DESIGN OF EXPERIMENT FOR ETHANOL-WATER MIXTURE IN DISTILLATION PROCESS

SAWALAK PHUNGTHAM

UTSANEE PHONJIT

WEERAWUT PONGSUTEENIWET

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นักศึกษา : นางสาว สวลักษ์ พึ่งธรรม
นางสาว อุษณีย์ พลจิตต์
นาย วีรวุฒิ พงศ์สุธีนิเวศ
สาขาวิชา : เทคโนโลยี ปิโตรเคมี (นานาชาติ)
พ.ศ. : 2546
อาจารย์ผู้ควบคุมวิทยานิพนธ์ : อ. มนตรี ทองคำ

บทคัดย่อ

โครงงานพิเศษนี้ศึกษาถึงผลกระทบของตัวแปร 4 ตัวแปรสำหรับการกลั่นเอทานอลกับน้ำโดยใช้การออกแบบการทดลอง (design of experiment) การออกแบบการทดลองมีหลายวิธี เนื่องจากโครงงานพิเศษนี้ต้องการศึกษาถึงผลกระทบของตัวแปร 4 ตัวแปรที่มีต่อการกลั่นได้แก่ ความเข้มข้นของ feed อุณหภูมิของ feed อัตราการไหลของ feed และ reflux ratio จึงเลือกวิธี 2^4 factorial design มาใช้ในโครงงานพิเศษนี้ ตัวแปรทั้งสี่จะถูกพิจารณาเป็น 2 ระดับคือระดับสูงและระดับต่ำ ดังนั้นจำนวนการทดลองจะมี 16 การทดลอง แต่เนื่องจากการทดลองถูกทำซ้ำ 2 ครั้ง จึงมีจำนวนการทดลองทั้งหมด 32 การทดลอง ก่อนเริ่มการทดลองจะต้องมีการเตรียมสารผสมของเอทานอลกับน้ำ สารผสมที่เตรียมไว้ในหนึ่งครั้งจะเพียงพอสำหรับการทดลองเพียง 16 การทดลอง ดังนั้นจึงต้องมีการเตรียมสารผสม 2 ครั้งสำหรับการทดลองนี้ เพื่อให้เพียงพอต่อจำนวนการทดลองทั้งหมด สารผสมที่เตรียมจะถูกพิจารณาให้เป็นบล็อก (block) ดังนั้นการทดลองนี้จึงมี 2 บล็อก ใน 1 บล็อกมีจำนวนการทดลอง 16 การทดลอง ลำดับของการทดลองในแต่ละบล็อกถูกจัดขึ้นจากการสุ่ม การออกแบบการทดลองในลักษณะนี้เรียกว่า การสุ่มในบล็อกแบบสมบูรณ์ (Randomized in Complete Block Design or RCBD) ดังนั้น แบบการทดลองที่ใช้ในโครงงานพิเศษนี้จึงเป็น 2^4 factorial design บนพื้นฐานของการสุ่มในบล็อกแบบสมบูรณ์ (2^4 factorial design in RCBD) ในการกลั่นเอทานอลกับน้ำหลังจากที่ระบบเข้าสู่สมดุล distillate จะถูกเก็บ หลังจากนั้นจึงนำ distillate ไปวัดหาค่า refractive index โดยใช้เครื่อง refractometer ค่า refractive index จะถูกเปลี่ยนเป็นความเข้มข้นโดยใช้ calibration curve เพื่อนำค่าความเข้มข้นเหล่านี้ไปคำนวณหาค่าผลกระทบของแต่ละตัวแปร หลังจากนั้นจึงใช้วิธีการวิเคราะห์ความแปรปรวน (analysis of variance) มาศึกษาอิทธิพลที่มีร่วมกันของตัวแปรทั้งสี่

จากการทดลองพบว่าเงื่อนไขที่ดีสำหรับการกลั่นเอทานอลกับน้ำคือที่ ความเข้มข้น 40 % ของ feed อุณหภูมิของ feed 80 องศาเซลเซียส อัตราการไหลของ feed 2 ลิตรต่อชั่วโมง และที่ reflux ratio 1:1 จากการวิเคราะห์ความแปรปรวนค่า F ของอิทธิพลร่วมของตัวแปรทั้งสี่ตัวแปรมีค่ามากกว่าค่า F ที่เปิดได้จากตาราง F-distribution นั่นคือค่า F ของอิทธิพลร่วมทั้งสี่ตัวแปรมีนัยสำคัญ ซึ่งมีความหมายว่าตัวแปรทั้งสี่ตัวแปรมีอิทธิพลร่วมกัน

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Student : Sawalak Phungtham
Utsanee Phonjit
Weerawut Pongsuteeniwet
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Thesis Advisor : Mr. Montree Thongkam

ABSTRACT

This research investigated the effect of four parameters for ethanol-water mixture in distillation process by using design of experiment. In the design of experiment, 2^4 factorial design was used to study the effect of the parameters. Four parameters were feed concentration, feed temperature, feed flow rate, and reflux ratio. They were varied to two values (high and low). There were 16 treatment combinations. Two replicates of the 2^4 factorial design did in this experiment. Therefore, there were 32 runs in this experiment. Raw material were considered as blocks, then 16 treatment combinations of the 32 treatment combinations were assigned to each block. Therefore, there were two blocks in the experiment. The treatment combinations in each block made in random order to minimize an error in the process. This design was called a randomized complete block design (RCBD). Consequently, the design in this experiment was called the 2^4 factorial design in RCBD. After each of the treatment combination was run, the distillate was collected. The distillates were measured by the refractometer to identify the refractive indexes. That were changed to concentrations by using the calibration curve. The effect of the parameters was then calculated and the analysis of variance (F-values) was used to study the interaction effect of the parameters.

It was found that the optimum condition for distillation of ethanol-water system was 40% of feed concentration, 80°C of feed temperature, 2 L/h of feed flow rate, and 1:1 of reflux ratio. Since the F-value of the ABCD interaction effect from a calculation was more than the F-value from the F-distribution table, so the F-value of the ABCD interaction effect was significant as shown in variance analysis. It was meant that the reflux ratio (A), the feed flow rate (B), the feed temperature (C), and the feed concentration (D) had interaction effect together.

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Sawalak Phungtham
Utsanee Phonjit
Weerawut Pongsuteeniwet

TABLE OF CONTENTS

Page

TABLE OF CONTENTS

TABLE OF CONTENTS (continue)

Page

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

LIST OF FIGURES (continue)

CHAPTER 1

INTRODUCTION

1.1 MOTIVATION

In recent years, there has been a revival of interest in experimental design. Many industries have been using designed experiment for their competitive success. All engineers will receive formal training in experimental design as part of their undergraduate education. It is a key factor in the future competitiveness of industrial base.

Distillation of ethanol-water mixture is the popular case for study, but it has many parameter to consider. Thus, design of experiment is the good tool to analyze data of distillation process for dominating the critical parameters, reducing operating time and operating costs.

1.2 OBJECTIVES

1. To study and compare the operating conditions of water and ethanol mixture in distillation.
2. To design and study the optimum operating condition for distillation of water and ethanol mixture by using design of experiment for statistical analysis of the data.

1.3 SCOPE OF STUDY

1. To short cut processing variables of critical parameter by using experimental design method.
2. To find the effects of critical parameters of distillation process on water-ethanol mixture system.
3. To investigate the optimum operating conditions of water and ethanol mixture in distillation.

1.4 EXPECTED RESULTS

- To know the optimum operating condition of water and ethanol mixture in distillation.
- To improve process yields by design the processes.
- To reduce variability and approach to target requirements.
- To neglect some parameters that do not affect to process.
- To reduce processing time and operating costs.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 LITERATURE REVIEW

S.Kauchali, C. McGregot and D. Hildebrandt [1] studied on an attainable region (AR) analysis, this is a geometrically-based method of optimization that has mainly been used for performing optimal reactor synthesis. They applied the AR theory to binary distillation where they constructed a constrained attainable region. They considered the optimum policy for the reflux ratio along the column where there was no cost associated with the processes used to control the reflux ratio. In their paper, they would like to investigate the effect of including costs for the processes used to control the reflux ratio on the operating policy and structure of the column. The attainable region, subject to the conditions discussed above, has been determined and the behavior shown graphically in a composition, cost and reflux/reboil space. They discussed the effects of changing the reflux/reboil ratio along the length of the column and examined the implications of the results obtained from the construction of the constrained AR for the design of conventional distillation columns.

M. Šoóš, E. Graczová, J. Markoš, A. Molnár and P. Steltenpohl [2] are presented the design of a separation column for recovery of 1,2-dichloropropane (DCP) from the off-gas released during propylenechlorhydrine (PCH) synthesis. The aim of this separation is to recover DCP with purity of 99.99 % by weight. The simulation of the separation column is performed by means of the professional simulation program HYSYS®. The design of the rectification column is based on complete experimental measurements. The calculation is compared with the design of a separation column, which uses for the computation of the equilibrium composition corresponding to database of the simulation program, and with the calculation, in which the complete set of equilibrium data is predicted from the UNIFAC method. By comparison of the results of the rectification column design quite different values of parameters which characterizing the rectification column were obtained.

L. Chau-Kuang Liau, T. Chung-Kuang Yang, and M. Tsai [3] used design of experiment to analyze the effect of the system input variables on the oil product qualities from crude oil distillation unit (CDU). An expert system of crude oil distillation unit (CDU) was developed to carry out the process optimization on maximizing oil production rate under the required oil product qualities. The expert system was established using the expertise of a practical CDU operating system provided by a group of experienced engineers. The input operating variables of the CDU system were properties of crude oil and manipulated variables; while the system output variables were defined as oil product qualities. The knowledge database of the CDU operating model can be built using the input–output data with an approach of artificial neural networks (ANN). The built ANN model can be applied on predicting the oil product qualities with respect to the system input variables. In addition, a design of experiment was implemented to analyze the effect of the system input variables on the oil product qualities. Optimal operating conditions were then found using the knowledge database with an optimization method according to a defined objective function. The built expert system can provide on-line optimal operating information of the CDU process to the operators corresponding to the change of crude oil properties.

Bimal P. Singh, L. Besra, and S. Bhattacharjee [4] stuied the factorial design of experiment to define the condition for an optimum performance in a complex system. The present investigation was aimed at studying the synergistic effects of different surface-active agents (SAA) on the stability of aqueous alumina suspensions. The SAA used were dibasic ammonium citrate as dispersant, albumin as binder and octanol-2 as an antifoaming agent. Stability of suspensions was assessed through measurement of the specific surface charge of the system, using the fact that the particles exhibit maximum repulsion between them at high magnitude of surface charge. The experiments were statistically designed to bring out the effect of each variable as well as the effect due to interactions. The results show that the strongest affects on stability of aqueous colloidal suspension is that of dibasic ammonium citrate and albumin. The effect of interactional parameters, though slightly favourable for increasing the stability of the suspension, is very small. Dibasic ammonium citrate and albumin, both highly negatively charged SAA, stabilise the suspension by increasing the overall surface charges of the ceramic particles which inturn increases the overall repulsive forces. On the other hand, the positive charge of octanol-2 neutralises/decreases the magnitude of negative surfaces charge and, consequently, decreases the stability of the suspension. It has been shown that factorial design of experiment approach is very helpful in defining conditions for an optimum performance in such complex systems.

D. Yoon, and Burtrand I. Lee [5] studied the optimization of the twenty-four kinds of $BaTiO_3$ slips for MLCC application were investigated using three different binder systems: one solvent-based, and two water-based with water-soluble acrylic binder and aqueous emulsion binder systems by using factorial design method. The half-fractional factorial design method was used for each system with four input factors with two levels for each factor. Tape casting, K-square preparation, sintering and characterization were conducted. Slip viscosity, mechanical properties of the green tapes, green and sintered density of K-squares, and dielectric permittivity were analyzed as output responses using statistical analysis methods. Most of the green body properties from solvent-based system such as tensile strength, tape morphology and bulk density depended on the ceramic powder. While, dispersant was the most significant factor for the two water-based systems. The sintered properties such as microstructure and dielectric permittivity for the three systems depended significantly on the type of ceramic powder. Finally, an optimization was performed for each system by means of a scorecard which was used to prioritize all samples to important output responses through the numerical ranking method.

I. L. Shih, Y. T. Van, and Y. N. Chang [6] employed the statistical experimental methods (SEM) to study the effects of glutamic acid, citric acid, glycerol and initial medium pH on the production of poly(γ-glutamic acid) (γ-PGA) by *Bacillus licheniformis* CCRC 12826 in shaken cultures. The results of first-order factorial design experiments showed that the liner terms of glutamic acid, citric acid and glycerol had significant positive effects, but the initial medium pH exhibited insignificant effect on γ-PGA production. The effects decreased in the order of glycerol, glutamic acid and citric acid. In addition, the interaction term of glutamic acid–glycerol exhibited a significant positive effect. Based on the results of the first-order factorial design experiment, the optimum composition was then investigated by using a central composite design (CCD). The experimental results of CCD were fitted with a second-order polynomial equation by a multiple regression analysis. The coefficient of determination (R^2) was 0.9078, the Fisher F-test was significant at upper 5% level and the lack of fit was insignificant at 5% level. All of these indicated a good adequacy of the second-order polynomial model proposed to explain the data observed.

The optimal γ-PGA yield (19.80±1.59 g/l) was determined by the CCD experiments and was predicted to be at the regions where respective concentrations of citric acid, glutamic acid and glycerol were around 24.50, 57.30 and 157.11 g/l, respectively. When the strain was cultivated using the optimized medium predicted by the model, the yield of γ-PGA production was 19.62±1.07 g/l (average of three repeats). The γ-PGA production by *B. licheniformis* CCRC 12826 was increased significantly by 372%, from 5.27 to 19.62 g/l when the strain was cultivated in the optimal medium developed by SEM, as compared to conventional medium E used in the literature. The γ-PGA thus produced was shown to be a homogeneous polymer of glutamic acid by thin-layer chromatography and amino acid analysis, and its molecular weight was over 2×10^6 Da by GPC

E. Batista, M. I. Rodrigues, and A. J. Meirelles [7] used factorial design to study the optimization of SRV extractive distillation in production of pure ethanol. SRV (Secondary Reflux Vaporization) distillation is based on heat exchange between the rectifying and stripping sections. This specific kind of distillation involves a large number of operating variables and details in design, and enormous computational efforts are traditionally necessary for its optimization. Factorial design and surface response analysis were used to optimize SRV extractive distillation in production of pure ethanol. Once such a distillation process is optimized, it involves substantially lower energy consumption than conventional ones.

D. Undurraga , A. Markovits, and S. Erazo [8] studied the effect of the initial ratio of stearic acid–POMF, initial humidity of the enzyme preparation and the enzyme–substrate ratio on the yield, mass productivity and specific productivity by using a factorial design. The production of a cocoa butter equivalent (CBE) through enzymic interesterification of palm oil midfraction (POMF) with stearic acid in a solvent free system using Novo lipase Lipozyme™ as a catalyst was analyzed. A two level factorial design was used to study the effect of the initial ratio of stearic acid–POMF, initial humidity of the enzyme preparation and the enzyme–substrate ratio on the yield, mass productivity and specific productivity. Studies were carried out both in batch and in a continuous packed bed reactor. The highest specific productivity obtained in shake flask was 0.0393 g/Batch Interesterification Unit (BIU) h at a stearic acid–POMF ratio of 1.6 and enzyme–

substrate ratio of 23 BIU/g. In the continuous packed bed reactor the highest mass productivity observed was 1.54 g/g·h, using an enzymic load of 73 BIU/g. Unreacted fatty acids were separated from the intereresterified products by short path distillation at 0.2 mbar and 140°C obtaining a product practically without free fatty acids. Thermograms of the products obtained by scanning differential calorimetry were similar to cocoa butter (CB), but exhibited several distinct peaks, due presumably to the presence of diglycerides and trisaturated triglycerides.

M. M. Esquível , M. A. Ribeiro, and M. G. Bernardo-Gil [9] investigated the optimum fractionation conditions by using two-level factorial design method. The experimental results of supercritical CO_2 extraction on summer savory (*Satureja hortensis* L.) oil at pressures ranging from 12 to 18 MPa and at a temperature of 313 K are presented. The optimum conditions achieved to obtain the maximum extraction yield were 12 MPa, 120 kg CO_2/h kg solid and 1 h of extraction. The extract was fractionated in three separators, operated in series. The optimum fractionation conditions which minimize the coextraction of unwanted compounds were investigated using a two-level factorial design approach. The extracts obtained were compared with summer savory essential oil isolated by steam distillation and by a modified Clevenger apparatus. A study of the antioxidant activity of summer savory extracts was performed using the Rancimat method.

J. Leboreiro and J. Acevedo [10] presented an optimization framework is proposed in this work for the synthesis and design of complex distillation sequences, based on a modified genetic algorithm (GA) coupled with a sequential process simulator. The use of a simulator facilitates the formulation of rigorous models for different process alternatives, while the genetic algorithm allows the solutions of the complex non-convex mathematical problem, involving discrete and continuous decisions. To reduce the computational requirements of the optimization procedure, several strategies are proposed, including a novel stopping criterion, which provides an efficient way to end the calculations when the optimal solution has been found. The implementation of these strategies resulted in reductions up to 60% in CPU time for the synthesis of complex distillation systems, succeeding in problems where deterministic mathematical algorithms had failed.

C. Noeres, K. Dadhe, R. Gesthuisen, S. Engell and A. Gorak [] , Their studied the benefits of using dynamic models of different complexity and size for process design optimal operation and control of catalytic distillation (CD) processes are discussed for the case study of the heterogeneously catalyzed reactive distillation (RD) of methyl acetate. Dynamic reactive distillation experiments at pilot plant scale were performed using the catalytic structured packing MULTIPAK. A dynamic rate-based model were developed which contains hydrodynamic effects as liquid holdup, liquid back mixing and pressure drop as well as reaction kinetics and which describes the process behavior accurately. For offline and online optimization and control, reduced order and simplified models were applied. A systematic control structure selection and controller design studies for the experimental column were conducted. The linear controller shows good performance over a wide range of operating conditions.

K. Sundmacher and Z. Qi [12] studied on the conceptual design of reactive distillation process configurations is presented, considering the reversible reaction $A_1 \leftrightarrow A_2$ in an ideal binary mixture as simple model system. The analyzed flow schemes are a reactor-distillation column sequence with an external recycle loop, the same recycle system with a prereactor, a non reactive distillation column on top of a reactive reboiler, a fully reactive distillation column, and a hybrid distillation column combining a reactive and a non reactive section. For these configurations, the design aspects are discussed in terms of the most important operating parameters, kinetic parameters and design parameters.

M. Tapp, S. Kauchali, B. Hausberger, C. McGregor, D. Hildebrandt and D. Glasser, [13] their interested in the use of residue curves for the preliminary design and sequencing of distillation columns. Residue curves are used not only to predict composition changes in separation processes, but also to determine the feasibility of proposed separations, and flow sheet development.

An experimental technique has been developed for the measurement of these residue curves. It can be shown that the time-dependent composition profiles obtained in a modified form of this apparatus are mathematically equivalent to the position-dependent profiles in a continuous distillation column. Hence, it is possible to experimentally simulate a distillation column profile in a small batch apparatus using only small quantities of material.

The modified apparatus consists of a still immersed in a heated oil bath so that a liquid feed is continuously supplied to the still. Samples of liquid are then analyzed over time using a gas chromatograph. The results from an experimental system have been compared to available information and simulations to determine the accuracy of the apparatus.

This technique has several advantages over working with distillation columns, firstly in the sample size required, and secondly in the ease of operation. The method allows quick and low-cost measurements of the concentration variables that model a distillation column. The information obtained this way could prove useful for the selection of feasible systems and for finding minimum reflux requirements. It could also be very valuable for screening of complex systems where only small amounts of material are available and simulations may be very difficult.

2.2 DISTILLATION [14]

The separation process known as distillation is a method for separating the various components of a liquid solution which depends upon the distribution of these components between a vapor phase and a liquid phase. All components are present in both phases. The vapor phase is created from the liquid phase by vaporization at the boiling point.

The basic requirement for the separation of components by distillation is that the composition of the vapor be different from the composition of the liquid with which it is in equilibrium at the boiling point of the liquid. Distillation is concerned with solutions where all components are appreciably volatile, such as ammonia-water or ethanol-water solutions, where both components will be in the vapor phase.

Distillation can be carried out by either of two main methods in practice. The first method of distillation involves the production of a vapor by boiling the liquid mixture to be separated in a single stage and recovering and condensing the vapors. No liquid is allowed to return to the single-stage still to contact the rising vapors. The second method of distillation involves the returning of a portion of the condensate to the still. The vapors rise through a series of stages or trays, and part of the condensate flows downward through the series of stages of trays countercurrent to the vapors. This second method is called *fractional distillation, distillation with reflux, or rectification.*

There are three important types of distillation that occur in a single stage of still and that do not involve rectification. The first method of these is equilibrium or flash distillation, the second is simple batch or differential distillation, and the third is simple steam distillation.

Equilibrium or Flash Distillation. In ***equilibrium*** or ***flash distillation***, which occurs in a single stage, a liquid mixture is partially vaporized. The vapor is allowed to come to equilibrium with the liquid, and the vapor and liquid phases are then separated. This can be done batchwise or continuously.

In Fig. 2-1 a binary mixture of components A and B flowing at the rate of F mol/h into a heater is partially vaporized.

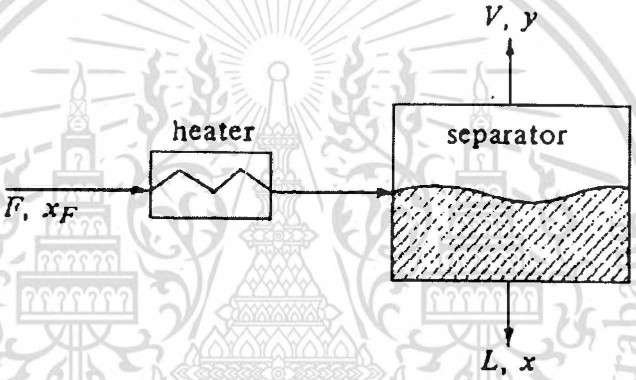


Figure 2-1. Equilibrium of flash distillation. [14]

Then the mixture reaches equilibrium and is separated. The composition of F is x_F mole fraction of A. A total material balance on component A is as follows:

$$Fx_F = Vy + Lx \tag{2-1}$$

Since $L = F - V$, Eq. (2-1) becomes

$$Fx_F = Vy + (F - V)x \tag{2-2}$$

Usually, the moles per hour of feed F, moles per hour of vapor V, and moles per hour of L are known or set. Hence, there are two unknowns x and y in Eq. (2-2). The other relationship needed in order to solve Eq. (2-2) is the equilibrium line. A convenient method to use is to plot Eq. (2-2) on the x-y equilibrium diagram. The intersection of the equation and the equilibrium line is the desired solution.

2.2.1 Simple Batch or Differential Distillation

In *simple batch* or *differential distillation*, liquid is first charged to a heated kettle. The liquid charge is boiled slowly and the vapors are withdrawn as rapidly as they form to a condenser, where the condensed vapor (distillate) is collected. The first portion of vapor condensed will be richest in the more volatile component A. As vaporization proceeds, the vaporized product becomes leaner in A.

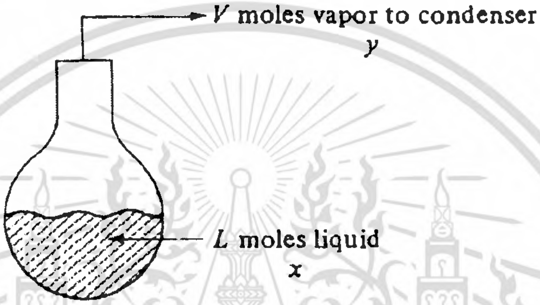


Figure 2-2. Simple batch or differential distillation. [14]

In Fig. 2-2 a simple still is shown. Originally, a charge of L_1 moles of components A and B with a composition of x_1 mole fraction of A is placed in the still. At any given time, there are L moles of liquid left in the still with composition x, and the composition of the vapor leaving in equilibrium is y. A differential amount dL is vaporized.

The composition in the still pot changes with time. In deriving the equation for this process, we assume that a small amount of dL is vaporized. The composition of the liquid changes from x to $x - dx$ and the amount of liquid from L to $L - dL$. A material balance on A can be made, where the original amount equals to the amount left in the liquid plus the amount of vapor:

$$xL = (x - dx)(L - dL) + ydL \tag{2-3}$$

multiplying out the right side,

$$xL = xL - xdL - Ldx + dxdL + ydL \tag{2-5}$$

Neglecting the term dx dL and rearranging,

$$\frac{dL}{L} = \frac{dx}{y - x} \tag{2-5}$$

Integrating,

$$\int_{L_2}^{L_1} \frac{dL}{L} = \ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{dx}{y-x} \tag{2-6}$$

where L_1 is the original moles charged, L_2 the moles left in the still, x_1 the original composition, and x_2 the final composition of liquid. The equilibrium curve gives the relationship between y and x. The integration of Eq. (2-6) can be done by calculating values of $f(x) = 1/(y - x)$ and numerically or graphically integrating Eq. (2-6) between x_1 and x_2. Equation (2-6) is known as the *Rayleigh equation*. The average composition of total material distilled, y_{av}, can be obtained by material balance:

$$L_1 x_1 = L_2 x_2 + (L_1 - L_2) y_{av} \tag{2-7}$$

2.2.2 Simple Steam Distillation

At atmospheric pressure high-boiling liquids cannot be purified by distillation, since the components of the liquid may decompose at the high temperatures required. Often the high-boiling substances are essentially insoluble in water, so a separation at lower temperatures can be obtained by *simple steam distillation*. This method is often used to separate a high-boiling component from small amounts of nonvolatile impurities.

If a layer of liquid water (A) and an immiscible high-boiling component (B) such as a hydrocarbon are boiled at 101.3 kPa absolute pressure, then, by the phase rule, Eq. (2-8), for three phases and two components,

$$F = 2 - 3 + 2 = 1 \text{ degree of freedom} \tag{2-8}$$

Hence, if the total pressure is fixed, the system is fixed. Since there are two liquid phases, each will exert its own vapor pressure at the prevailing temperature and cannot be influenced by the presence of the other. When the sum of the separate vapor pressures equals the total pressure, the mixture boils and

$$P_A + P_B = P \tag{2-9}$$

where P_A is vapor pressure of pure water A and P_B is vapor pressure of pure B. Then the vapor composition is

$$y_A = \frac{P_A}{P} \quad \text{and} \quad y_B = \frac{P_B}{P} \tag{2-10}$$

As long as the two liquid phases are present, the mixture will boil at the same temperature, giving a vapor of constant composition y_A. The temperature is found by using the vapor-pressure curves for pure *A* and pure *B*.

Note that by steam distillation, as long as liquid water is present, the high-boiling component *B* vaporizes at a temperature well below its normal boiling point without using a vacuum. The vapors of water (*A*) and high-boiling component (*B*) are usually condensed in a condenser and the resulting two immiscible liquid phases separated. This method has the disadvantage that large amounts of heat must be used to evaporate the water simultaneously with the high-boiling compound. The ratio moles of *B* distilled to moles of *A* distilled is

$$\frac{n_B}{n_A} = \frac{P_B}{P_A} \tag{2-11}$$

Steam distillation is sometimes used in the food industry for the removal of volatile taints and flavors from edible fats and oils. In many cases vacuum distillation is used instead of steam distillation to purify high-boiling materials. The total pressure is quite low so that the vapor pressure of the system reaches the total pressure at relatively low temperatures.

Van Winkle [15] derives equations for steam distillation where an appreciable amount of a nonvolatile component is present with the high-boiling component. This involves a three-component system. He also considers other cases for binary batch, continuous, and multicomponent batch steam distillation.

2.3 DISTILLATION WITH REFLUX AND McCABE-THIELE METHOD

2.3.1 Introduction to Distillation with Reflux

Rectification (fractionation) or stage distillation with reflux, from a simplified point of view, can be considered to be a process in which a series of flash-vaporization stages are arranged in a series in such a manner that the vapor and liquid product from each stage flow countercurrent to each other. The liquid in a stage is conducted or flows to the stage below and the vapor from a stage flows upward to the stage above. Hence, in each stage a vapor stream *V* and a liquid stream *L* enter, are mixed and equilibrated, and a vapor and a liquid stream leave in equilibrium. This process flow diagram was shown in Fig. 2-3 for a single stage.

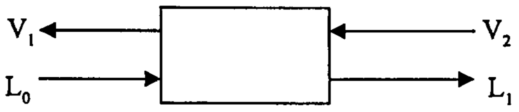


Figure 2-3. Single-state equilibrium process. [14]

For the countercurrent contact with multiple stages in Fig. 2-4, the material-balance or operating-line equation (2-12) was derived, which relates the concentrations of the vapor and liquid streams passing each other in each stage.

$$y_{n+1} = \frac{L_n x_n}{V_{n+1}} + \frac{V_1 y_1 - L_0 x_0}{V_{n+1}} \tag{2-12}$$

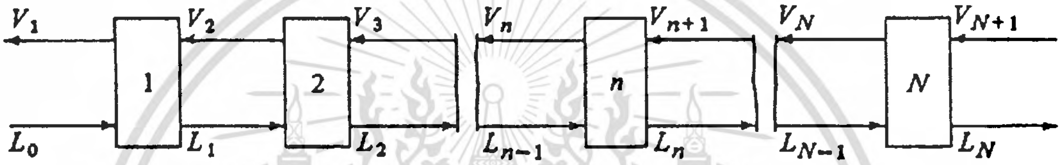


Figure 2-4. Countercurrent multiple-state process. [14]

In a distillation column the stages (referred to as *sieve plates* or *trays*) in a distillation tower are arranged vertically, as shown schematically in Fig. 2-5

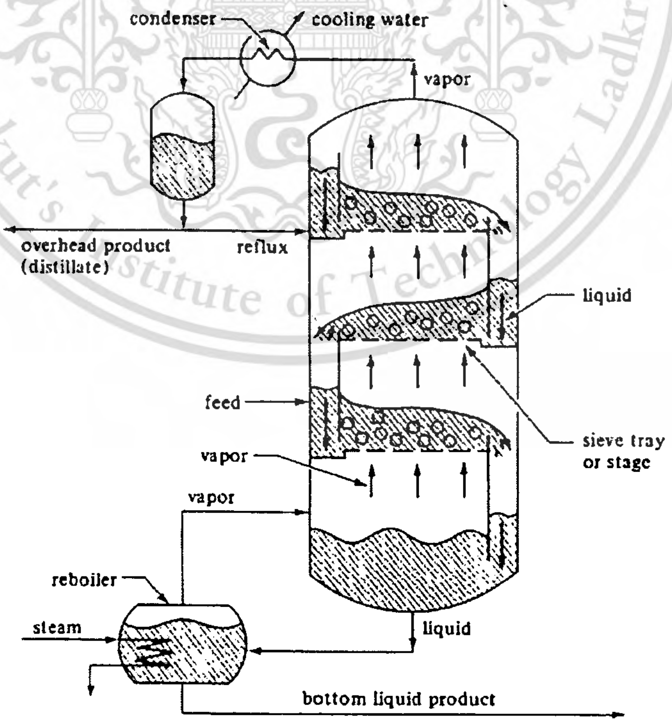


Figure 2-5. Process flow of a fractionating tower containing sieve trays. [14]

The feed enters the column in Fig. 2-5 somewhere in the middle of the column. If the feed is liquid, it flows down to a sieve tray or stage. Vapor enters the tray and bubbles through the liquid on this tray as the entering liquid flows across. The vapor and liquid leaving the tray are essentially in equilibrium. The vapor continues up to the next tray or stage, where it is again contacted with a downflowing liquid. In this case the concentration of the more volatile component (the lower-boiling component *A*) is being increased in the vapor from each stage going upward and decreased in the liquid from each stage going downward. The final vapor product coming overhead is condensed in a condenser and a portion of the liquid product (distillate) is removed, which contains a high concentration of *A*. The remaining liquid from the condenser is returned (refluxed) as a liquid to the top tray.

The liquid leaving the bottom tray enters a reboiler, where it is partially vaporized, and the remaining liquid, which is lean in *A* or rich in *B*, is withdrawn as liquid product. The vapor from the reboiler is sent back to the bottom stage or tray. Only three trays are shown in the tower of Fig. 2-5. In most cases the number of trays is much greater. In the sieve tray the vapor enters through an opening and bubbles up through the liquid to provide intimate contact between the liquid and vapor on the tray. In a theoretical tray the vapor and liquid leaving are in equilibrium. The reboiler can be considered as a theoretical stage or tray.

2.3.2 McCabe-Thiele Method of Calculation for Number of Theoretical Stages

2.3.2.1 Introduction and assumptions

A mathematical-graphical method for determining the number of theoretical trays or stages needed for a given separation of a binary mixture of *A* and *B* has been developed by McCabe and Thiele. The method uses material balances around certain parts of the tower, which give operating lines somewhat similar to Eq. (2-12), and the *x-y* equilibrium curve for the system. The main assumption made in the McCabe-Thiele method is that there must be equimolar overflow through the tower between the feed inlet and the top tray and the feed inlet and bottom tray. This is shown in Fig. 2-6, where liquid and vapor streams enter a tray, are equilibrated, and leave. A total material balance gives

$$V_{n+1} + L_{n-1} = V_n + L_n \tag{2-13}$$

A component balance on *A* gives

$$V_{n+1}y_{n+1} + L_{n-1}x_{n-1} = V_n y_n + L_n x_n \tag{2-14}$$

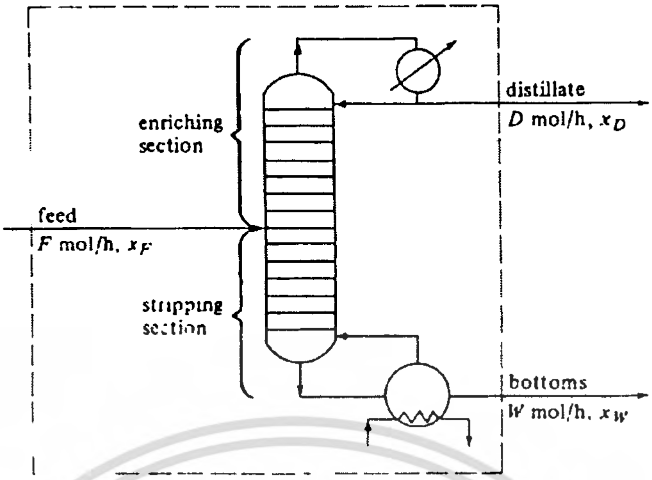


Figure 2-7. Distillation column showing material-balance sections for MaCabe-Thiele method. [14]

In Fig. 2-8a the distillation-tower section above the feed, the enriching section, is shown schematically. The vapor from the top tray having a composition y_1 passes to the condenser, where it is condensed so that the resulting liquid is at the boiling point. The reflux stream L mol/h and distillate D mol/h have the same composition, so $y_1 = x_D$. Since equimolal overflow is assumed, $L_1 = L_2 = L_n$ and $V_1 = V_2 = V_n = V_{n+1}$. Making a total material balance over the dashed-line section in Fig. 2-8a,

$$V_{n+1} = L_n + D \tag{2-17}$$

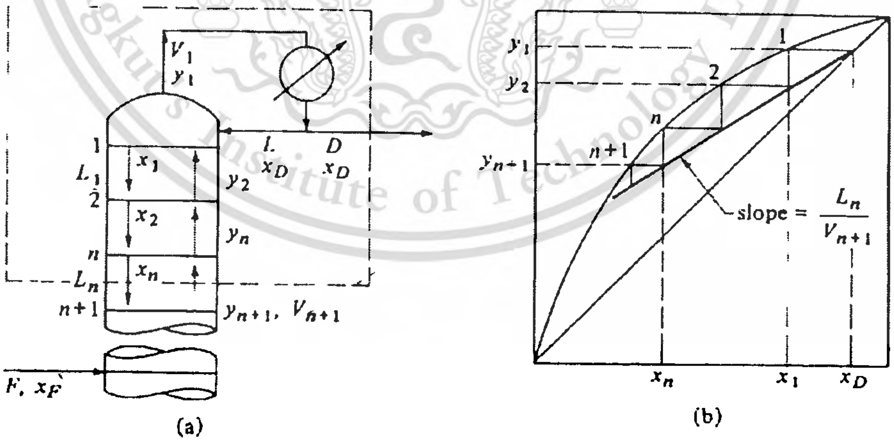


Figure 2-8. Material balance and operating line for enriching section: (a) schematic of tower, (b) operating and equilibrium. [14]

Making a balance on component A,

$$V_{n+1}y_{n+1} = L_n x_n + Dx_D \tag{2-18}$$

Solving for y_{n+1}, the enriching-section operating line is

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{Dx_D}{V_{n+1}} \tag{2-19}$$

Since $V_{n+1} = L_n + D$, $L_n/V_{n+1} = R/(R + 1)$ and Eq. (2-19) becomes

$$y_{n+1} = \frac{R}{R+1} x_n + \frac{x_D}{R+1} \tag{2-20}$$

where $R = L_n/D$ = reflux ratio = constant. Equation (2-19) is a straight line on a plot of vapor composition versus liquid composition. It relates the compositions of two streams passing each other and is plotted in Fig. 2-8b. The slope is L_n/V_{n+1} or $R/(R+1)$, as given in Eq. (2-20). It intersects the $y = x$ line (45° diagonal line) at $x = x_D$. The intercept of the operating line at $x = 0$ is $y = x_D/(R + 1)$.

The theoretical stages are determined by starting at x_D and stepping off the first plate to x_1. Then y_2 is the composition of the vapor passing the liquid x_1. In a similar manner, the other theoretical trays are stepped off down the tower in the enriching section to the feed tray.

2.3.2.3 Equations for stripping section

Making a total material balance over the dashed-line section in Fig. 2-9a for the stripping section of the tower below the feed entrance,

$$V_{m+1} = L_m - W \tag{2-21}$$

Making a balance on component A,

$$V_{m+1} y_{m+1} = L_m X_m - Wx_W \tag{2-22}$$

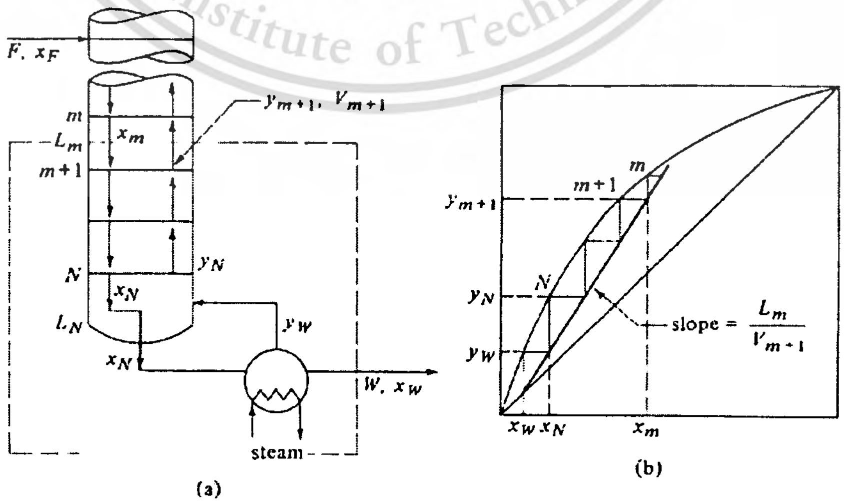


Figure 2-9. Material balance and operating for stripping section: (a) schematic of tower, (b) operating and equilibrium lines. [14]

Solving for y_{m+1}, the stripping-section operating line is

$$y_{m+1} = \frac{L_m}{V_{m+1}} X_m - \frac{W x_W}{V_{m+1}} \tag{2-23}$$

Again, since equimolal flow is assumed, $L_m = L_N$ = constant and $V_{m+1} = V_N$ = constant. Equation (2-23) is a straight line when plotted as y versus x in Fig. 2-9b, with a slope of L_m/V_{m+1}. It intersects the $y = x$ line at $x = x_W$. The intercept at $x = 0$ is $y = -Wx_W/V_{m+1}$. Again the theoretical stages for the stripping section are determined by starting at x_W, going up to y_W, and then across to the operating line, and so on.

2.3.2.4 Effect of feed conditions

The condition of the feed stream F entering the tower determines the relation between the vapor V_m n the stripping section and V_n in the enriching section as well as between L_m and L_n. If the feed is part liquid and part vapor, the vapor will add to V_m to give V_n. For convenience, we represent the condition of the feed by the quantity q, which is defined as

$$q = \frac{\textit{heat needed to vaporized 1 mol of feed at entering conditions}}{\textit{molar latent heat of vaporization of feed}} \tag{2-24}$$

If the feed enters at its boiling point, the numerator of Eq. (2-24) is the same as the denominator, and $q = 1.0$. Equation (2-24) can also be written in terms of enthalpies:

$$q = \frac{H_V - H_F}{H_V - H_L} \tag{2-25}$$

where H_V is the enthalpy of the feed at the dew point, H_L the enthalpy of the feed at the boiling point (bubble point), and H_F the enthalpy of the feed at its entrance conditions. If the feed enters as vapor at the dew point, $q = 0$. For cold liquid feed $q > 1.0$, for superheated vapor $q < 0$, and for the feed being part liquid and part vapor, q is the fraction of feed that is liquid.

We can also look at q as the number of moles of saturated liquid produced on the feed plate by each mole of feed added to the tower. In Fig.2-10 a diagram shows the relationship between flows above and below the feed entrance. From the definition of q, the following equations hold:

$$L_m = L_n + q_F \tag{2-26}$$

$$V_n = V_m + (1-q)F \tag{2-27}$$

The point of intersection of the enriching and the stripping operating-line equations on an x-y plot can be derived as follows. Rewriting Eqs. (2-18) and (2-22) as follows without the tray subscripts:

$$V_n y = L_n x + D x_D \tag{2-28}$$

$$V_m y = L_m X - W x_W \tag{2-29}$$

where the y and x values are the point of intersection of the two operating lines. Subtracting Eq. (2-28) from (2-29),

$$(V_m - V_n) y = (L_m - L_n) x - (D x_D + W x_W) \tag{2-30}$$

Substituting Eqs. (2-16),(2-26), and (2-27) into Eq. (2-30) and rearranging,

$$y = \frac{q}{q-1} x - \frac{x_F}{q-1} \tag{2-31}$$

This equation is the q-line equation and is the locus of the intersection of the two operating lines. Setting $y = x$ in Eq. (2-31), the intersection of the q-line equation with the 45° line is $y = x = x_F$, where x_F is the overall composition of the feed.

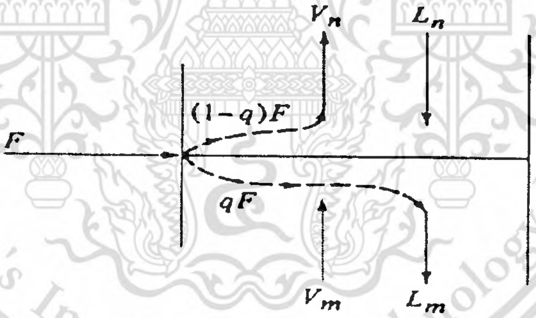


Figure 2-10. Relationship between flows above and below the feed entrance. [14]

In Fig. 2-11 the q line is plotted for various feed conditions given below the figure. The slope of the q line is $q/(q - 1)$. For example, for the liquid below the boiling point, $q > 1$, and the slope is > 1.0, as shown. The enriching and operating lines are plotted for the case of a feed of part liquid and part vapor, and the two lines intersect on the q line. A convenient way to locate the stripping operating line is to first plot the enriching operating line and the q line. Then draw the stripping line between the intersection of the q line and enriching operating line and the point $y = x = x_W$.

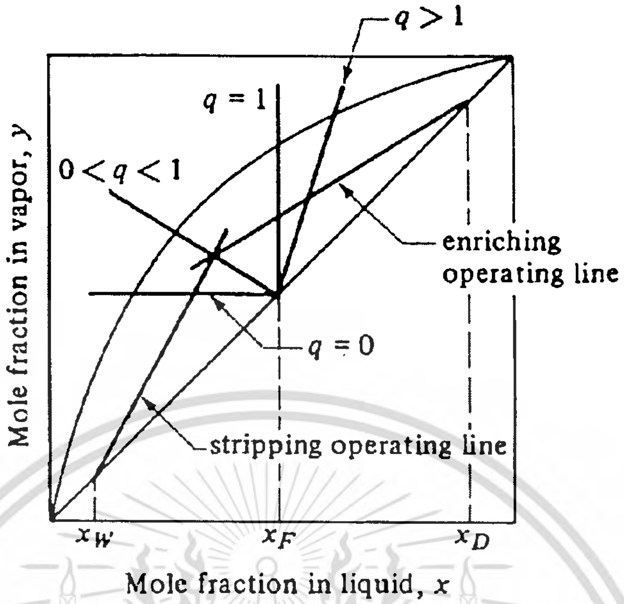


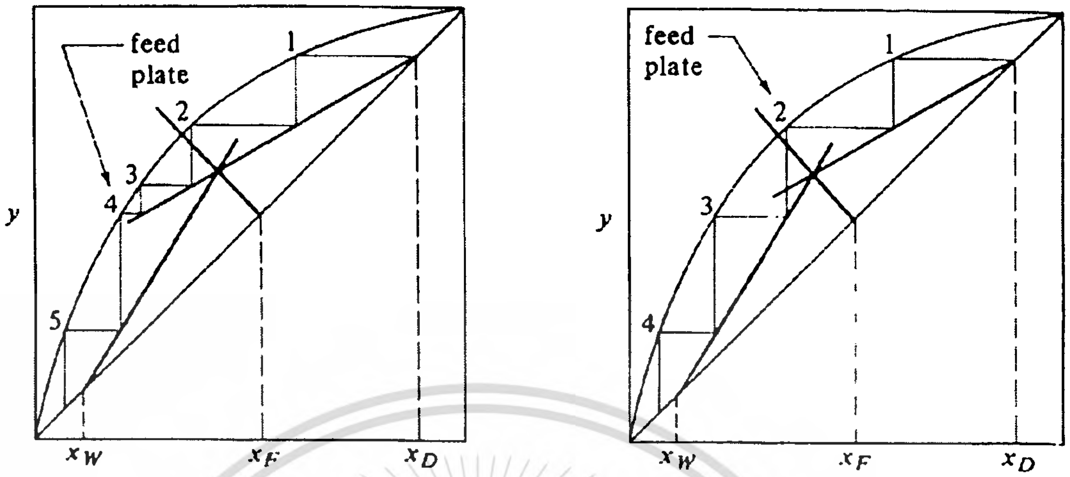
Figure 2-11. Location of the q line for various feed conditions: liquid below boiling point (q>1), liquid at boiling point (q=1), liquid+vapor(0<q<1),saturated vapor(q=0). [14]

2.3.2.5 Location of the feed tray in a tower and number of trays

To determine the number of theoretical trays needed in a tower, the stripping and operating lines are drawn to intersect on the *q* line, as shown in Fig. 2-12. Starting at the top at x_D, the trays are stepped off. For trays 2 and 3, the steps can go to the enriching operating line, as shown in Fig. 2-12a. At step 4 the step goes to the stripping line. A total of about 4.6 theoretical steps are needed. The feed enters on tray 4.

For the correct method, the shift is made on step 2 to the stripping line, as shown in Fig. 2-12b. A total of only about 3.7 steps are needed, with the feed on tray 2. To keep the number of trays to a minimum, the shift from the enriching to the stripping operating line should be made at the first opportunity after passing the operating-line intersection.

In Fig. 2-12b the feed is part liquid and part vapor, since $0 < q < 1$. Hence, in adding the feed to tray 2, the vapor portion of the feed is separated and added beneath plate 2 and the liquid added to the liquid from above entering tray 2. If the feed is all liquid, it should be added to the liquid flowing to tray 2 from the tray above. If the feed is all vapor, it should be added below tray 2 and join the vapor rising from the plate below.



(a) (b)

Figure 2-12. Method of stepping off number of theoretical trays and location of feed plate: (a) improper location of feed on tray 4, (b) proper location of feed on tray 2 to give minimum number of steps. [14]

Since a reboiler is considered a theoretical step, when the vapor y_W is in equilibrium with x_W, as in Fig. 2-12b, the number of theoretical trays in a tower is equal to the number of theoretical steps minus one.

2.3.3 Total and Minimum Reflux Ratio for McCabe-Thiele Method

2.3.3.1 Total reflux

In distillation of a binary mixture *A* and *B*, the feed conditions, distillate composition, and bottoms composition are usually specified and the number of theoretical trays are to be calculated. However, the number of theoretical trays needed depends upon the operating lines. To fix the operating lines, the reflux ratio $R = L_n/D$ at the top of the column must be set. One of the limiting values of reflux ratio is that of total reflux, or $R = \infty$. Since $R = L_n/D$ and, by Eq. (2-32),

$$V_{n+1} = L_n + D \tag{2-32}$$

then L_n is very large, as is the vapor flow V_n. This means that the slope $R/(R+1)$ of the enriching operating line becomes 1.0 and the operating lines of both sections of the column coincide with the 45° diagonal line, as shown in Fig. 2-13.

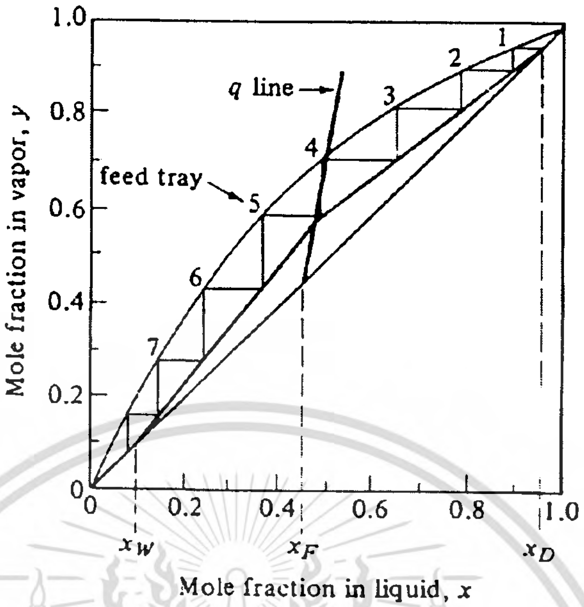


Figure 2-13. Total reflux and minimum number of trays by McCabe-Thiele method. [14]

The number of theoretical trays required is obtained as before by stepping off the trays from the distillate to the bottoms. This gives the minimum number of trays that can possibly be used to obtain the given separation. In actual practice, this condition can be realized by returning all the overhead condensed vapor V from the top of the tower back to the tower as reflux, that is, total reflux. Also, all the liquid in the bottoms is reboiled. Hence, all the products distillate and bottoms are reduced to zero flow, as is the fresh feed to the tower.

This condition of total reflux can also be interpreted as requiring infinite sizes of condenser, reboiler, and tower diameter for a given feed rate.

If the relative volatility α of the binary mixture is approximately constant, the following analytical expression by Fenske can be used to calculate the minimum number of theoretical steps N_m when a total condenser is used:

$$N_m = \frac{\log\left(\frac{x_D}{1-x_D}\frac{1-x_W}{x_W}\right)}{\log \alpha_{av}} \tag{2-31}$$

For small variations in α, $\alpha_{av} = (\alpha_1 \alpha_W)^{1/2}$, where α_1 is the relative volatility of the overhead vapor and α_W is the relative volatility of the bottoms liquid.

2.3.3.2 Minimum reflux ratio

The minimum reflux ratio can be defined as the reflux ratio R_m that will require an infinite number of trays for the given desired separation of x_D and x_W. This corresponds to the minimum vapor flow in the tower, and hence the minimum reboiler and condenser sizes. This case is shown in Fig. 2-14. If R is decreased, the slope of the enriching operating line $R/(R + 1)$ is decreased, and the intersection of this line and the stripping line with the q line moves farther from the 45° line and closer to the equilibrium line. As a result, the number of steps required to give a fixed x_D and x_W increases.

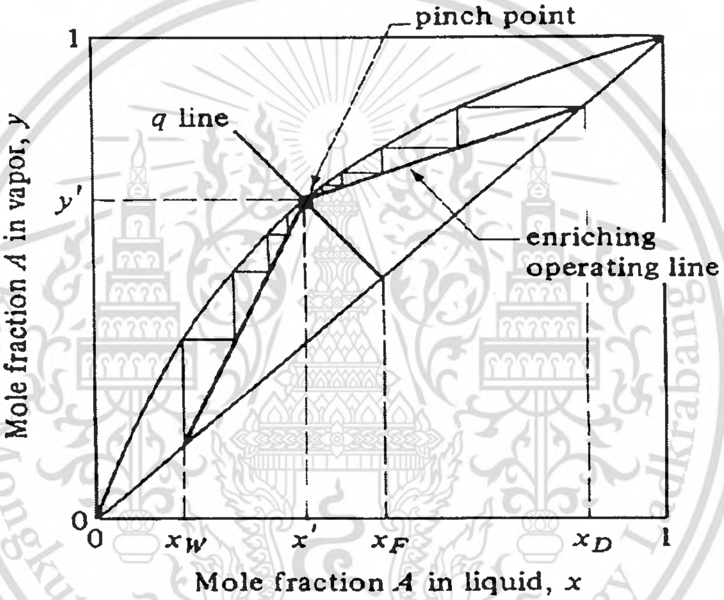


Figure 2-14. Minimum reflux ratio and infinite number of trays by McCabe-Thiele method [14]

When the two operating lines touch the equilibrium line, a "pinch point" at y' and x' occurs, where the number of steps required becomes infinite. The slope of the enriching operation line is as follows from Fig. 2-14, since the line passes through the points x', y', and x_D ($y = x_D$):

$$\frac{R_m}{R_m + 1} = \frac{x_D - y'}{x_D - x'} \tag{2-32}$$

In some cases, where the equilibrium line has an inflection in it as shown in Fig. 2-15, the operation line at minimum reflux will be tangent to the equilibrium line.

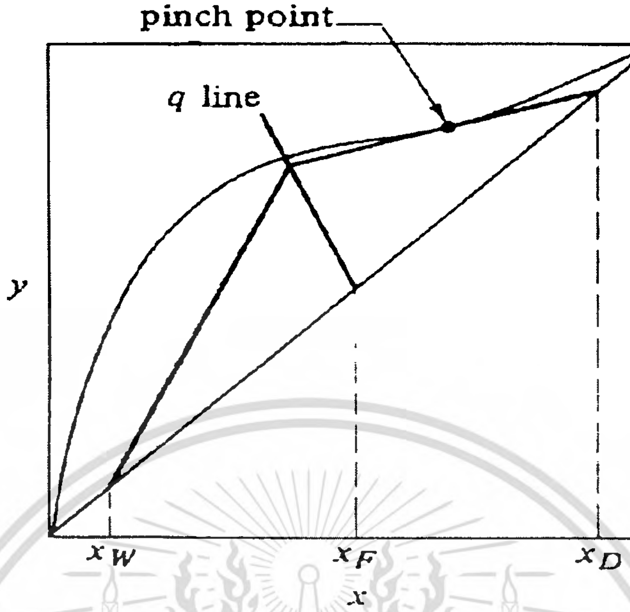


Figure 2-15. Minimum reflux ratio and infinite number of trays when operating line is tangent to equilibrium line. [14]

2.3.3.3 Operating and optimum reflux ratio

For the case of total reflux, the number of plates is a minimum, but the tower diameter is infinite. This corresponds to an infinite cost of tower as well as steam and cooling water. This is one limit in the tower operation. Also, for minimum reflux, the number of trays is infinite, which again gives an infinite cost. These are the two limits in operation of the tower.

The actual operating reflux ratio to use lies between these two limits. To select the proper value of R requires a complete economic balance on the fixed costs of the tower and operation costs. The optimum reflux ratio to use for lowest total cost per year is between the minimum R_m and total reflux. This has been shown for many cases to be at an operating reflux ratio between $1.2R_m$ and $1.5\ R_m$. [3]

2.4 DESIGN OF EXPERIMENT [16]

2.4.1 Strategy of Experimentation

Experiment is performed by investigators in virtually all fields of inquiry, usually to discover something about a particular process or system. Literally, an experiment is a test. More formally, we can define an experiment as a test or series of tests in which proposeful changes are made to the input variables of a process or system so that we may observe and identify the reasons for changes in the output response.

2.4.2 Some Typical Applications of Experimental Design

Experiment design methods have found broad application in many disciplines. In fact, we may view experimentation as part of the scientific process and as one of the ways we learn about how systems or processes work. Generally we learn through a series of activities in which we make conjectures about a process, perform experiments to generate data from the process, and then use the information from the experiment to establish new conjectures, which lead to new experiments, and so on.

Experimental design is a critically important tool in the engineering world for improving the performance of a manufacturing process. It also has extensive application in the development of new processes. The application of experimental design techniques early in process development can result in

1. Improved process yields.
2. Reduced variability and closer conformance to nominal or target requirements.
3. Reduced development time.
4. Reduced overall costs.

Experimental design methods also play a major role in engineering design activities, where new products are developed and existing ones improved. Some applications of experimental design in engineering design include

1. Evaluation and comparison of basic design configurations.
2. Evaluation of material alternatives.
3. Selection of design parameters so that the product will work well under a wide variety of field conditions, that is, so that the product is robust.
4. Determination of key product design parameters that impact product performance.

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2.4.3 Basic Principles

By the statistical design of experiments, we refer to the process of planning the experiment so that appropriate data that can be analyzed by statistical methods will be collected, resulting in valid and objective conclusions. The statistical methods will be collected, resulting in valid and objective conclusions. The statistical approach to experimental design is necessary if we wish to draw meaningful conclusions from the data. When the problem involves data that are subject to experimental errors, statistical methodology is the only objective approach to analysis. Thus, there are two aspects to any experimental problem: the design of the experiment and the statistical analysis of the data. These two subjects are closely related since the method of analysis depends directly on the design employed.

The three basis principles of experimental design are replication, randomization and blocking.

Replication has two important properties. First, it allows the experimenter to obtain an estimate of the experimental error. Second, if the sample mean (e.g.) is used to estimate the effect of a factor in the experiment, then replication permits the experimenter to obtain a more precise estimate of this effect.

Randomization is the cornerstone underlying the use of statistical methods in experimental design. By randomization we mean that both the allocation of the experimental material and the order in which the individual runs or trials of the experiment are to be performed are randomly determined. Statistical methods require that the observations (or errors) be independently distributed random variables. Randomization usually makes this assumption valid. By properly randomizing the experiment, we also assist in "averaging out" the effects of extraneous factors that may be present.

Blocking is a technique used to increase the precision of an experiment. A block is a portion of the experimental material that should be more homogeneous than the entire set of material. Blocking involves making comparisons among the conditions of interest in the experiment within each block.

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By the statistical design of experiments, we refer to the process of planning the experiment so that appropriate data that can be analyzed by statistical methods will be collected, resulting in valid and objective conclusions. The statistical methods will be collected, resulting in valid and objective conclusions. The statistical approach to experimental design is necessary if we wish to draw meaningful conclusions from the data. When the problem involves data that are subject to experimental errors, statistical methodology is the only objective approach to analysis. Thus, there are two aspects to any experimental problem: the design of the experiment and the statistical analysis of the data. These two subjects are closely related since the method of analysis depends directly on the design employed.

The three basis principles of experimental design are replication, randomization and blocking.

Replication has two important properties. First, it allows the experimenter to obtain an estimate of the experimental error. Second, if the sample mean (e.g.) is used to estimate the effect of a factor in the experiment, then replication permits the experimenter to obtain a more precise estimate of this effect.

Randomization is the cornerstone underlying the use of statistical methods in experimental design. By randomization we mean that both the allocation of the experimental material and the order in which the individual runs or trials of the experiment are to be performed are randomly determined. Statistical methods require that the observations (or errors) be independently distributed random variables. Randomization usually makes this assumption valid. By properly randomizing the experiment, we also assist in "averaging out" the effects of extraneous factors that may be present.

Blocking is a technique used to increase the precision of an experiment. A block is a portion of the experimental material that should be more homogeneous than the entire set of material. Blocking involves making comparisons among the conditions of interest in the experiment within each block.

2.4.4 Guidelines for Designing Experiments

To use the statistical approach in designing and analyzing an experiment, it is necessary that everyone involved in the experiment have a clear idea in advance of exactly what is to be studied, how the data are to be collected, and at least a qualitative understanding of how these data are to be analyzed. An outline of the recommended procedure is

1. Recognition of and statement of the problem. It is necessary to develop all ideas about the objectives of the experiment. Usually, it is important to solicit input from all concerned parties: engineering, quality assurance, manufacturing, marketing, management, the customer, and operating personal (who usually have much insight and who are too often ignored). A clear statement of the problem often contributes substantially to a better understanding of the phenomena and the final solution of the problem. For this reason, a term approach to designing experiments is recommended.

2. Choice of factors, levels, and ranges. The experimenter must choose the factors to be varied, and the specific level at which runs will be made. Thought must also be given to how these factors are to be controlled at the desired values and how they are to be measured.

3. Selection of the response variable. In selecting the response variable, the experimenter should be certain that this variable really provide useful information about the process under study. Most often, the average or standard deviation (or both) of the measured characteristic will be the response variable. Multiple responses are not unusual.

4. Choice of experimental design. F the pre-experimental planning activities above are done correctly this step is relatively easy. Choice of design involves the consideration of sample size (number of replicates), the selection of a suitable run order for the experimental trials, and the determination of whether or not blocking or other randomization restrictions are involved.

5. Performing the experiment. When running the experiment, it is vital to monitor the process carefully to ensure that everything is being done according to plan.

6. Statistical analysis of the data. If the experiment has been design correctly and if it has been performed according to the design, then the statistical methods required are not elaborate. There are many excellent software packages designed to assist in data analysis, and many of the programs used in step 4 to select the design provide a seamless, direct interface to the statistical analysis.

7. Once the data have been analyzed, the experimenter must draw *practical* conclusions about the results and recommend a course of action. Graphical methods are often useful in this state, particularly in presenting the results to others. Follow-up runs and confirmation resting should also be performed to validate the conclusions from the experiment.

2.5 2^k FACTORIAL DESIGN [16]

2.5.1 Introduction

Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response. However, there are several special cases of the general factorial design that are importance because they are widely used in research work and also because they form the basis of other designs of considerable practical value.

The most important of these special cases is that of *k* factors, each at only two levels. There levels may be quantitative, such as two values of temperature, pressure, or time; or they may be qualitative, such as two machines, two operators, the "high" and "low" levels of a factor, or perhaps the presence and absence of a factor. A complete replicate of such a design requires $2 \times 2 \times \cdots \times 2 = 2^k$ observations and is called a 2^k factorial design.

This report focuses on this extremely important class of designs. Throughout this report we assume that (1) the factors are fixed. (2) the designs are completely randomized, and (3) the usual normality assumptions are satisfied.

The 2^k design is particularly useful in the early states of experimental work, when there are likely to be many factors to be investigated. It provides the smallest number of runs with which k factors can be studied in a complete factorial design. Consequently, these designs are widely used in factor screening experiments

Because there are only two levels for each factor, we assume that the response is approximately linear over the range of the factor levels chosen. In many factor screening experiments, when we are just starting to study the process or system, this is often a reasonable assumption. We will present a simple method for checking this assumption, and discuss what action to take if it is violated.

2.5.2 The general 2^k design

The methods of analysis that we have presented thus far may be generalized to the case of a 2^k factorial design, that is, a design with k factors each at two levels. The statistical model for a 2^k design would include k main effects, two-factor interactions, three-factor interactions, . . . , and one k-factor interaction. That is, for a 2^k design the complete model would contain $2^k - 1$ effects. The notation introduced earlier for treatment combinations is also used here. For example, in a 2^5 design abd denotes the treatment combination with factors A, B, and D at the high level and factors C and E at the low level. The treatment combinations may be written in standard order by introducing the factor at a one time, with each new factor being successively combined with those that precede it. For example, the standard order for 2^4 design is (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, and abcd.

The general approach to the statistical analysis of the 2^k design is summarized in Table 2-1. As we have indicated previously, a computer software package is usually employed in this analysis process.

The sequence of steps in Table 2-1 should, by now, be familiar. The first step is to estimate factor effects and examine their signs and magnitudes. This gives the experimenter preliminary information regarding which factors and interactions may be important, and in which directions these factors should be adjust to improve the response. In forming the initial model for the experiment, we usually choose the full model, that is, all main effects and interactions, provide that at least one of the design points has been replicated. Then in step 3, we use the analysis of variance to formally test for significance of main effects and interaction. Table 5.2-2 shows the general form of an analysis of variance for a 2^k factorial design with n replicates. Step 4, refine the model, usually consists of removing any non significant variables from the full model. Step 5 is the usual residue analysis to check for model adequacy and to check assumptions. Sometimes model refinement will occur after residual analysis, if we find that the model is inadequate or assumptions are badly violated. The final step usually consists of graphical analysis—either main effect or interaction plots, or response surface and contour plots.

Although the calculations described above are almost always done with a computer, occasionally it is necessary to manually calculate an effect estimate or sum of squares for an effect. We must first determine the contrast associated with that effect. This can always be done by using a table of plus and minus signs. However, for large values of k this is awkward, and we can use an alternative method. In general, we determine the contrast for effect AB · · · K by expanding the right-hand side of

$$Contrast_{AB\wedge K} = (a \pm 1)(b \pm 1)\mathrm{K}\ (k \pm 1) \qquad (2\text{-}33)$$

In expanding Equation, ordinary algebra is used with "1" being replaced by (1) in the final expression. The sign in each set of parentheses is negative if the factor is included in the effect and positive if the factor is not included.

To illustrate the use of Equation 2-33, consider a 2^3 factorial design. The contrast for AB would be

$$\begin{aligned} \text{ContrastAB} &= (a-1)(b-1)(c+1) \\ &= abc + ab + c + (1) - ac - bc - a - b \end{aligned}$$

As a further example, in a 2^5 design, the contrast for ABCD would be

ContrastABCD = (a-1)(b-1)(c-1)(d-1)(e+1)

= abcde + cde + bde + ade + bce + ace + abe + e + abcd + ad + bd + ad + bc + ac + ab + (1) – a – b – c – abc – d – abd – acd – ae – be – ce – abce – de – abde – acde – bcde

Once the contrasts for the effects have been computed, we may estimate the effects and compute the sum of square according to

$$AB\wedge K = \frac{2}{n2^k}(Contrast_{AB\wedge K}) \qquad (2\text{-}34)$$

and

$$SS_{AB\wedge K} = \frac{1}{n2^k}(Contrast_{AB\wedge K})^2 \qquad (2\text{-}35)$$

Respectively, where n denotes the number of replicates. We will present another method for estimating the effects in the 2^k design.

2.5.2.1 2^4 factorial design

Suppose that four factors, A, B, C, and D, each run at two levels, are of interest. The design is called a 2^4 factorial design. The levels of the factors may be arbitrarily called "low" and "high". Using the "+" and "-" notation to represent the low and high levels of the factors, we may list the sixteen runs in the 2^4 design as in Table 2-1. This is sometimes called the design matrix.

By convention, we denote the effect of a factor by a capital letter. Thus "A" refers to the effect of factor A, "B" refers to the effect of factor B, "C" refers to the effect of factor C, and

"AB" refers to the AB interaction.

The sixteen treatment combinations in the design are usually represented by lowercase letters, as shown in Table 2-2. We see from the Table 2-2 that the high level of any factor in the treatment combination is denoted by the corresponding lowercase letter and that the low level of a factor in the treatment combination is denoted by the absence of the corresponding letter. Thus, a represents the treatment combination of A at the high level, B at the low level, C at the low level, and D at the low level. By convention, (1) is used to denote four factors at the low level. This notation is used throughout the 2^k factorial.

In a two-level factorial design, we may define the average effect of a factor as the change in respond produced by a change in the level of that factor averaged over the levels of the other factor. Also the notations (1), a, b, ab, c, ac, bc, abc, d, ad, bd, abd, cd, acd, bcd, and abcd now represent the total of all n replicates taken at the treatment combination, as illustrated in Table 2-2. Now the effect of A at the low level of B, C, and D is [a - (1)] / n. Similarly the effect of A .

Table 2-1 The design matrix [16].

Run	Factor			
	A	B	C	D
1	-	-	-	-
2	+	-	-	-
3	-	+	-	-
4	+	+	-	-
5	-	-	+	-
6	+	-	+	-
7	-	+	+	-
8	+	+	+	-
9	-	-	-	+
10	+	-	-	+
11	-	+	-	+
12	+	+	-	+
13	-	-	+	+
14	+	-	+	+
15	-	+	+	+
16	+	+	+	+

when B is at the high level and C, D are at the low level is [ab - b] / n. The effect of A when C is at the high level and B, D are at the low level is [ac -c] / n. The effect of A when D is at the high level and B, C are at the low level is [ad - d] / n. The effect of A when B is at the low level and C, D are at the high level is [acd - cd] / n. The effect of A when C is at the low level and B, D are at the high level is [abd - bd] / n. The effect of A when D is at the low level and B, C are at the high level is [abcd - bcd] / n. Average these eight quantities yields the main effect of A:

Table 2-2 Treatment combinations in the 2^4 design [16].

Run	Factor				Labels
	A	B	C	D	
1	-	-	-	-	(1)
2	+	-	-	-	a
3	-	+	-	-	b
4	+	+	-	-	ab
5	-	-	+	-	c
6	+	-	+	-	ac
7	-	+	+	-	bc
8	+	+	+	-	abc
9	-	-	-	+	d
10	+	-	-	+	ad
11	-	+	-	+	bd
12	+	+	-	+	abd
13	-	-	+	+	cd
14	+	-	+	+	acd
15	-	+	+	+	bcd
16	+	+	+	+	abcd

$$A = \frac{1}{8n} \{ [a-(1)] + [ab-b] + [ac-c] + [ad-d] + [acd-cd] + [abd-bd] + [abc-bc] + [abcd-bcd] \}$$

$$A = \frac{1}{8n} [a - (1) + ab - b + ac - c + ad - d + acd - cd + abd - bd + abc - bc + abcd - bcd] \quad (2\text{-}36)$$

In a similar manner, the main effect of B, C, and D are:

$$B = \frac{1}{8n} [b - (1) + ab - a + bc - c + bd - d + bcd - cd + abd - ad + abc - ac + abcd - acd] \quad (2\text{-}37)$$

$$C = \frac{1}{8n} [c - (1) + ac - a + bc - b + cd - d + bcd - bd + acd - ad + abc - ab + abcd - abd] \quad (2\text{-}38)$$

$$D = \frac{1}{8n} [d - (1) + ad - a + bd - b + cd - c + bcd - bc + acd - ac + abd - ab + abcd - abc] \quad (2\text{-}39)$$

A measure of the *AB* interaction is the difference between the average *A* effects at the two levels of *B*. By convention, one-half of this difference is called the *AB* interaction. Symbolically,

<u>B</u>	<u>Average A Effect</u>
High(+)	$\frac{[(ab-b)+(abc-bc)+(abd-bd)+(abcd-bcd)]}{4n}$
Low (-)	$\frac{\{[a-(1)]+(ac-c)+(ad-d)+(acd-cd)\}}{4n}$

Difference

$$\frac{[ab-b+abc-bc+abd-bd+abcd-bcd-a+(1)-ac+c-ad+d-acd-cd]}{4n}$$

Since the *AB* interaction is one-half of this difference,

$$AB = \frac{[ab-b+abc-bc+abd-bd+abcd-bcd-a+(1)-ac+c-ad+d-acd-cd]}{8n}$$

(2-40)

In a similar manner, the AC, BC, AD, BD, and CD interaction are

$$AC = \frac{[ac-c+abc-bc+abd-bd+abcd-bcd-a+(1)-ab+b-ad+d-abd+bd]}{8n}$$

(2-41)

$$BC = \frac{[bc - c + abc - ac + abcd - acd + bcd - cd - ab + a - b + (1) - abd + ad + bd + d]}{8n}$$

(2-42)

$$AD = \frac{[ad - d + abd - bd + acd - cd + abcd - bcd - a + (1) - ab + b - ac + c - abc + bc]}{8n}$$

(2-43)

$$BD = \frac{[bd - d + abd - ad + bcd - cd + abcd - acd - ab + a - b + (1) - abc + ac - bc + c]}{8n}$$

(2-44)

$$CD = \frac{[cd - d + acd - ad + bcd - bd + abcd - abd - c + (1) - ac + a - bc + b - abc + ab]}{8n}$$

(2-45)

The *ABC* interaction is defined as the average difference between the AB interaction for the two different levels of C. Thus,

$$ABC = \frac{1}{8n}\ [\mathrm{abcd - bcd - acd + cd - abd + bd + ad - d + abc - bc - ac + c - ab + b + a - (1)}]$$

(2-46)

In the same manner, the *ABD*, *ACD*, and *BCD* interactions are

$$ABD = \frac{1}{8n}\ [\mathrm{abcd - bcd - acd + cd + abd - bd - ad + d - abc + bc + ac - c - ab + b + a - (1)}]$$

(2-47)

$$ACD = \frac{1}{8n}\ [\mathrm{abcd - bcd + acd - cd - abd + bd - ad + d - abc + bc - ac + c + ab - b + a - (1)}]$$

(2-48)

$$BCD = \frac{1}{8n}\ [\mathrm{abcd + bcd - acd - cd - abd - bd + ad + d - abc - bc + ac + c + ab + b - a - (1)}]$$

(2-49)

The *ABCD* interaction is defined as

$$ABCD = \frac{1}{8n}\ [\mathrm{abcd - bcd - acd + cd - abd + bd + ad - d - abc + bc + ac - c + ab - b - a + (1)}]$$

(2-50)

In many experiments involving 2^k designs, we will examine the magnitude and direction of the factor effects to determine which variables are likely to be important. The analysis of variance can generally be used to confirm this interpretation. There are several excellent statistics software packages that are useful for setting up and analyzing 2^k designs. There are also special time-saving methods for performing the calculations manually.

In Equations (2-35) through (2-50), the quantities in the brackets are **contrasts** in the treatment combinations. A table of plus and minus signs can be developed from the contrasts and is shown in Table 2-3. Signs for the main effects are determined by associating a plus with the high level and a minus with the low level. Once the signs for the main effects have been established, the signs for the remaining columns can be obtained by multiplying the appropriate preceding columns, row by row. For example, the signs in the AB column are the product of the A and B column signs in each row. The contrast for any effect can be obtained easily from this table.

Table 2-3 Algebraic Signs for Calculating Effects in the 2^4 design [16].

Treatment Combination	Factorial Effect															
	I	*A*	*B*	*AB*	*C*	*AC*	*BC*	*ABC*	*D*	*AD*	*BD*	*ABD*	*CD*	*ACD*	*BCD*	*ABCD*
(1)	+	-	-	+	-	+	+	-	-	+	+	-	+	-	-	+
a	+	+	-	-	-	-	+	+	-	-	+	+	+	+	-	-
b	+	-	+	-	-	+	-	+	-	+	-	+	+	-	+	-
ab	+	+	+	+	-	-	-	-	-	-	-	-	+	+	+	+
c	+	-	-	+	+	-	-	+	-	+	+	-	-	+	+	-
ac	+	+	-	-	+	+	-	-	-	-	+	+	-	-	+	+
bc	+	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+
abc	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-
d	+	-	-	+	-	+	+	-	+	-	-	+	-	+	+	-
ad	+	+	-	-	-	-	+	+	+	+	-	-	-	-	+	+
bd	+	-	+	-	-	+	-	+	+	-	+	-	-	+	-	+
abd	+	+	+	+	-	-	-	-	+	+	+	+	-	-	-	-
cd	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-	+
acd	+	+	-	-	+	+	-	-	+	+	-	-	+	+	-	-
bcd	+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
abcd	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

Table 2-3 has several interesting properties (1) Expect for column *I*, every column has an equal number of plus and minus signs. (2) The sum of the products of the signs in any two columns is zero. (3) column I multiplied times any column leaves that column unchanged. That is, *I* is an **identity element.** (4) The product of any two columns yields a column in the table. For example, $A \times B = AB$, and

$$AB \times B = AB^2 = A$$

The sum of squares for any contrast can be computed. In the 2^4 design with n replicates, the sum of squares for any effect is

$$SS = \frac{(Contrast)^2}{16n}$$

CHAPTER 3

EXPERIMENTAL DETAILS

3.1. MATERIALS

3.1.1 Ethanol (EtOH)

Carlo Erba Reagenti

Via G.Winckelmann, 1-20146 Milano-Italy

Grade: AR grade

Properties of the ethanol are shown in Table 3-1.

Table 3-1 Properties of the ethanol [17].

Chemical Formula	CH_3CH_2OH
Molecular Weight	46.07
Weight of 1 Gallon	6.59 lbs (100% / 200 proof) , 6.80 lbs (95% / 190 proof)
Density in Grams / cm^3	0.791 (100%) , 0.815 (95%)
Surface Tension in Dynes / cm^2	21.38 @ 40°C
Freezing and Melting Point	-117.3°C / -178.6°F
Boiling Point	78.5°C / 173.3°F
Critical Temperature	243°C

3.1.2 Distilled Water

Sanyo Gallenkamp PLG

Serial No. L9806011 Model No. WSC008. MH34

Properties of the distilled water are shown in Table 3-2.

Table 3-2 Properties of the distilled water. [18]

Chemical Formula	H_2O
Molecular Weight	18.015
Weight of 1 Gallon	8.33 lbs
Density in Grams / cm^3	1.0
Surface Tension in Dynes / cm^2	54.9 @ 40°C
Freezing and Melting Point	0°C / 32°F
Boiling Point	100°C / 212°F
Critical Temperature	374.2°C

3.2 APPARATUS

1. Volumetric flask 50 ml
   ITALMAR CO., LTD
2. Burette 50 ml
   ITALMAR CO., LTD
3. Pipette 2 ml
   ITALMAR CO., LTD
4. Beaker 600 ml
   ITALMAR CO., LTD
5. Dropper
   ITALMAR CO., LTD
6. Funnel
   ITALMAR CO., LTD
7. Cylinder 50mL , 1000mL
   ITALMAR CO., LTD
8. Stirring rod
   ITALMAR CO., LTD

9. Distillation Tower System

ILUDEST Destillationsanlagen GmbH - Dachdeckerstr. 2 – D-97297 Waldbuttelbrunn

Operating Manual Control by Micropure V 4.234

The distillation tower system are consist of feed tank, reboiler, column, controller and condenser as shown in Fig. 3-1. and Fig. 3-2.

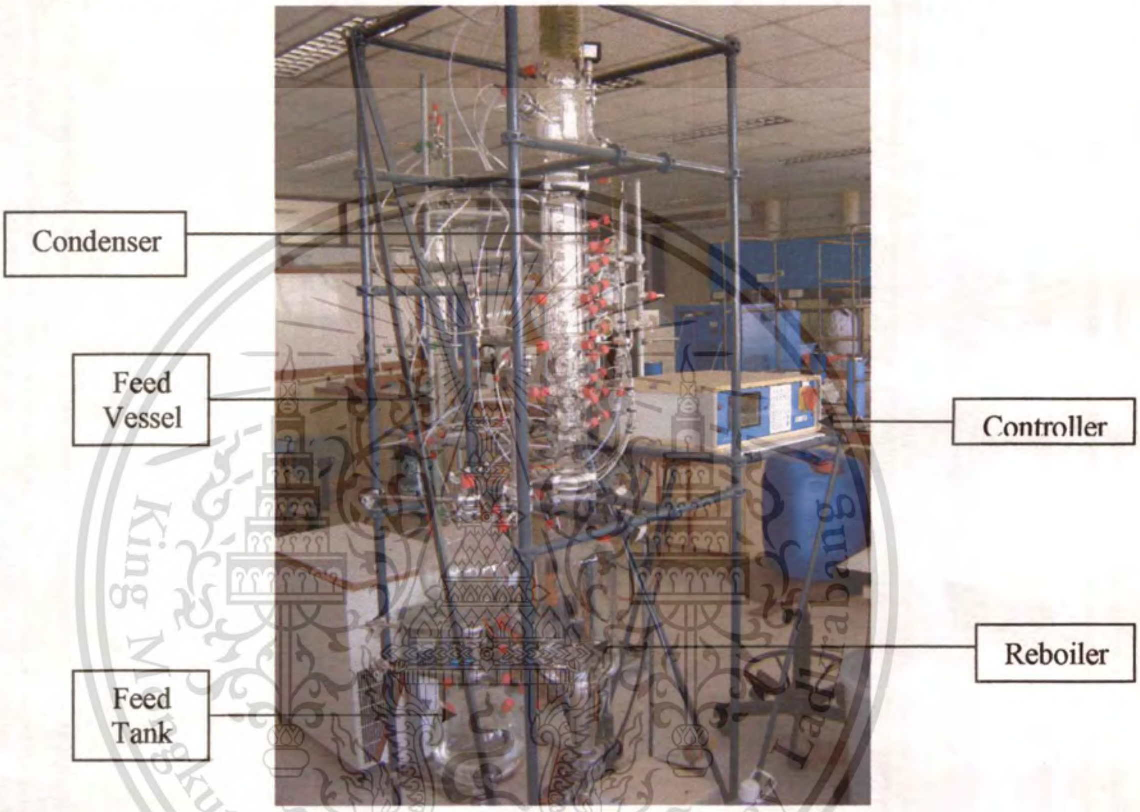


Figure 3-1. Overview of distillation tower machine.

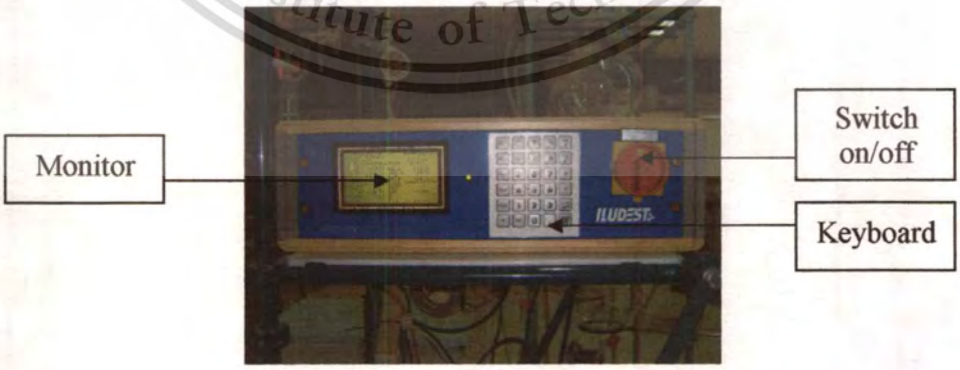


Figure 3-2. Detail of the controller.

10. Refractometer

Model NAR-1T Serial NO. 911412 ATAGO CO.,LTD

Detail of Refractometer is shown in Fig. 3-3

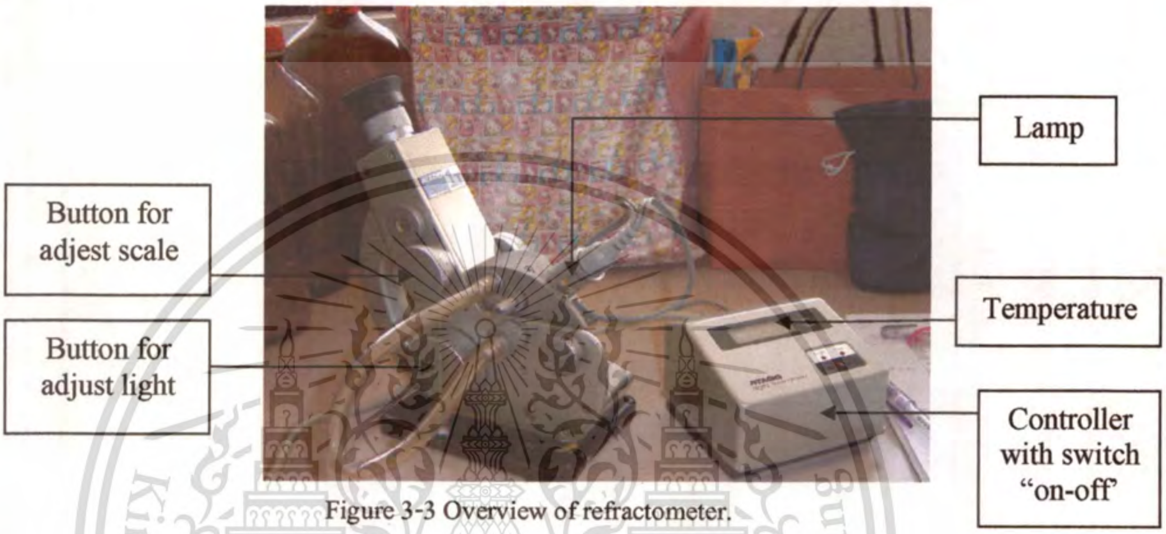


Figure 3-3 Overview of refractometer.

3.3 PREPARATION OF FEED

3.3.1 Preparation of 40 % by volume of ethanol

Mixed 4 L of ethanol and 6 L of distilled water in a container. Stirred the mixture before pouring in the feed tank.

3.3.2 Preparation of 50 % by volume of ethanol

Mixed 5 L of ethanol and 5 L of distilled water in a container. Stirred the mixture before pouring in the feed tank.

3.4 CALIBRATION CURVE FOR AN ETHANOL AND WATER SYSTEM

1. Preparation of 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100 % by volume of ethanol in 50 ml volumetric flasks which are shown in Table 3-3.

Table 3-3 Concentration by volume of the ethanol for calibration curve.

Flask	Concentration by volume	Volume of ethanol	Volume of distilled water
1	10%	5 ml	45 ml
2	20%	10 ml	40 ml
3	30%	15 ml	35 ml
4	40%	20 ml	30 ml
5	50%	25 ml	25 ml
6	60%	30 ml	20 ml
7	70%	35 ml	15 ml
8	80%	40 ml	10 ml
9	90%	45 ml	5 ml
10	100%	50 ml	0 ml

2. The refractometer was then calibrated by distilled water.
3. Refractive index (RI) was measured for each concentration with refractometer.
4. Plot graph of refractive index versus concentration with microsoft excel program.

3.5 INVESTIGATION OF PROCESSING PARAMETERS

In this experiment, four parameters were investigated (k = 4). They were feed temperature, feed concentration, flow rate of feed, and reflux ratio. The 2^4 factorial design was used in the experiment, then all parameters were varied to two values (high and low values.) The feed temperature was varied to 70°C and 80°C. The feed concentration was varied to 40 and 50 percent by volume of ethanol. The flow rate of feed was varied to 1 and 2 liters per hour and the reflux ratio was varied to 1:1 and 10:1. There were 16 runs in the experiment as shown in Table 3-4.

Table 3-4 Values of all parameters in each treatment combination.

Treatment combination	FACTORS			
	Reflux ratio (A)	Flow rate (B)	Temperature (C)	Composition (D)
(1)	1:1	1	70	40
a	10:1	1	70	40
b	1:1	2	70	40
ab	10:1	2	70	40
c	1:1	1	80	40
ac	10:1	1	80	40
bc	1:1	2	80	40
abc	10:1	2	80	40
d	1:1	1	70	50
ad	10:1	1	70	50
bd	1:1	2	70	50
abd	10:1	2	70	50
cd	1:1	1	80	50
acd	10:1	1	80	50
bcd	1:1	2	80	50
abcd	10:1	2	80	50

3.6 DESIGN OF EXPERIMENT

Suppose that the 2^k factorial design had been replicated two times. Therefore, there were 32 runs in the experiment. It was impossible to perform all of the runs in a 2^k factorial experiment in one time because the prepared ethanol-water mixture was not enough to make all of the required runs.

The design technique used in this situation was blocking. There were four blocks in the experiment, each set of the runs defined a block, and each replicate was run in one of the blocks. The runs in each block would be made in random order. The order of the runs in each block was shown in Fig. 3-4.

Replicate I Block 1	Replicate II Block 2
ac	bc
abd	abd
(1)	(1)
abc	d
abcd	acd
bc	a
b	ad
ab	bcd
a	cd
bcd	c
cd	bc
c	b
ad	bd
d	abc
acd	abcd
bd	ac

Figure 3-4. The order of the runs in each block

Before the operation was run, the distillation tower system should be checked by following steps which were shown in Appendix C.

Step 1: The first order of the run was the ac treatment combination. Poured 40 % by volume of ethanol into the feed tank and the reboiler, then turned on the main switch of the distillation tower system as shown in Fig. 3-5.

Figure 3-5. Main switch of the distillation tower system

Step 2: Turned on the computer, chose the Mic_top icon Fig. 3-6a, and then double clicked at the online button to link the computer to the distillation tower system as shown in Fig. 3-6b.

Figure 3-6a. Mic Top icon on desktop

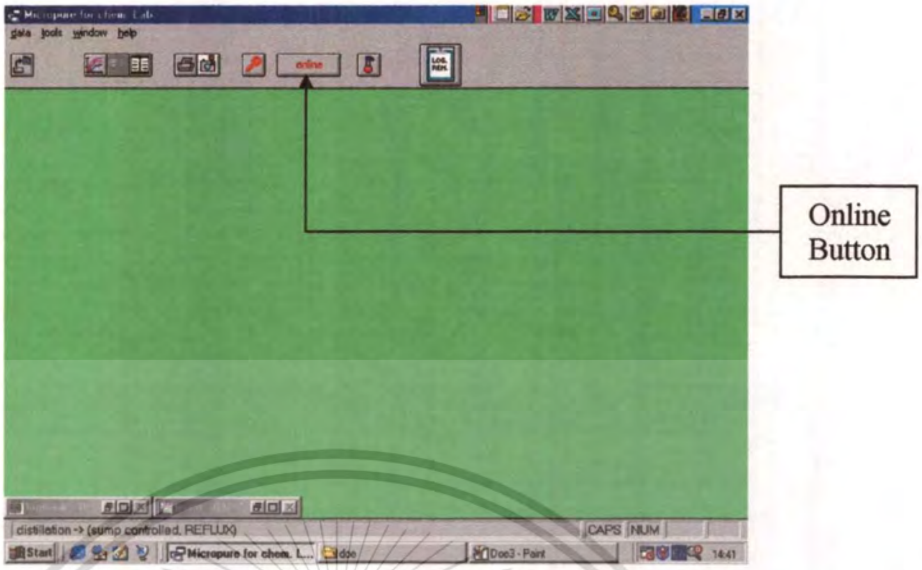
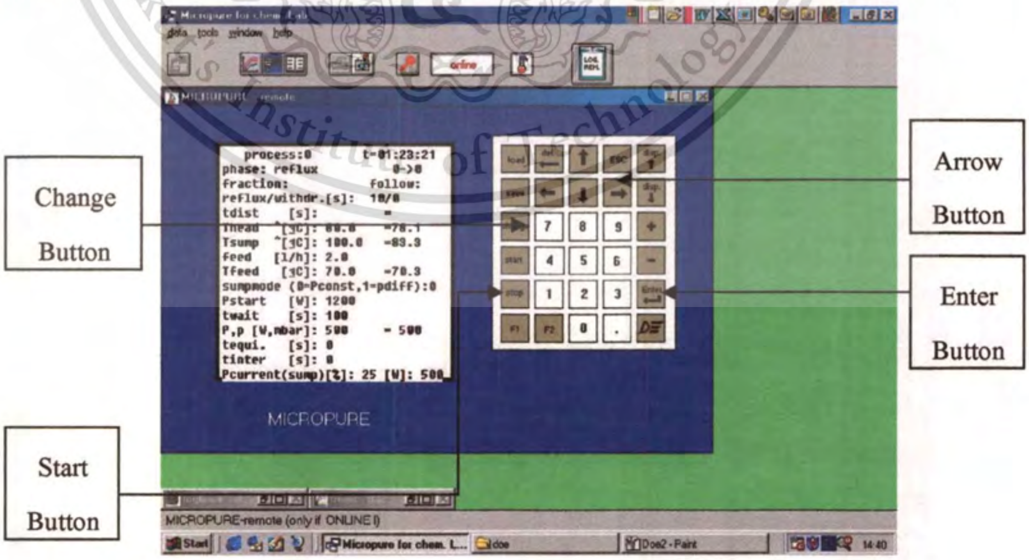


Figure 3.6b. Online button in Mic top program

The reflux ratio (A) was 10:1, the feed flow rate (B) was 1 liter per hour, and the feed temperature (C) was 80°C for the ac treatment combination. The method of setting all the parameters were shown in Appendix D.

Step 3: Set these values of all the parameters for the ac treatment combination by clicking at change button. After selected the change button, the cursor appeared. The cursor was then moved by clicking at the arrow buttons. After the values of all the parameters were set, clicked at the enter button as shown in Fig. 3-7. The definition of these preset values were shown in Appendix E.



```
  process:0        t-01:23:21
phase: reflux            0->0
fraction:             follow:
reflux/withdr.[s]:  10/0
tdist    [s]:           -
Thead   ^[ɟC]: 80.0    -78.1
Tsump   ^[ɟC]: 100.0   -83.3
feed   [l/h]: 2.0
Tfeed    [ɟC]: 70.0    -70.3
sumpmode (0=Pconst,1=pdiff):0
Pstart    [W]: 1200
twait     [s]: 100
P,p [W,mbar]: 500      - 500
tequi.    [s]: 0
tinter    [s]: 0
Pcurrent(sump)[%]: 25 [W]: 500
```

Figure 3-7. Operation button

Step 4: Clicked at the start button to run the distillation tower system, and then clicked at the graph button. After clicked at the graph button, the graph line was shown on the screen as shown in Fig. 3-8

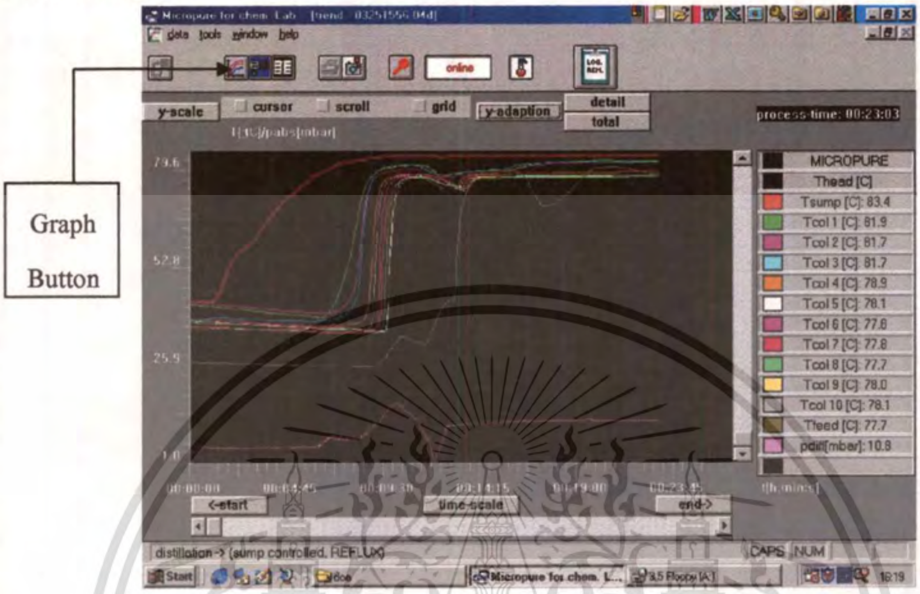


Figure 3-8. Operating screen

All the lines represented the temperature of trays and feed. When the system reached to the equilibrium, all the lines were straight and smooth lines. The system was reaching to the equilibrium when the distillate collected. Measured the refractive index of the distillate by using the refractometer.

Step 5: Plotted the refractive index of the distillate on the calibration curve to find its concentration.

The other treatment combinations (replicate I and replicate II) did in the same manner form step 1 to step 5.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 CALIBRATION CURVE FOR ETHANOL AND WATER SYSTEM

From the various concentration of ethanol-water mixture in weight percent, refractive index of each concentration were measured. The results were shown in Table 4-1

Table 4-1 Refractive index of ethanol-water mixture

Flask	Conc. (%)	RI
1	0	1.3297
2	10	1.336
3	20	1.3407
4	30	1.3457
5	40	1.3497
6	50	1.3537
7	60	1.3557
8	70	1.3578
9	80	1.3587
10	90	1.3588
11	100	1.3579

The plot between refractive index and concentration or calibration curve was shown in Appendix A.

From Table 4.1, the refractive index was increased when the concentration of ethanol in water was increased. RI was increased until 90% concentration of ethanol in water and when concentration 100% of ethanol in water, RI was constant. It was meant that ethanol was more significant to RI than water.

4.2 INVESTIGATION OF PROCESSING PARAMETER

In this experiment, four parameters were considered in the distillation of ethanol-water system. Each parameter has two levels (low and high), These levels are quantitative values of reflux ratio, temperature, flow rate and concentration. Negative symbol represents the low level of parameters whereas positive symbol represents the high level of parameters. It was shown in Table 4.2

Table 4-2 Level for parameter.

Symbol	Factors	Low (-)	High (+)
A	Reflux ratio	1:1	10:1
B	Feed flow rate	1 L/h	2 L/h
C	Temperature	70°C	80°C
D	Concentration	40%	50%

The treatment combinations of design are represented by lower case letters, as shown in Table 4.3. We can see from the table that the high level of any factor in the treatment combination is denoted by the corresponding lower case letter and that is the low level of a factor in the treatment combination of A at the high level and B, C, D at the low level. For example b represent A, B, C at the low level and B at the high level; ab represents both A, B at the high level and C, D at the low level and abcd represents all factors at the high level. By convention, (1) is used to denote all factors at the low level. This notation is used throughout the 2^k series.

From refractive index of each treatment in Table 4-3, we could find the concentration of each treatment by using the calibration curve of ethanol-water system in Appendix A. The concentration of each treatment were shown in Table 4-4. For example, parameters of treatment combination 1 were reflux ratio at 1:1, feed flow rate at 1 L/h, temperature at 70°C and 40% of ethanol-water mixture concentration. Let symbol y_j and y_i represents concentration and total concentration.

Table 4-3 Refractive index of treatment.

Treatment combination	Factors				Refractive index	
	A	B	C	D	Replicate I	Replicate II
1	1:1	1	70	40	1.3576	1.3582
a	10:1	1	70	40	1.3576	1.3566
b	1:1	2	70	40	1.3572	1.3575
ab	10:1	2	70	40	1.3578	1.3577
c	1:1	1	80	40	1.3567	1.3576
ac	10:1	1	80	40	1.3567	1.3571
bc	1:1	2	80	40	1.3572	1.3577
abc	10:1	2	80	40	1.3565	1.3566
d	1:1	1	70	50	1.3556	1.3561
ad	10:1	1	70	50	1.3561	1.3561
bd	1:1	2	70	50	1.3571	1.3560
abd	10:1	2	70	50	1.3557	1.3561
cd	1:1	1	80	50	1.3578	1.3567
acd	10:1	1	80	50	1.3577	1.3577
bcd	1:1	2	80	50	1.3576	1.3567
abcd	10:1	2	80	50	1.3566	1.3565

From Table 4-4 the percent of concentration of ethanol from distillation for the treatment combinations 1, ab, cd and acd were quite high (about 70% yield). It was meant that selection of treatment 1, ab, cd and acd to run the distillation process, we would get high purity of ethanol from the distillation process.

Table 4-4 Concentration of treatment

Treatment combination	Concentration (y_j)		Total (y_i)
	Replicate I (%)	Replicate II (%)	
1	68.8	73.4	142.2
a	68.8	64	132.8
b	66.7	68.2	134.9
ab	70	69.3	139.3
c	64.4	68.8	133.2
ac	64.4	66.2	130.6
bc	66.7	69.3	136
abc	63.6	64	127.6
d	59.5	61.8	121.3
ad	61.8	61.8	123.6
bd	66.2	61.4	127.6
abd	60	61.8	121.8
cd	70	64.4	134.4
acd	69.3	69.3	138.6
bcd	68.8	64.4	133.2
abcd	64	63.6	127.6
Total	1053	1051.7	2104.7

Consider treatment combination d, abd and ad, the percent of concentration of ethanol from distillation was quite low when compare to the other. It was proposed that these treatments were less effective to distillation of ethanol-water system. If we ran these values, it would get low purity of ethanol from the distillation process.

4.3 DESIGN OF EXPERIMENT

The 2^4 factorial in RCBD was used in this experiment. The reflux ratio (A), flow rate of feed (B), feed temperature (C), and feed composition (D) were investigated in the distillation of ethanol-water mixture. These parameters were varied to be two values (high and low values). Run two replicates of the 2^4 design was considered in this research. Consequently, there were 32 runs in this experiment.4.

4.3.1 Mass flow rate

From the various concentrations of the ethanol-water mixture, the distillate and the liquid at the bottom of the distillation system were collected. The refractive indexes of the liquids were measured by the refractometer as shown in Table 4-5

Table 4-5 Refractive indexes of the distillate and the bottom

Treatment combination	Distillate		Bottom	
	Replicate I	Replicate II	Replicate I	Replicate II
(1)	1.3576	1.3582	1.3498	1.3512
a	1.3576	1.3566	1.3502	1.3485
b	1.3572	1.3575	1.3482	1.3496
ab	1.3578	1.3577	1.3502	1.3497
c	1.3567	1.3576	1.3496	1.3501
ac	1.3567	1.3571	1.3493	1.3502
bc	1.3572	1.3577	1.3492	1.3497
abc	1.3565	1.3566	1.3492	1.3495
d	1.3556	1.3561	1.3518	1.3526
ad	1.3561	1.3561	1.3527	1.3526
bd	1.3571	1.3560	1.3526	1.3521
abd	1.3557	1.3561	1.3526	1.3527
cd	1.3578	1.3567	1.3467	1.3517
acd	1.3577	1.3577	1.3518	1.3517
bcd	1.3576	1.3567	1.3517	1.3528
abcd	1.3566	1.3565	1.3530	1.3522

From Table 4-5, the refractive indexes were changed to concentrations by using the calibration curve which shown in Appendix A. The concentrations and averages of these concentrations were shown in Table 4-6.

Table 4-6. The concentrations and the average concentrations

Treatment combination	Distillate			Bottom		
	Replicate I	Replicate II	Average	Replicate I	Replicate II	Average
(1)	68.8	73.4	71.1	40.25	43.75	42
a	68.8	64	66.4	41.125	37	39.06
b	66.7	68.2	67.45	38.75	39.75	39.25
ab	70	69.3	69.65	41.125	40	40.56
c	64.4	68.8	66.6	39.75	41.125	40.44
ac	64.4	66.2	65.3	38.875	41.25	40.06
bc	66.7	69.3	68	38.625	40	39.31
abc	63.6	64	63.8	38.75	39.5	39.13
d	59.5	67.8	60.65	45.25	47.25	46.25
ad	67.8	67.8	67.8	47.5	47.25	47.38
bd	66.2	67.4	63.8	47.25	46	46.63
abd	60	67.8	60.9	47.25	47.5	47.375
cd	70	64.4	67.2	32.5	45	38.75
acd	69.3	69.3	69.3	45.25	45	45.13
bcd	68.8	64.4	66.6	45	47.75	46.38
abcd	64	63.6	63.8	48.5	46.25	47.38

From Table 4-6, the average of these concentrations were changed to mole fractions by divided with a hundred as shown in Table 4-7.

Table 4-7 Mole fraction of the distillates and the bottoms

Treatment combination	Mole fraction of the distillate (x_D)	Mole fraction of the bottom (x_W)
(1)	0.7110	0.4200
a	0.6640	0.3906
b	0.6745	0.3925
ab	0.6965	0.4056
c	0.6660	0.4044
ac	0.6530	0.4006
bc	0.6800	0.3931
abc	0.6380	0.3913
d	0.6065	0.4625
ad	0.618	0.4738
bd	0.638	0.4663
abd	0.609	0.4738
cd	0.672	0.3875
acd	0.693	0.4513
bcd	0.666	0.4638
abcd	0.638	0.4738

From Table 4-7, the mass flow rates of the feed and the bottoms could be calculated as shown in Appendix F. The mass flow rates were shown in Table 4-8.

Table 4-8 Mass flow rates of the feeds and the bottoms

Treatment combination	Mass flow rate of the feed (F)	Mass flow rate of the bottom (W)
(1)	19.88 mol/h	21.25 mol/h
a	19.88 mol/h	19.20 mol/h
b	39.77 mol/h	38.71 mol/h
ab	39.77 mol/h	40.54 mol/h
c	19.88 mol/h	20.21 mol/h
ac	19.88 mol/h	19.93 mol/h
bc	39.77 mol/h	38.81 mol/h
abc	39.77 mol/h	38.37 mol/h
d	19.43 mol/h	14.37 mol/h
ad	19.43 mol/h	15.90 mol/h
bd	38.85 mol/h	31.22 mol/h
abd	38.85 mol/h	31.31 mol/h
cd	19.43 mol/h	11.75 mol/h
acd	19.43 mol/h	15.52 mol/h
bcd	38.85 mol/h	31.89 mol/h
abcd	38.85 mol/h	32.65 mol/h

The mass flow rate of feed (F) should be more than the mass flow rate of the bottom (W). If the mass flow rate of the bottom is more than the mass flow rate of feed, the system will waste the energy. The system will need more energy to heat the liquid at the bottom of the system. If the system need more energy, the operating cost will be high. Therefore, the mass flow rate of the bottom should be less than the mass flow rate of the feed.

From Table 4-8, the mass flow rate of feed was more than the mass flow rate of the bottom in the treatment combination a, b, bc, abc, d, ad, bd, abd, cd, acd, bcd, and abcd.

4.3.2 Main effect and interaction effect.

The main effect and interaction effect of these parameters was first calculated as shown in Appendix G. By convention, we denoted the effect of a factor by a capital letter. Thus "A" refers to the effect of factor A, "B" refers to the effect of factor B, "AB" refers to the effect of AB interaction, "ABC" refers to the effect of ABC interaction. The main effect and interaction effect of all the parameters were shown in Table 4-9.

Table 4-9 Main effect and interaction effect

Treatment	Concentration		Total	Effect	Factor
	I	II			
(1)	68.8	73.4	142.2		
a	68.8	64	132.8	-1.306	(A)
b	66.7	68.2	134.9	0.619	(B)
ab	70	69.3	139.3	-0.544	(AB)
c	64.4	68.8	133.2	1.006	(C)
ac	64.4	66.2	130.6	1.331	(AC)
bc	66.7	69.3	136	0.244	(BC)
abc	63.6	64	127.6	1.106	(ABC)
d	59.5	61.8	121.3	-3.831	(D)
ad	61.8	61.8	123.6	-0.506	(AD)
bd	66.2	61.4	127.6	1.119	(BD)
abd	60	61.8	121.8	1.081	(ABD)
cd	70	64.4	134.4	0.419	(CD)
acd	69.3	69.3	138.6	1.619	(ACD)
bcd	68.8	64.4	133.2	-0.694	(BCD)
abcd	64	63.6	127.6	-3.031	(ABCD)

According to Table 4-9, the main effect of A (reflux ratio) was negative value, this suggested that increasing A from the low level (1:1) to the high level (10:1) would decrease the yield. The main effect of B (feed flow rate) was positive; this suggested that increasing B from the low level (1L/h) to the high level (2L/h) would increase the yield. The main effect of C (temperature) was positive; this suggested that increasing C from the low level (70°C) to high level (80°C) would increase the yield. The main effect of D (concentration) was negative; this suggested that increasing D from the low level (40%) to the high level (50%) would decrease the yield.

4.3.3 Analysis of variance for the experiment

Analysis of variance is a method for testing a hypothesis. In 2^k factorial design, the interaction effect of the factors is first tested. If there is no interaction effects between the factors, then the main effect will be calculated later. Consequently, a hypothesis of the interaction effect was first tested in this experiment.

The test of interaction effect must begin from the interaction effect of all factors in the experiment.

The hypothesis for testing in the 2^4 factorial design in RCBD is

H_0: interaction of ABCD = 0

H_a: interaction of ABCD $\neq$ 0

After the hypothesis was set, we did the analysis of variance to test the hypothesis of this experiment.

Step 1: Calculation of the correction factor, as shown in Appendix H.

Step 2: Calculation of sum of square for block, treatment, all the effects of factorial, and error, as shown in Appendix H.

Step 3: Calculation of mean square for block, all the effects of factorial, and error, as shown in Appendix H.

Step 4: Calculation of F-Value for block, and all the effect of factorial, as shown in Appendix H.

Then the data were analyzed by using analysis of variance. The notation for sum of square and the degree of freedom were shown in Table 4-10.

Table 4-10 Analysis of variance for a 2^4 design in RCBD

Source of variation	Sum of square	Degree of freedom
Four main effects		
A	SS_A	(a-1)=1
B	SS_B	(b-1)=1
C	SS_C	(c-1)=1
D	SS_D	(d-1)=1
Two factor interactions		
AB	SS_{AB}	(a-1)(b-1)=1
AC	SS_{AC}	(a-1)(c-1)=1
AD	SS_{AD}	(a-1)(d-1)=1
BC	SS_{BC}	(b-1)(c-1)=1
BD	SS_{BD}	(b-1)(d-1)=1
CD	SS_{CD}	(c-1)(d-1)=1
Three factors interactions		
ABC	SS_{ABC}	(a-1)(b-1)(c-1)=1
ABD	SS_{ABD}	(a-1)(b-1)(d-1)=1
ACD	SS_{ACD}	(a-1)(c-1)(d-1)=1
BCD	SS_{BCD}	(b-1)(c-1)(d-1)=1
Four factors interactions		
ABCD	SS_{ABCD}	(a-1)(b-1)(c-1)(d-1)=1
Error	SS_E	(abcd-1)(n-1) = 15
Total	SS_T	30

Degree of freedom of A was (a-1), symbol "a" mean number of level for factor A (in this case factor A is reflux ratio). Thus, degree of freedom of A is equal to 2-1=1.

The test procedure was summarized of analysis of variance, as shown in Table 4-11.

Table 4-11 Analysis of variance

Source of variation	Degree of freedom	Sum square	Mean square	F-test value
Block	1	0.053	2.053	2.578
Treatment	15	290.1897	19.346	3.655
A	1	13.650	13.650	2.578
B	1	3.063	3.063	0.579
C	1	2.365	2.365	0.447
D	1	8.1	8.1	1.530
AB	1	14.178	14.178	2.678
AC	1	0.475	0.475	0.090
AD	1	9.790	9.790	1.849
BC	1	117.428	117.428	22.181
BD	1	2.05	2.05	0.387
CD	1	10.013	10.013	1.891
ABC	1	9.353	9.353	1.767
ABD	1	1.403	1.403	0.265
ACD	1	20.963	20.963	3.960
BCD	1	3.850	3.850	0.727
ABCD	1	73.508	73.508	13.885
error	15	79.456	4.966	
Total	46	369.645		

Compare the F value from calculation with F value and F distribution table as shown in Appendix I (degree of freedom =1,15, α= 0.05).

If the value of F to calculation was less than F value from F distribution table, it should be accepted H_o. If the value of F from calculation was more than F value from F distribution table, it should be reject H_o and accept H_a This was meant that the F-test value was so significant. The results was shown as follow:

$F_A = 2.578 < F_{0.05(1,15)} = 4.54$

$F_B = 0.579 < F_{0.05(1,15)} = 4.54$

$F_C = 0.447 < F_{0.05(1,15)} = 4.54$

$F_D = 1.530 < F_{0.05(1,15)} = 4.54$

$F_{AB} = 2.678 < F_{0.05(1,15)} = 4.54$

$F_{AC} = 0.090 < F_{0.05(1,15)} = 4.54$

$F_{AD} = 1.849 < F_{0.05(1,15)} = 4.54$

$F_{BC} = 22.181 > F_{0.05(1,15)} = 4.54^{*}$

$F_{BD} = 0.387 < F_{0.05(1,15)} = 4.54$

$F_{CD} = 1.891 < F_{0.05(1,15)} = 4.54$

$F_{ABC} = 1.767 < F_{0.05(1,15)} = 4.54$

$F_{ABD} = 0.265 < F_{0.05(1,15)} = 4.54$

$F_{ACD} = 3.960 < F_{0.05(1,15)} = 4.54$

$F_{BCD} = 0.727 < F_{0.05(1,15)} = 4.54$

$F_{ABCD} = 13.885 > F_{0.05(1,15)} = 4.54^{*}$

It was found that, the interaction of ABCD was so significant, so we reject H_o and accept H_a. This suggested that all factors had the interaction effect. It was not necessary to analyze the main effect of A, B, C, and D because the ABCD had already interaction to each other. The calculation with multiple comparison should be further studied to investigate the couple of all factors.

4.3.4 Multiple Comparison

For interpreting the results of this experiment, it was helpful to use the student Newman-Keuls Procedure (SNK) to analyze the interaction effect of all the factors in this experiment.

1. Calculation of the average concentration of each level for the interaction effect of ABCD and then ranking of the average concentration from low value to high value.

No.	1	2	3	4
Factors	D	A	C	B
Treatments	d	a	c	b
Average concentration	60.65	66.4	66.6	67.45

2. Find the interval range(k) of these two averages.

k = the interval range between number of experiment. Thus, k = 2, 3 and 4

3. Finding of upper-tail critical value or $q_\alpha(k,v)$ from studentized range from Appendix J

v = degree of freedom at mean square error. Thus v = 15

$q_{0.05}(2,15) = 3.01$

$q_{0.05}(3,15) = 3.67$

$q_{0.05}(4,15) = 4.08$

4. Calculation of W_k, from $q_\alpha(k,v)\sqrt{\frac{MSE}{n}}$

$W_2 = 4.897$

$W_3 = 5.970$

$W_4 = 6.638$

5. Calculation the different between the average concentration of each factor and compare with W_k.

B-D = 6.8 > 6.638

B-A = 1.05 < 5.970

B-C = 0.85 < 4.897

C-D = 5.95 < 5.970

C-A = 0.2 < 4.897

A-D = 5.75 > 4.897

From different comparison between the average concentration of each factors and W_k, if the different values between the average concentration were more than W_k it was meant that there were interaction to each other. Thus, the results were

B and C had an interaction

B and A,C did not have an interaction

A and D had an interaction

C and D did not have an interaction

A and C did not have an interaction

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 CONCLUSIONS

This research was investigated on critical parameters which had interaction to each other in ethanol-water mixture of distillation process. Four parameters were considered; temperature 70°C and 80°C, feed flow rate 1 L/h and 2 L/h, concentration 40% and 50% and reflux ratio 1:1 and 10:1. The experiment was designed in the form of 2^4 factorials in randomized complete of two blocks design.

5.1.1 Main effect

The main effect of reflux ratio(A), feed flow rate(B), temperature(C),and concentration(D) was concluded as follows:

1. For 1:1 reflux ratio, the yield was better than using other reflux ratio.
2. For 2 L/h feed flow rate, the yield was better than using the other flow rate.
3. For temperature of 80°C, the yield was better than using other temperature.
4. For the 40% concentration, the yield was better than using other concentration.

From the conclusion of main effect, the better conditions for ethanol-water mixture in distillation process were 1:1 reflux ratio, 2 L/h feed flow rate, 80°C and 40% concentration.

5.1.2 Analysis of variance

Considered the interaction for 16 treatments by using analysis of variance with F-test method. It was found that only 2 treatments have shown the interaction, it was concluded as follows:

1. The F value from F-test of BC interaction was significant.
2. The F value from F-test of ABCD interaction was so significant.

It was not necessary to consider BC interaction because there were only two parameters. The important thing was ABCD interaction which had more parameters than BC interaction.

It was indicated that reflux ratio, feed flow rate, temperature and concentration were co-influenced parameters. All factors had an interaction to each other. It was not only one factor influence in the process, but also other parameter had significant roles. Multiple comparison was continued study to consider the interaction to consider of AB, AC, AD, BC, BD and CD.

5.1.3 Multiple Comparison

From multiple comparison, the interaction of AB, AC, AD, BC, BD and CD were concluded as follows :

1.Reflux ratio (A) and feed flow rate (B) had an interaction. Therefore, if reflux ratio was fixed at some point and varied the value of feed flow rate or the flow rate was fixed and varied reflux ratio, the results of the distillation of ethanol-water was not changed.

2. Reflux ratio (A) and temperature (C) was not had an interaction. If the value of reflux ratio was fixed at some point and varied the value of temperature or temperature was fixed and varied reflux ratio, the result of the distillation of ethanol-water was not changed.

3. Reflux ratio (A) and concentration (D) had an interaction. It was meant that if the value of reflux ratio was fixed and varied concentration or concentration was fixed and varied reflux ratio, the result of the distillation of ethanol-water was changed.

4. Feed flow rate (B) and temperature (C) was not had an interaction. It was meant that if flow rate if flow rate was fixed and varied temperature or temperature was fixed and varied flow rate, the result of the distillation of ethanol-water was not changed.

5. Feed flow rate (B) and temperature (C) was not had an interaction. It was meant that if feed flow rate was fixed and varied concentration or concentration was fixed and varied feed flow rate, the result of the distillation of ethanol-water was changed.

6. Temperature (C) and concentration (D) was not had an interaction. It was meant that if temperature was fixed and varied concentration or concentration was fixed and varied feed flow rate, the result of the distillation of ethanol-water was not changed.

Temperature was influenced in the distillation of ethanol-water mixture when considered only the main effect, but temperature was not had an influence in the process when considered from multiple comparison. This could be concluded that changing temperature (during 70 $^{\circ}$C to 80°C) was not necessary in the distillation of ethanol-water mixture when compare with reflux ratio, feed flow rate and concentration.

5.2 RECOMMENDATION

- We should study on other software such as HYSYS®, CHEMCAD® and MATHLAB® to compare the results of distillation process between ethanol-water mixture with the results from experiment.

- We should study on SPSS program to determine the effect of each parameter and compare with F-test method.

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Appendix A Calibration curve of ethanol and water mixture

The plot between refractive index and concentration or calibration curve was shown in below.

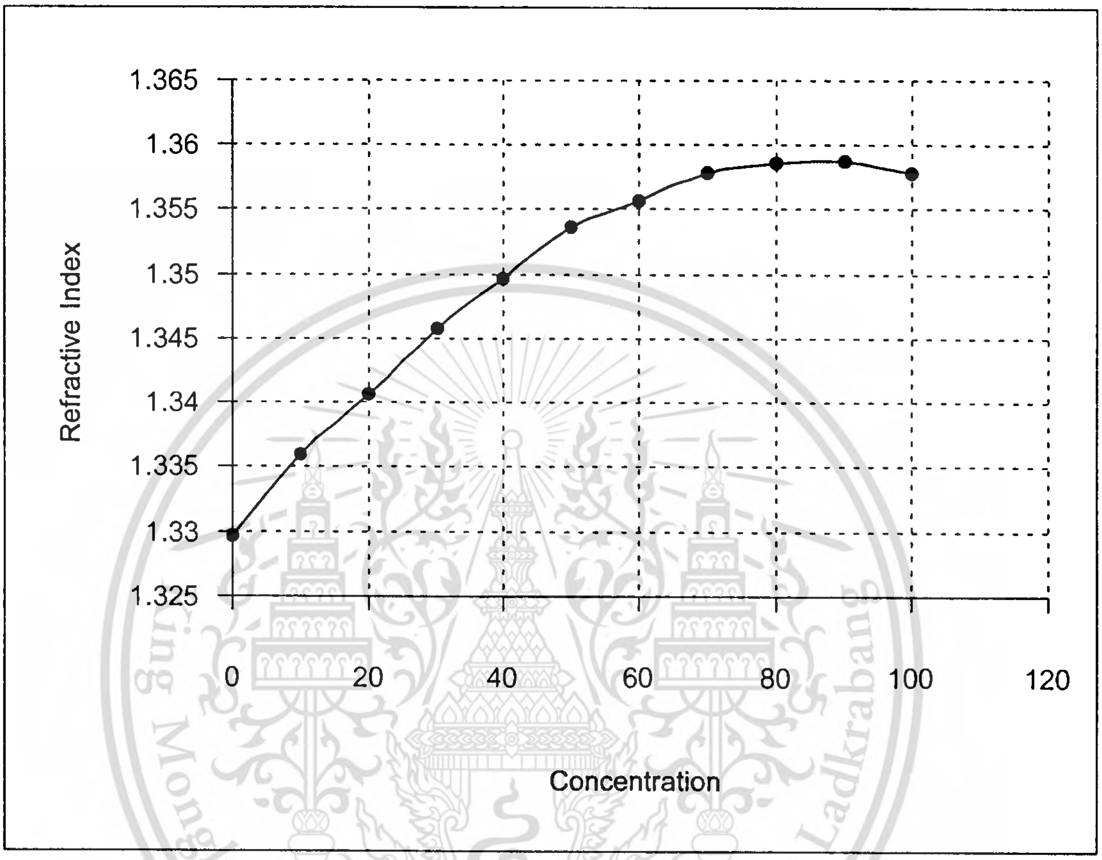


Fig A1. Calibration curve for ethanol-water mixture between refractive index and concentration

Appendix B Density of ethanol-water mixture

Density of water equal to 1 g/cm^3 and density of pure ethanol equals to 0.791 g/cm^3 as density of ethanol-water mixture was received from plotting density of water and pure ethanol.

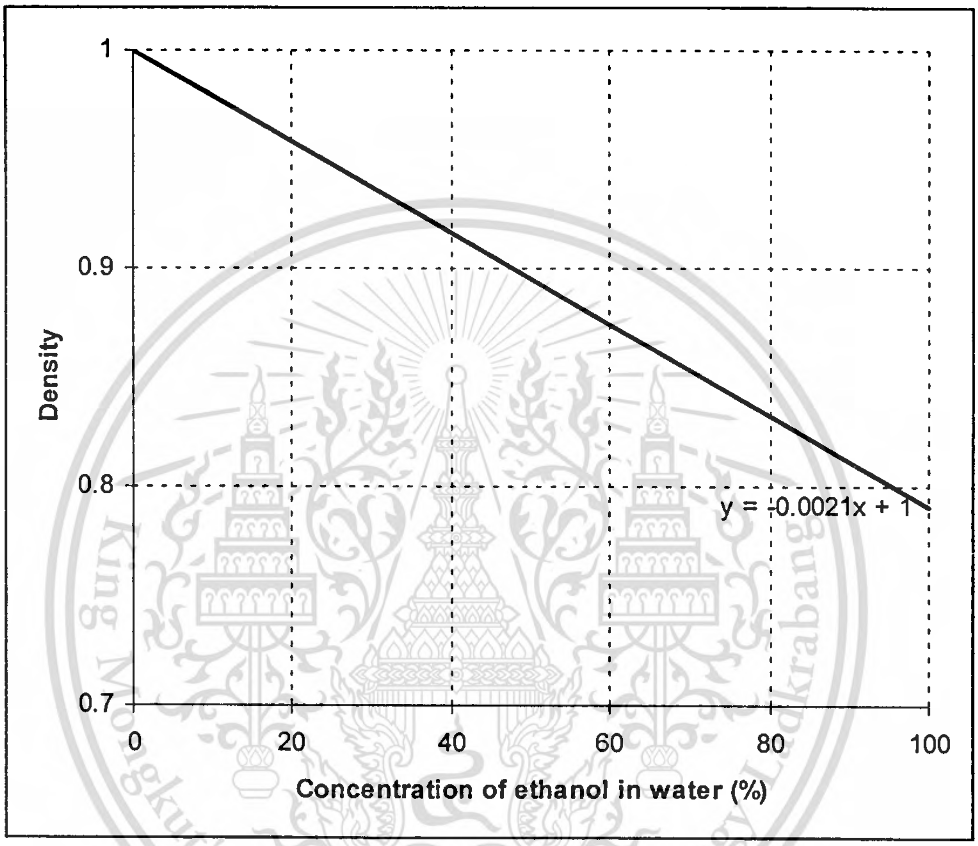


Fig B1. graph of density of ethanol in water at different concentration

From calculation of linear equation, the density of 40% by volume of ethanol-water mixture was 0.916 g/cm^3 and the density of 50% by volume of ethanol-water mixture was 0.895 g/cm^3.

Appendix C Preparation of operation

After the design of experiment, the following operation should checked:

- Are all filling points closed?
- Is the plane vented?

  Totally closed distillation plants over-pressure will occur in the plant when it is heat up. This may damage the glass parts.
- Is there any leakage to be seen under the plant?

At continuously working plants:

- is there enough feed product?

Dry running may damage the feed pump.

- Are receiver vessels big enough?
- Make sure that the place where the plant is operated, has vent sufficiently

Seals or valves leaking will lead to immense amount of toxic or flammable liquids or vapor.

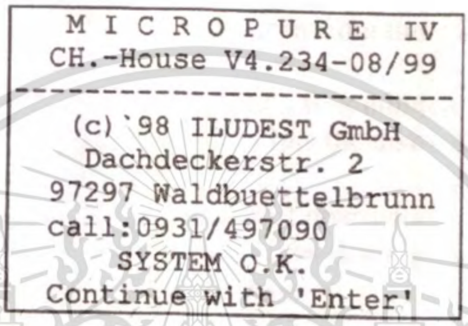
- when handling flammable liquids, it should be avoid flames.

Appendix D How to operating

After the design of experiment it should be checked the equipment. The procedure of the running process are shown below

1. After switching on the unit, the opening window containing the version number and the hotline is displayed:

2. Press the “ENTER” key of the control unit to display the parameters.



```
 M I C R O P U R E  IV
CH.-House V4.234-08/99
-----------------------
  (c)`98 ILUDEST GmbH
   Dachdeckerstr. 2
97297 Waldbuettelbrunn
call:0931/497090
     SYSTEM O.K.
Continue with 'Enter'
```

Fig.D1. First displayed on the screen.

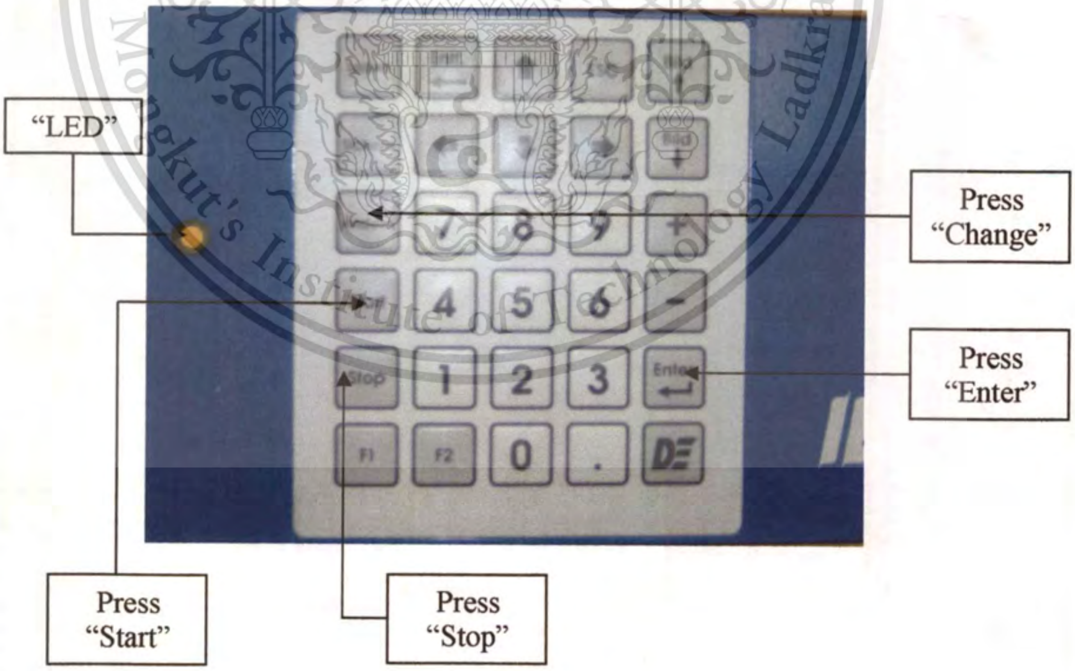
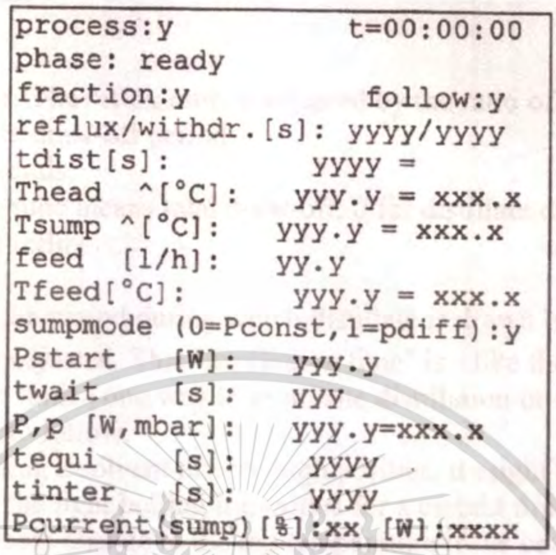


Fig D2. Detail of key control

3. Enter the necessary data for the distillation. These could be as follows:



```
process:y               t=00:00:00
phase: ready
fraction:y               follow:y
reflux/withdr.[s]: yyyy/yyyy
tdist[s]:            yyyy =
Thead  ^[°C]:     yyy.y = xxx.x
Tsump ^[°C]:    yyy.y = xxx.x
feed  [l/h]:    yy.y
Tfeed[°C]:        yyy.y = xxx.x
sumpmode (0=Pconst,1=pdiff):y
Pstart     [W]:    yyy.y
twait      [s]:    yyy
P,p [W,mbar]:     yyy.y=xxx.x
tequi      [s]:      yyyy
tinter     [s]:      yyyy
Pcurrent(sump)[%]:xx [W]:xxxx
```

Fig D3. Parameters control on the screen.

4. If you want to change the data, just press “Change” key and set the data, confirm by the “Enter” key.

5. To start the process, press “Start” key, the set of parameters valid gets active: the LED in the front panel of the controller changes its color from orange to green, the clock starts running and the reboiler is run with the heating power Pstart.

6. When starting a distillation process, the cooling water valve is opened automatically.

Fig D4. Cooling water is opened automatically when start the process.

7. Reboiler temperature is controlled from the beginning. And top temperature is controlled when t_{equi} is over.

8. Collecting the distillate when the system reach to the equilibrium.

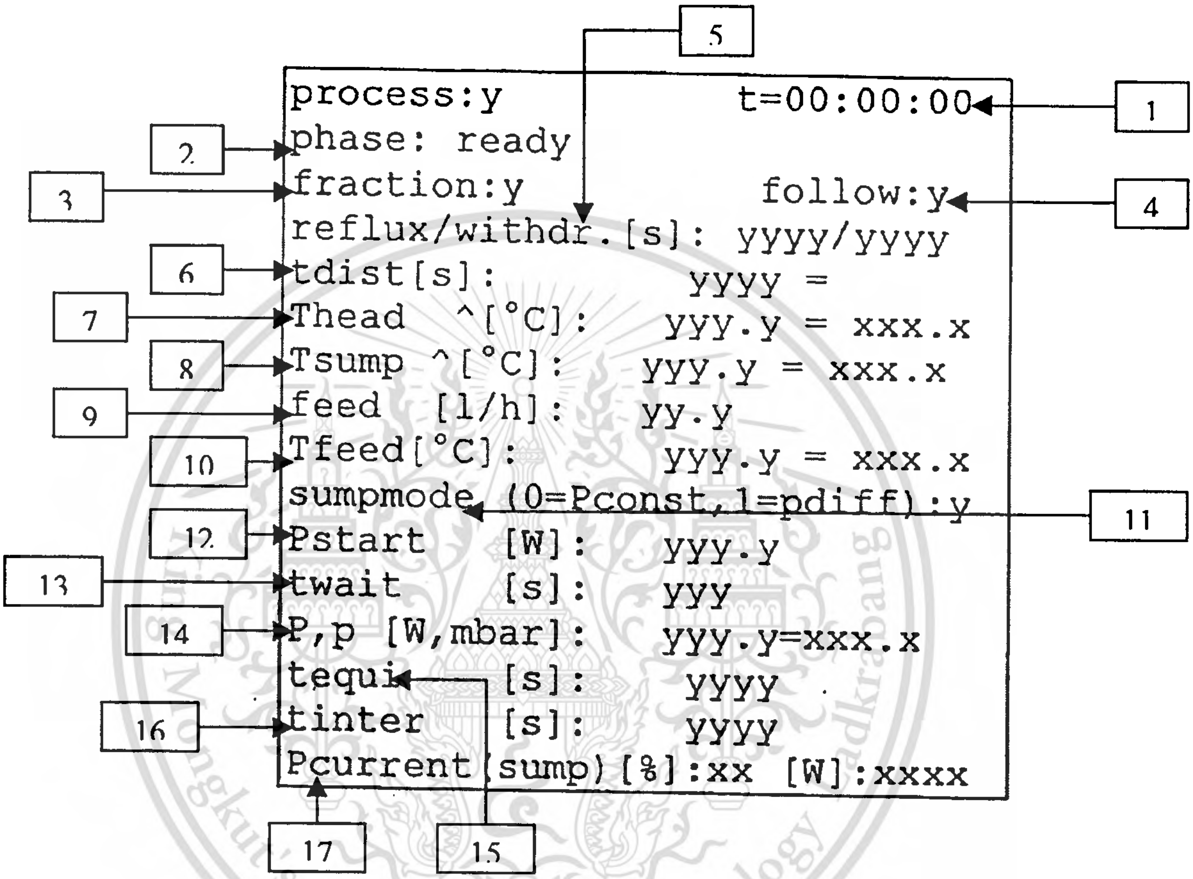
9. Measuring the refractive index by using the refractometer.

10. By pressing the stop-key, the distillation process can be terminated at any time.

11. The cooling water valve will remain open for a period preset in the master-mode, this is shown on the display.

Appendix E The definition of parameters on distillation machine

Many parameter were set following the design of experiment. The definition of parameters on distillation machine are shown in Fig E1. and Table E2.



```
process:y                t=00:00:00
phase: ready
fraction:y                 follow:y
reflux/withdr.[s]: yyyy/yyyy
tdist[s]:             yyyy =
Thead   ^[°C]:      yyy.y = xxx.x
Tsump  ^[°C]:      yyy.y = xxx.x
feed   [l/h]:      yy.y
Tfeed[°C]:           yyy.y = xxx.x
sumpmode (0=Pconst,1=pdiff):y
Pstart     [W]:    yyy.y
twait      [s]:    yyy
P,p [W,mbar]:     yyy.y=xxx.x
tequi      [s]:     yyyy
tinter     [s]:     yyyy
Pcurrent (sump)[%]:xx  [W]:xxxx
```

Fig E1. The number of parameters on screen.

Table E1. The definition of each numbers on screen.

NO.	Symbol	Definition
1	time	- Indicates the lasting of a distillation run. Specified in hours, minutes and seconds.
2	phase	- Every distillation consists of separate phases which are started automatically by the program. Ready (before starting, after terminating a process), P_{start}, t_{equi}, W, R, t_{inter}; explanations see below. So the status of the distillation can be seen from this value.

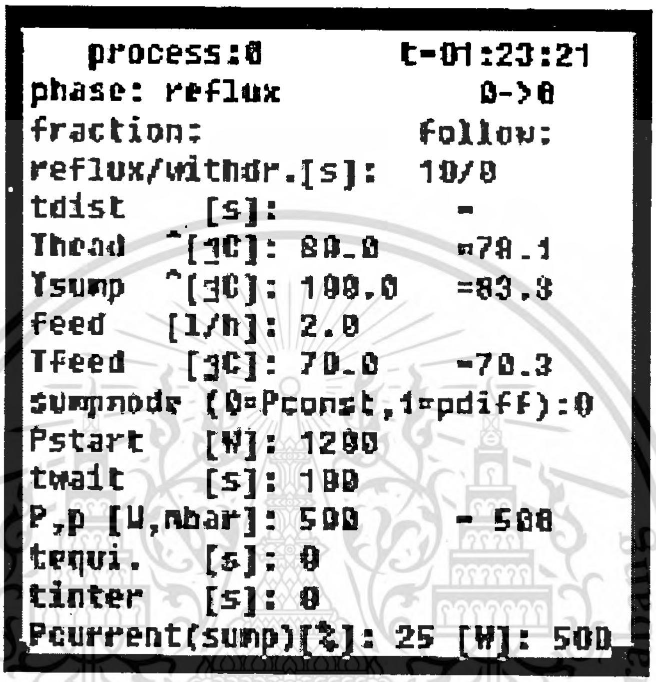
NO.	Symbol	Definition
3	fraction	- This number indicates, which fraction is combined with the actual process, this is, by what product line the distillate is drawn off.
4	follow	- It is possible to start another process after the actual one has ended. If this shall happen, the number of the process to follow is to be entered here. If the distillation shall be stopped when a refering creterion is given (see t_{dist}, T_{head}) this parameter has to be deleted (see below).
5	Reflux ratio	- The reflux ratio is adjusted by the ratio of reflux and distillate draw-off period. - Input in seconds : 0 for reflux time means total draw-off, 0 for distillate draw-off time means total reflux.
6	T_{dist}	- Determines the period during which distillate is drawn off by the reflux ratio adjusted. This "distillation time" is – like the top temperature limit – one way to terminate distillation or to start the process to follow. - When cleaning a solvent to very high purities, it might be advisable to draw off the light boiling impurities for a certain time, as there is no detectable change in the top temperature if the concentration of impurities is very low. - When distilling, the period for which the distillate has already been drawn off is indicated behind the equal (=). - Input in s.
7	T_{head}	- The draw - off of distillate is stopped when the column top temperature reaches this limit. Depending on the actual set of parameters this may lead to the termination of the distillation process or may activate another set of parameters (see also follow and t_{inter}).

NO.	Symbol	Definition
7(cont)	T_{head}	- The value measured is displayed behind the equal (=). As the temperature measured during the start up period (t_{equi}) might be higher than the preset limit, T_{head}: is not valid before the draw – off of distillate. - Although a distillation plant has no electrical fraction changer, the ILUDEST – MICROPURE controller allows to take off separate fractions very easily: 1) be sure no figure at all is indicated at "fraction" 2) enter the number of another process behind the "follow" field: When – during distillation of the first fraction – the entered limit for the head temperature is reached, the draw off of product will be interrupted (total reflux) and a corresponding message will be displayed on the screen.
8	T_{sump}	- Maximum allowed temperature for the reboiler content. If this value is exceeded by any reason, a corresponding message will be displayed on the screen and the plant will be shut off. The temperature limit is to be entered behind the colon, the actual value is displayed behind the equal.
9	Feed	- Throughput of the feed pump. The indicated set point is only valid, if the maximum throughput of the connected pump has been entered correctly (this is done under MASTERMODE "pump") and if the used pump has been calibrated with the corresponding feed mixture. *- Important note: The difference, whether the distillation system should be used in continuous mode or batch*

NO.	Symbol	Definition
9(cont)	Feed	*mode is recognized* *by the controller while checking this parameter. If a "0" is set as feed rate or the field is deleted, this means, that the distillation system is used batchwise (feed and discharge pumps are not active then). Values >=0 mean continuous operation mode.*
10	T_{feed}	- Temperature for the feed heater in continuous operation mode. The preset temperature should be near to the boiling temperature of the feed mixture. - Sump – mode: it can be defined, how the heating of the reboiler content is done.
11	Sump – mode	- To the evaporator during distillation should be kept constant, the value here must be a "0" behind the equal. If a constant pressure difference at the separation column should be achieved, the value here must be a "1" behind the equal.
12	P_{start}	- Start – up power for the heating rod of the circulating evaporator. A high power can be preset so to achieve boiling of the evaporator content as fast as possible. The maximum indicated and applied power will be not more than 80% of the maximum possible for safety reasons. Input in W
13	t_{wait}	- Because of a high start up heating power the column may flood. When the first vapor reaches the head temperature probe, the heating power is switched off for the period of t_{wait} to end the flooding of the column.
14	P	- The set point for the power to the heating circulator during distillation, as soon as the start – up phase P_{start} is over. For a good separation of the column, it is

NO.	Symbol	Definition
14 (cont)	P	advisable to run the distillation plant with low to moderate heating power.
15	t_{equi}	- When vapor reaches the head, P_{start} is ended automatically and the equilibration time t_{equi} starts: - the heating power to the reboiler is controlled as defined by the the chosen sumpmode (Pconst or pdiff) and the corresponding parameters under P, p (W or mbar). The plant runs under total reflux for the period of t_{equi}. - This ensures that the column efficiency is at its maximum when distillate is drawn off. - Input in s. - When t_{equi} is over, the top product is drawn off by the reflux ratio preset.
16	t_{inter}	- Intermitting period: When a certain top temperature (see T_{head}) is exceeded, draw off is changed to total reflux. If the top temperature will decrease under the limit (T_{head}) during t_{inter}, distillate draw – off will be continued, otherwise the actual process will be terminated. This intermitting mode is useful to draw off some light boiling components almost completely (in batchwise operation).
17	$P_{current}$	- The real power (actual value) to the evaporator is displayed in % of the maximum heating capacity and directly in W.

Variable parameters in this experiment were reflux/withdraw [5], feed [9] and Tfeed [10]. Therefore the other were constant parameters. For this experiment, the constant parameters shown in Fig. E2



```
   process:0           t=01:23:21
phase: reflux             0->0
fraction:              follow:
reflux/withdr.[s]:  10/0
tdist      [s]:          -
Thead   ^[3C]: 80.0     =78.1
Tsump   ^[3C]: 100.0    =83.8
feed    [1/h]: 2.0
TFeed     [3C]: 70.0     =70.3
sumpmode (0=Pconst,1=pdiff):0
Pstart     [W]: 1200
twait      [s]: 100
P,p [W,mbar]: 500       - 508
tequi.     [s]: 0
tinter     [s]: 0
Pcurrent(sump)[%]: 25 [W]: 500
```

Fig. E2. Operation parameters

Appendix F Calculation of a mass flow rate

From chapter 2, the overall material balance around the entire column states that the entering feed of F mol/h must equal the distillate D in mol/h plus the bottom W mol/h:

$$F = D + W \tag{1}$$

which F is feed flow rate in mol/h.

D is distillate flow rate in mol/h.

W is bottom flow rate in mol/h.

A total material balance on component A (ethanol) gives

$$Fx_F = Dx_D + Wx_W \tag{2}$$

which x_F is mole fraction of ethanol in feed.

x_D is mole fraction of ethanol in distillate.

x_W is mole fraction of ethanol in bottom.

Rewrite Eq. (1), becomes

$$D = F - W \tag{3}$$

Substitute Eq. (3) into Eq. (2), gives

$$F x_F = (F - W)x_D + W x_W$$

$$F x_F = F x_D - W x_D + W x_W$$

$$F x_F = F x_D + W(x_W - x_D) \tag{4}$$

From Eq. (4), the mole fraction of ethanol in feed, distillate, and bottom were known which shown in Table 4-7. The flow rate of feed known also but it was the flow rate in L/h. The feed flow rate in mol/h was required in this calculation. Therefore, the unit of feed flow rate was changed first by multiplying with density of the mixture and then dividing with molecular weight of ethanol as shown below.

Treatment combination (1)

The feed flow rate was 1 L/h and the feed composition was 40% by volume in treatment combination (1). The density equals the mass dividing by the volume as shown below.

$$D = M/V \tag{5}$$

From the graph of the density of the ethanol-water mixture in Appendix B, the density of 40% by volume of ethanol-water mixture was 0.916 g/cm^3.

The density was multiplied by a thousand for changing the unit from g/cm^3 to g/L. Therefore, the density became 916 g/L.

The density and the volume of feed were substituted into Eq. (5) which shown below.

$$M = (916\ \text{g/L})(1\ \text{l})$$

$$M = 916\ \text{g}$$

The mass in gram was divided by a molecular weight of ethanol (46.07) then the mole of ethanol obtained.

$$\text{Mol} = 916\ /\ 46.07$$

$$\text{Mol} = 19.88$$

Therefore, the mass flow rate of feed (F) in treatment combination (1) was 19.88 mol/h. The mass flow rate of feed for other treatment combinations were calculated in the same manner.

The mass flow rate of feed and the mole fractions were substituted into Eq. (4) to find the mass flow rate of the bottom (W) as shown below.

$$F\,x_F = F\,x_D + W(x_W - x_D)$$

$$(19.88)(0.4) = (19.88)(0.711) + W(0.42 - 0.711)$$

$$W = 21.246\ \text{mol/h}$$

The mass flow rate of bottom was 21.246 mol/h in treatment combination (1).

The mass flow rate of bottom for the other treatment combinations calculated in the same manner. The calculated mass flow rate of feed and bottom were shown in Table 4-8 (chapter 4).

<u>Appendix G</u> Calculation of main effect and interaction effect

- <u>Main effect</u>

The results of effect at each treatment combination from Table 4-5. are solved by

$$A = \frac{1}{8n}\ [a - (1) + ab - b + ac - c + ad - d + acd - cd + abd - bd + abc - bc + abcd - bcd]$$

$$A = \frac{1}{8(2)}[132.8-142.2+139.3-134.9+130.6-133.2+123.6-121.3+138.6-134.4+121.8-127.6+127.6-136+127.6-133.2]$$

$$A = -1.306$$

In a similar manner, the main effect of B, C, and D are:

$$B = \frac{1}{8n}\ [b - (1) + ab - a + bc - c + bd - d + bcd - cd + abd - ad + abc - ac + abcd - acd]$$

$$C = \frac{1}{8n}\ [c - (1) + ac - a + bc - b + cd - d + bcd - bd + acd - ad + abc - ab + abcd - abd]$$

$$D = \frac{1}{8n}\ [d - (1) + ad - a + bd - b + cd - c + bcd - bc + acd - ac + abd - ab + abcd - abc]$$

Interaction effect of Ab

$$AB = \frac{[ab - b + abc - bc + abd - bd + abcd - bcd - a + (1) - ac + c - ad + d - acd - cd]}{8n}$$

$$AB = \frac{1}{8(2)}[139.3-134.9+127.6-136+121.8-127.6+127.6-133.2-132.8+142.2-130.6+133.2-123.6+121.3-138.6-134.4]$$

$$AB = -0.544$$

In a similar manner, the AC, BC, AD, BD, and CD interaction are

$$AC = \frac{[ac - c + abc - bc + abd - bd + abcd - bcd - a + (1) - ab + b - ad + d - abd + bd]}{8n}$$

$$BC = \frac{[bc - c + abc - ac + abcd - acd + bcd - cd - ab + a - b + (1) - abd + ad + bd + d]}{8n}$$

$$AD = \frac{[ad - d + abd - bd + acd - cd + abcd - bcd - a + (1) - ab + b - ac + c - abc + bc]}{8n}$$

$$BD = \frac{[bd - d + abd - ad + bcd - cd + abcd - acd - ab + a - b + (1) - abc + ac - bc + c]}{8n}$$

$$CD = \frac{[cd - d + acd - ad + bcd - bd + abcd - abd - c + (1) - ac + a - bc + b - abc + ab]}{8n}$$

The *ABC* interaction is defined as the average difference between the AB interaction for the two different levels of C. Thus,

$$ABC = \frac{1}{8n}\ [\text{abcd - bcd - acd + cd - abd + bd + ad - d + abc - bc - ac + c - ab + b + a - (1)}]$$

In the same manner, the *ABD*, *ACD*, and *BCD* interactions are

$$ABD = \frac{1}{8n}\ [\text{abcd - bcd - acd +cd + abd - bd - ad + d - abc + bc + ac - c - ab + b + a - (1)}]$$

$$ACD = \frac{1}{8n}\ [\text{abcd - bcd + acd - cd - abd + bd - ad + d - abc + bc - ac + c + ab - b + a - (1)}]$$

$$BCD = \frac{1}{8n}\ [\text{abcd + bcd - acd - cd - abd - bd + ad + d -abc - bc + ac + c + ab + b - a - (1)}]$$

The *ABCD* interaction is defined as

$$ABCD = \frac{1}{8n}\ [\text{abcd - bcd - acd + cd - abd + bd + ad - d - abc + bc + ac - c + ab - b - a + (1)}]$$

Appendix H Analysis of variance

Calculation of correction factor (CF)

$$CF = \frac{[\sum y_i]^2}{n(a \times b \times c \times d)}$$

$$= \frac{1}{32}[142.2 + 132.8 + 134.9 + 139.3 + 133.2 + 130.6 + 136 + 127.6$$

$$+ 121.3 + 123.6 + 127.6 + 121.8 + 134.4 + 138.6 + 133.2 + 127.6]^2$$

$$= \frac{[2104.7]^2}{2 \times (2^4)}$$

$$= 138430.07$$

Calculation of sum of square

- Total sum of square (SS_T)

$$SS_T = \sum y_j{}^2 - CF$$

$$SS_T = [68.8^2+68.8^2+66.7^2+70^2+64.4^2+64.4^2+66.7^2+63.6^2+59.5^2+61.8^2+66.2^2+60^2+70^2$$
$$+69.3^2+68.8^2+64^2+73.4^2+64^2+68.2^2+69.3^2+68.8^2+66.2^2+69.3^2+64^2+61.8^2+61.8^2$$
$$+61.4^2+61.8^2+64.4^2+69.3^2+64.4^2+ 63.6^2]- 138430.07$$

$$SS_T = 369.645$$

- Sum of square of block (SS_R)

$$SS_R = \frac{(\sum y_{1j})^2 + (\sum y_{2j})^2}{a \times b \times c \times d} - CF$$

$$\sum y_{1j} = 68.8 + 68.8 + 66.7 + 70 + 64.4 + 64.4 + 66.7 + 63.6 + 59.5 + 61.8 + 66.2$$
$$+ 60 + 70 + 69.3 + 68.8 + 64$$

$$= 1053$$

$$\sum y_{2j} = 73.4 + 64 + 68.2 + 69.3 + 68.8 + 66.2 + 69.3 + 64 + 61.8 + 61.8 + 61.4$$
$$+ 61.8 + 64.4 + 61.8 + 64.4 + 69.3 + 64.4 + 63.6$$

$$= 1051.7$$

$$= \frac{1053^2 + 1051.7^2}{2^4} \qquad = \frac{2104.7^2}{32}$$

$$= 0.053$$

- Sum of square of treatment (SS_{tr})

$$SS_{tr} = \sum \frac{y_i^{\,2}}{n} - CT$$

$$= (142.2)^2+(132.8)^2+(134.9)^2+(139.3)^2+(133.2)^2+(130.6)^2+(136)^2+(127.6)^2$$

$$+(121.3)^2+(123.6)^2+(127.6)^2+(121.3)^2+(123.6)^2+(127.6)^2+(121.8)^2$$

$$+(134.4)^2+(138.6)^2+(133.2)^2+(127.6)^2$$

$$= 290.1897$$

- Sum square error SS_E

$$SS_E = SS_T - SS_R - SS_{tr}$$

$$= 369.6447 - 0.052825 - 290.1897$$

$$= 79.402175$$

- Sum of square due to the effect of factorial ($SS_{AB...K}$)

$$SS_{(AB...K)} = \frac{1}{n \cdot 2^k}[AB...Kcontrast]^2$$

$$SS_A = \frac{1}{2 \cdot 2^4}[a-(1)+ab-b+ac-c+ad-d+acd-cd+abd-bd+abc$$
$$-bc+abcd-bcd]^2$$

$$SS_A = \frac{1}{2 \cdot 2^4}[132.8\text{-}142.2\text{+}139.3\text{-}134.9\text{+}130.6\text{-}133.2\text{+}123.6\text{-}121.3\text{+}138.6\text{-}134.4$$
$$+121.8\text{-}127.6\text{+}127.6\text{-}136\text{+}127.6\text{-}133.2]$$

$$SS_A = 13.650$$

In the same manner

$$SS_B = \frac{1}{2 \cdot 2^4}[b - (1) + ab - a + bc - c + bd - d + bcd - cd + abd - ad + abc - ac$$

$+ abcd - acd]$

Substitute the value of contrast to find other sum of square for each treatment. The results were shown in Table 4-7.

Calculation of mean square

- Mean square (MS)

$$\mathrm{MS}_{(AB...K)} = \frac{SS_{(AB...K)}}{Df_{(AB...K)}}$$

$$\mathrm{MS}_{A} = \frac{SS_A}{Df_A}$$

$$= \frac{13.650}{1}$$

$$= 13.650$$

$$MS_B = \frac{SS_B}{Df_B}$$

$$= \frac{3.063}{1} = 3.063$$

Substitute the sum of square value to find mean square for each treatment. The results were shown in Table 4-7.

- Mean square of block (MS_R)

$$MS_R = \frac{SS_R}{r-1}$$

$$= \frac{0.053}{2-1}$$

$$= 0.053$$

- Mean square of treatment (MS_{tr})

$$MS_{tr} = \frac{SS_{tr}}{(t-1)}$$

$$= \frac{290.1897}{16-1}$$

$$= 19.346$$

- Error mean square (MS_E)

$$\mathrm{MS}_E = \frac{SS_E}{(r-1)(abcd-1)}$$

$$= \frac{79.402}{(2-1)(16-1)}$$

$$= 5.293$$

Calculation of F-Value

- F-Value of block

$$F_R = \frac{MS_R}{MS_E}$$

$$= \frac{0.053}{5.293}$$

$$= 0.010$$

- F-Value of treatment

$$Ftr = \frac{MS_{tr}}{MS_E}$$

$$= \frac{19.346}{5.293}$$

$$= 3.655$$

- F-Value of effects

$$F_A = \frac{MS_A}{MS_E}$$

$$= \frac{13.650}{5.293}$$

$$= 2.579$$

$$F_B = \frac{MS_B}{MS_E}$$

$$= 0.579$$

The other F-Values for another effect could be computed in the same manner, the results were shown in Table 4-8 (Chapter 4).

<u>Appendix I</u> Percentage points of $F_{0.05}$ contribution

$F_{0.05}$ contribution was used to compare with F from calculation to determine of each treatment combination.

$F_{0.05,\nu_1,\nu_2}$

ν_2 \ ν_1	Degrees of Freedom for the Numerator (ν_1) 1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
Degrees of Freedom for the Denominator (ν_2) 1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	243.9	245.9	248.0	249.1	250.1	251.1	252.2	253.3	254.3
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.43	19.45	19.45	19.46	19.47	19.48	19.49	19.50
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.74	8.70	8.66	8.64	8.62	8.59	8.57	8.55	8.53
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.77	5.75	5.72	5.69	5.66	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.53	4.50	4.46	4.43	4.40	4.36
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.84	3.81	3.77	3.74	3.70	3.67
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.51	3.44	3.41	3.38	3.34	3.30	3.27	3.23
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.12	3.08	3.04	3.01	2.97	2.93
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.90	2.86	2.83	2.79	2.75	2.71
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77	2.74	2.70	2.66	2.62	2.58	2.54
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.61	2.57	2.53	2.49	2.45	2.40
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.51	2.47	2.43	2.38	2.34	2.30
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.42	2.38	2.34	2.30	2.25	2.21
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.35	2.31	2.27	2.22	2.18	2.13
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.29	2.25	2.20	2.16	2.11	2.07
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.24	2.19	2.15	2.11	2.06	2.01
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.19	2.15	2.10	2.06	2.01	1.96
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.15	2.11	2.06	2.02	1.97	1.92
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.11	2.07	2.03	1.98	1.93	1.88
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.08	2.04	1.99	1.95	1.90	1.84
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.25	2.18	2.10	2.05	2.01	1.96	1.92	1.87	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.23	2.15	2.07	2.03	1.98	1.94	1.89	1.84	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.20	2.13	2.05	2.01	1.96	1.91	1.86	1.81	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.18	2.11	2.03	1.98	1.94	1.89	1.84	1.79	1.73
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.16	2.09	2.01	1.96	1.92	1.87	1.82	1.77	1.71
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.15	2.07	1.99	1.95	1.90	1.85	1.80	1.75	1.69
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.13	2.06	1.97	1.93	1.88	1.84	1.79	1.73	1.67
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.12	2.04	1.96	1.91	1.87	1.82	1.77	1.71	1.65
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22	2.18	2.10	2.03	1.94	1.90	1.85	1.81	1.75	1.70	1.64
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.89	1.84	1.79	1.74	1.68	1.62
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.00	1.92	1.84	1.79	1.74	1.69	1.64	1.58	1.51
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.92	1.84	1.75	1.70	1.65	1.59	1.53	1.47	1.39
120	3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96	1.91	1.83	1.75	1.66	1.61	1.55	1.55	1.43	1.35	1.25
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.52	1.46	1.39	1.32	1.22	1.00

Appendix J Upper percentage points q_{α}

Error df	α	p — number of									
		2	3	4	5	6	7	8	9	10	11
5	.05	3.64	4.60	5.22	5.67	6.03	6.33	6.58	6.80	6.99	7.17
	.01	5.70	6.97	7.80	8.42	8.91	9.32	9.67	9.97	10.24	10.48
6	.05	3.46	4.34	4.90	5.31	5.63	5.89	6.12	6.32	6.49	6.65
	.01	5.24	6.33	7.03	7.56	7.97	8.32	8.61	8.87	9.10	9.30
7	.05	3.34	4.16	4.68	5.06	5.36	5.61	5.82	6.00	6.16	6.30
	.01	4.95	5.92	6.54	7.01	7.37	7.68	7.94	8.17	8.37	8.55
8	.05	3.26	4.04	4.53	4.89	5.17	5.40	5.60	5.77	5.92	6.05
	.01	4.74	5.63	6.20	6.63	6.96	7.24	7.47	7.68	7.87	8.03
9	.05	3.20	3.95	4.42	4.76	5.02	5.24	5.43	5.60	5.74	5.87
	.01	4.60	5.43	5.96	6.35	6.66	6.91	7.13	7.32	7.49	7.65
10	.05	3.15	3.88	4.33	4.65	4.91	5.12	5.30	5.46	5.60	5.72
	.01	4.48	5.27	5.77	6.14	6.43	6.67	6.87	7.05	7.21	7.36
11	.05	3.11	3.82	4.26	4.57	4.82	5.03	5.20	5.35	5.49	5.61
	.01	4.39	5.14	5.62	5.97	6.25	6.48	6.67	6.84	6.99	7.13
12	.05	3.08	3.77	4.20	4.51	4.75	4.95	5.12	5.27	5.40	5.51
	.01	4.32	5.04	5.50	5.84	6.10	6.32	6.51	6.67	6.81	6.94
13	.05	3.06	3.73	4.15	4.45	4.69	4.88	5.05	5.19	5.32	5.43
	.01	4.26	4.96	5.40	5.73	5.98	6.19	6.37	6.53	6.67	6.79
14	.05	3.03	3.70	4.11	4.41	4.64	4.83	4.99	5.13	5.25	5.36
	.01	4.21	4.89	5.32	5.63	5.88	6.08	6.26	6.41	6.54	6.66
15	.05	3.01	3.67	4.08	4.37	4.60	4.78	4.94	5.08	5.20	5.31
	.01	4.17	4.83	5.25	5.56	5.80	5.99	6.16	6.31	6.44	6.55
16	.05	3.00	3.65	4.05	4.33	4.56	4.74	4.90	5.03	5.15	5.26
	.01	4.13	4.78	5.19	5.49	5.72	5.92	6.08	6.22	6.35	6.46
17	.05	2.98	3.63	4.02	4.30	4.52	4.71	4.86	4.99	5.11	5.21
	.01	4.10	4.74	5.14	5.43	5.66	5.85	6.01	6.15	6.27	6.38
18	.05	2.97	3.61	4.00	4.28	4.49	4.67	4.82	4.96	5.07	5.17
	.01	4.07	4.70	5.09	5.38	5.60	5.79	5.94	6.08	6.20	6.31
19	.05	2.96	3.59	3.98	4.25	4.47	4.65	4.79	4.92	5.04	5.14
	.01	4.05	4.67	5.05	5.33	5.55	5.73	5.89	6.02	6.14	6.25
20	.05	2.95	3.58	3.96	4.23	4.45	4.62	4.77	4.90	5.01	5.11
	.01	4.02	4.64	5.02	5.29	5.51	5.69	5.84	5.97	6.09	6.19
24	.05	2.92	3.53	3.90	4.17	4.37	4.54	4.68	4.81	4.92	5.01
	.01	3.96	4.54	4.91	5.17	5.37	5.54	5.69	5.81	5.92	6.02
30	.05	2.89	3.49	3.84	4.10	4.30	4.46	4.60	4.72	4.83	4.92
	.01	3.89	4.45	4.80	5.05	5.24	5.40	5.54	5.65	5.76	5.85
40	.05	2.86	3.44	3.79	4.04	4.23	4.39	4.52	4.63	4.74	4.82
	.01	3.82	4.37	4.70	4.93	5.11	5.27	5.39	5.50	5.60	5.69
60	.05	2.83	3.40	3.74	3.98	4.16	4.31	4.44	4.55	4.65	4.73
	.01	3.76	4.28	4.60	4.82	4.99	5.13	5.25	5.36	5.45	5.53
120	.05	2.80	3.36	3.69	3.92	4.10	4.24	4.36	4.48	4.56	4.64
	.01	3.70	4.20	4.50	4.71	4.87	5.01	5.12	5.21	5.30	5.38
∞	.05	2.77	3.31	3.63	3.86	4.03	4.17	4.29	4.39	4.47	4.55
	.01	3.64	4.12	4.40	4.60	4.76	4.88	4.99	5.08	5.16	5.23

AUTHOR BIOGRAPHY

Name : Sawalak Phungtham

Date of Birth : 14 July 1980

Place of Birth : Bangkok

Education : Triamudomsuksa School

Name : Utsanee Phonjit

Date of Birth : 4 Sep 1980

Place of Birth : Sakonnakorn

Education : Sakonrajwittayanukul School

Name : Weerawut Pongsuteeniwet

Date of Birth : 7 Sep 1981

Place of Birth : Nakornsrithammarat

Education : Technologyratchamongkol