構，包含回收程序的反應，分離與能源整合。在製程可行性評估中，可依照產品和原料的價格以下列公式來計算：

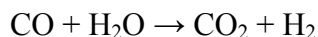
[經濟可行性]=[每年產品營收]-[每年原料成本]-[每年公用物料成本]-[每年總資金成本]

其中原料的成本與化學計量式有關，例如在氨的製造中，氫氣的來源是從天然氣中的甲烷反應而得，其化學式分別如下：



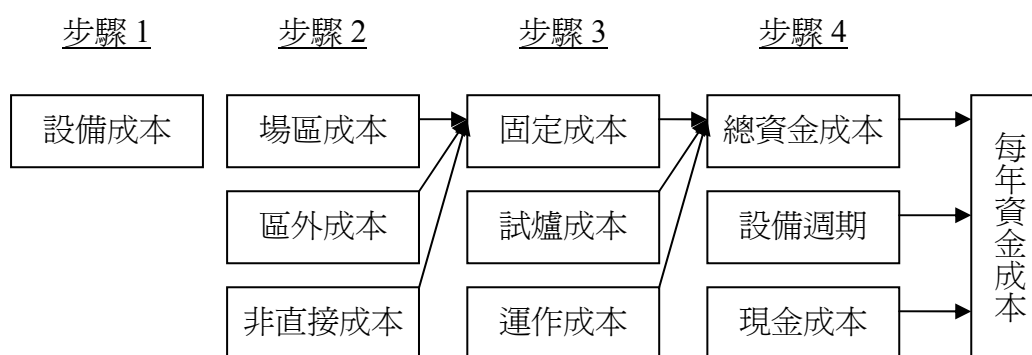
但若可考量在甲烷在空氣不足的情況下燃燒，然後將生成的一氧化碳再行水解反應，其反應式如下：





則每莫耳的甲烷可產生的氫氣可從 2 莫耳增加到 3 莫耳，如此足可省了 1/3 的甲烷成本。但需考量增加分離一氧化碳，以及水解反應所需的設備。

在計算總資金成本時，使用啟發法(Heuristics)進行推估，這種方法雖然普遍運用，但仍需考量通膨與相關物價的波動，例如原油價格。在下圖中，說明資金需求計算的架構。



設備成本的預估需由製造流程來計算設備數量，再從文獻資料中，加上通膨進行推估，甚至可向設備廠商要求估價以求得更精確的數字。接著，場區的成本依經驗為設備成本的 4 倍，但需考量建場當地的物價水準，可從該地區的勞工薪資進行斟酌。區外的成本包括電力及蒸汽的供應及其他額外的建築物，以及管理及技術支援成本，一般為場區成本的 0.45 倍。非直接成本包括建造成本及室內設施工程，通常為場區成本與區外成本的 0.25 倍。上述合計為固定成本，約為 7.2 倍的設備成本。

試爐期間會需要較多的工程師和操作員，大約為 0.1 倍固定成本。運作初期，雖還未產出，仍有購料後的庫存成本，即為運作成本，約總資金成本的 0.15 倍。合計總資金成本為 9.4 個設備成本。

設備週期一般為十年，投入資金假設為 15%，則可計算每年資金成本為：

$$[\text{每年資金成本}] = \frac{[\text{總資金成本}]}{10\text{年}} (1.15)^{10} = \frac{4.0}{\text{年}} [\text{設備成本}]$$

以上是大宗化學品的經濟評估，其假設將投入到一個現有產品市場，且有競爭者的產品售價當參考，成功的條件在能長時間創造出以更低廉於競爭對手的成本。但當考量市場上尚未銷售的新產品時，則以淨現值(net present value)作為其經濟競爭力的評估標準，淨現值與從開發到上市時間，以及資金的時間價值

(time value)有關。

二、分離與下游加工

本課程的目的在研習以化學作用為基礎，進行批次分離(batch separations)的理論與實務；分離的選擇與連續性；以物理分離法進行產品區隔，包括液-液萃取，結晶化，噴灑乾燥及冷凍乾燥，氣相及液相吸收，離子交換，色層分析法，電泳，超過濾及微過濾法。

色層分析(Chromatography)又稱色譜法，主要分為固定相和移動相，在將欲分析的物質加入後，藉由移動相流經固定相，因不同的移動速率而分離出各成份。固定相可為固相或液相，移動相則通常為液相。不過近年來發展到應用氣相，使得氣、液、固相可交互組合使用，讓色層分析成為更迅速、精確的分析方法。

色層分析技術可依據不同的技術背景再進行分類。以色層分析床型來進行分類有柱層析法，平面層析法，及紙層析法，薄層層析法。以移動相的物理狀態來區分有氣相層析法，液相層析法，親和層析法，超臨界流體層析法。以分離機構來區分有離子交換層析法，體積排除層析法。其他的尚包括置換層析法，反相層析法，二維層析法等等。

色層分析是預備分離的物質分子在固定相與流動相之間分佈平衡的過程，不同的物質在兩相之間的分佈會有所不同，隨著流動相流動速度的差異，不同成份在固定相上相互分離。依據分離機制，分為以下類別。吸附層析法利用固定相對物質的吸附能力差異而產生分離。分配層析法則利用分離成份在固定相與流動相中不同的溶解度來進行分離。離子交換層析利用分離成份與固定相間的離子交換能力進行分離，其固定相一般為離子交換樹脂，樹脂的結構中可存在許多可以電離的活性中心，分離成份與這些活性中心進行離子交換，最終在兩相之間產生平衡。

液液萃取(LLE)的三個主要步驟為將液相充份混合，進行相間質傳以及液相分離。其使用的機會通常是在其他分離方法，例如蒸餾，無法使用的情形下，或者對溫度較為敏感的物质，尤其是對製藥業而言。對於溶劑有相當多的選擇，但通常有以下特性。(a)對於欲萃取的物質具有高選擇性，此特性也決定所需萃取板數；(b)萃取物質在溶劑與進料中溶解度的比例，此特性影響溶劑的選擇性與需求量；(c)進料與溶劑密度的差異愈大，愈易於相分離；(d)應儘量選擇低黏度(小

於 10 CP)，黏度愈大，增加相間質傳與分離；(e)高表面張力有助於溶液的沈澱與共溶，但會阻礙質傳；(f)揮發性需作為與進料和萃取物質間的參考；(g)對於製程的條件應具穩定性，減少減損耗及需再純化的需要；(h)腐蝕性要低；(i)不具毒性；(j)成本要低。

液液萃取的設備有幾種型式，依照操作的不同，可分為較簡單的批式及連續式。批式反應器的攪拌器若放置在重相(heavy phase)，則輕相(light phase)會變成分散相(dispersed phase)，反之亦然，通常會先加入輕相後，再加入重相，可以讓分散效果更佳。

其他非機械式攪拌接觸器的最主要優點就是沒有任何零件需要移動，增加的內部零件包括擋板，填充物和多孔板，缺少軸向混合，卻因增加了分散相的滯留時間而提升了質量傳遞，增加液滴共溶，但減少了塔容量(column capacity)。填充塔(packed column)並不適合含有懸浮固體或高表面張力的液體。

另一種液液萃取設備為混合沉澱器(mixer settler)，其包含一個混合區及另一個含有幾個間隔的沉澱區。兩接觸相在混合區充份混合後進入沉澱區，分散相溶合而兩相進行分離。其優點為可以控制接觸塔所無法控制的體積流量，缺點則是需要佔用的面積較大，因而成本較高。

在選擇設備上有幾個條件需要列入考量，包括需要的流通量，可提供的空間，資金及維護成本及潔淨度。通常會依照下列的原則，(a)如果有乳化可能或兩密度差異小，則使用離心萃取器；(b)需要小體積者，可選擇批式反應器或離心式；(c)小於 5 個理論板，用離心式或混合沉澱式；(d)大於 5 個理論板用塔式；(e)具高界面張力者則需用攪拌幫助分散；(f)低界面張力者則用重力系統。

所謂吸附(adsorption)是指溶質因受物理力量而停留並連結在多孔固體的內部表面上。而離子交換(ion exchange)則指溶質在多孔固體內受化學力量而停留或與離子群連結。用於離子交換的吸附劑有矽膠，活性礬土，活性碳，沸石，聚合物和樹脂以及天然黏土(clays)。

氣體吸附程序包括應用在純化程序的加熱擺盪吸附法(Thermal swing adsorption，簡稱 TSA)和鈍氣吹驅擺盪吸附法(Inert purge swing)，以及大量分離程序的加壓擺盪吸附法(Pressure swing adsorption，簡稱 PSA)、真空擺盪吸附法(Vacuum swing adsorption，簡稱 VSA)和置換吹驅吸附法(Displacement purge

adsorption)。以上氣體吸附法的應用均在固定床，然而近來亦有以移動床吸附程序增加的驅勢。

三、應用工程實習

本課程的目的在培養對工程裝置的實務技術，工程製程的操作能力，以及加強結合理論與實驗工作之間的關聯。灌輸重要的安全觀念，例如化學危害與風險評估等。同時也培養數據分析，報告寫作以及簡報技巧的能力。

1. 控制危害健康物質(COSHH)

英國政府在 2002 通過控制危害健康物質條例(Control of Substances Hazardous to Health Regulations, COSHH)，要求僱主必須控制勞工與其他人員因暴露在有害物質環境中所產生的風險。暴露的風險，內容及程度的評估均需製作記錄在 COSHH 評估表中，請參見附錄一。

學校依照 COSHH 規定，評估表由大學安環單位進行管制，並要求系所儘可能使用較不具危害性物質的替代物，或禁止在密閉空間中使用。在無可避免的情形下，應以技術性儘可能降低暴露存在的風險。非正常狀態下的暴露及危急情況發生時的採行措施應公布在任何可輕易看見的地方。

COSHH 的風險評估的步驟有八項，分別如下：

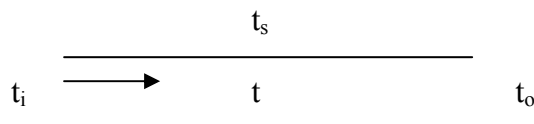
- (I) 評估風險：評估工作場所使用或產生的危險性物質對健康帶來的風險。
- (II) 決定需要什麼防範：決定需要採取的行動以排除或減少這些風險，使能達到可接受的程度。
- (III) 預防或適當地控制暴露：例如改變程序以避免或減少危害物質產生，或以其他安全的方法取代。
- (IV) 確保採用和適當維持各種控制措施：僱主有責任採取適度的步驟確保施行。
- (V) 監測暴露：如果評估有暴露的風險，必需要有適當的量測。
- (VI) 對健康進行適當監控：對僱員進行暴露風險之必要健康檢查。
- (VII) 預定計畫和步驟以應付意外、事件和緊急情況。
- (VIII) 確保僱員適當地得到通知、培訓和監督。

我們公司內容對於工安的要求更甚於此，在此提出此管制內容，一來借作參考，截長補短，二來，進入實驗室之前，特別安排課程，教授有關安全、衛生等觀念，使所有教導更為完整，第三，所有人員均依要求填具表格，對於落實要

求，均審慎施行，毫不馬虎，印象十分深刻。

2. 薄膜與滴狀的冷凝效應(Film and dropwise condensation)

此實驗的目的在計算蒸汽的薄膜及滴狀冷凝在一大氣壓下的熱傳導係數。實驗裝置包括一銅管，內有冷卻水流動，而蒸汽在管外冷凝。當管內外有熱流率 Q ，其與管表面積 A 及溫度驅動力 $\Delta t = (t_s - t)$ 成正比，即 $Q = UA \Delta t_{lm}$ ，其中 U 為比例常數，即總熱傳係數。

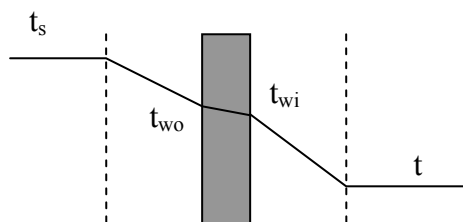


若水的溫度由進口溫度到出口溫度，驅動力應為對數平均溫差，即

$$\Delta t_{lm} = \frac{(t_s - t_i) - (t_s - t_o)}{\ln \left[\frac{(t_s - t_i)}{(t_s - t_o)} \right]}$$

總熱傳係數即可由上面各式推導而得。

理想的狀況下，從蒸汽到水的溫度梯度可如下圖表示：



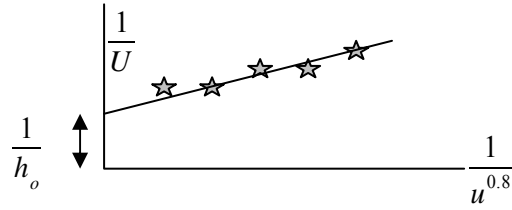
$Q = h_o A (t_s - t_{wo}) = h_w A (t_{wo} - t_{wi}) = h_i A (t_{wi} - t) = UA (t_s - t)$ 其中， h_o 和 h_i 各自是管外和管內的薄膜熱傳係數，而 h_w 則是管壁熱傳導係數。這些係數為傳導係數，為阻抗力的倒數。因此可以下式表示：

$$\frac{1}{U} = \frac{1}{h_o} + \frac{1}{h_w} + \frac{1}{h_i} \quad \text{且,} \quad h_w = \frac{k_w}{x_w}$$

其中 k_w 和 x_w 為管壁的熱傳導率及厚度。管壁阻抗力可逕行忽略。當管內流動為擾流時，下式可成立：

$$Nu = 0.023 Re^{0.8} Pr^{0.4}$$

其中 Nu ， Re 及 Pr 分別為紐塞數，雷諾數及普蘭特數。因此，



$$h_i \propto u^{0.8}$$

其中 u 為流體流速。

所以當以 $1/U$ 對 $1/u^{0.8}$ 作圖時，在 $1/u^{0.8}=0$ 時， $h_i \rightarrow \infty$ ，所得截距為 $1/h_o$ 。

此即為威爾森圖(Wilson plot)，提供一個取得外部薄膜係數的方法。

此實驗結果以簡報方式進行報告。製作投影本向指導教授說明實驗內容及結果和討論，並回答教授相關的提問。

3. 控制閥(Control valve)

閥在工業製程中使用得相當廣泛，用來控制液體，氣體和粉末的流量。絕大多數的閥以手動操作，通常只作為開和關的裝置。然而製程中重要的操作需要精確地對物質的流動進行控制，以便調整系統的操作。可能只是簡單地避免液位，溫度，壓力超出操作範圍，不過卻是控制化學反應必要的元件。控制閥亦可以手動操作，但大多時候是以動力空氣或電力來進行驅動，並針對來自製程量測元件的轉換訊號進行回應動作。根據製程的需要來選擇各種型式的閥，同時閥的作動位置與產生的流量都必須能夠預測得到。然而製造廠商所製造出的閥，可能會有相當多種的安裝方式和位置，塔槽，管線位置，管徑等等都會影響到閥的性能。因此必需瞭解並分辨出閥的固有特性(inherent characteristic)及安裝特性(installed characteristic)的差別，前者為閥的本身特性，後者則與裝設在工場的特定位置有關。

實驗的裝置及控制閥的拆解圖，以及流體流經閥體的流向，如下圖所示：

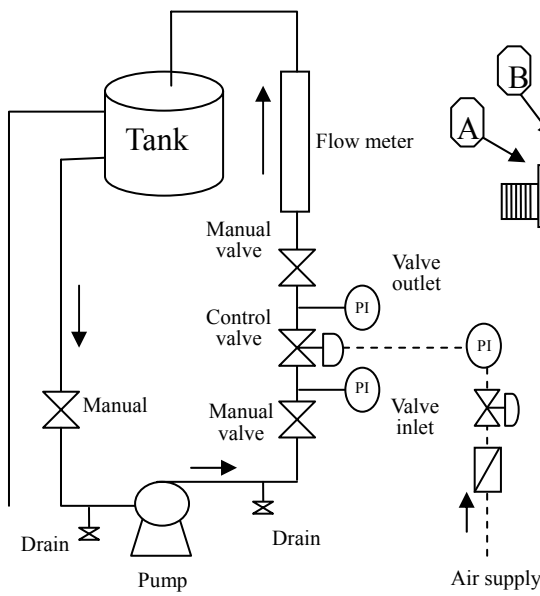


Figure 1: Flow Diagram

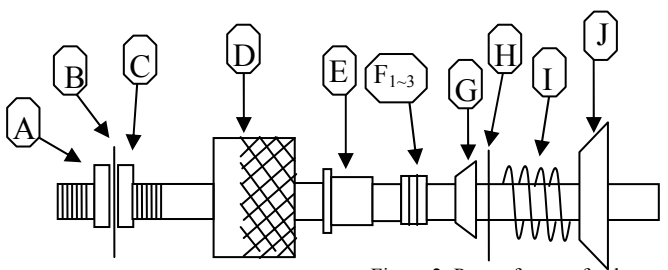


Figure 2: Parts of stem of valve

- A, C: Nut
- B: Spacer
- D: Knurled nut
- E: Packing gland
- F₁₋₃: PTFE washer
- G: Packing follower
- H: Spacer
- I: Spring
- J: Seat

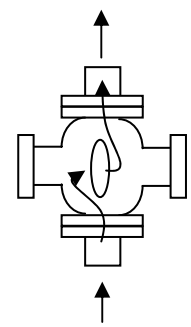


Figure 3: Flow pattern through the valve

非壓縮流體流經控制閥的流動方程式為 $Q=C_v\sqrt{(\Delta P/SG)}$ ，其可推導自白努力定律(Bernoulli's equation)，其中 Q 為體積流量， ΔP 為流經閥所產生的壓降， SG 為流體相較於水的相對密度，而 C_v 即為閥係數。當流體雷諾數低於 4000 時，此方程式需考量黏度的影響。

閥的固有特性決定於閥的開度及其柱塞的形狀，在單位壓降下，每分鐘流經閥體的流量，即為其固有特性流量。依據閥的開度，在差壓不變的情況下，繪製與流量變化的關係，即為固有特性曲線。依照固有特性曲線，可將控制閥分為幾種型式。快速開啟型(Quick opening)，在開度不大的時候，即能產生極大的流量變化，適用於安全釋放閥的用途。線型(Linear)，流量和閥開度成正比例。等比例型(Equal percentage)，閥的增加的開度與流量增加比例相當。

另一個閥的特性是安裝特性，相較於固有特性屬於製造廠家在出廠時，為該閥所測量得到的，買家也通常能從製造廠家取得新購閥的固有特性曲線圖。當閥安裝在製程上某一位置時，受到上下游設備的影響，產生不同的壓降，同時也影響到該閥的特性曲線，此即為安裝特性。安全閥的受驅動力的作用，再分成失效關閉(Fail-closed)及失效開啟(Fail-opened)，或者稱作空氣作動開(Air-to-open)及空氣作動關(Air-to-close)，其目的在於操作時的安全考量，當動力來源消失時，

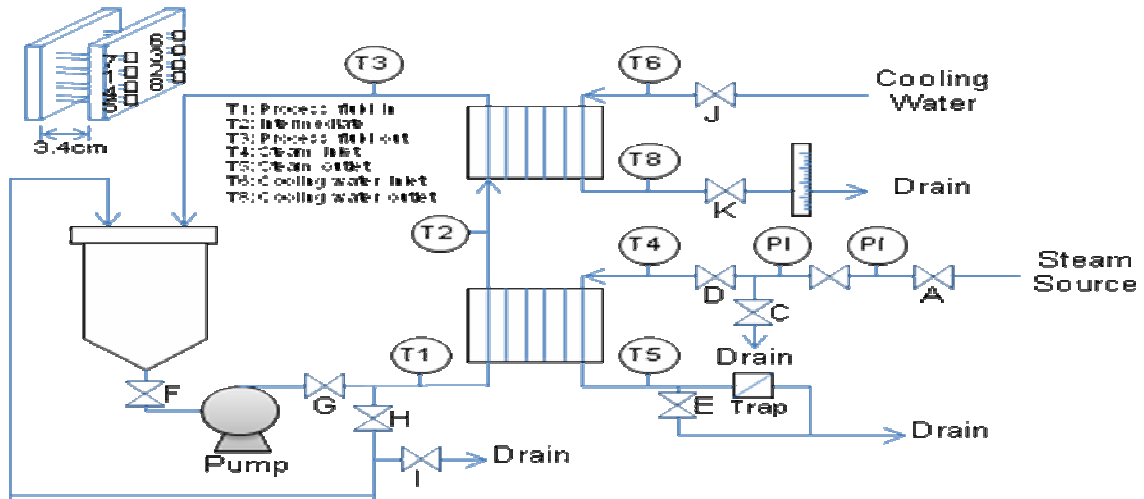
其作動的方向應以系統安全為最大考量。此外，驅動力對閥為正作動(direct acting)或逆作動(reverse acting)，亦為類似考量。在現今的控制系統中，亦可在控制室DCS系統中進行規劃，以符合需求。

另外欲探討有關閥的現象是遲滯效應(Hysteresis effect)。以彈簧為例，由虎克定律說明，彈簧的變化量與施力成正比，但事實上，當施力由零逐漸增加與由最大施力逐漸減少，對彈簧的影響應該是不同的。此即為磁滯效應，在實驗操作中，我們調整空氣來源壓力，改變控制閥開度，來印證此一現象。現今的控制閥為避免此一現象所產生出來的困擾，多安裝閥定位器(valve positioner)，來使得指令訊號與閥開度能夠一致同步，且能具有再現性。

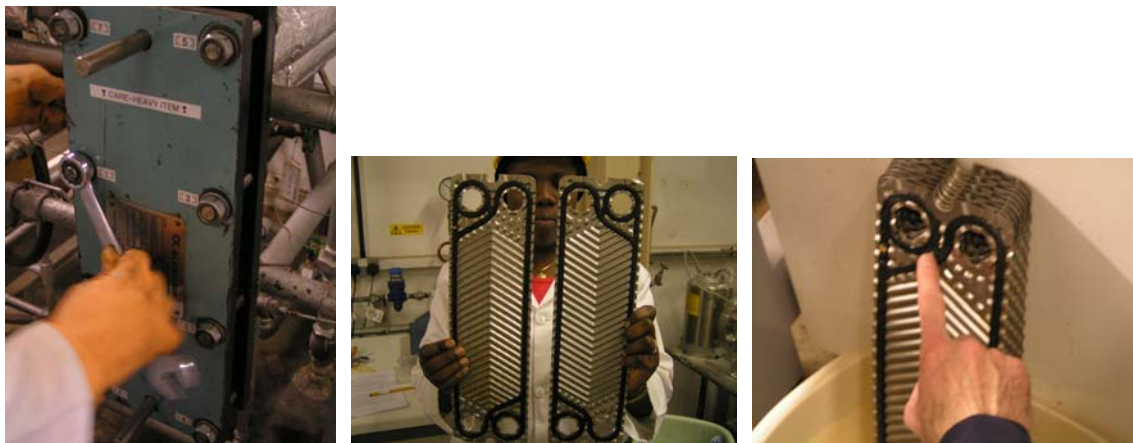
此實驗結果以海報方式進行報告。其特點為海報能提供的空間有限，必須儘量將重點節錄出，將成果展現並作說明以及接受提問。

4. 板式換熱器(Plate heat exchanger)

幾乎所有的製程操作都會有流體間的換熱，最常見的就是管殼式換熱器。不過當流體的黏度大時，容易在換熱表面結垢，影響換熱效率且污染產品，這類的換熱器便不符合需求。板式換熱器便能應付這種狀況，其由許多薄板片所組成，冷熱流體交相川流其中。薄板之間隙相當小，在表面常成皺狀，可加強薄板硬度，並使流體擾動。薄板放置在一邊為固定板，一邊為移動板的平板之間，並以螺絲加鎖予以固定。薄板的數量依所需之換熱面積而定，少則低於10片，多則高達100片以上。薄板之間以橡膠墊片間隔，並且引導流體進出換熱器。實驗內容包括對板式換熱器的拆解，安裝，以及利用冷熱流體的熱量交換，計算出熱傳係數。實際裝置的流程與換熱器裝置的示意圖如下所示。



實驗裝置的流程為，製程流體從儲槽經泵浦出後，經過兩個換熱器再回到儲槽。第一個換熱器 A 以蒸汽將製程流體加熱，第二個換熱器 B 則使用冷卻水換熱進行冷卻。在泵浦出口設有一回流管線可控制製程流體流經換熱器的流量。另外尚包含各溫度偵測點與冷卻水流量計。



上左圖為薄板構造之差異比較，上中圖手指處為流體流經薄板之位置，右圖為安裝後之加鎖過程。

冷卻水吸收的熱量(Q_1)可由下式估算出：

$$Q_1 = M_{cw} * C * (T_8 - T_6)$$

其中， $C = 4220 \text{ J/kg K}$ ， M_{cw} = 水的質量流率(kg/s)。

此吸收熱應與製程流體所放出的熱(Q_2)相等：

$$Q_2 = M_{pf} * C' * (T_2 - T_3)$$

其中， M_{pf} = 製程流體流量(kg/s)，此時即可求出製程流體的比熱(C')。

在計算換熱器 B 的熱傳係數可用下式：

$$Q_1 = U_B * A_B * \Delta T_B$$

其中， A_B 為換熱器B的熱傳面積(0.36m^2)，而 ΔT_B 為冷熱流體間的有效平均溫差，由對數平均溫差公式求出。

$$\Delta T_B = \frac{(T_3 - T_6) - (T_2 - T_8)}{\ln \left[\frac{(T_3 - T_6)}{(T_2 - T_8)} \right]}$$

利用稍早求出的製程流體的比熱(C')，可計算出換熱器A所傳遞的熱量，再計算出其熱傳係數(U_A)：

$$Q_1 = U_A * A_A * \Delta T_A = M_{pf} * C' * (T_2 - T_1)$$

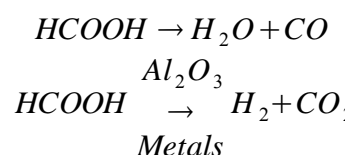
其中， A_A 為換熱器A的熱傳面積(0.22m^2)。因熱流體由蒸汽冷凝成液態水，故對數平均式並不適用於換熱器A，因此其有效平均溫差(ΔT_A)以估計為 60K 取代。此實驗結果以報告寫作的方式報告，為使能有效練習正式報告的寫作，寫作的要點摘錄於附錄中。

四、應用異相催化程序

本課程的目的在探討影響工業觸媒效能的物理及化學因素，著重在觸媒的設計、製造、特性、活性衰減及再生，以及化學動力學與輸送效應在觸媒反應器最佳設計中所扮演的角色。首先介紹催化的背景，歷史和觸媒製程的發展，以及觸媒材料與製備，觸媒試驗與特性，包括組成及結構，表面積與孔隙大小分佈。在吸附與動力學部份，將介紹蘭幕爾(Langmuir)、弗倫德里希(Freundlich)及 BET 等溫線，溫度程控脫附作用，LHHW(Langmuir- Hinshelwood-Hougen-Watson) 及其他動力模式。在觸媒孔洞內的擴散作用，如等溫氣相擴散(isothermal gaseous diffusion)，表面擴散(surface diffusion)，液相擴散(liquid diffusion)，有效性因子(effectiveness factor)，選擇性的擬擴散 (diffusional disguise of selectivity)及希爾模組(Thiele modulus)。此外還將介紹觸媒反應器的設計，包括工業觸媒反應器(industrial catalytic reactors)、薄膜反應器(Membrane catalysis)以及微流體裝置(Microfluidic devices)，如微反應器(microreactors)、酵素微反應器(enzyme microreactors)以及觸媒基體(catalyst supports)。另外對於觸媒蒸餾(Catalytic

distillation)與離子交換催化(ion-exchange catalysis)，酵素催化(enzyme catalysis)，燃料電池與催化(fuel cells and catalysis)，固體超酸(solid superacids)以及以碳為催化基體(carbon as a catalysis support.)等之介紹均包含在課程專題中。

觸媒為能使化學反應加速平衡，但本身卻不因參與反應而改變的一種物質。這種現象則稱為催化反應。基本的原理為觸媒使反應的活化能降低，使反應容易進行，但卻不會改變其熱力學平衡位置。換句話說，觸媒只能讓符合熱力學的反應增加反應速率，若無法符合熱力學定律，也無法誘使其進行反應。在觸媒的存在下，當正反應的反應常數 k_f 增加時，其逆反應的反應常數 k_i 也會增加，但全反應的反應常數 $K=k_f/k_i$ 並不會受觸媒影響改變的。對於某些反應物可能進行不只一種的反應，觸媒可能會促使其選擇較低活化能的路徑。例如甲酸的分解反應，在有無觸媒的存在下，可能會有不同的產物。



同相催化(Homogeneous Catalysis)指製程中觸媒可與反應物之一溶解，例如酯類藉由同為液態的酸進行水解反應。這種催化反應容易在實驗室內進行研究，但不易商業化的操作，工業界的使用也有限。至於異相催化(Heterogeneous Catalysis)則指觸媒與反應物為不同相態，例如固態氧化鋅觸媒使氣態一氧化碳進行氧化反應。此類反應具有較複雜的反應機構，相反地，不易在實驗室內進行研究，但卻便於商業化操作，並且廣泛地在工業界使用。

酵素催化(Enzyme Catalysis)使用一種蛋白質分子，既非同相也非異相，通常用於生物製程，具有極佳的效率，僅在某產業界使用，例如製藥，啤酒等。以其與異相催化的效率作比較，在 10%(w/w)Ni/Al₂O₃催化的苯加氫反應中，反應速度為 4*10¹⁷分子/秒-克 觸媒，但在酵素催化H₂O₂分解的反應速度為 6*10²⁶分子/秒-克 觸媒，可見得酵素催化的效率遠較異相催化高許多。

異相觸媒通常製成顆粒的形式，實際的反應常數 k_T 決定於表面的化學性，若受限於進入孔洞或外部表面的緩慢擴散，會降低成觀察到的反應常數 k_0 ，降低的程度決定於製程條件及觸媒性質。

因為有孔洞的關係而擁有大面積的觸媒，同時也稱作多孔性觸媒。這些孔

洞可允許小分子進入而將大分子阻擋在外，因此凡具有這種孔洞作用的物質稱作分子篩。天然的分子篩有粘土(clay)和沸石(zeolite)，也有合成的結晶矽酸鋁(crystalline aluminosilicates)。分子篩可作為各式觸媒的基底，其孔洞則能控制不同的分子靠近觸媒活性表面的時間，因此即可只准許特定的分子進行反應。

然而並非所有的觸媒都需要多孔性結構來增加表面積，有些已經具有足夠活性，努力再讓其成多孔性也成多餘。非多孔性觸媒稱作單體觸媒(monolithic catalysts)，主要使用在以散熱為主要考量的程序上，因此過多的觸媒表面積只會讓熱傳遞效果更糟糕。即使目的相近，也可能使用不同類型的觸媒。例如在汽車排放廢氣中，欲減少污染的催化氧化作用，福特和克萊斯勒使用單體觸媒，而通用和美國汽車則使用多孔觸媒，不過，兩種觸媒都是以白金金屬作為主要觸媒材料。

部份觸媒的形式為極細微顆粒的活性物質，散佈在較無活性的材質上，此材質稱作載體(support)。活性物質通常為純金屬或金屬合金，而此類觸媒稱之為載體觸媒(supported catalysts)，反之則稱非載體觸媒(unsupported catalysts)，後者的活性成份為其他的主要部份的物質，稱作促進劑(promoters)，來增加活性。例如煉油廠常見的白金-氧化鋁觸媒。

多數觸媒無法長期保有活性，即為活性衰減(deactivation)，意指經過一段時間後，觸媒的活性降低的現象。觸媒的活性衰減可能是因為老化(aging)現象，例如表面的活性結構逐漸改變，或者有其他物質沉積在觸媒表面的活性部份。其中後者的過程稱之為觸媒的中毒(poisoning)或結垢(fouling)。活性衰減的速度可能相當快，例如輕油或重油裂解，在反應區很短的時間內即在觸媒上累積相當多的焦炭，因此需儘快移除將焦炭燒除。

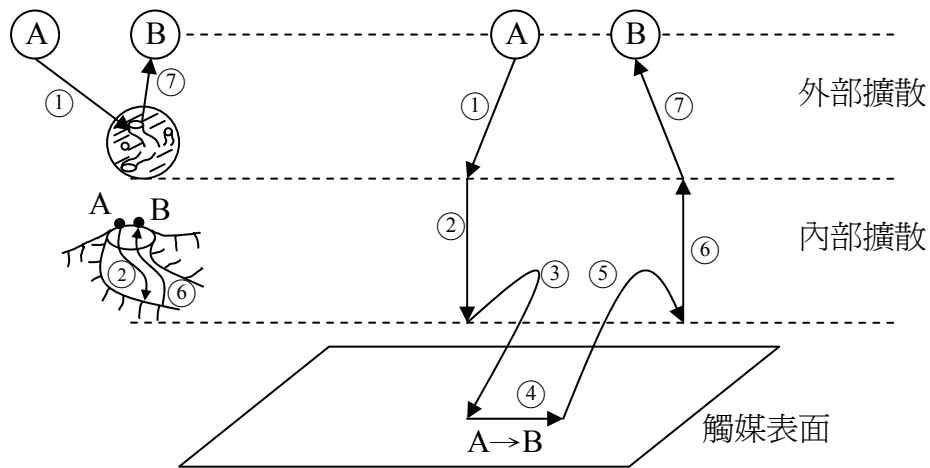
考慮一固體催化上的氣相反應，催化反應產生，意指至少一個，但通常是全部的反應物附著在表面上。這種附著即為吸附(adsorption)，一種為物理吸附(physical adsorption)，一種為化學吸附(chemisorption)。物理吸附類似冷凝(condensation)，其過程為放熱性，吸附熱通常相當低，在一階反應中僅只有 15 kcal/g mol。氣體分子與固體表面間的吸引力很弱，此類的凡得瓦力(van der Waals forces)包括下列相互的作用，有永久偶極之間(permanent dipoles)，永久偶極與感應偶極(induced dipole)之間以及中性原子與分子之間。溫度上升，氣體的物理吸

附會下降，當超過其臨界溫度時，只有相當少量的物質能夠被物理性吸附。

化學吸附能影響化學反應速率，被吸附的原子或分子與表面間以共價鍵連結，如同分子內的原子鍵結一樣。化學吸附也是放熱性，但放熱量與化學反應一樣大，在 10~100 kcal/g mol 之間。若催化反應涉及到化學吸附，則應在反應物的化學吸附可行的範圍內進行。

催化反應並非能在所有的固體觸媒表面上進行，而是發生在某些活性基 (active sites) 上。活性基可視為觸媒表面的一個點，能從此與吸附的原子或分子形成強力的化學鍵。每個活性基每秒所能進行反應的分子數目稱為轉換數 (turnover number, TON)，可量化觸媒的活性。

催化反應的步驟如下圖所示：



整體反應速率即為反應機構中最慢步驟的速率。若擴散步驟(①, ②, ⑥, ⑦)相對較快，則輸送與擴散不會影響整體反應速率。若反應步驟(③, ④, ⑤)相對較快，則反之，此時改變流體流經觸媒的條件，則會改變整體反應速率。

當氣體反應物A吸附於觸媒表面時，其反應式為 $A + S \rightleftharpoons A \cdot S$ ，其中S為活性基。則吸附速率可表示為 $k_A P_A C_v$ ，脫附速率為 $k_{-A} C_{A \cdot S}$ ，其中 k_A 與 k_{-A} 分別為吸附及脫的反應常數，為 P_A 氣體A的平衡壓力， C_v 為尚未吸附的活性基濃度， $C_{A \cdot S}$ 則為被 $A \cdot S$ 吸附的活性基濃度。整個吸附反應速率為

$$r_{AD} = k_A P_A C_v - k_{-A} C_{A \cdot S} = k_A \left(P_A C_v - \frac{C_{A \cdot S}}{K_A} \right)$$

其中， K_A 為吸附平衡常數。因活性基總濃度 $C_t = C_v + C_{A \cdot S}$ ，且當平衡時 r_{AD} 為 0，

所以 $C_{A \cdot S} = K_A C_v P_A = K_A P_A (C_t - C_{A \cdot S})$ 。整理後可得到下式：

$$C_{A \cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A}$$

此即為著名的蘭幕爾等溫式(Langmuir isotherm)。若將上式再整理可得下式：

$$\frac{P_A}{C_{A \cdot S}} = \frac{1}{K_A C_t} + \frac{P_A}{C_t}$$

即可繪出以 $P_A / C_{A \cdot S}$ 為 P_A 函數的直線圖形。

若 A 為雙分子氣體，而吸附時會先解離成兩個原子再進行吸附，則其蘭幕爾等溫式為：

$$C_{A \cdot S} = \frac{(K_A P_{A_2})^{1/2} C_t}{1 + (K_A P_{A_2})^{1/2}}$$

其中， P_{A_2} 為雙分子氣體時的壓力。同樣可重新整理成下式：

同樣可繪出 $(P_{A_2})^{1/2} / C_{A \cdot S}$ 為 $(P_{A_2})^{1/2}$ 函數的直線圖形。

$$\frac{(P_{A_2})^{1/2}}{C_{A \cdot S}} = \frac{1}{C_t (K_A^{1/2})} + \frac{P_{A_2}^{1/2}}{C_t}$$

$$C_{A \cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_B P_B}$$

兩種氣體反應物 A 與 B 進行催化反應為最常見到的討論形式，故在此仍列舉出其蘭幕爾等溫式。

其中反應物 A 與 B 均為一階吸附反應，脫附也為一階反應，吸附時均為分子形式，意即不會先解離成原子。蘭幕爾等溫式的重要的假設是，對於每個分子與活性基而言，每個吸附發生的機率是相等的，也就是假設吸附表面是平整的。

相較於蘭幕爾等溫式著重要氣體分子單層吸附在觸媒的固體表面上，BET 理論提出多層吸附，且符合下列假設。(a) 氣體分子可無限制在固體表面上進行多層物理吸附；(b) 每一層吸附之間，彼此並無影響；(c) 蘭幕爾理論可應用在每層吸附上。因此可得出下面之 BET 等溫式：

$$\frac{1}{v[(P_0/P)-1]} = \frac{c-1}{v_m c} \left(\frac{P}{P_0}\right) + \frac{1}{v_m c}$$

其中，P 與 P_0 為在吸附溫度下，被吸附物質的平衡壓力及飽和壓力，v 為被吸附氣體體積量， v_m 為單層被吸附氣體體積量，c 為 BET 常數。c 的表示式為：

$$c = \exp\left(\frac{E_1 - E_L}{RT}\right)$$

其中， E_1 為第一層的吸附熱， E_L 第二層以上的吸附熱，即為液化(liquefaction)熱。同樣地，此式也可經由線性化，作出 $1/v[(P_0/P)-1]$ 對 (P_0/P) 的 BET 圖形。此式的線性關係只適用於 $0.05 < (P_0/P) < 0.35$ 之間。

在前面反應物 A 吸附於固體表面上的例子中，其反應式可寫為：

$$\frac{-dP_A}{dt} = k_2 \left(\frac{K_A P_A}{1 + K_A P_A} \right)$$

若吸附和脫附過程為決定步驟，即 $k_A P_A \ll 1$ ，反應速率式改寫成：

$$\frac{-dP_A}{dt} = k_2 K_A P_A$$

即為 1 階反應。若反應過程為決定步驟，即 $k_A P_A \gg 1$ ，則反應速率式將改成：

$$\frac{-dP_A}{dt} = k_2$$

則為零階反應。

在雙分子反應中，反應式為：

$$\frac{-dP_A}{dt} = k_2 \left(\frac{K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2} \right)$$

若同樣吸附和脫附過程為決定步驟，即 $k_A P_A, k_B P_B \ll 1$ ，則反應式可改寫為：

$$\frac{-dP_A}{dt} = k_2 K_A K_B P_A P_B$$

為二階反應。若 B 的吸附相對於 A 的吸附強，則反應式可改寫為：

$$\frac{-dP_A}{dt} = k_2 \frac{K_A P_A}{K_B P_B}$$

在此情況下，對反應物 A 而言，反應物 B 成為佔著活性基，而抑制反應物 A 的吸附，最大的反應速率會發生在吸附表面由兩反應物各佔一半的情形下。此即為蘭幕爾-辛希爾伍德機構(Langmuir Hinshelwood mechanism)。

燃料電池是一種電化學裝置，能將儲存的化學能直接轉成電能。此裝置包含一種電解質，夾層在兩薄多孔性電極之間。一為正極，提供燃料，通常為氫氣。另一為負極，提供氧化劑，通常為氧氣。燃料電池所需的氧氣通常以輸入空氣供

應。電解質液可供離子傳導。所有的燃料電池都有相同的基本原理，即將供應的燃料進行催化反應，此時電子會從燃料中釋出，經外部電路提供電力，離子則經電解液往相對電極移動，然後在負電極上出現副產物，主要為水和二氧化碳。隨著提供燃料和電極的不同，可進行不同的化學反應。

燃料電池主要是提供由陽極到陰極間的電子流所產生的直流電，電流量則視燃料的化學活性與數量，以及本身電池組消耗的電力而定。燃料電池的設計可藉化學反應保持電量，所以其可使用的時間依提供反應物的量來決定。大多數單獨的燃料電池很小，僅可提供 0.5 到 0.9V 的直流電。欲產生較大電壓可經由組合而得。

依照電解液的不同，可形成不同型式的燃料電池。分別如下說述。磷酸燃料電池(phosphoric acid fuel cell, PAFC)以高濃度的磷酸溶液作為電解液，以白金作為陰陽兩極的電極，操作溫度在 180~220°C，但一般在 200°C 左右，溫度不高，可使用較小的散熱器。相較於其他酸性溶液，使用濃磷酸的相對穩定度高，因此 PAFC 會在醫院，資料處理站或軍事基地受選用。其效率較低，大約只有 30~40%。以系統發展來看，PAFC 算是最成熟的燃料電池技術，而且已經進入商業化階段。

鹼性燃料電池(Alkaline fuel cell, AFC)使用氫氧化鉀水溶液當作電解液，電極的選擇很多，包括鎳、氧化金屬、尖晶石(spinel)及貴金屬等。當使用高濃度氫氧化鉀(85%)時，操作溫度會高於 PAFC 到 250°C，但也可使用較低濃度(35~50%)，操作溫度可小於 120°C。只能用氫氣作燃料，產生的一氧化碳具毒性，或二氧化碳會與氫氧化鉀反應成碳酸鉀，破壞電解液。AFC 曾在美國阿波羅號太空船登陸月球時使用，但也是唯一目前的用途，且有逐步被淘汰的跡象。其優點是方便設計，使用的電解液較為便宜。

熔融碳酸鹽燃料電池(Molten carbonate fuel cell, MCFC)使用熔融的碳酸鹽混合液作為電解液，此溶液的組成有多種變化，但主要還是包括碳酸鋰和碳酸鉀。其操作溫度約在 650°C 高溫，此溫度有助於溶液中的離子傳導，也因此不需要貴重金屬作為電極，一般可使用鎳或與鉻、鋁的合金作陽極，以氧化鎳作陰極。此燃料電池的操作性能受溫度影響大，從 650°C 的操作溫度降至 600°C，可使電壓下降 15%，其主要原因為離子和電子阻力增加。MCFC 已在具規模的工場中進行測試，且能達到 50~60%的效率，因其操作溫度高，所產生的廢熱亦能拿來

發電，整個熱效率更能達到 85%。缺點是電解液具腐蝕性，需持續供應二氧化碳到陰極，以產生碳酸根離子。

固態氧化物燃料電池(Solid oxide fuel cell, SOFC)使用一種陶瓷固相電解質，可減少腐蝕性和儲存的問題。為使適量的離子能進行傳導，系統的操作溫度約在 650~1000°C。高密度與氧化釷平衡的氧化鋯是較佳的電解質，其可提供在高溫下帶負電荷氧良好的傳導性。SOFC 陽極一般採用多孔鎳-氧化鋯或鈷-氧化鋯之陶瓷金屬複合物，陰極則通常採用塗鎂或鋇之錳酸鋇。由於操作溫度高，其廢熱仍可回收利用提升燃料效率，不過缺點是耐熱的製作成本較高，啟動時間較久。不過因為電解質為固態，電池可鑄成各種形狀，如管狀，球狀或單體狀(monolithic)。其效率可達到 50~60%的電效率，85%的總熱效率。

燃料電池程序整個基本設計包括燃料儲槽、燃料處理及燃料電池。燃料處理主要是將碳氫化合物和其他有機燃料轉換成含氫的成份並淨化處理供燃料電池運作。燃料可包括如石油腦及汽油的石油衍生液體，如甲烷及丙烷的石油衍生氣體，以及其他如甲醇及乙醇的燃料。產品氫氣則需在燃料電池所需的溫度、濕度及純淨度下供用。

燃料處理系統有一連串的处理程序，將燃料逐步轉變成符合燃料電池的需求。此外，另包含一個蒸氣供應系統，提供所需蒸氣。首先將燃料的硫份去除，這個步驟相當重要，通常要將硫份降到幾個 ppb 以下，可以接下來的流程更順利進行，且可確保產品高純度。尤其在初級處理中，將硫化氫的去除可免除像鎳基觸媒受到中毒。

其次的初級處理是將燃料分解成主要為氫氣、二氧化碳及一氧化碳的產物，使用的方式有催化蒸汽重組，自動熱重組，部份氧化重組及其他等等。催化蒸汽重組將碳氫化合物燃料和觸媒、蒸汽混合，再另加入熱量進行化學反應，此方式的效率高，且蒸汽能讓氫氣的產量增加。自動熱重組將碳氫化合物燃料和觸媒、蒸汽及氧氣混合，部份燃料用來產生反應所需的熱量，此法可適用各種不同形式的燃料進行重組。部份氧化重組與自動熱重組類似，但此法的操作系統較簡單，規模也較小，不用蒸汽，所產的氫氣也較其他方法少。

接下來的步驟為移轉轉換(shift conversion)，目的在減少產品內含一氧化碳的含量，同時也增加氫氣含量的比例。之後，選擇性氧化器繼續將一氧化碳降至

10 ppm 以下，目的在保護燃料電池的觸媒，最後的處理包括淨化及調節步驟，即將氨去除及將處理後產品的溫度與濕度調節符合燃料電池的進料條件。

一種新穎的微流體燃料電池(microfluidic fuel cell)，不用薄膜將燃料與氧化劑隔離，且以薄流的方式操作，提升鹼性燃料電池的效率，為小型電子設備提供便宜的電源。大型的燃料電池，在兩股流體匯流時，因擾流而產生混合；但在微型電池，流經兩併行的窄渠道而不混合，利用此種薄流的優點，可設計出更有效率的燃料電池。典型的燃料電池包含兩個電極和一個燃料源，一個氧化劑以及隔離氧化劑的薄膜。陽極的反應從燃料中的氫原子釋出質子和電子。質子穿過薄膜到陰極，與氧氣結合形成水。電子則經外部電路供應電子設備電流。新式燃料電池設備不用薄膜，而使用 Y 型渠道，將燃料與氧化劑兩細流合併而不混合，在兩個觸媒包覆的電極間，僅一釐米寬的渠道中且繼續平行流動。這樣的設計並不需要昂貴的薄膜，且其隔離的效果也不好，降低電池效能。

鹼性燃料電池的效能比酸性的好，不過因為使用薄膜的燃料電池卻不適用鹼性化學反應，主要是因為薄膜允許酸性燃料電池的質子通過，但在鹼性燃料電池中扮演同樣角色的較大氫氧離子卻不易通過。而且鹼性反應會產生碳酸鹽，而導致薄膜阻塞。但在微流體燃料電池中，氫氧離子可在燃料與氧化劑間自由擴散，而穩定的流動也可將碳酸鹽沖淨，不致於將裝置阻塞。

五、流體觸媒裂解工場之程序模擬器基礎控制設計

介紹

流體觸媒裂解工場由於能生產高品質的汽油，在煉油廠的角色舉足輕重。下圖為UOP公司的流體觸媒裂解製程，該工場主要的產量隨裂解的反應器操作溫度上升而增加，但受限於設備的機械性能。因此，為得到較高的產量，系統的操作應儘可能以較高的煉量在接近設備的容許溫度下操作，同時也必須注意避免超過在安全及環境考量下的限制，包括系統可能操作不穩定之時。裂解反應為吸熱反應，所以也應儘可能在較高溫度下操作，以得到較高的產量。此外，為使觸媒能充份再生，再生器也和反應器一樣，也必須在設備的機械性能容許下，儘可能在高溫操作。¹操作的限制尚包括煙囪對於一氧化碳排放，亦可能對環境造成影響。²反應器與再生器之間的差壓對於觸媒循環有重大的影響，也因此深深地影響到其他重要的製程變數，必須限制其變動。反應器與再生器的操作壓力限制則在建廠時選用的機械材料已決定。適合製程的最佳操作必需在最高煉量下，將所有限制因素列入考量，獲得最大的產量。以下兩種操作變數組合將可達到這項目標：

(I) 將總進料流量(包含新鮮進料以及 slurry recycle)納入可操作變數。這些參數對於所有的製程變數都有相當大的影響，因此可作為非常有效的可操作變數。然而，在這條件下，必須避免因總進料流量變動所導致產量下降。

(II) 將進料流量設定成常數，可得到預估的產量，接著在可操作的輸入變數中，

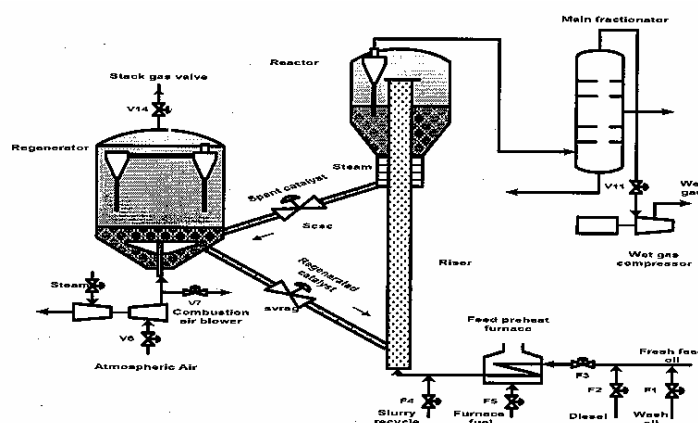


Fig. 1. UOP type Fluid Catalytic Cracking Unit.

選出無進料流量的控制變數結構，可妥善地控制製程。

¹ 再生器高溫操作，雖可儘量將coke燒除，亦需考量觸媒的耐熱性。

² RFCC製程因有CO爐的設計，若操作正常，並無CO的排放，但視進料油品，有NO_x和SO_x的排放考量。

UOP FCC 工場之動態模組與開放性迴路模擬

UOP 的流體觸媒裂解製程在世界上的許多煉油廠廣泛使用，因此作者選用該製程作為研究標的。FCC 工場在煉油廠中扮演一個極重要的角色，其生產汽油及柴油，也生產乙烯、丙烯及異丁烯等高價值的氣體。進料則包含常壓製氣油，真空製氣油和加氫裂解塔底油。FCC 工場現今石油煉製業中所扮演著重要的經濟角色，吸引學術界及業界相當大的興趣，加強研發及其模組控制演算，來提升其效率。其已被模組化的主要部份包括進料系統，預熱系統，反應器，再生器，空氣鼓風器，濕氣壓縮機，觸媒循環管線以及主分餾塔。將工業上 FCC 工場模組化實際上相當困難，因為製程變數之間有強烈地緊密關聯，以及反應器內裂解反應的動力行為，焦炭沉積導致觸媒活性衰減和再生器內焦炭燒除程序等具有較大不確定性。

已被開發出的 FCCU 模組程式，能基本地涵蓋該類操作中工場的描述與操作資訊，並能相當複雜地攫取實際發生在 FCCU 系統的主要動態效果，其多重變數彼此緊密關聯，且高度非線性。所開發出的模擬器能描繪出一般商業化 FCC 製程的主要動態特性。其他的模組包括能預測高價值產品的產率及汽油辛烷值的產率模組等。

動態模擬器被用來研究製程的動態行為，建立在非線性模組的 FCCU 的模擬系統已可運作且進行研究。研究 FCCU 的動態行為可使用開放性迴路及封閉性迴路，使用 PID 控制運算可使封閉性迴路變得穩定。不同的控制結構可用來作為操作中嚴重擾動的研究，最常見的即是進料流量的改變。在這份研究中，5% 的擾動在 1.5 小時內即趨於穩定。

FCCU 的控制結構選擇與多變數 PID 控制器

最佳的控制系統是能將在限制界限的擾亂降至最低，並將系統在最短時間內恢復正常操作。PID 控制器經研究來測試不同的控制結構，使用相對增益陣列 (relative gain array, 簡稱 RGA) 來判斷出工場的本質控制性質。RGA 的定義為在其他迴路在良好的控制之下，一輸入值 j 與輸出值 i 之間的開放迴路增益與其閉路迴路增益之比值。RGA 是多重輸出輸入值 (multi-input-multi-output, 簡稱 MIMO) 系統中，輸入值與輸出值之間關聯的好用的量測工具。RGA 線性系統在不同的操作點對非線性矩陣系統線性化時，會有不同的配對。

當輸入值與輸出值之間的相對增益接近 1 時，表示對這些獨立的控制迴路為最好的控制配對。在這份研究中，顯示出在不同的控制結構中置入了 PID 控制器，並且在 6 個研究控制組合中，得出一個最佳的結果。這個控制組合使用再生器溫度(Treg)及反應器升舉管溫度(Tr)等兩個控制變數，以及加熱爐燃料流量(F5)與含碳觸媒控制閥(svsc)等操作變數。其他的組合因與部份控制迴路間有相當強烈的關聯性，而沒有明確的結果。

MIMO 系統設計使用來模擬兩個獨立控制迴路的 PID 控制。在這份研究中，測試每個控制器用來控制 Tr 及 Treg。例如以操作加熱爐燃料流量來控制反應器升舉管溫度，以含碳觸媒控制閥控制再生器溫度，可達到不影響其他控制變數的穩定環境，得出良好的結果。此外，受增加新鮮進料流量的擾動用來研究 PID 控制器的表現。

結論

用來模擬的 FCCU 動態模組包含了幾個主要的系統，尤其包含反應再生系統複雜的動力學和分餾塔的動態模組，以及可預測高價值產品的產率和汽油辛烷值的模組和升舉管部份的動力模組，為其新穎之處。

動態模擬器可用來研究製程的動態行為。進行這些模擬時，可藉由設定點與擾動變化的不同組合，避免取消特定輸出動態值的可能。利用依據簡單的 RGA 矩陣的可控制性分析，來研究製程變數間的相互關係。PID 運算則用來測試不同的控制結構，結果顯示有些控制迴路間有強烈地牽連，使得 PID 控制器的參數很難調整至符合所有的輸出結果。所以這些控制器必須謹慎使用，否則容易使程序產生失敗。因此，非常需要一個更先進的多變數控制器，來掌控動態製程中具較強的連結，所以使用具 PID 控制器的 MIMO 系統來達成控制目標。

參、研習心得與建議事項

- 一、此次研習的主要內容，包括五個主題，分別為化學產品設計、分離與下游加工、應用工程實習與應用異相催化，以及與該研究所博士生討論有關流體觸媒裂解工場之研究。研習的地點在英國羅浮堡大學，化學工程研究所高階方法工程的碩士課程。
- 二、化學產品設計為一個相當實用的方法學。通常化學工程的學生，都是把學習的重點放在製程研究上，卻很難有機會去瞭解一個化學產品開發的過程。從顧客的需求來判斷需要什麼樣的產品，並利用這些需求去建構出更明確的產品規範。然後提出構想來滿足這些需求，然而好的構想並不容易找尋，通常需要許多的構想才能出現一個好點子，藉由整理與編輯，並使用矩陣篩選法最好的幾個構想。接著用更詳細的科學和工程計算，來確認最佳的選擇。如果新產品是一個化學產品，則可能先用現有的設備批次製造。如果涉及到化學變化，則需要機械工程來建立製造技術。最後，考量的經濟層面的問題，是否申請專利或保留為商業機密，以及投入的資金成本計算，都需要慎密的評估。
- 三、分離與下游加工課程的目的在研習以化學作用為基礎，進行批次分離(batch separations)的理論與實務；分離的選擇與連續性；以物理分離法進行產品區隔，包括液-液萃取，結晶化，噴灑乾燥及冷凍乾燥，氣相及液相吸收，離子交換，色層分析法，電泳，超過濾及微過濾法。
- 四、應用工程實習課程的目的在培養對工程裝置的實務技術，工程製程的操作能力，以及加強結合理論與實驗工作之間的關聯。灌輸重要的安全觀念，例如化學危害與風險評估等。同時也培養數據分析，報告寫作以及簡報技巧的能力。
- 五、應用異相催化程序課程的目的在探討影響工業觸媒效能的物理及化學因素，著重在觸媒的設計、製造、特性、活性衰減及再生，以及化學動力學與輸送效應在觸媒反應器最佳設計中所扮演的角色。首先介紹催化的背景，歷史和觸媒製程的發展，以及觸媒材料與製備，觸媒試驗與特性，包括組成及結構，表面積與孔隙大小分佈。
- 六、在研習期間，與該所博士班學生 Redah Alsabei 共同討論有關流體觸媒裂解

工場之研究。這項研究的主要目的是研發出一種便於使用者的程序模擬器，其使用以目標為導向的程式環境，可用於瞭解製程動態，操作員訓練，控制結構設計以及控制器調整。由於正好與筆者過去之經驗相關，遂提供交換實務上之操作經驗供其參考。

七、為使報告更充份完整，遂將在國外研習期間所完成大部份完整的報告及簡報內容附錄於后。其中部份的內容可能與其他研究生經小組討論後，或者分工合作所完成。除了供指導教授評閱外，並無在其他期刊文物發表過。但內容所參考之文獻，均列於各篇之末。

八、非常感謝有這機會能到國外研習，尤其是在工作數年之後，仍能回到學校再次進修，彌足珍貴。在國外求學的這段期間，除充份感受英國的學術氣息，也與來自世界各地的同學在此萍水相逢，收獲甚為豐富。

九、公司有此美意培養員工到國外研習，不僅能提升員工視野以及競爭力，也希望能夠為公司的未來發展有所助益。如由員工自行選擇訓練機構，自然能依本身需求，得到適切的效果。但可能因為個人資源有限，能選擇的選項自然較少。若公司在提供這樣機會的同時，能同時考量提供其他相關的資源，相信對公司或個人均能有更大的助益。例如能透過公司與國外專業訓練機構聯繫，選擇適合員工培訓的項目，可在內容、時間及經費上獲得最佳的效果。

肆、 附錄

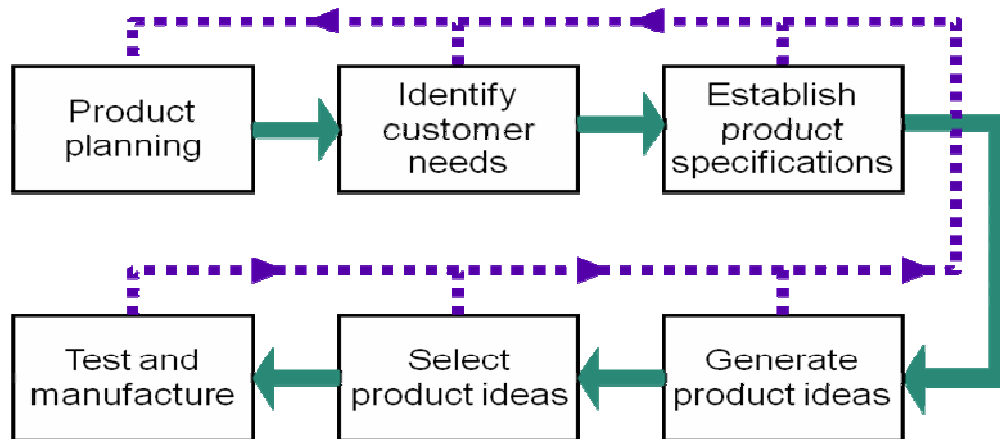
一、 Total Solution Technology On Aircraft Deicing

Executive summary

-The objectives of the product development and the conclusions

The aircraft de-icing method has been developed since aircraft has been invented. There are also many reviews about aircraft de-icing to be edited. We can find them in many published reports. In order to analyse and solve this kind of problem, we can probably classify the procedure into several steps which will be demonstrated later. We also care about the customers need as well as environmental impact. Sort and discuss them in order to pursue the best resolve method. So we will list the specification of the product and provide our recommendations.

The content of this report is mainly to follow the project report list and also the generic design process, which is the core of the module of Chemical product design. The introduction will be induced the purpose of the product and the existing technology. Then review these methods and identify the customer needs. The summarization and more findings and details of the deicing product will also be described. These methods will subsequently be estimated and screened out three ideas. Through selection, we will have a conclusion at last.



Introduction

-the purpose of the product and the existing technology

Since human beings discovery wheel, they always think of arriving at farther place fast and timesavingly. Aircraft is nowadays the best choice for transportation which can carry people around the world. But as proverb says, the water can float the boat, as well can capsize the boat. This kind of human being's great invention also brings several disadvantages and one of them is safety. Federal Aviation Administration

(FAA) requires the deicing and anti-icing of aircraft surface to ensure the safety of passengers. Normally airport deicing operation may result in severe environmental impact if discharges don't have been well-performed. The toxicity of additives added to deicing and anti-icing agent may also lead to the potential aquatic life and human health impact. We need to consider alternative methods or substitutes which can improve this kind of awkward situation and to look after the compatibility of aircraft safety and reduction of environmental impact.

Deicing is to remove snow, fog, and ice from aircraft surface while anti-icing is to prevent the accumulation of snow, fog, and ice on the same surface. The procedures can be divided into two categories, i.e. using mechanical means and through the application of chemical agents. Mechanical means includes brushes, booms, and plows but it depends on the weather condition to use them. The most common usage of de-icing/anti-icing airplanes is using aircraft de-icing fluids (ADFs). The aim is to remove snow, frost and ice from aircraft surfaces. The main component of ADFs is either ethylene glycol (EG) or propylene glycol (PG). The rest compositions include corrosion inhibitors, wetting agents, surfactants, thickeners, and other chemicals. The primary environmental concern with using ADFs is high chemical oxygen demand (COD) or biological oxygen demand (BOD) of untreated wastewater as well as the potential toxic effects from additives, especially corrosion inhibitors. In order to reduce the impact of environment, it is considered to look for alternative fluids or methods for de-icing airplanes which is much less environmentally harmful. Subsequently, there are some existing technologies to be introduced.

When deicing/anti-icing progress, ADFs mixed with additives are sprayed to the target aircraft with deicing facilities. There are four classes of ADFs presently: Type I, Type II, Type III and Type IV. Type I is commonly used for deicing procedure while the others are developed to anti-ice aircraft. Each of them has different composition and allowed holdover time which is the interval between the aircraft treated and taken-off. Normally Type I can be recycled rather than others, so some airports separate into two-step procedure of deicing and anti-icing. Type II and Type IV are used for all kinds of aircrafts while Type III is suitable for smaller and commute airplane. Some airlines choose Type IV exclusively for only anti-icing because of its longer holdover time. Others choose Type II due to less expensive because Type IV needs extra facility. All researches focus on how to reduce or eliminate the usage volume of ADFs as much as possible and so less environmental impact. Such as looking for substitutes of ADFs, alternative methods to deicing/anti-icing or combining them. There are also some recommendations suggesting on improving the operation efficiency such like shortening the spraying distance and strengthening the skill of operators. The estimated benefit will be extremely large by summing up all

airplane landings and taking-offs annually.

There are some other nonchemical methods used to replace ADFs and reduce environmental impact. They are mechanical and thermal means but quite depend on the weather condition. Dry and powdered snow can be swept by booms and brushes. This method can only be used in the early morning because of time- and labour-intensive work. Hot air blower can also be used to remove snow mechanically and make air pollution in the airport area. The thermal mean is using infrared (IR) to heat the aircraft. This method can deice but can't anti-ice the airplane, so Type IV is needed to apply following IR deicing. Although using thermal mean cannot completely replace glycol-based fluids, it greatly reduces the volume required.

Although there are many ways to deicing/anti-icing aircraft, most of them are developed from using ADFs which is very harmful to the environment. When considering pollution prevention, there are several ways we can do some efforts. First, developing alternative fluids friendly to the environment can eliminate the glycol-based fluids. Second, minimizing the fluids applied to aircraft by developing better fluids, improving operation management, or developing another technologies combined or replaced into some or all the procedure. Third, developing the glycol recycling technology.

At present, there are several organization and professionals trying to develop the alternative fluids of deicing/anti-icing fluids, which must be environmental benign product. Most of them are thought at preliminary stage and need some time to become commercial product. Substitute products should be biodegradable and have the same effect on deicing/anti-icing procedure as well as the cost should not be too expensive. One of the researches is exploring the structure of antifreeze molecules which can exhibit ice crystal growth.

Needs

-review the methods for identifying customer needs and summarise your findings for the de-icing product

Without removing ice or any other containment, there really exists potential danger on aviation safety. That is why Federal Aviation Administration (FAA) insists on the deicing/anti-icing of aircraft to ensure the safety of passengers. However, the present method using aircraft deicing fluids (ADFs), no matter more or less, indeed results in environmental impact. The different improving directions described above. Here will be discussed further about these methods and meet the customer needs.

Alternative substitute product is the first for consideration because this is the best way to eliminate environmental impact from glycol-based aircraft deicing fluids.

There are several researches is under in progress but it seems only at the preliminary stage to be brought to the commercial products. The characteristics of substitute products should be environmentally harmful, less toxic, and biodegradable. In addition, they should be as effective to deice aircraft as present ADFs and noncorrosive to aircraft as well. We cannot expect too much on this method but fund on the project and concern the progress if possible.

Now that we cannot have alternative substitute products at once, the reduction of usage ADFs would be more practicable. This strategy could consist of several sub strategies. To reduce the consumption of ADFs means to reduce environmental impact, also to reduce the cost of purchasing chemicals and subsequently wastewater treatment. Reduction of application and operational rates is very practicable and applicable. Improving the application and operation management could be effective and noticeable to reduce the usage of ADFs, such like training staff well, shortening the applying distance, optimizing the composition ratio applied and reducing secondary deicing operations.

Otherwise, there are different deicing techniques we can use to partially replace or reduce the usage of ADFs. They cannot be applied to replace the usage of ADFs totally because of restrictions to be found, such like weather conditions and safety reasons. But no mention about restrictions, these techniques indeed could be helpful to reduce the usage of ADFs in some suitable occasions.

Two Step Deicing is to separate the deicing procedure by applying ADF type I and II in different steps is to be considered to reduce the usage of ADF noticeably. It is because ADF type I is recyclable but type II is non-recyclable. In addition, after applying type I, type II can be determined what quantity should be applied according to the weather condition and the deicing concept at an airport. This application could really reduce the usage of ADF type II. By separating recyclable and non-recyclable fluids, the cost of post-treatment would be also reduced.

Hot Water Deicing is to use very low glycol concentrations of ADFs. This could only be applied without precipitation and on centralized area. Although it seems a practicable way to reduce the ADF usage and so is less environmental impact, hot fluid cannot melt all the ice and snow on the aircraft surface and low glycol concentrations lead to refreeze water on the aircraft surface, especially at the critical part of the aircraft. This results in significant aviation safety concern and would also have environmental impact if ADF type II is applied to compensate this considerable problem.

Hot Air Deicing is to pressure air to remove frozen accumulations from aircraft surface. This aims to reduce ADF usage but would make air pollution at airports more serious. The air is pressurized by a turbine jet engine mounted on a special vehicle

and cannot be applied at any angle and height. At the same situation, ADF type II would also be applied after deicing procedure and the improvement to environmental impact is still limited.

Infrared Deicing is another choice to deice aircraft. There are three ways to apply this technology nowadays and each belongs to its own company. One is a fixed-hanger deicing system, another is a mobile system and the rest one is computer-controlled infrared laser. All of them also need to apply ADF type II after deicing procedure.

Glycol Recycling is to recover glycol from ADF-containment wastewater and is applied at many airports. The concept of this method is to remove water, suspended solids, surfactants, corrosion inhibitors, and other additives from ADF-contaminated wastewater. Typically, this process includes a series of filtration, ion exchange, nanofiltration, flocculation, reverse osmosis, evaporation and distillation. Each of them has its purpose of removing certain containments. Using distillation can produce products with concentrate glycol as high as 98 percent, however, it is an energy-intensive separation way.

Airports collect wastewater from aircraft deicing/anti-icing operation and prevent or minimize discharges to sewage treatment system. There are a variety of collection methods, including storm sewer plugs, designated aircraft deicing pads, storm drain valves, gate and ramp area drainage collection systems, temporary aircraft deicing pads, and specially designed glycol-vacuum vehicles. The combination of these methods would be used and vary with different certification.

In order to collect wastewater more efficiently, some airports like Minneapolis-St. Paul International Airport, constructed aircraft deicing pads, where provisions for containment and collection.

Metrics

-discuss the product specifications and metrics and present the results from the “sanity check” calculations (detailed calculations should be placed in an appendix)

There are many methods to be considered to an alternative substitute or method. According to the situation of the recent development of these technologies, they will be estimated by four aspects. The applicable or practicable item is targeted at if the technique would be easily achieved. The cost down or benefit item is estimated if the new technique would bring more profit than the old ones. Although our aim is to reduce environmental impact, it is necessary to notice if the impact is really to be reduced. At last, aviation safety is still our top priority and any discount on this item won't be allowed.

Alternative method \ Estimate item	Applicable or practicable	Cost down or benefit	Environmental impact	safety
Substitute chemicals				
antifreeze molecules	!	*	***	***
Alternative methods of removing snow				
Two step deicing	**	*	*	**
Hot water deicing	**	*	*	!
Hot air deicing	*	*	*	!
Infrared deicing	**	*	*	*
Improved sewage treatment	**	**	**	*
Glycol Recycling	***	***	**	*

Three-level ranking: *essential* (* * *); *desirable* (* *); *useful* (*); *latent needs* (!)

We can't find any substitute which can totally replace ADFs. Antifreeze molecules are still under very preliminary stage and far from to be applicable, although this technique is substantial to overcome completely the icing problem we face on now.

Since ADFs cannot be totally replaced at present technology, there are many methods to be developed to minimum the usage of ADFs. These methods are mostly applied to practical use, but there are some restrictions on using them. In addition, these techniques are applied to deice aircraft and it should be to apply chemicals to anti-ice aircraft. This also cannot avoid having environmental impact. Another concern is the refreezing phenomenon just after the deicing procedure and this results in the safety concern of aircraft.

Presently, the most important and practicable application to airports is to improve sewage treatment. No matter to reduce environmental impact or recycle ADFs fluids, you can only expect to have good collection system and treatment. Due to applying deicing/anti-icing agents is to spray, it is not easy to control recovering the chemicals. That's why we put more weight on this technology.

Glycol Recycling can reproduce the product and reduce the impact to the environment. In addition, recycling can make profit by selling products and lower the cost on the deicing/anti-icing operation. This is discussed mostly at our group and this would be more interesting and discussable to present issue. This technique is less relative to aviation safety but if we can operation it well, it is also helpful to reduce environmental impact as well as the impact potential aquatic life and human health.

Ideas

-discuss the generation of ideas and the sorting into categories

IDEA 1:

At the Minneapolis-St. Paul International Airport, Inland Technologies, Ltd. installed its first U.S.-based glycol recycling facility in the spring of 1997. The facility processes glycol-contaminated storm water from aircraft deicing/anti-icing operations and also recovers glycol from spent deicing fluid collected at Des Moines International Airport in Iowa. The main recycle product is the more profitable propylene glycol. The purity of the product is only 50% glycol solutions but the demand for pure and concentrated glycol product is generally greater. We hope to develop the facility to recover higher concentrated glycol product from Inland facility product.

IDEA 2:

Due to the similarity of boiling points of ethylene glycol and propylene glycol, mixtures of them are difficult and expensive to separate. Recovered product including of mixture may be difficult to sell. We hope to develop more efficient equipment to separate the mixture.

IDEA 3:

It is not easy to recovery all wastewater from aircraft deicing/anti-icing operation, especially during the heavy snowfalls and to transport it to designated collection areas. Most aircraft deicing/anti-icing operations are at passenger terminals and parking ramps, snow collected at these places should be contaminated with ADFs. We hope to develop a suitable pad used to store snow contaminated with deicing/anti-icing chemicals.

Selection

-review the various stages of selection, showing the results of crude and detailed concept screening (include calculations, as necessary, in an appendix)

After reading as many as possible materials searched from available sources, we conclude three ideas as above. Actually we can have more ideas to put into the development of solving problems due to aircraft deicing/anti-icing operation. Now we only choose three of them to be considered because of their importance.

IDEA 1 is based on the recycling glycol product, which is not concentrated enough and the market need is high concentrated recycling glycol, which is more profitable than diluted solution. While IDEA 1 is focus on the concentration of recycling glycol, IDEA 2 is trying to separate mixture of ethylene glycol and propylene glycol. The profit is also different between mixture solution and mono-solution. So it should be profitable to purify the mixture. IDEA 3 is different

from the above two ideas as it would like to improve present using pad to collect and store contaminated snow wastewater.

IDEA 1 would be the first one solution we can get involved. Because glycol recycling not only can solve the problem of drainage of wastewater containing too much glycol-based fluids, but also make profit to airports by recovering glycol and reproducing ADFs fluids. Although the glycol recycling is applied, the concentration product of glycol is not high enough, which doesn't meet the demand of the market.

Conclusions

-justify and recommend your choice of product technology; obtain, through the literature and using calculations, a detailed set of final product specifications

Most of the present technologies of deicing/anti-icing are reviewed at this document. The target is to find a substitute or alternative method for deicing plane which is much harmful environmentally. A total solution technology is considered and comprises substitute chemicals, improved sewage treatment, recycling of the glycol or substitute and alternative methods of removing snow. After reviewing existing technology, we focus on improved sewage treatment and glycol recycling, and provide three ideas for customer needs. Subsequently, glycol recycling is chosen for our devotion to throw in.

Now that the Minneapolis-St. Paul International Airport in Minnesota is applied as the study case in our class, we can investigate the situation at this airport. Inland Technologies, Ltd., a waste management company based in Truro, Nova Scotia, installed its first U.S.-based glycol recycling facility in the spring of 1997 at the Minneapolis-St. Paul airport. Inland processes glycol-contaminated storm water from aircraft deicing/anti-icing operations and operates the glycol recycling system. The fee based on the unit operating costs is approximately \$0.10 to \$0.20 per gallon of recovered product. The sale of the recovered product has always covered the operating costs. Since the capacity of this recovering system is sufficient enough, the facility also recovers glycol from spent deicing fluid collected at Des Moines International Airport in Iowa. The amount is approximately 4,000 to 5,000 gallons of ADF-contaminated wastewater each winter.

Since Inland's facilities at Minneapolis-St. Paul International Airport on recover the profitable propylene glycol and the recycling product is only 50% glycol solutions, we can develop better facility to produce more concentrated glycol solution and meet the demand for pure, concentrated glycol product.

Further Recommendations

-make recommendations about how to protect the intellectual property related to the

product technology; note any further information that would be required before process design and manufacture, detailing any experimental work required to collect data, or for proof of concept

It is really very short time to complete this project assignment. We don't have enough time to fully understand the whole deicing/anti-icing industry even though to write a report providing further recommendations. But as an employer or company manager, it is impossible to allow you to have much time for looking for the information and understanding them. Your boss, completers, and even clients won't wait for you. So this time we are fortunate to have a direction which giving by professor and narrow the range to only finding the alternative way of deicing/anti-icing methods, not including of airport/airline management, government relationship, also relative industries and etc. We have to admit all the relative issues could not be neglected in practice. Sometimes we have to emphasis the Health and safety and risk management on site operation and the operator won't just tell you that is or isn't good for use. They might complain more about this and we chemical engineer cannot handle.

It is good for us to have brainstormed at the beginning of the semester, especially the first week. Actually I thought we have a honeymoon at the first month and take easy to know everything here. I just arrived at Loughborough for one week and it is not ready for arranging my accommodation at that time. We have to quickly acquaint with the environment and sources for study and research. Without this report and assignment, it should take longer time to know the resource in the library and university network. Besides, it is better for me to spend more time in the library. We don't have enough time to know team member and just discuss the project with each other although we all come from different countries and this makes the discussion more difficult.

References

-provide a list of references cited in the body of the report (www addresses are quite acceptable as reference sources); ensure that the report is properly referenced.

EPA, U. S. (August 2000). *Preliminary Data Summary*. Washington, DC: <http://www.epa.gov/waterscience/guide/airport/airport.pdf>.

Hoffmann, A. (1998). *An Investigation of The Feasibility of Recycling Deicing Materials at Munich Airport*. Loughborough, United Kingdom: Loughborough University.

Valerie A. Bennett, T. S. (2005). Comparative overwintering physiology of Alaska and Indiana populations of the beetle *Cucujus clavipes* (Fabricius): roles of antifreeze proteins, polyols, dehydration and diapause. *Journal of Experimental Biology* , 208, 4467-4477.

二、Aircraft Deicing Recycling



AIRCRAFT DEICING Recycling

Group F

Introduction

This project was embarked on to attempt solving the following deicing issues:

- Safety (***)
- Environmental impact (***)
- Cost (***)
- Time (**)
- Profitability (**)
- Mechanical impact (**)

*** - essential

** - desirable

Identified product ideas

- Substitute chemicals
- Heating methods
- Mechanical methods
- Separation and recycle
- Waste treatment
- Aircraft alteration
- Hybrid

Advantages of glycols

- The most common technique
- Low freezing point (-47C)
- Biodegradability
- Ease of handling
- Low corrosive nature to metals
- Low flammability
- 10 to 1,000 gallons of ADF may be used on a single aircraft



The high biochemical oxygen demand of glycols

Oxygen Measure	Ethylene Glycol	Propylene Glycol
Literature values for BOD (at 20EC), mg O ₂ /L glycol	400,000 - 800,000	1,000,000
Literature values for BOD (at 20EC), g O ₂ /g glycol	0.4 - 0.7	1
Ethylene glycol manufacturer values for theoretical oxygen demand (i.e., ultimate BOD), g O ₂ /g glycol	1.3	1.7
Propylene glycol manufacturer values for average COD:BOD ratio	2.08	2.23

Waste water + high fees

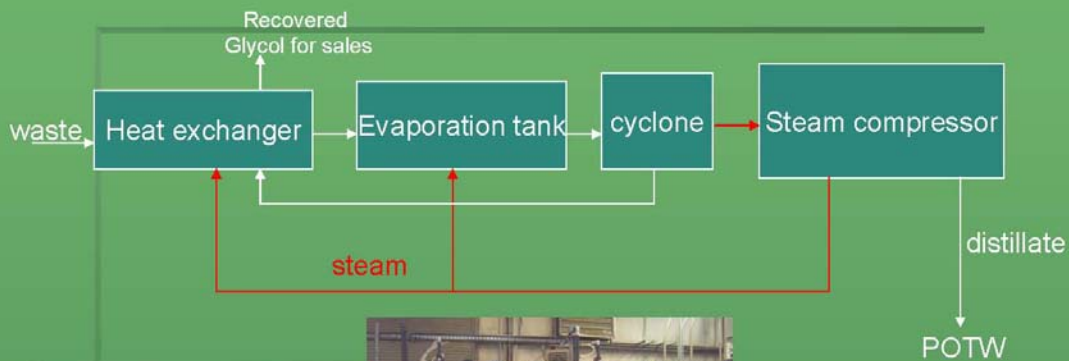


RECYCLING GLYCOLS

Recycling method selection

	Flocculation+distillation	Evaporation+distillation	Ion exchange+distillation	Flocculation + reverse osmosis	Evaporation
Concentration of glycol	98%	99%	55%	18-20%	50-60%
Energy requirements	High intensive	High intensive	High intensive	Low intensive	Low intensive
Operating cost	High	High	High	Low	Low
Wastewater with glycol	10%	2%	less than 1.5%	At least 10%	At least 5%
Ability to separate mixture of propylene and ethylene glycols	No	No	No	No	No

Mechanical Vapor Recompression (based on evaporation)



Advantages

- Self-contained and portable
- Energy for HEX is supplied by steam produced during the process and by hot recovered product
- High recovery of product (50-60%)
- High unit capacity (264 gph)
- Low cost (\$0.10 - 0.20 per gallon of recovered product)
- Coverage of operational costs by sale of recovered product

Disadvantages

- Can not separate mixtures of glycols
- 50% solution is to be concentrated to obtain market value

Perspectives

- To produce reformulated Type I fluid by blending 50% glycol product with additives such as wetting agents, corrosion inhibitors, and flame retardants.

三、Separation and Products from Milk and Cheese Whey

Summary

The products from milk and cheese whey are common in our daily life. The separation of milk and whey proteins into individual components has been a considerable interest. The common properties of these products will be introduced as well as the common separation methods that are widely used in the food, the pharmaceutical and the related industries will also be described in the Introduction section.

The attention is focused on the products and ingredients separated from milk and cheese whey. The most recent reports are reviewed and the separations of these products are described in the discussion section.

According to the discussion below, some important ingredients contained in milk are of significant function which can't be ignored. For example, according to (M.S. Noble, M.B. Wheeler & W.L. Hurley, 2000), α -Lactalbumin shows its high value by engaging itself in the process of lactation, plays as an essential role. β -lactoglobulin also suggests its value in the transport among important proteins in milk by binding to several hydrophobic molecules (Jost, R. 1993). Immunoglobulin G can be efficiently used for eluting which is consistent with measurement of immunoglobulin G titers in most frozen storage of ascites monoclonal antibodies (Mabs) for more than one year. The Mabs can be serotyped of outer membrane antigen (Angeley Davis & Reitz, 2006). IGF-I belongs to the multi-functional regulatory peptides for cell growth and survival. It also can be part of a complex system that cells use to communicate with their physiologic environment. Some neurotrophic factors, just like IGF-I, (Kuncl, 2001) can be used for the protection of the postnatal motor neurons from slow glutamate injury in organotypic spinal cord. When it is applied at the time of human spinal cord injury, IGF-1 treatment can rescue substantially, even if the chronic neurodegeneration has been a 7-8 week process and the motor neurons have been injured already.

For separation, several separation methods are widely applied. Electrophoresis, Liquid phase separation, Mass Spectrometry, High-Performance Liquid Chromatography (HPLC) are mentioned as below. And for these important proteins in milk, scientists have worked out a few effective ways to separate them out of raw material. For instance, liquid-solid extraction system based on Tween 80/phosphate and immobilized metal affinity chromatography are proved to be two methods to separate α -Lactalbumin out of milk whey. The separation of β -Lactoglobulin from milk whey can also be achieved by applying liquid-solid extraction system and preparative-scale ion-exchange chromatographic process. In addition to the two main proteins mentioned above, Immunoglobulin G is also a kind of product of great value

and commercial productivity which can be obtained by anion- and cation-exchange columns. Last but not least, heparin affinity chromatography and immunomagnetic separation (IMS) are also discovered by researchers as practicable methods to extract IGF-I and Escherichia coli from milk.

Introduction

The separation of whey proteins into individual components has been a considerable interest. Each whey protein has its own functionalities and properties which are of value in many industries, such as the food, the pharmaceutical, and the related ones. Some important physical properties of the major proteins found in milk are summarized as below.

Table 1. Characteristics of major whey proteins (2)

Protein	Concentration [g/L]	Molecular weight [g/mol]	Isoelectric pH
β -Lactoglobulin (β -Lg)	2.7	18,362	5.2
α -Lactalbumin (α -La)	1.2	14,147	4.5–4.8
Bovine serum albumin (BSA)	0.4	69,000	4.7–4.9
Immunoglobulin (Ig)	0.65	150,000–1,000,000	5.5–8.3

Table 1. Characteristics of major whey proteins (Ritchie, 2007)

The reduction of the fat and lactose content of milk commercially uses membrane processes. For example, a two-stage ultrafiltration process for obtaining an α -La enriched product from raw acid whey or mixed whey. (Roger, 1984) The other example is to obtain an α -La purification greater than 10-fold for whey protein isolate using two-stage high performance tangential flow filtration (HPTFF). (Cheang, 2004)



Fig 1 Hoefer SE 400 Sturdier Electrophoresis units

Accessed by 30, Oct, 2008

<<http://homepages.gac.edu/~cellab/chpts/chpt4/figure4-1.html>>

The purpose of this document aims at the possible products from milk and cheese whey. The discussion section will demonstrate products and separations of all we have found.

There are many separation methods used to separate ingredients from milk and cheese whey. The common methods are electrophoresis, liquid phase separation, mass spectrometry, performance liquid-chromatography, cel-electrophoresis and polyacrylamide-gel. The introduction of these common methods will be described as below.

Electrophoresis may be the main technique for molecular separation because of its powerful technique and reasonably and inexpensive and becoming commonplace. Electrophoresis can be one dimensional or two dimensional. One dimensional electrophoresis is used for most routine protein and nucleic acid separations, while two dimensional separations of proteins are used for finger printing.

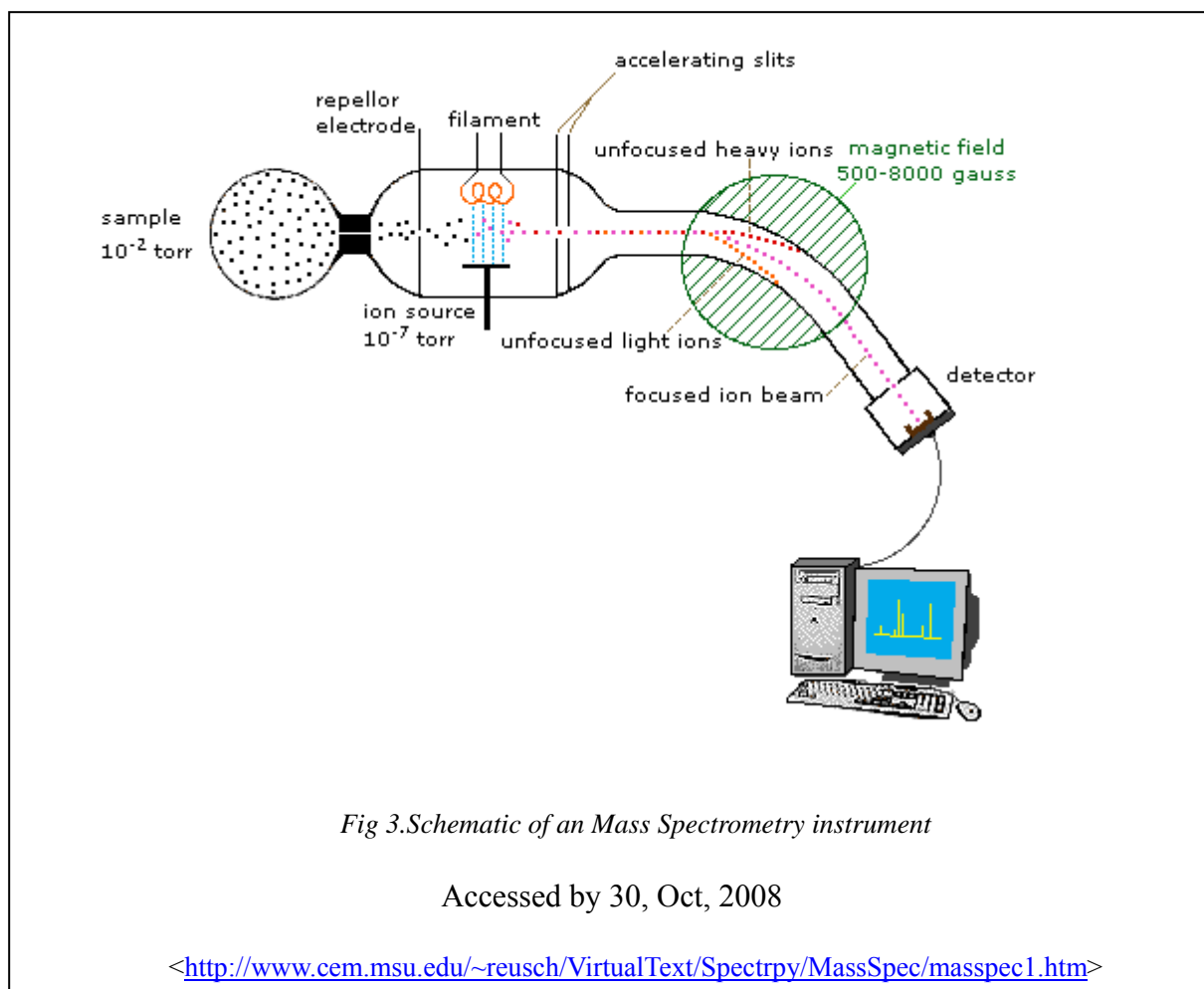
The support medium for electrophoresis can be formed into a gel within a tube or it can be layered into flat sheets. The tubes are used for easy one-dimensional separations, and the sheets have a larger surface area and are better for two-dimensional separations. **Gel-electrophoresis** is used to separate macromolecules like DNA, RNA and proteins. **Polyacrylamide Gel** is a kind of gels used for

gel-electrophoresis.

Liquid phase separation is used to separate either dissolved or undissolved particles in water. Several types of separation techniques are briefly described below.

1. **Filtration** is the physical process whereby particles suspended in water are separated by forcing the fluid through a porous medium. The suspended particles are trapped in the filter. Filtration relies on the pore size of the membrane, which can be varied to remove particles and molecules of various sizes.
2. Simple **Distillation** is a process in which heat is applied to a liquid, causing a portion of the liquid to vaporize. Contaminants with different boiling points from water are thereby separated.
3. **Freeze Crystallization** freezes contaminated water. When the solution is slowly frozen, water crystals form on the surface, from which they are separated from the remaining solution.
4. **Membrane pervaporation** uses several permeable membranes to preferentially sorb volatile organic compounds (VOCs) from contaminated water. Contaminated water heated, causing the VOCs to change into the vapour phase.
5. **Reverse Osmosis** uses a selectively permeable membrane that allows water to pass through it, but which traps heavy metals and radionuclide ions on the other side of the membrane.

Mass Spectrometry converts individual molecules to ions so that they can be moved about and manipulated by external electric and magnetic fields. The three essential functions of mass spectrometer and the associated components are the ion source, a small sample of compound is ionized, usually to cations by loss of an electron; the mass analyzer, the ions are sorted and separated according to their mass and charge; the detector, the separated ions are then detected and tallied, and the results are displayed on a chart.



High-Performance Liquid Chromatography (HPLC) is a form of liquid chromatography to separate compounds that are dissolved in solution. HPLC instruments consist of a reservoir of mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by injecting a plug of the sample mixture onto the column. The different components in the mixture pass through the column at different rates due to differences in their partitioning behaviour between the mobile liquid phase and the stationary phase.

There are a lot of products made of milk and whey, including Yoghurt, butter, cheese, ice cream and so on. Yoghurt is a semi-solid fermented milk product. Its popularity has grown and is now consumed in most parts of the world. Although milk of various animals has been used for yogurt production in various parts of the world, most of the industrialized yogurt production uses cow's milk. Whole milk, partially skimmed milk, skim milk or cream may be used. Butter is made by beating cream, the thickest, fattiest part of milk. As the cream is beaten, the fat globules begin to stick together, forcing the cream to form a solid mass of milkfat, also known as butter. Curdling or coagulation is the separation of the solid from liquid components, such as whey separation, which is achieved by adding ripening cultures. All cheeses are put through this process. There are two basic curdling methods and there are determined according to the type of cheese being made. One is sour-curd cheeses, which are made by adding lactic acid bacteria to milk. The other is rennet cheeses, which are made by adding an enzyme and then the formation of larger grains of curd appears. Some cheeses are made by mixing both sour curd and rennet. Ice cream is a frozen mixture of a

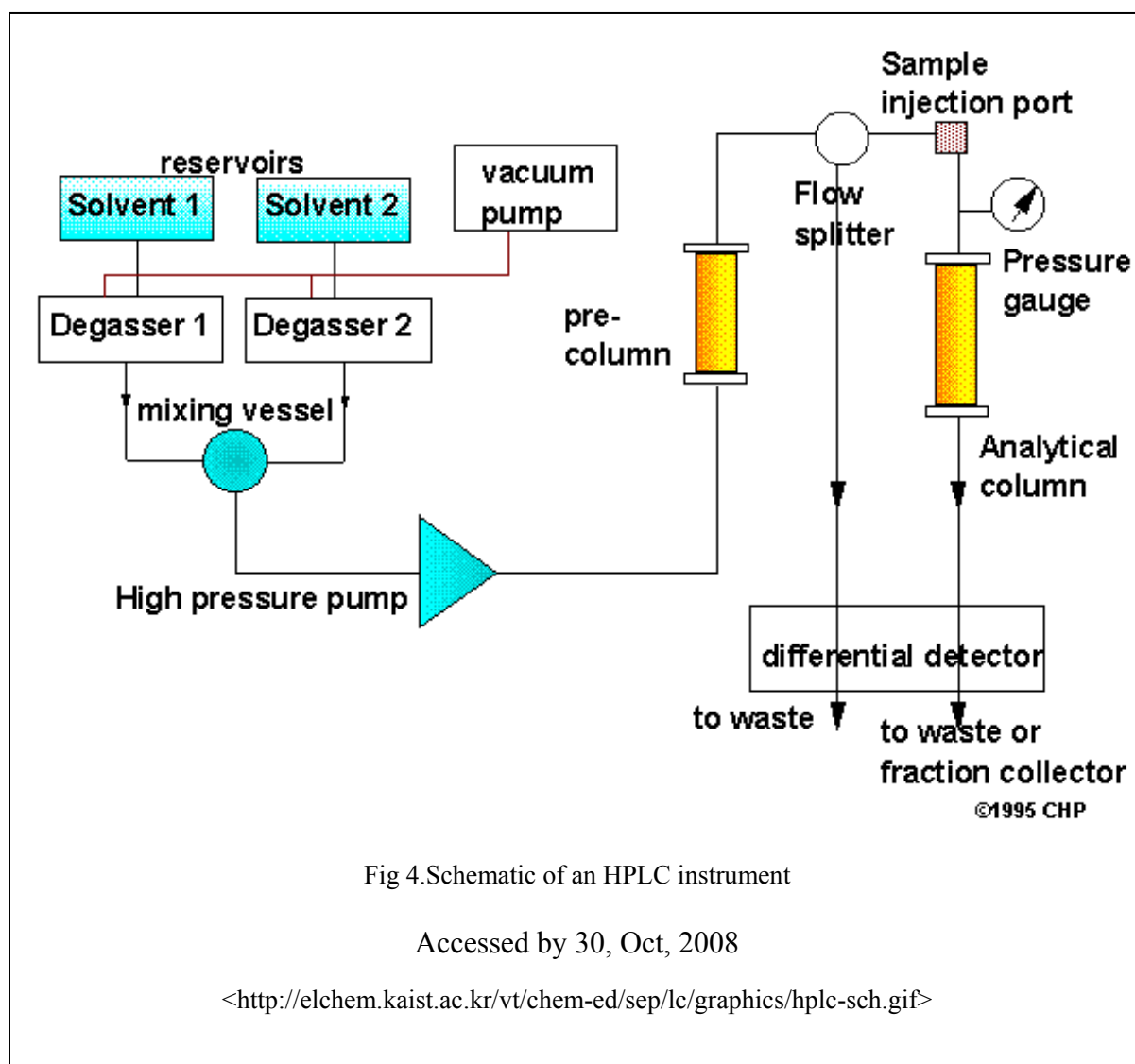


Fig 4.Schematic of an HPLC instrument

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<<http://elchem.kaist.ac.kr/vt/chem-ed/sep/lc/graphics/hplc-sch.gif>>

combination of components of milk, sweeteners, stabilizers, emulsifiers and flavouring. Other ingredients such as egg products, colourings and starch hydrolysates may be added also. The mixture is pasteurized and homogenized before freezing, which involves rapid removal of heat while agitating vigorously to incorporate air, then imparting the desirable smoothness and softness of the frozen product. In order to follow the project appraisal, the ingredients and its separation will be discussed in great detail in later Discussion section.

Discussion

(1) α -Lactalbumin

One of the main whey proteins in milk is Alpha-lactalbumin (α -LA) which is made by the mammary epithelial cells during the period of lactation. In the milk, α -Lactalbumin should be considered as an important ingredient since it generates a complex of important function with enzyme and galactosyltransferase (Galactosyltransferase usually get it involved in the course of glycosylation of proteins in mammary cells). During the time of lactation, lactose synthase, which takes its responsibility to make lactose, is produced by α -LA complexes and galactosyltransferase as well as enzyme activity. Lactose, which is counted as the major carbohydrate in milk, makes the digestion of milk easier for the next generation by providing a readily digestible energy source. The synthesis of lactose draws water into the milk producing cells of the mammary gland. During this process, synthesis of α -Lactalbumin plays a role to control the volume of milk produced.

In experiments where the α -LA has been changed and mice are involved, scientists find that mothers can not generate lactose until they give birth and mice are not able to lactate or support their litters. Such experiment can illustrate the importance of α -LA in the process of lactation. It is still a viable question that whether an increase in milk production can be achieved by increasing α -LA production by the mammary gland. (M.S. Noble, M.B. Wheeler and W.L. Hurley)

Separation Method 1: (Liu, Sun, & Li, 2006) noted that effective separation for α -Lactalbumin from milk whey can be achieved by a convenient liquid-solid extraction system. In this process, the improved convenient liquid-solid extraction system should be based on Tween 80/phosphate. And in order to get satisfactory results, particular conditions (9 wt% Tween 80, 1.6 : 1 (molar ratio) K_2HPO_4 : NaH_2PO_4 , 1.25 mol/L total phosphate, pH= 7.4) should be given. After this manipulation, water and salt are introduced and make the solid phase be able to form a new liquid-solid extraction system. In that case, a satisfactory recovery rate (85.1%) for α -Lactalbumin from the former into the new salt aqueous phase can be achieved.

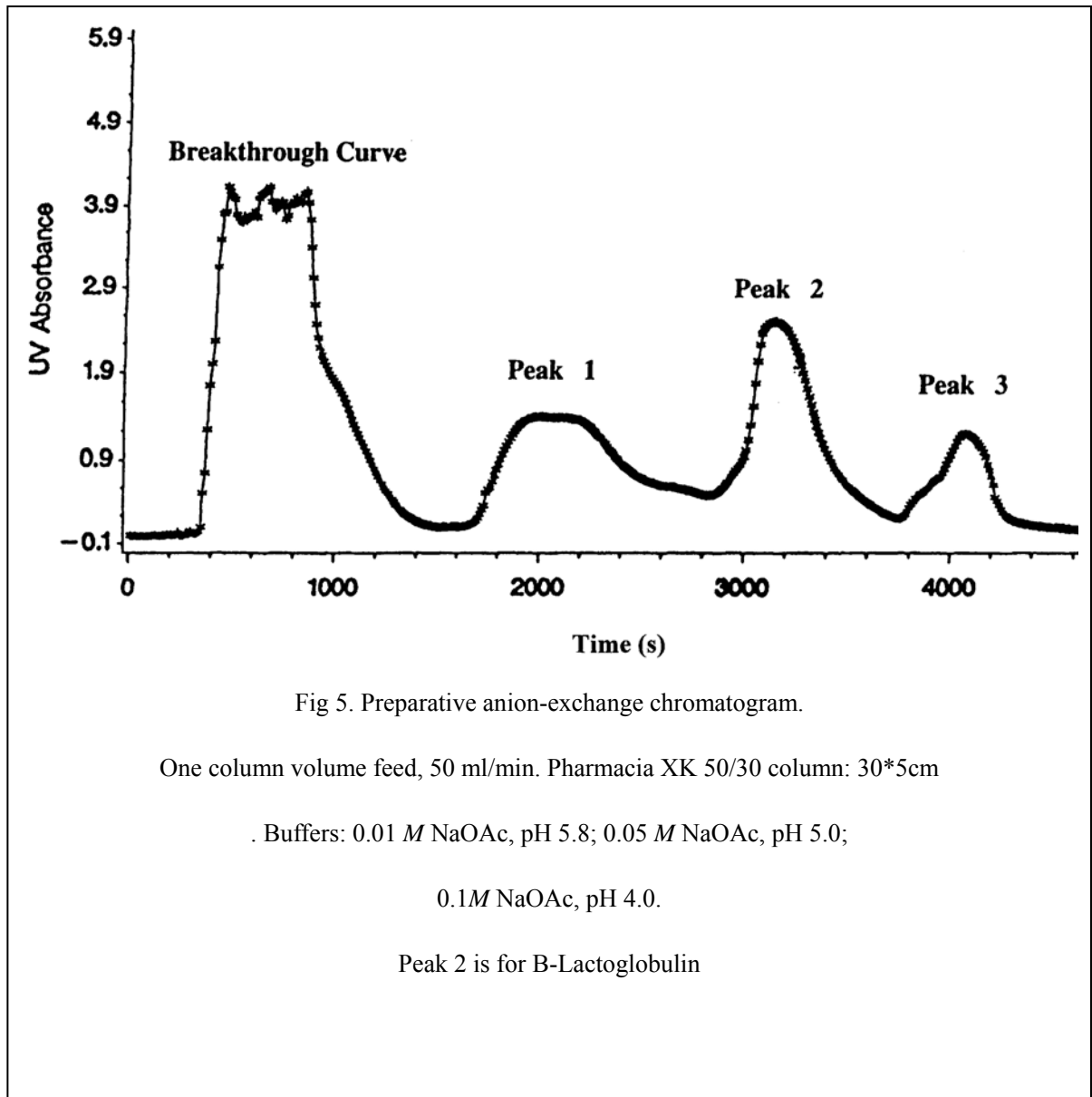
Separation method 2: According to (A., et al., 1997), a material can serve as a stationary phase in IMAC (immobilized metal affinity chromatography) to make α -lactoalbumin separated from bovine milk whey. This material can be obtained when making some modification to silica gel surface with β -diketoamine groups by reacting the silanol from the silica surface with 3-aminopropyl-triethoxysilane and 3-bromopentanedione. This material can extract copper ions out of aqueous solutions, and an amount of $0.67 \text{ m mol g}^{-1}$ of organic groups attached to the support and $0.63 \text{ m mol g}^{-1}$ of copper was given by chemical analysis of the silica-gel-immobilized acetylacetone. Since the chelated copper has a high and collective attraction for α -lactoalbumin functional groups, a good separation of the protein with a high purity can be achieved. Additionally, the silica matrix can also serve as a role to give the system more chemical and mechanical resistibility.

(2) β -Lactoglobulin

β -lactoglobulin is also a kind of main whey proteins in milk and its function is still unclear to human-beings. However, due to its properties which can change to be negative or positive in dairy products and processing, β -lactoglobulin have become a great interest in food industry^[4]. β -lactoglobulin, which only with an 18.4 kDa molecular weight (1 Dalton being defined as 1 molecular weight unit), should be considered as a small protein of just 162 residues. (Jost, R. 1993)

Separation method 1: Still according to (Liu, Sun, & Li, 2006), the liquid-solid extraction system created by can not only be used to adsorb α -Lactalbumin from milk whey, but also show its high performance with recovery rating at 98.2% in selecting β -Lactoglobulin. Same conditions (9 wt% Tween 80, 1.6 : 1 (molar ratio) K_2HPO_4 : NaH_2PO_4 , 1.25 mol/L total phosphate, pH= 7.4) are literally required. However, the effects of water and salt are not needed since they are specially applied to make α -La extracted into the new salt aqueous phase.

Separation method 2: It is evident from the article written by (Gerberding & Byers, 2008) that preparative-scale ion-exchange chromatographic process can also be established for the separation of B-Lactoglobulin from milk. In that experiment, when



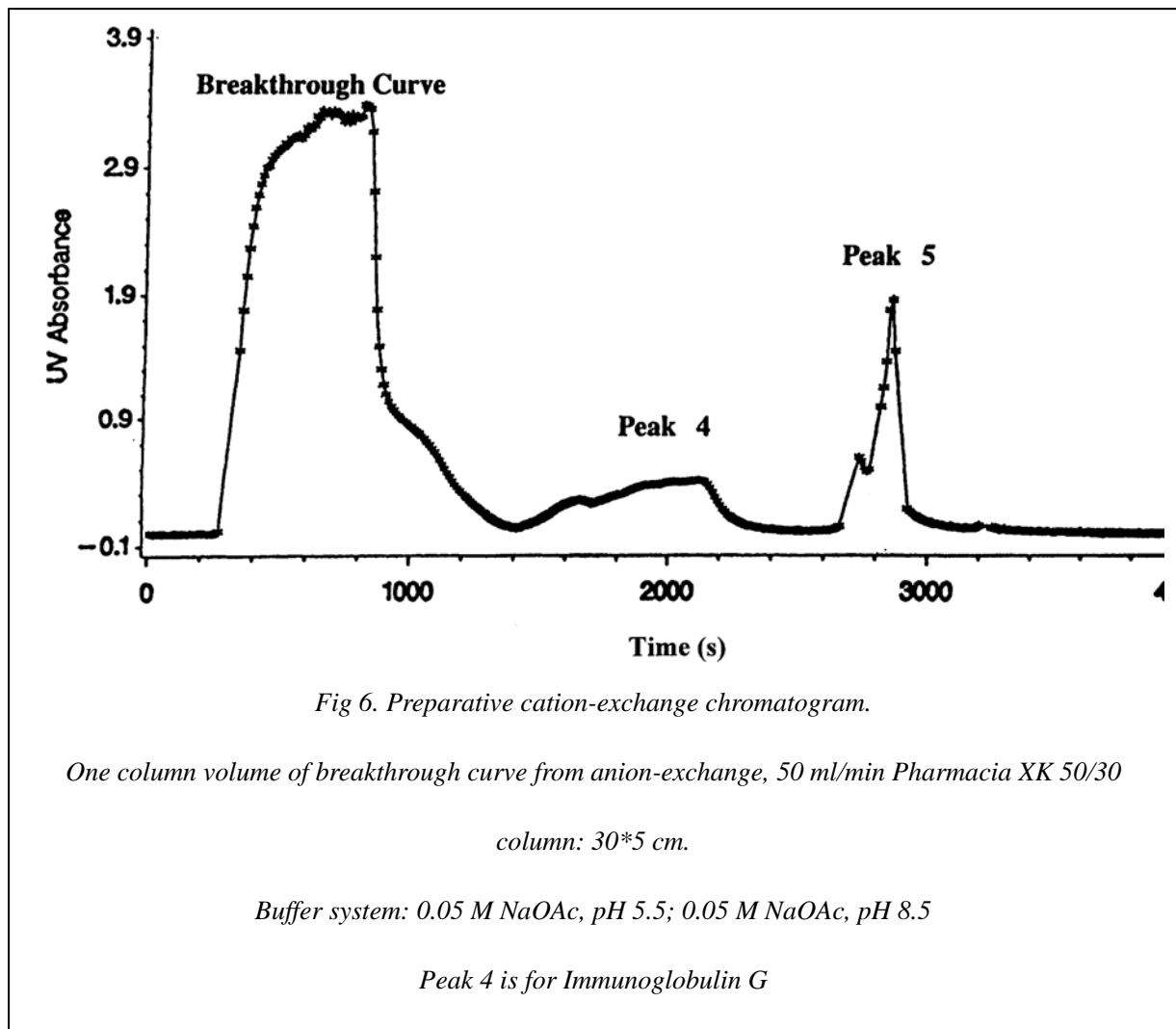
the cleaning of ion-exchange column was done, the first step was to load a column volume of whey feed on to the anion-exchange column. Because of the affinity varied in different ingredients, the proteins α -lactalbumin, b-lactoglobulin and BSA were bound by the column which let IgG to pass through without adsorption. The next stage was to wash out any material (like IgG) which was not adsorbed by resin and one column volume of this buffer was needed. When this was finished, variable ingredients could be washed out independently due to their different pI s. B-Lactoglobulin could be firstly washed out by two column volumes of 0.05 M sodium acetate, pH 5.0 and the recovery turned out to be quite high. This method should be counted as a practicable for B-Lactoglobulin separation. Scale-up can also

be obtained if maintenance of the column bed length, superficial velocity and particle size is put into performance.

(3) Immunoglobulin G

Immunoglobulin G presents strong function in the field of health and commerce. For example, immunoglobulin G can be efficiently used for eluting which is consistent with measurement of immunoglobulin G titers in most frozen storage of ascites monoclonal antibodies (Mabs) for more than one year. The Mabs can be serotyped of outer membrane antigens of *N.meningitidis* by dot-blot ELISA after a simple filter paper method (Ferraz et al, 2008). The immunoglobulin G proteins also can be used for the fabricate and optical quality linear grating for microcontact printing and the demonstration of potential biosensing applications (Angeley Davis & Reitz, 2006).

Separation method: Immunoglobulin G is entitled to be effectively separated from dairy whey by (Gerberding & Byers, 2008) This goal can be achieved if both anion- and cation-exchange column are applied. For the beginning, both columns needed to be washed by a column volume of 1 M sodium hydroxide and one column volume of deionized water. The following step was to use two and a half column volumes of 0.1 M acetic acid to make the pH lower so that the whey feed with a Ph of 5.8 could be loaded on to the column directly. Since Immunoglobulin G differed itself from other main proteins like a-Lactalbumin and b-Lactoglobulin in whey by showing no affinity to the anion-exchange column, it could run through the column and leave other main protein attached to the resin. Then, the one column volume loading of the anion-exchange breakthrough curve fraction needed to be optimized before loaded onto the cation-exchange column. After loading, a column volume of the initial buffer would served as a cleaner to wash out any material which was not absorbed by column. Finally, two column volumes of the buffer (0.05 M, sodium acetate, pH 8.5) were introduced to elute the bound IgG. This was the last step which is done to Immunoglobulin G with high purity.



(4) IGF-1

IGF-I belongs to the multi-functional regulatory peptides for cell growth and survival. It also can be part of a complex system that cells use to communicate with their physiologic environment. Some neurotrophic factors such as IGF-I (Kuncl, 2001) can be used for the protection of the postnatal motor neurons from slow glutamate injury in organotypic spinal cord. When it is applied at the time of human spinal cord injury, IGF-1 treatment can rescue substantially, even if the slow neurodegeneration has been a 7-8 week process and the motor neurons have been injured already.

Separation method: The separation of IGF-1 from whey had been proved to be practicable by (Ben ounis, Gauthier, Turgeon, Roufik, & Pouliot, 2008). During the operation, heparin affinity chromatography was chosen to extract minor protein ingredients from two whey protein isolates which were obtained by ion-exchange chromatography (IEC-WPI) and the second by microfiltration/ultrafiltration (MF/UF-WPI) respectively. After a calculation, scientists found that IGF-1 was

enriched by factors of 24-38 in the fraction made less concentrated by 0.5 m NaCl from IEC-WPI and MF/UF-WPI nevertheless only 1–13% of major proteins were extracted by heparin column. The existence of minor proteins including transthyretin, angiogenin, β_2 -microglobulin and heart fatty acid-binding protein was also presented by two-dimensional gel electrophoresis of this fraction from IEC-WPI. Thus, they came to a conclusion that heparin affinity chromatography can not only show its value in separating the main proteins included in some WPIs, but also highlight its importance in concentrating the minor cationic proteins and some milk growth factors.

(5) *Escherichia coli*

Separation method: According to Vasqu (Rojas, Vasquez, Reyes, Martinez, & Medina, 2006), with the help of immunomagnetic separation (IMS), the recovery of *Escherichia coli* O₁₅₇:H₇ milk cream is no longer out of reach. Before the manipulation of ISM, people should make a confirmation on the efficiency of various pre-enrichments broths and give their consideration and analysis to different agars (differential and/ or selective) for the purpose of plating of the immunobeads. Parts of 25 g from screams, which were previously planted with pathogen low levels (50, 10 and 1 cell/g), were made richer in buffered peptone water with vancomycin (BPW-V), buffered peptone water with vancomycin and cefixime (BPW-VC) and triptone soya broth with vancomycin, cefixime and tellurite (TSB-VCT) being incubated 35 degrees C/18 hours. What came to the next is to apply the IMS and make the immunobeads plated onto sorbitol MacConkey agar (SMA), sorbitol MacConkey agar with cefixime and tellurite (SMA-CT) and chromogenic agar with tellurite and cefixime (CRGA-TC). It was discerned obvious differences ($p < 0.05$) in the recovery ratios according to the pre-enrichment broth applied, being achieved the highest recovery rates with the help of TSB-VCT for the three inocula levels. The number used to describe the recovery rate did not change hugely ($p < 0.05$) among the agars which were applied, however, the quantity for inoculated cells decreases the recovery ratios, being larger since it raise the inocula. At last, they could come to a conclusion that while choosing a method to separate *Escherichia coli* O₁₅₇:H₇ for milk creams, IMS would not lose its place.

Conclusions

According to the content above, the separations of those products from milk and whey have been proved to be practicable and effective. Special attention should be given to ion-exchange chromatographic process since this method is easy manipulated and shows high performance in the separation of main proteins from milk with satisfactory recovery. However, there are still some aspects of these processes which can be improved. For instance, due to the limitation of current technology, some

products gained from the milk are microweight, even if the raw material is enough. What is more, some other components are damaged under some special conditions, in order to obtain the certain product, improvement should be made to enhance the quality of separation. What we would like to make clear is that some of other valuable ingredients contained in milk are detected, however, the separation of them is far satisfactory. A good example is Glycomacropeptide (GMP).

Glycomacropeptide (GMP) located in milk protein casein- κ -a peptide fragment, is a new kind of functional factor with many of the biological activity. It combines cholera and enterotoxin for inhibiting bacteria and viruses to keep away the attaching of the intestinal secretion in order to promote and regulate the growth of bifidobacterium immune response(Lee & Chang, 2002). In order to make most advantage of milk, further separation method should be established. Last but not least, in order to meet the huge demand from the global market, scale-up is extremely needed. Thus, Scientists and researchers still need to put more effort to enlarge the scale of separation. Though there is a long way ahead, scale-up in some fields is far from dim since 'scale-up can also be obtained if maintenance of the column bed length, superficial velocity and particle size is put into performance, just like the conditions we talked about in method 2 for B-Lactoglobulin separation. However, with the progression of theory and technology in the field of separation, those products can sooner or later be separated and serve as a role to contribute to human health and medical science. There is a good saying that 'where there is a will, there is a way', no matter how hard the separations are, they will be defeated by human-beings, sooner or later, in the future, we believe.

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E19 FILM AND DROPWISE CONDENSATION

ShihSheng Chang
27.Nov.2008



Context



- Fluids is always to be either heated or cooled in the chemical processes, i.e. heat is to be given out or absorbed
- Furnances、Evaporators、Distillation units、Driers and reaction vessels
- Alternatively, prevent the loss of heat
- The overall heat transfer coefficient (U) is needed to be determined

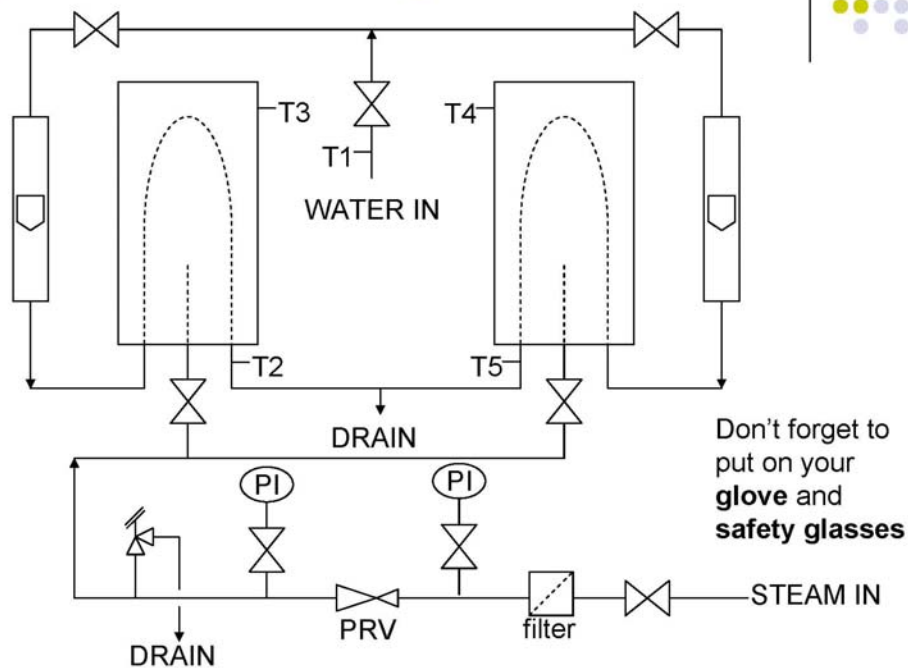


Purpose of Experiment

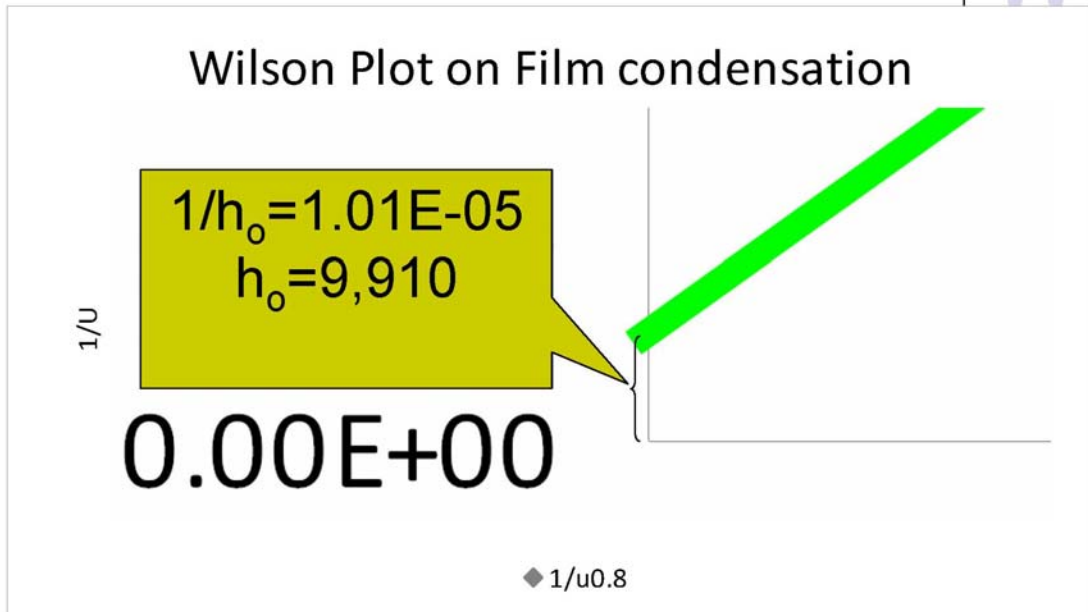
- Determination of film coefficients
 - Method 1: requires measuring the temperatures of both fluids and the surface of separation
 - Method 2: is put forward by Wilson*
 - Suppose steam to be condensing on the outside of a tube through which water is passed at various velocities. ([more](#))
- Comparison with dropwise condensation
 - Heat do not have to flow through a film by conduction, much higher transfer coefficients are obtained. ([more](#))

*WILSON, E.E.: Trans. Am. Soc. Mech. Eng. 37(1915)546. A basis for rational design of heat transfer apparatus

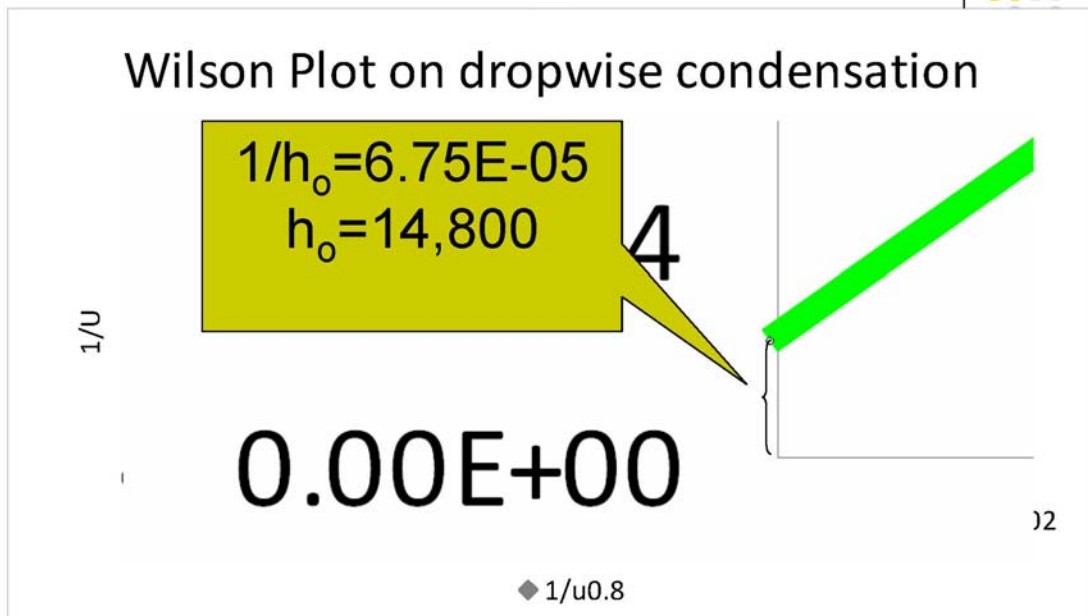
Experimental Diagram



Results



Results





Discussion

- Transfer coefficient of steam (h_o) obtained
 - film condensation is 9,910 W/m²K
 - dropwise condensation is 14,800 W/m²K
- $Nu = 0.023 Re^{0.8} Pr^{0.4}$ is valid for $Re > 10,000$
- Steam supply is not steady
- Oleic acid not spreads very well
- Reference results
 - Film condensation is 8032.8 W/m²K
 - Dropwise condensation is 28866 W/m²K



Heat Transfer Equation

- $Q = UA \Delta T_{lm}$
 - Q: the heat transferred per unit time
 - A: the area available for the flow of heat
 - ΔT_{lm} : the difference in temperature between hot and cool fluid ([more](#))
 - U: the overall heat transfer coefficient



Wilson Method

- Steam condensed on the outside of a tube
- Water pass at various velocities
- The overall and film transfer coefficients

$$\frac{1}{U} = \frac{1}{h_o} + \frac{1}{h_k} + \frac{1}{h_i} \quad \text{more}$$

- The transfer area on each side of the tube is approximately the same
- For conditions of turbulent flow of the transfer coefficient for the water side $h_i = \varepsilon u^{0.8}$



Wilson Method

- The coefficient for the condensate film is almost independent of the water velocity

$$\frac{1}{U} = (\text{constant}) + 1 / \varepsilon u^{0.8}$$

- $1/U$ is plotted against $1/u^{0.8}$ a straight line is obtained with slope $1/\varepsilon$ and intercept equal to the value of the constant
- ε represents the value of the film coefficient h_i for unit water velocity





Dropwise Condensation

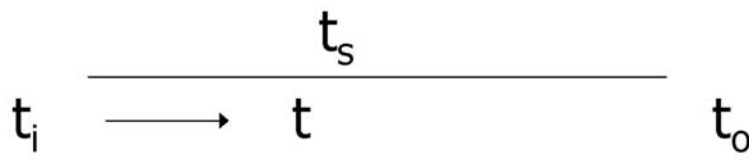
- Droplets formed without wetting the surface
- Expose fresh condensing surface
- heat transferred without flowing through a film by conduction
- Much higher transfer coefficients obtained
- Mercaptans and oleic acid could be used but little practical application at present
- Exceptionally high values of h won't give a corresponding increase in the overall coefficient
- Helpful in experimental work to reduce the thermal resistance on one side of a surface to negligible value



Definition of ΔT_{lm}

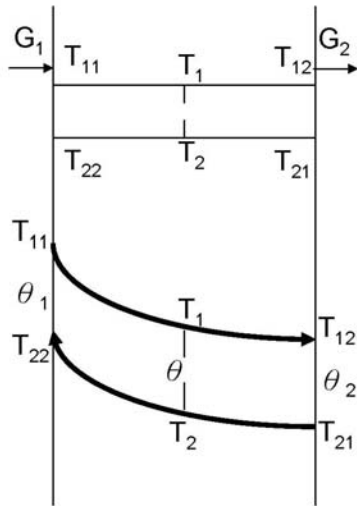
- The logarithmic mean temperature difference

$$\Delta T_{lm} = \frac{(t_s - t_i) - (t_s - t_o)}{\ln \left(\frac{t_s - t_i}{t_s - t_o} \right)}$$



[Derivation of \$\Delta T_{lm}\$](#)

Derivation of ΔT_{lm}



$$\text{Let } \theta = T_1 - T_2$$

$$d\theta = dT_1 - dT_2$$

$$\text{Heat given out by hot stream} = dQ = -G_1 C_{p1} dT_1$$

$$\text{Heat taken up by cold stream} = dQ = G_2 C_{p2} dT_2$$

$$d\theta = -\frac{dQ}{G_1 C_{p1}} - \frac{dQ}{G_2 C_{p2}} = -dQ \left(\frac{G_1 C_{p1} + G_2 C_{p2}}{G_1 C_{p1} * G_2 C_{p2}} \right) = -\Psi dQ$$

$$\theta_1 - \theta_2 = \Psi dQ$$

$$U dA \theta = dQ$$

$$-\Psi \int_0^A dA = \int_{\theta_1}^{\theta_2} d\theta / \theta$$

$$-\Psi UA = -\ln(\theta_1 / \theta_2)$$

$$\theta_1 - \theta_2 = \Psi Q = \Psi UA \theta_m = \ln \frac{\theta_1}{\theta_2}$$

$$\Delta T_{lm} \equiv \theta_m = \frac{\theta_1 - \theta_2}{\ln(\theta_1 / \theta_2)}$$

Overall heat transfer coefficient

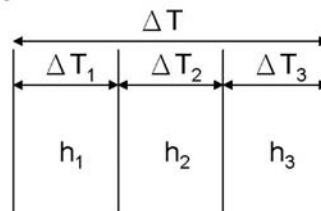


$$Q = h_1 A \Delta T_1 = h_2 A \Delta T_2 = h_3 A \Delta T_3$$

$$\Delta T_1 = \frac{Q}{A h_1} \quad \Delta T_2 = \frac{Q}{A h_2} \quad \Delta T_3 = \frac{Q}{A h_3}$$

$$\Delta T = \Delta T_1 + \Delta T_2 + \Delta T_3 = \frac{Q}{A} \left(\frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3} \right) = \frac{Q}{A U}$$

$$\frac{1}{U} = \frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3}$$



Conclusion



- Good understanding of Heat transfer and film condensation
- Determination of steam transfer coefficient
- Comparison with dropwise condensation
- Good Practice at laboratory experiment

Further development



- Change the supplement of pressure of steam
 - The source of steam should be more stable
- Determination of other vapors or mixed vapors
- Find out substitute of oleic acid
 - Mercaptans or others which is better to be applied
- The goal is to reduce resistance or make more heat transfer as much as possible

EA-56 CONTROL VALVES

Chemical Engineering Department (CGP668) Applied Engineering Practice,

Introduction:

An important operation in any process is the precise control of the flow of materials in order to regulate the operation of the system. This might simply be to prevent excessive level, temperature or pressure but could be an essential part of the control of a chemical reaction. Control valves play the roles and are commonly driven by pneumatic or electrical actuators in response to an automatic signal derived from a process measurement. In order to have a good control, the relationship between the valve movement and the produced flow needs to be more precise and should be predictable in advance. The purpose of this experiment is to have good understanding of valve characteristics by the plot obtained from the result of actuating the valve and observing the differences in the flow rate. In addition, hysteresis occurs at a difference in the flow measured at the same diaphragm pressure depending on whether the diaphragm pressure is being increased or decreased. The valve is dismantled and identified as each of its components as well as the matching seat inside the valve body. The procedure before and after dismantling is also important.

Experimental:

The setup consists of pneumatic control valve, a tank with pump for continuous water circulation and rota meter for the flow measurement. An arrangement is made to measure pressure at the valve inlet and outlet in terms of psi. An air regulator and pressure gauge is provided for the control valve actuation. During start-up procedure, check that drain valves are closed and all other manual valves are open. The main tank is filled to the appropriate level. Turn on the air supply valve, start the pump and check the flow is steady. Adjust and increase the diaphragm pressure in 1 psi steps up to 15 psi and read the rota meter and water pressure gauges. Then in reducing steps to 1 psi.

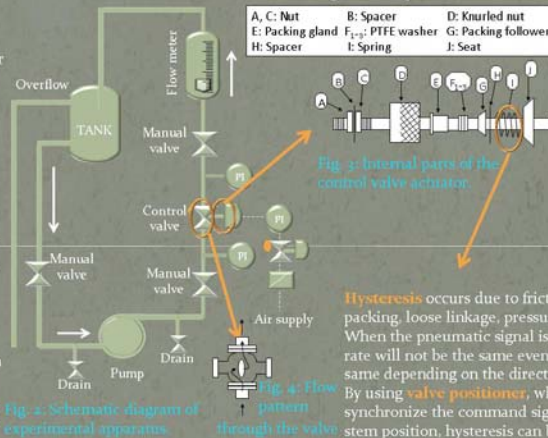


Fig. 2: Schematic diagram of experimental apparatus.

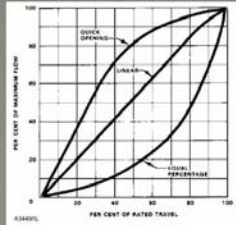


Fig. 1: Inherent flow characteristics

Installed valve characteristic refers to when the valve is installed with other fluid handling equipment in processing systems and subjected to variable pressure drop, flow and other changes of the system and differs from that of any single component.

Fig. 3: Internal parts of the control valve actuator.

Hysteresis occurs due to friction between the stem and packing, loose linkage, pressure drop, and stiction. When the pneumatic signal is going up and down, the flow rate will not be the same even though the command signal is same depending on the direction of signal change. By using **valve positioner**, which is a controller which can synchronize the command signal and its corresponding valve stem position, hysteresis can be overcome.

Inherent Valve characteristic are determined by the valve orifice and the plug geometry. It refers to the flow characteristic when there is a constant pressure drop across the control valve. There are three types and can be represented graphically as illustrated in Figure 1. **Quick Opening** provides a maximum change in flow rate at low travels and small changes when the valve plug is near maximum. **Linear** shows that the flow rate is directly proportional to the valve travel. **Equal Percentage** shows that equal increments of valve travel produce equal percentage changes in the existing flow.

Direct or Reverse action: Since the valve is fail-closed (FC) in this experiment, when the valve opening is increased by the increment of diaphragm pressure, this valve is **DIRECT** acting. Otherwise, when its opening is decreased by the same case, it is **reverse** acting. A FC valve must be closed when the energy supply fails for the sake of safety consideration.

Results and Discussion:

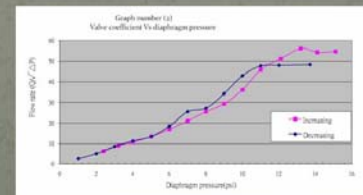
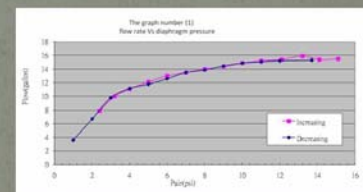
- The graph number 1 shows that the flow rate versus the diaphragm pressure in increasing and decreasing operations where Hysteresis phenomena is occurring.
- The graph number 2 shows that the flow rate versus the valve coefficient where Inherent characteristic is taking place. A change in the valve coefficient is occurring in increasing and decreasing diaphragm pressure when the control valve is being opened and closed.

Conclusions:

- By measuring the flow rate and the diaphragm pressure across the valve, the design and the size of the control valve can be identified to be appropriate for the operation in terms of characteristics and selectivity.
- The valve coefficient (Cv) is depending on the valve position.
- Valve manufacturers can shape the valve characteristics by arranging the way the area of the valve orifice varies with valve position.

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六、EA-58 Plate heat exchanger

Introduction

Almost heat exchangers used in the chemical processes are the shell and tube types, which can provide the best heat transfer for most fluids. However, they are not satisfied while processing the high viscosity fluids due to the surfaces of the exchangers could be fouled quickly and therefore a loss of performance and contamination of the product appear. For these conditions plate heat exchangers are more appropriate. This kind of exchangers is made of many thin plates with the heating or cooling fluid on one side and the process fluid on the other. The plates are mounted between a fixed head plate and a moveable follower plate and are corrugated to give them rigidity and to produce turbulence. The number of plates can be determined by the needed heat exchanger area, which provides heat to go through. A rubber gasket is used for sealing each pair of plates and therefore the inlet and outlet flow paths can be defined for the two fluids.

Experimental

1. Firstly, the exchanger A is to be dismantled. By following the steps, we first measure the gaps between the two end plates at each four corner of the exchanger A. Normally, each of the gap is 3.4 cm. This could be shown as fig. 1.
2. Next check the valves A, D, H and are closed and C and E are open for releasing the remained pressure in the pipe and exchanger. Close the pump isolation valve (G) and open the drain valve (I). Then the exchanger A starts to be dismantled by removing the nuts.

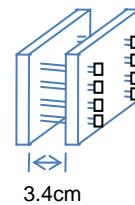


Fig. 1: a sketch shows the measurement of the exchanger before dismantling.



Fig. 2: The two different kinds of the plates which compose the exchanger alternately.

3. While drawing off the follower plate, the order and orientation of the plates should be carefully noted. The two different kinds of the plates which compose the exchanger alternately. By following the arrangement, the hot and cold fluids can flow through the exchanger across every one other plate. Therefore, the two fluids can sufficiently heat exchange.
4. Wash and clean the plates and make sure the gaskets are good for use and there is no dirt or contamination remained on the plates.
5. Replace the plates and follower in the correct sequence and then put on the nuts to hand tightness. The final tightening should be carried out on alternate sides by following the numbered sequence shown on the follower. Check that the separation of the follower and header is equal to the value measured initially all around the plates.
6. Before start the pump, check that steam inlet valve (A) and process drain valve (I) are closed and the by-pass valve (H), the pump inlet and outlet isolation valves (F,G) are open. Turn on the pump and check that some process fluid emerges from the outlet pipes above the tank and then gradually close the by-pass valve.

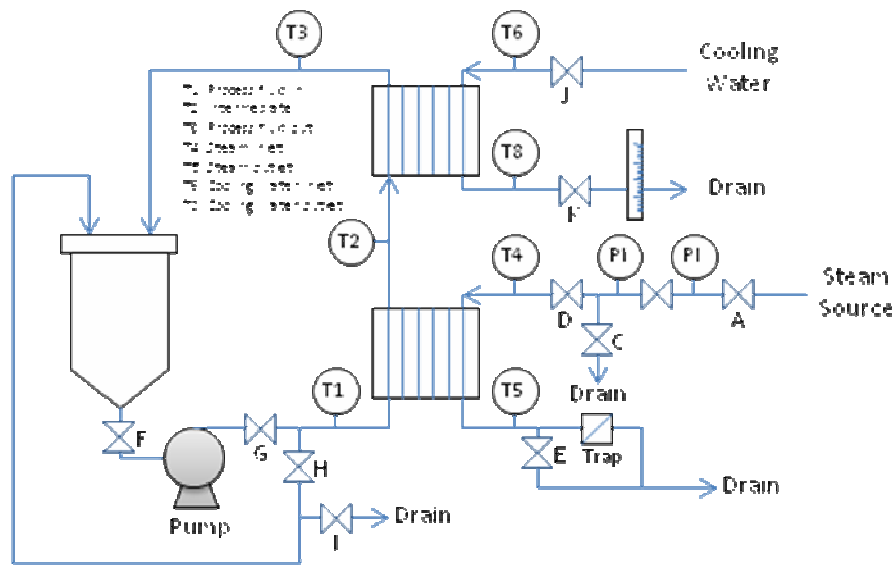


Fig. 3: the flowchart of EA-58 experiment

7. Open the cooling water control (K) and inlet valves (J). Turn on the temperature indicator and select channel 2. Make sure that the process fluid temperature is less than 85°C .
8. Steam is supplied by opening the isolation valves and closing by-pass, vent and drain valves. The steam main should be at 7 bar(g) and on this rig the steam is reduced to 1 bar(g).
9. Wait until the system reach equilibrium temperature and adjust the cooling water flow rate until the process fluid temperature at the inlet to the first heat exchanger and the outlet from the second are approximately equal.
10. Read all the temperatures and the cooling water flow rate. Measure the mass flow of process fluid (M_{pf}) with a stopwatch by diverting the flow return into a container and weighing.
11. Reduce the process fluid flow until the temperature of the intermediate point of the heat exchangers rises by about 10°C .
12. Repeat the step 10 and 11 again for a temperature (T_2) of about 80°C .
13. On completion of this section, close the by-pass, isolating and steam inlet valves and open the vent and trap by-pass valves.
14. Close the cooling water inlet valve and turn off the pump and temperature indicator after the system has cooled.

Results and Discussion

1. The raw data and the calculated results are presented in the appendix.
2. The heat capacity of the process fluid (C') decreases while the temperature of it increases at the intermediate point, i.e. 4102.85 J/kg.K at 54.3°C , 3897.14 at 70.6 and 2887.29 at 77.6 . That also means the

viscosity of the process fluid also changes with the fluid temperature and is high at low temperature. High heat capacity makes the process fluid temperature not easy to increase or decrease although the heat transfer is already large as the result of run 1.

3. Although the steam temperature is over 100°C, the steam supply is not sufficient enough and so the temperature of the process fluid increases very slowly. After adjusting the pressure reducing valve by a supervisor, the process fluid temperature has obviously changed.
4. The signals from transmitters seem to be a little strange because the reading on the indicator sometimes decreases to a non-reasonable value but recovers to a normal value after the channel is switched to another and turn back. This means the signal wire is probably fatigued and needed to be changed in order to get a stable reading.
5. We need to wait for a longer time until the inlet temperature of the process fluid to the first heat exchanger and the outlet temperature from the second are approximately equal. Therefore, the system reaches equilibrium and then the results would be more reliable in this experiment.

Conclusion

1. Plate heat exchanger is used to process the heat transfer of high viscosity fluids.
2. Plate heat exchanger is dismantled for taking a look at the inside. The procedure should be noticed that the arrangement of the plates in the right direction and the distance between the head and follower is recovered to the original state after dismantling.
3. Due to process high viscosity fluids, the equipment should be kept high efficiency by cleaning it carefully.

Appendix

The raw data obtained from the experiment.

Run	Time1 (sec)	Weigh1 (kg)	Time2 (sec)	Weigh2 (kg)	T ₁	T ₂	T ₃	T ₄	T ₅	T ₆	T ₈	Flowrate (cm)
1	9.75	2.23	11.78	2.65	31.7	54.3	35.8	102.9	39.2	7.1	12.2	16.75
2	21.25	2.254	21.40	2.310	34.9	70.6	38.1	104.3	93.8	10.2	14.3	16.5
3	29.33	1.856	24.92	1.545	30.0	77.6	30.0	105.0	106.0	10.5	20.7	2.0

The results obtained from calculation.

Q1=Q2	C'	ΔT_B	U_B	U_A	Q3
17217.6	4102.85	34.97	1367.5	1593.44	21033.39
13553.2	3897.14	40.45	930.68	1127.86	14887.71
8608.8	2887.29	34.92	684.71	652.182	8608.80

$$Q_1 = M_{CW} \cdot C \cdot (T_8 - T_6) \text{ the heat gained by the cooling water}$$

where: $C = 4220 \text{ J/kgK}$ $M_{CW} = \text{water MASS flow (kg/s)}$

$$Q_2 = M_{pf} \cdot C' \cdot (T_2 - T_3) \text{ the heat given up by the process fluid}$$

where: $M_{pf} = \text{process fluid flow (kg/s)}$

C' is the specific heat capacity of the process fluid

$$Q_1 = U_B \cdot A_B \cdot \Delta T_B$$

where A_B is the area for heat transfer (0.36 m^2)

$$\Delta T_B = \frac{(T_3 - T_6) - (T_2 - T_8)}{\ln\left(\frac{T_3 - T_6}{T_2 - T_8}\right)}$$

$$Q_3 = U_A \cdot A_A \cdot \Delta T_A = M_{pf} \cdot C' \cdot (T_2 - T_1)$$

where A_A is 0.22 m^2

七、Biodiesel Production

1.0 BACKGROUND

Biodiesel has been gaining worldwide popularity as an alternative energy source because it is non toxic, biodegradable and non flammable and has fewer emissions than petroleum based diesel when burned. Biodiesel is an eco-friendly, alternative diesel fuel that runs in diesel engine cars, buses, trucks, construction equipment, boats, generators and oil home heating units. Biodiesel functions in current diesel engines and is a possible candidate to replace fossil fuels as the world's primary transport energy.

Biodiesel is a substitute fuel for compression ignition internal combustion engines. It is produced by the transesterification of waste or vegetable oils and animal oils or fats with lower alcohols. Most vegetable oils can be converted into biodiesel but the cost of the vegetable oil feedstock is now a key factor in the least cost production of biodiesel for blending with fossil fuel. Biodiesel has many environmentally beneficial properties. The main benefit is that it can be described as “carbon neutral”. This means that the fuel produces no net output of carbon in the form of carbon dioxide. It also has good lubricant properties that extend the engine shelf life, its high cetane number, its high flash point and its acceptable cold filter plugging point which makes it attractive as an alternative fuel.

A method used to produce biodiesel is the transesterification reaction by a heterogeneous catalyst. The catalyst used in this write up is calcium oxide which promotes the transesterification reaction without catalyst loss. In this process, the catalyst is stable with no metal leaching and no formation of either glycerate salts or metal soaps. By eliminating the formation of soap, heterogeneous method further prevents the formation of emulsion in the mixture which could complicate the separation and purification process. Basically, there are three types of heterogeneous catalysts used in the transesterification process; i.e. acid, base (alkali) and enzyme.

Biodiesel has recently experienced a major surge worldwide. A rapid expansion in production capacity is being observed not only in developed countries such as Germany, Italy, France, and the United States but also in developing countries such as Brazil, Argentina, Indonesia, and Malaysia. Interest in and expansion of the production of the renewable fuel has been fostered by mandates and financial incentives offered by governments. This interest can be mostly attributed to the commonly cited advantages of biofuels, mainly that they

- Reduce the emission of gases responsible for global warming

- Promote rural development.
- Contribute towards the goal of energy security.
- Are renewable,
- And reduce pollution.

Another feature that proponents of biodiesel put forward is that the fuel can be used without modification in engines currently in use. Over the past three decades the desires to establish national energy self-reliance and to develop alternatives to finite fossil fuel resources have resulted in the development of fuel technologies that are based on the use of renewable agriculture-based materials as feedstock. Information on the production, quality specifications, performance and emission properties of biodiesel has accumulated steadily over the past three decades. In addition to extensive laboratory testing, millions of miles have been travelled by test and demonstration vehicles running on biodiesel. Announcements of its adoption by municipalities, school districts, businesses, governmental agencies, entrepreneurs, and show business entertainers appear on a regular basis. Thus, biodiesel technology is making the transition from a research endeavour to a worldwide commercial enterprise. In support of this increasing consumption there have been substantial increases in biodiesel production in recent years, a trend that is expected to continue. Europe and the US are the leading biodiesel producers at this time. This growth is the result of the construction of new production plants and the expansion of existing ones.

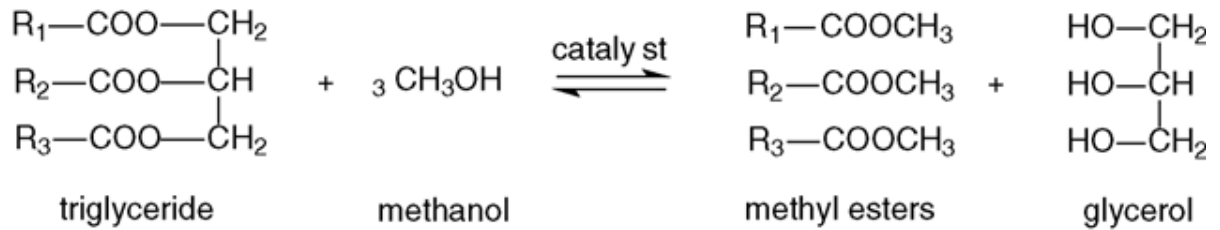
The choice of feedstock in the production of biodiesel is based on such variables as local availability, cost, government support and performance as a fuel. A variety of different types of reaction configurations can be employed in biodiesel synthesis, and may involve inorganic acid, inorganic base or enzymatic catalysis, biphasic or monophasic reaction systems, and ambient or elevated pressures and temperatures.

2.0 METHODOLOGY

Transesterification process is a main process in biodiesel production from vegetable oils. With the current demand and technologies, many types of heterogeneous catalysts have been explored in order to enhance existing production capacity and quality. Heterogeneous catalysts have many advantages when compared to homogenous catalysts. As a heterogeneous catalyst, Calcium Oxide (CaO) has basic sites stronger and it has been studied as a solid strong base catalyst by many

researchers. It also has a longer catalyst lifetime and better stability than current homogeneous catalyst.

The transesterification of triglycerides to fatty acid methyl esters (FAME) with methanol is a balanced and catalyzed reaction, as illustrated in Fig. 1. An excess of methanol is required to obtain a high degree of conversion.



with R1, R2, R3 = hydrocarbon chain from 15 to 21 carbon atoms

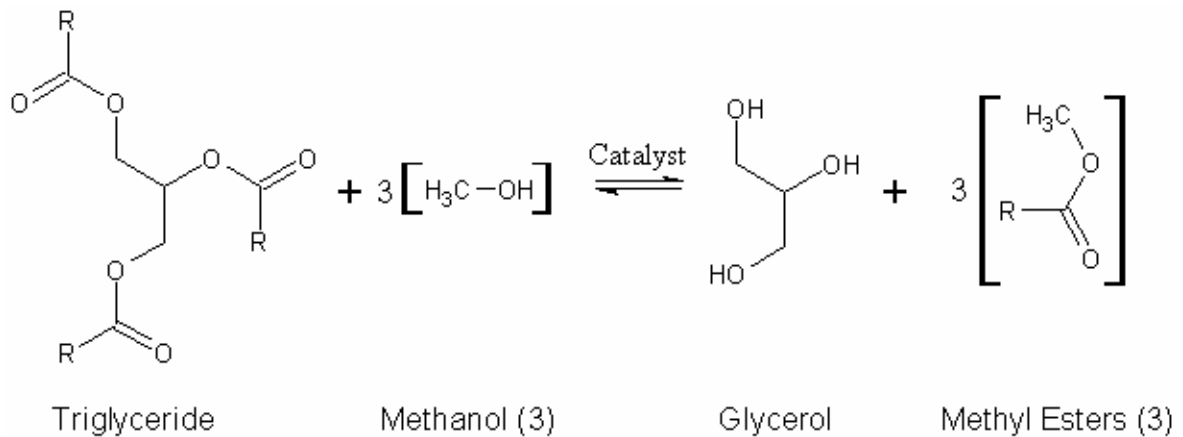


Fig. 1: Overall reaction for vegetable oils methanolysis

In this continuous process, the transesterification reaction is promoted by a completely heterogeneous catalyst without catalyst loss. In heterogeneous catalyst processes, the reaction is performed at higher temperature and pressure with an excess of methanol. However, this excess is removed by vaporization and recycled to the process with fresh methanol.

In order to meet the standard specifications, two stages of reaction and glycerol separation were built to shift equilibrium of methanolysis. The flow diagram of this process is presented in Fig. 2. The catalyst section includes two fixed bed reactors fed with vegetable oil and methanol at a given ratio. Excess of methanol is removed after each reactor by partial evaporation, and then esters and glycerol are separated in a

settler. Glycerol outputs are gathered and the residual methanol is removed by evaporation. In order to obtain biodiesel at the European specifications, the last traces of methanol and glycerol have to be removed. The purification section of methyl ester output coming from decanter 2 consists of finishing methanol vaporization under vacuum followed by a final purification in an adsorber for removing the soluble glycerol.

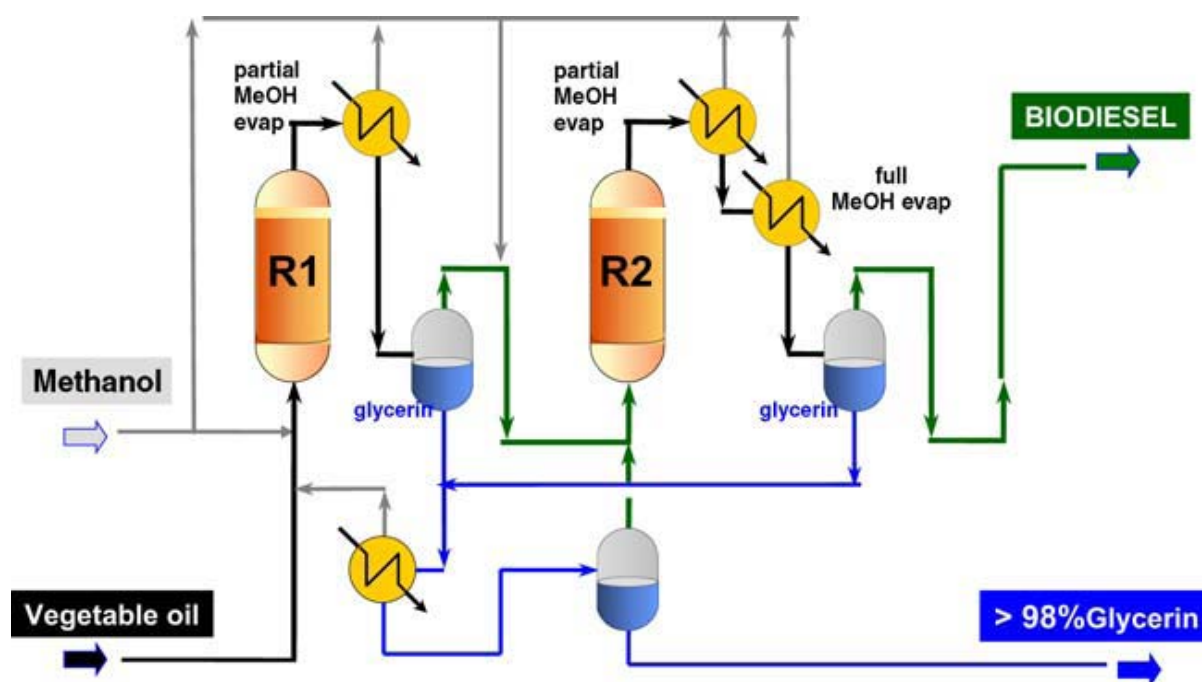


Fig. 2: Simplified flow sheet of the new heterogeneous process, Esterfif-HTM

In conventional biodiesel production process, vegetable oil methanolysis is achieved using a homogeneous catalyst system which is operated in either batch or continuous mode. Normally, sodium hydroxide or sodium methylate will be used as catalyst in this process. After transesterification reaction, sodium will be recovered as sodium glycerate, sodium methylate, and sodium soaps in the glycerol phase. Sodium soaps generally occur as side reactions from this process. The sodium soaps are soluble in the glycerol phase and must be isolated after neutralization by decantation as fatty acids.

Soaps may allow emulsification that causes the separation of the glycerol and ester phases to be less sharp. Soap formation also produces water that can hydrolyze the triglycerides and contribute to the formation of more soap. Further, catalyst that has been converted to soap is no longer available to accelerate the reaction.

3.0 NOVELTY

Heterogeneous base catalysts are better than homogeneous base catalysts because of the great property of being noncorrosive, friendly to the environment and presenting very few disposal problems. That is the reason that they are easily separated from the liquid products and used for design with higher activity, selectivity and longer catalyst lifetimes. There are a lot of types of heterogeneous catalysts explored for transesterification of vegetable oils to biodiesel. One of them is CaO, which owns stronger basic sites and many researchers use it as a solid strong base catalyst for study. By using CaO to produce biodiesel as a solid base catalyst, the advantages are higher activity, mild reaction conditions, long catalyst lifetimes and low catalyst cost. Reddy (2006) used Nanocrystalline Calcium Oxides to produce biodiesel under room-temperature but the reaction rate was slow as it required 6-24 h to have a high conversion with the most active catalyst. Liu et al. (2008) found that adding a little water into methanol can enhance the catalytic activity of CaO in the transesterification of soybean oil to biodiesel. They also proposed the transesterification reaction mechanism in the presence of a little water in methanol. Because of the presence of a little water, CaO can produce more methoxide anions. Methoxide anions are the real catalysts of transesterification of glyceride to biodiesel. Therefore, the transesterification reaction rate is enhanced and can be accelerated. The yield of biodiesel is also increased due to a short reaction time. The best amount of water is no more than 2.8% by weight of soybean oil.

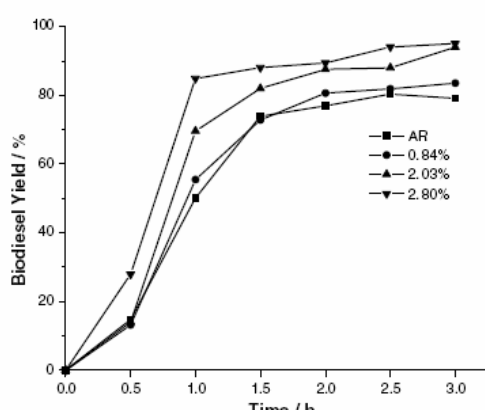


Fig. 3: Effect of water content of methanol on biodiesel yield. CaO/oil mass ratio: 8%; reaction temperature: 65 °C; methanol/oil molar ratio: 6:1. (Liu et al (2008))

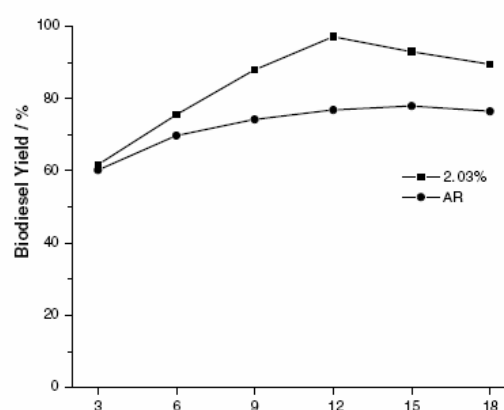
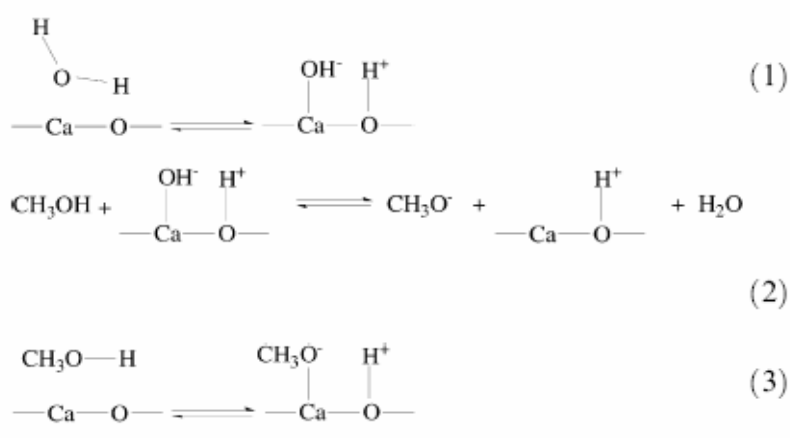


Fig. 4: Effect of molar ratio of methanol to oil on biodiesel yield. CaO/oil mass ratio: 8%; reaction temperature: 65 °C; reaction time: 1.5 h; water content: 2.03%. (Liu et al (2008))

Fig. 3 shows that the various amounts of the water contained in methanol affect the biodiesel yield. When the water content in methanol increased, the biodiesel yield

raised. It took 3 h when analytical reagent methanol was used by only 80%. Meanwhile, 95% of the biodiesel yield reached when the water was added up to an excess of 2.03%. That is because OH groups were formed on the CaO surface by adsorbing water molecules dissociatively. (Eq. (1)) and they can accelerate the transesterification reaction rate. The content of water in methanol should not be more than 2.8% in order to prevent the formation of soap.

Fig. 4 indicates that when the molar ratio increased, the biodiesel yields grew. By using analytical reagent methanol with 12:1 molar ratio of methanol to oil, the yield was only 75%.



In contrast, at a 2.03% water content in methanol, the biodiesel yield reached 97% when the molar ratio was 12:1. This is the best molar ratio of methanol to oil because the catalyst content decreased at higher molar ratio. The result shows the biodiesel yield was only 90% at 18:1.

In the reaction mixture, there constitutes a three-phase system in the presence of heterogeneous catalysts. The diffusion resistance occurs between different phases and the reaction rate decreases. Raising the reaction temperature can accelerate the reaction rate, but at high temperatures, methanol would be vaporized and form lot of bubbles. It is not good to the reaction on the three-phase interface. According to the result, the best temperature for the reaction was 65°C.

The mass ratio of catalyst to oil can affect biodiesel yield. The amount of CaO increases to improve the biodiesel yield. When the CaO/oil mass ratio was 8%, 90% of biodiesel yield can be obtained by 3 h. In contrast, when CaO/oil mass ratio was 2%, the yield only was 55%. The reason was that alkalinity can affect greatly the catalytic activity, but when the amount of CaO to oil was more than 8%, the effect of CaO on biodiesel yield was slight. Therefore, the importance of the mass transfer increases at this moment rather than the increasing the amount of catalyst.

Although the heterogeneous solid base catalysts for the transesterification of vegetable oils to biodiesel consist of CaO, $K_2CO_3/\gamma-Al_2O_3$ and $KF/\gamma-Al_2O_3$, CaO is more stable and has better activity in this reaction. CaO catalysts can produce excessive 86% biodiesel yields at 65 °C and 1 h in each experiment. After used for 20 times, the activity remains high and the biodiesel yield only decreases slightly. However, $K_2CO_3/\gamma-Al_2O_3$ and $KF/\gamma-Al_2O_3$ catalysts are sensitive to water and the activity of them decrease rapidly at each time to produce biodiesel repeatedly. The reason is that alkali metal compounds are dissolvable in methanol, which corrodes the active ingredients. Therefore, the biodiesel yields decreases.

The novelty of this research is using CaO catalysts to produce highly yield of biodiesel. It is an important impact on biodiesel yield to add water at an approximate level in the transesterification of soybean oil to biodiesel. The best composition is a 12:1 molar ratio of methanol to oil; addition of 8% CaO catalyst, 65 °C and 2.03% water content in methanol and the biodiesel yield can exceed 95% at 1.5 h.

4.0 POTENTIAL IMPACTS

The potential for the use of biodiesel is to enhance the chemical process industry to produce environmentally friendly biofuel using heterogeneous catalyst.

Bioenergy should play an essential part in reaching targets to replace petroleum-based transportation fuels with a viable alternative, and in reducing long-term carbon dioxide emissions, if environmental and economic sustainability are considered carefully. Here, different platforms, crops, and biotechnology-based improvements for sustainable bioenergy are reviewed.

Bioenergy refers to renewable energy from biological sources that can be used for heat, electricity and fuel, and their co-products. There has been a resurgence of interest in bioenergy recently. The potential impact of the biotechnology on renewable energy has been already addressed.

Second generation micro algal systems have the advantage that they can produce a wide range of feedstocks for the production of biodiesel,

The main advantages of second generation micro algal systems are that:

- Have higher photon conversion efficiency.
- Can utilize salt and waste water streams, thereby greatly reducing freshwater use
- Can couple CO_2 -neutral fuel production with CO_2 sequestration.
- Produce non-toxic and highly biodegradable biofuels.

Biodiesel is the most immediate alternative to diesel oil and many environmental, social, and economic benefits would readily arise from its utilization in both the transportation and energy sectors. In Brazil, there has been an increasing interest in developing such an alternative, but the economics of producing biodiesel from vegetable oils has always been negative. However, several factors indicate that changes are just around the corner. These include the severe turbulence recently observed in the international petroleum market, the recent achievements toward the production of a good-quality biodiesel from cheaper and more readily available lipid sources and the development of new catalysts for alcoholysis.

Therefore, biodiesel may soon become competitive and its use to replace diesel oil will increase steadily.

A new biodiesel process has been introduced to the chemical process industry which is the Mcgyan process. In this process, a better biodiesel process has been developed with no waste products and lower costs.

The metal oxide microspheres are the key to the process because they are highly soluble catalysts, even under extreme temperature and pressure and show no loss of conversion efficiency over time.

All excess alcohol is recycled back through the reactor, so the process does not produce waste any products.

The Benefits of the process;

- Can utilize a variety of inexpensive, not food grade feedstocks [like fat and garbage food waste]
- Can produce biodiesel in seconds not hours
- Does not produce any waste
- Small in physical size
- No washing, refining or neutralizing of the biodiesel is necessary [can be 88% of the cost of biodiesel]
- Sulphated zirconia catalyst never needs replacing

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