การสกัดครูดบาราคอลจากใบขี้เหล็กโดยใช้เครื่องสกัดแบบแพ็กเบด

นางสาวกีรติ ศรวัฒนะ

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CRUDE BARAKOL EXTRACTION FROM *Cassia siamea* USING PACKED BED EXTRACTOR

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for the Degree of Master of Engineering in Chemical Engineering

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ทำการศึกษาตัวแปรที่มีผลต่อการสกัดครูดบาราคอลจากใบขี้เหล็กโดยใช้เครื่องสกัดแบบแพ็กเบด ใช้เอทานอล 15% โดยปริมาตรเป็นตัวทำละลาย เพื่อหา ภาวะที่เหมาะสมที่สุดในการสกัดและหาค่า effective diffusivity ทำการทดลองในภาวะที่ทิศทางการไหลของสายป้อนตัวทำละลาย (ตัวทำละลายไหลขึ้นและไหลลง) ขนาดอนุภาคของใบขี้เหล็ก (0.42, 0.59 และ 0.84 มม.) และความเร็วสายป้อนตัวทำละลาย (18.44, 29.36 และ 37.96 มิลลิลิตรต่อนาที สำหรับทิศทางตัวทำละลายไหลขึ้น และ 14.80, 23.68 และ 30.88 มิลลิลิตรต่อนาที สำหรับทิศทางตัวทำละลายไหลลง) โดยป้อนตัวทำละลายใหม่ตลอดช่วงเวลาการสกัด 3 ชั่วโมง พบว่า อนุภาคขนาดเล็กให้ผลการสกัดมากกว่าอนุภาคขนาดใหญ่ แต่ที่อนุภาคขนาดเล็กมีปัญหาการยกตัวของเบด ความเร็วสายป้อนเพิ่มขึ้นผลการสกัดครูดบาราคอลจะมากขึ้นตาม และทิศทางการไหลของสายป้อนตัวทำละลายเป็นแบบไหลขึ้นให้ผลการสกัดที่ดีกว่าแบบไหลลง ภาวะที่ดีที่สุดในการสกัด คือ อนุภาคมีขนาด 0.59 มม. ความเร็วสายป้อนเป็น 37.96 มม.ต่อนาที และทิศทางการไหลของสายป้อนตัวทำละลายเป็นแบบไหลขึ้น ปริมาณสารบาราคอลที่สกัดได้เท่ากับ 71.80 มิลลิกรัมบาราคอลต่อกรัมผงใบขี้เหล็กแห้ง

หลังจากนั้นนำผลการทดลองนี้มาเปรียบเทียบกับการสกัดครูดบาราคอลในเครื่องสกัดแบบแพ็กเบดแบบมีการหมุนเวียนตัวทำละลาย พบว่าการสกัดครูดบาราคอลในเครื่องสกัดแบบแพ็กเบดโดยใช้ตัวทำละลายใหม่ตลอดช่วงเวลาการสกัดให้ผลการสกัดที่ดีกว่าการสกัดครูดบาราคอลแบบมีการหมุนเวียนตัวทำละลายแต่จะเสียค่าใช้จ่ายในการแยกสารสกัดครูดบาราคอลที่สกัดได้ออกจากตัวทำละลาย และอัตราส่วนระหว่างน้ำหนักผงใบขี้เหล็กต่อปริมาตรตัวทำละลายที่ให้ค่าการสกัดสูงสุดสำหรับการทดลองนี้ คือ อัตราส่วน 1: 60 สำหรับค่าสัมประสิทธิ์การถ่ายโอนมวลของสารสกัดครูดบาราคอลในตัวทำละลายเอทานอล 15 เปอร์เซนโดยปริมาตรมีค่าเพิ่มขึ้นเมื่ออัตราการป้อนตัวทำละลายเพิ่มขึ้น ส่วนค่า effective diffusivity เฉลี่ยของสารสกัดครูดบาราคอลในตัวทำละลายเอทานอล 15 เปอร์เซนโดยปริมาตรเท่ากับ $8.16*10^{-11}$ เมตร^2/วินาที

ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อนิสิต.....

สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่ออาจารย์ที่ปรึกษา.....

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KEYWORD: SOLID LIQUID EXTRACTION / PACKED BED EXTRACTOR / BARAKOL

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The effects on crude barakol extraction from *Cassia siamea* leaves in a packed bed extractor, using 15%(V/V) ethanol as solvent, were studied to determine suitable operating conditions as well as determine effective diffusivities. A series of experiments were carried out at various conditions with directions of feed solution both in an upward and downward direction, with particle sizes between 0.42, 0.59 and 0.84 mm and solvent flow rates between 18.44, 29.36 and 37.96 ml/min for the upward direction of feed solution and 14.80, 23.68 and 30.88 ml/min for the downward direction of feed solution. In a first set of experiments lasting 3 hours, the packed bed was contacted only with fresh solvent. It was found that the reduction of particle size enhanced barakol extraction yield. But, if too fine a particle size is used, the bed behaves as a fluidized bed. An upward direction of feed solution resulted in a barakol extraction yield which was superior than using a downward direction of flow. A set of suitable operating conditions found was a particle size of 0.59 mm, a solvent flow rate of 37.96 ml/min and an upward direction of flow and yielded 71.80 mg of barakol/g of dried *Cassia siamea* powder.

Comparing the yield of barakol extraction in the previous system which did not include a recycle stream with a system with recycle, it was found that the yield of barakol extraction in a system without recycle was superior to the barakol extraction system with recycle however there is a cost associated with recovery of barakol from the solvent. The ratio of solid to solvent (W/V) which gives the highest extracted yield was 1:60. The mass transfer coefficient of crude barakol extraction with 15%(V/V) ethanol as solvent increased with increasing feed flow rate. The average effective diffusivity of crude barakol extraction with 15%(V/V) ethanol as solvent was $8.16*10^{-11}$ m^2/s.

Department…….Chemical Engineering…….Student's signature…..……..……...

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Academic year…….2000……..……Co-advisor 's signature ……..……

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NOMENCLATURES

C	:	Barakol concentration in the laminate ($mg/g_{inert\ solid}$)
C_0	:	Initial barakol concentration ($mg/g_{inert\ solid}$)
D_{eff}	:	Effective diffusivity (m^2/s)
l	:	Thickness of laminate (m)
t	:	Time (s)
γ	:	Fraction of residual in laminate $= \frac{C}{C_0}$
ε	:	Void fraction
τ	:	Tortuosity
Bi	:	Biot number $= \frac{kma}{D}$
k	:	mass transfer coefficient in the extract
a	:	the characteristic dimension of the solid
D	:	the diffusivity in the solid
m	:	$(\frac{Y}{X})_{\infty}$ the equilibrium distribution ratio
Y	:	the solute concentration in the extract
X	:	the solute concentration in the solid

CHAPTER 1

INTRODUCTION

1.1 General

In the past century, the use of herbal medicine in Thailand has been on the decline, due largely to the introduction of modern medicine which apparently is more effective and simpler to use. However, medicines of natural origin are used worldwide as they are believed to possess less harmful side effects than modern medicine. Thailand's long seacoast, its rivers and its multitudes of forested mountains are home to an abundance of diverse plant species believed to possess medicinal properties. Base on this abundance of diverse plants species, herbal medicines could be developed by combining pharmacology and chemical engineering processes to extract and produce more efficiency herbal medicines. The sought after active ingredients in herbs are deposited in the leaves, stems and roots. Therefore the separation of active ingredients in herbs generally use solid-liquid extraction and leaching, which are important unit operations particularly in the food and pharmaceutical industry.

Any people in Thailand have developed stress-related problems leading to anxiety and insomnia. Anxiety and insomnia are amenable to treatment with drugs that exert a depressant effect on the central nervous system (CNS). Most prescription drugs in these categories involve risks of overdose, tolerance, habituation and addiction. The herbs commonly used for their sedative effects do not generally have these drawbacks.

Barakol, a major constituent found in the leaves and flowers of *Cassia siamea*, have an effect on the central nervous system and have the low toxicity. Moreover, the report showed a 15% (V/V) ethanol solution in water can yield the highest extract of anhydrobarakol. It was also found that young leaves yield higher content of anhydrobarakol than flower and old leaves, respectively. [Sripunya, 1997]

In 1978, the isolation of barakol from young *Cassia siamea* by solvent extraction and precipitation was reported. It was revealed that 3 g of the lemon yellow needle crystals precipitated out of 3 kg of fresh leaves. [Chaichanthipayuth, 1978]

In 1998, a study was conducted on the barakol extraction from *Cassia siamea* with 15% (V/V) ethanol solution in shake flasks. The experimental results indicated that the most suitable conditions were a concentration of 10 grams of dried powder of *Cassia siamea* leaves per 100 ml of solution with a powder size smaller than 500 μ and an extraction time of 2 hours. The content of barakol in leaves is 0.8% (W/W). The disadvantage of this process is the low concentration of barakol extracted and its high-energy consumption because of the highly viscous solution. [Tangsrisamruang, 1998]

No previous studies make use of solid-liquid packed bed extractors for crude barakol extracted from *Cassia siamea*. Solid- liquid packed bed extractors may have many advantages as follows:

1. Extracts with high concentrations.
2. Large quantities of raw materials may be processed per extractor volume
3. Simple design and easy operation.

In this study, an attempt is made to understand the effects of variables (such as particle size, feed flow rate, direction of feed solution and solid to solvent ratio) on barakol extraction from *Cassia siamea* in a solid liquid packed bed extractor.

1.2 Objective of the study

1. To investigate factors which affect crude barakol extraction from *Cassia siamea* in a solid liquid packed bed extractor.
2. To determine optimum conditions for crude barakol extraction from *Cassia siamea* in a solid liquid packed bed extractor.

1.3 Scope of the study

1. Study the effect of various factors on crude barakol extraction from *Cassia siamea* a using solid liquid packed bed extractor as follows:
    1.1 Particle size (0.42 mm, 0.59 mm and 0.84 mm).
    1.2 Feed flow rate of 15% ethanol solution (18.44 ml/min, 28.96 ml/min and

37.96 ml/min for the upward direction of feed solution and 14.80 ml/min, 23.68 ml/min and 30.88 ml/min for the downward direction of feed solution).

1.3 *Cassia siamea* powder to feed solution ratio (ratio of 1:60, 1:50 and 1:33.33 (W/V)).

2. Compare the extracted yield, obtained from item 1. in terms of crude barakol concentration, initial rate of extraction and total amount of extractable barakol.

3. Compare the extracted yield for an upward and downward direction of feed solution.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to *Cassia siamea* Lamk.

Cassia siamea is a medium size tree plant widely distributed in South East Asia and is known in Thai as 'Khi-lekyai' as shown in Figure 2.1. Various local names, 'Khi-lekban', 'Khi-lekluang', 'Khi-lekkindok', 'Khi-lek' and 'Ya-ha', are also given to it. [Farnsworth et al.; 1992]

Young leaves and flowers are eaten as vegetable or taken as medicine in several countries. Leaves are said to be used as diuretic; flowers for insomnia as well as an antiasthma and an antidandruff; the stem-bark is used for haemorrhoids treatment; the hardwood is used as a laxative and an anthelmintic and the roots as a febrifuge. [Chaichanthipayuth, 1978]

Figure 2.1 Characteristic of the leaves and a *Cassia siamea* tree

2.2 The chemical nature of Barakol

In 1969, Barakol, a major constituent found in leaves and flowers of *Cassia siamea* was extracted [Chaichanthipayuth, 1978] and the structure was identified in 1970 as 3a, 4-dihydro-3a,8-dihydroxy-2,5-dimethyl-1,4-dioxaphenilene ($C_{13}H_{12}O_4$) [Bycroft et al.; 1970] as shown in Figure 2.2

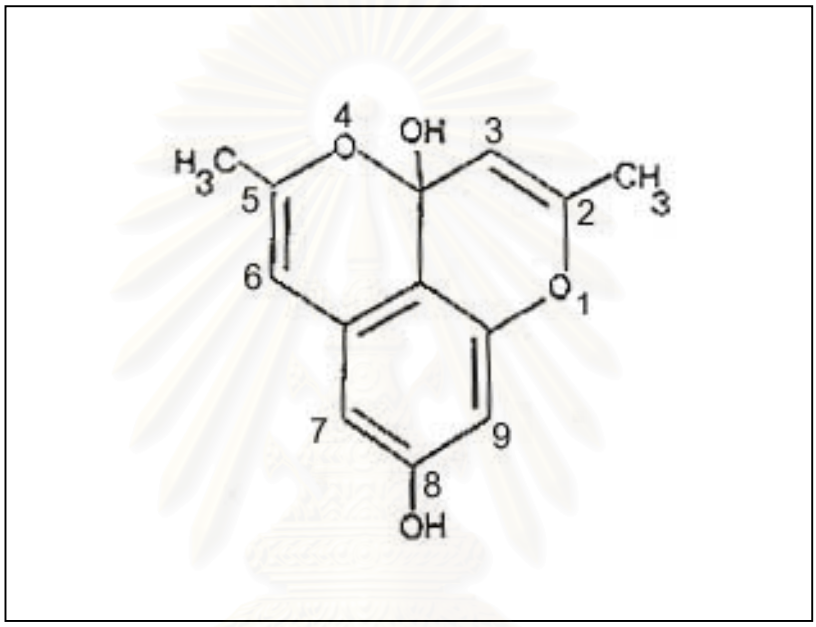


Figure 2.2 Chemical structure of Barakol

Barakol can be obtained from the acid treatment of 2-methyl-5-acetonyl-7-hydroxy chromone found in the leaves of *Cassia siamea* [Wagner et al.; 1978] and can be crystallized from aqueous methyl alcohol or ethyl alcohol as pale yellow needles, with a melting point of 165 °C (decomposed) and is stable in hydroxylic solvents or in a moist atmosphere. The chemical dehydration of Barakol can be achieved over phosphorous pentoxide or in a vacuum. The resulting dark green amorphous compound, anhydrobarakol, $C_{13}H_{10}O_3$, is extremely unstable. Table 2.1 shows the chemical properties of Barakol.

Anhydrobarakol can be reconverted into barakol by dissolution in aqueous methanol. The strong basic character of barakol was demonstrated by the lack of crystalline hydrobromide and hydrochloride derivatives, $C_{13}H_{10}O_3$, HX, salts of the anhydro-base, and

can be prepared by addition of concentrated hydrobromic or hydrochloric acid to a methanolic solution of barakol. [Chaichanthipayuth, 1978]

Table 2.1 Chemical properties of Barakol, Anhydrobarakol and Anhydrobarakol hydrochloride

	Barakol	Anhydrobarakol	Anhydrobarakol hydrochloride
Molecular formula	$C_{13}H_{12}O_4$	$C_{13}H_{10}O_3$	$C_{13}H_{12}ClO_3$
Molecular weight	232	214	251.4
Color	yellow	Green	Pale yellow
Melting point (°C)	166-170	163	208-210

Bycroft et al. [1970] presented the possible biogenesis of barakol from polyketide derived from seven acetate units by forming the intermediate compound (I) as shown in Figure 2.3. The scheme is illustrated below.

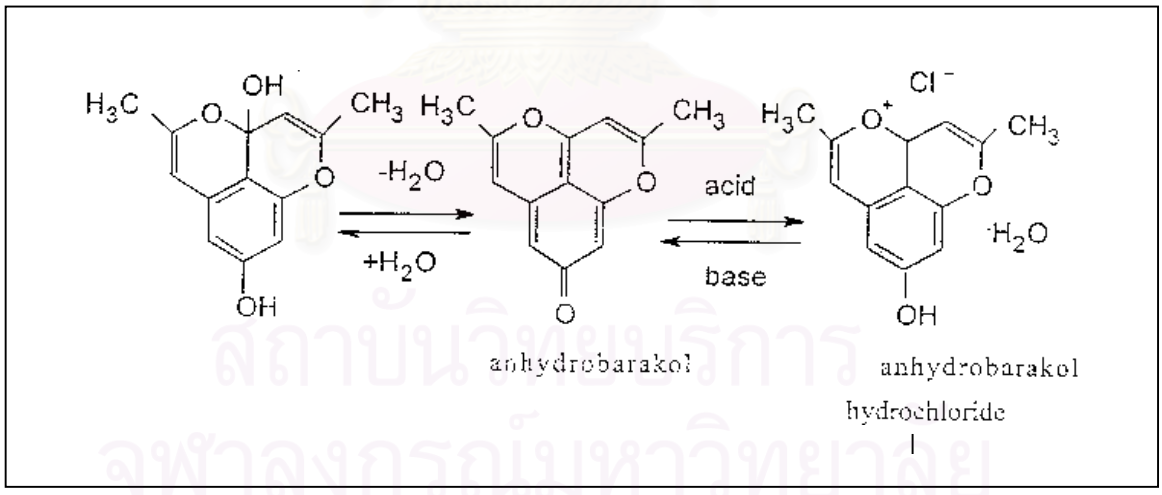


Figure 2.3 Schematic of Derivation of the possible biogenesis of barakol from polyketide

Crystallization of compound I to barakol can be regarded as an interaction of enolate anions with the chromone carbonyl. [Chaichanthipayuth, 1978]

2.2.1 The effect of barakol

Arunluksana et al. [1949] claimed that the extract of *Cassia siamea* leaves have some effects on the central nervous system and is used orally fed or injected into test animals. The study showed that tested animals developed depressed symptoms, slow movements and were mostly in a sleeping position but without falling asleep. They also found the extract have tranquilizing and analgestic effects, anticonvulsant properties, smooth muscle stimulation properties and effected the circulatory system, without change in heart rate and blood vessel contraction, and effected the respiratory system and diuretic activities.

Thongsaard et al. [1996] investigated the effect of water extract of *Cassia siamea* on behavioral changes compared with diazeparn by using an elevated plus-maze, a novel test for anxiolytic drug. The results indicated that barakol had anxiolytic properties similar to diazeparn from diazeparn in that it also increased exploratory and locomotor behavior.

In 1992, Suwan et al. [1992] proposed that the hypotensive effect of barakol extracted from *Cassia siamea* leaves were investigated in rats and cats. They found that intraveneous injections of barakol caused significantly loss of dependent hypotensive effects in bolts systolic and diastolic blood pressure in rats and cats. Besides, this study suggested that the hypotensive effects of barakol in rats and cats could be due to peripheral vasodilatation, possibly is via an endothelium derived relaxing factor (EDRF) and/or direct action on vascular smooth muscle in rats, while in cats, the effect could be mediated through muscarinic cholinergic receptors.

2.3 Solid-liquid Extraction

Solid-liquid extraction, or leaching, the transfer of solutes from a solid to an adjacent fluid, is used to extract sugar, vegetable oils, coffee, tea, gelatin, pectin and many other food solutes. Solute transfer can occur because of convection, molecular diffusion or eddy diffusion. Convection and eddy diffusion influence transfer in the extract, but diffusion due to random molecular motion dominates in the solid. Convection and eddy diffusion are greater

than molecular diffusion; and in the leaching of food, molecular diffusion in the solid is usually rate controlling. [Schwartzberg et al.; 1982]

2.3.1 Application of solid-liquid extraction

The solid-liquid extraction process is an important unit operations in the food and pharmaceutical industry as illustrated in Table 2.2 and Table 2.3.

Table 2.2 The Variety of Products Obtained through Leaching Processes [Schwartzberg, 1980]

Product	Raw Material	Solvent	Extraction Time
Sugar	Sugar Beets Sugar Cane	Water	20-90 min 25-60 min
Vegetable Oils	Oil Seeds	Hexane	18-45 min for Soybeans 60-85 min for cottonseed
Pickles	Cucumbers, Tomatoes, Onions, Cauliflower	Water	5 d for Large Pickles, 15 min for Relish
Softened Corn Kernels	Dry Corn Kernels	Water + % SO_2	30-50 h
Soluble Coffee	Roasted and Ground Coffee	Water	2-3 h
Soluble Tea	Dried Tea Leaves	Water	45 min – 2 h

Table 2.2 (continue) The Variety of Products Obtained through Leaching Processes

Product	Raw Material	Solvent	Extraction Time
Decaffeinated Coffee	Green Coffee Beans	Trichlorethylene (in the past) Methylene Chloride, Vegetable Oils	8-12 h
Gelatin	Collagen	Water or Dilute Acid	Successive 4-hour cooks
Pectin	Apple Pomace	Dilute Acid	0.5-2 h Sometimes Two Cooks
Cassava	Manioc	Water	_
Vanilla	Vanilla Beans	35% Ethanol, 65% Water	1 week
Carageenan	Kelp	Water	-
Zein	Corn	90% Ethanol, 10% Water	-
Iodine	Seaweed	H_2SO_4	-
Fish Protein Concentrate	Trash Fish	Ethylene Dichloride, Ethanol, Butanol, Hexane	15-60 min
Prune Juice	Dried Prunes	Water	-
Fish Oil	Fish	Ethylene Dichloride, Butanol, Hexane	15-60 min
Alfalfa Protein Concentrate	Heat or Solvent Coagulated Alfalfa Protein	Acetone, Ethanol, Butanol, Isopropanol	5-15 min

Table 2.3 Drug Extraction by leaching processes [List et al.; 1989]

Reference	Year	Drug/Plant	Solvent	Investigated Parameters
Astakhova Minina	1977	Scopolia tangutica	Chloroform	Intermediate maceration time, Percolation rate, Degree of comminution, Solvent-drug material ration, packing density of drug material
Ferrada, J. et al.	1977	Solanum tomatillo	5% Acetic acid in water	Temperature, Initial content of drug material, Solvent-drug material ration
Lipkovskii, A.	1975	Strophanthus seeds	Ethanol Acetone/Water	Influence of acetone
Muravev, I.	1972	Glycyrrhiza uralensis	1% aqueous ammonia solution	Intermediate maceration time, Numbers of percolators, Solvent-drug material ration
Zinko, M.	1977	Garlic	70% aqueous ethanol	Detail study of battery of 6 percolators

2.3.2 Extraction by solid-liquid packed bed extractor

In 1993, Vuorela et al. [1993] investigated suitable operation conditions of a medium pressure solid-liquid extraction process, a forced flow technique for the extraction of plant material. A column was filled with leaves using chloroform as an extractant. The medium particle size of the leaf material were 0.87, 0.67 and 0.40 mm, equilibrium times took 1,2 and 3 hours and the solvent volumes pumped through the column were 45, 90 and 135 ml. The results showed that the efficiency of extraction is more strongly influenced by the equilibrium time than by the medium particle size whereas the volume of the extractant is of less importance. According to the results, a medium particle size of 0.67 mm, a volume of 90 ml

and an equilibrium time of 2 hours were selected as the optimum conditions for an efficient extraction process.

Hulbert et al. [1998] studied the method for extraction of caffeine from ground and whole guarana seed cores with methylene chloride. For extraction of ground seeds used shaking flasks at 25 or 30°C in water baths at three solid-liquid ratios(1:4, 1:6 and 1:8 W/W). This results indicated that a solid-liquid ratio of 1:6 was adequate at 30°C but not at 25°C. For caffeine extract from whole seeds, 100 g of seeds were extracted in a packed bed extractor with a solid/liquid ratio of 1:50 (W/W) at three different solvent flow rates (456, 522 and 667 ml/min) and two temperatures (21 and 30°C). The results showed that caffeine extraction at 30°C continued to increase with solvent flow rate due to a higher diffusivity. There were no significant difference between extraction rates at 21°C for solvent flow rate of 522 and 667 ml/min, indicating that caffeine diffusivity was limiting the mass transfer. The calculated diffusivities at 21 and 30°C were $0.29*10^{-6}$ cm^2/s and $0.95*10^{-6}$ cm^2/s. For industrial applications, design of a solid/liquid packed bed extractor operating at high temperature and high solvent flow capabilities would probably be economically justified.

Sionero et al. [1996] pointed out that the mechanism of polyphenol extraction from sunflower press cake, as 96%(V/V) ethanol solvent, in a semicontinuous pulsed-flow-immersion extractor and in a conventional immersion extractor depends to a large degree on internal diffusion. The effective diffusion can be estimated by the equation:

$$D_{eff}\frac{\partial^2 C}{\partial^2 x} = \frac{\partial C}{\partial t} \qquad 2.1)$$

After calculation, they plotted ln(Y) against time (t). A linear behavior must be observed, according to

$$\ln(Y) = \ln(\frac{8}{\pi^2}) - \frac{\pi^2 D_{eff} t}{4i^2} \qquad 2.2)$$

In Figure 2.4, a plot of ln(Y) against time is shown. It indicates that the plot is not linear up to 485 minutes, probably because the model cannot be reduced to only one term.

After 485 minutes, a linear behavior is observed since in this time range the equation can be reduced to only one term as illustrated in Figure 2.4. There were three effective difusivities for the pulsed-flow-immersion extractor, whereas for the nonpulsed-flow-immersion extractor two values of effective diffusivities are shown in Table 2.4

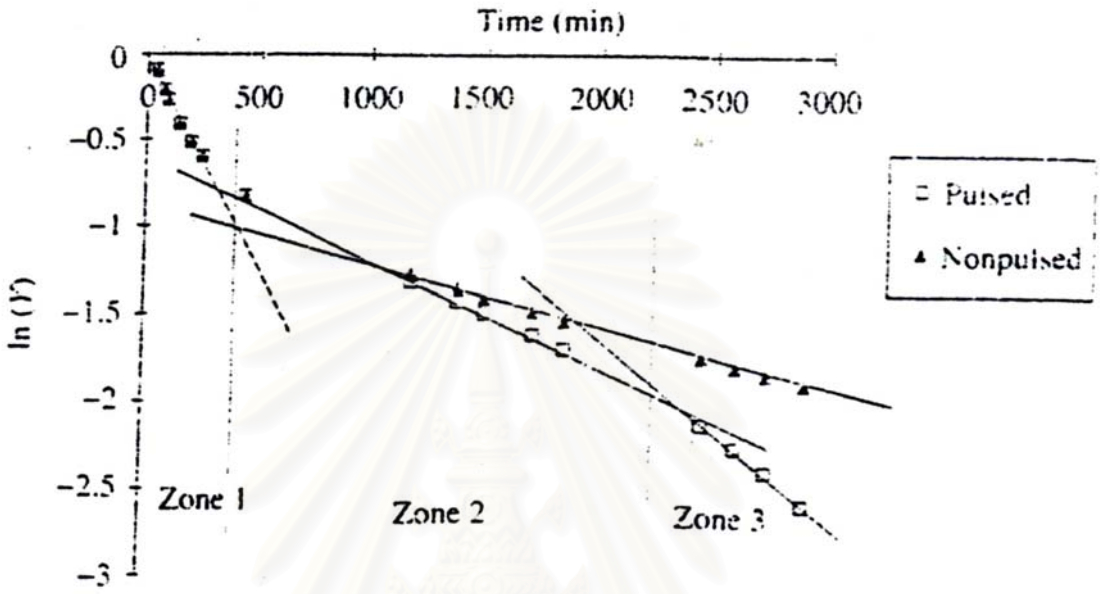


Figure 2.4 A plot ln (Y) against time according to equation 2.2)

Table 2.4 Effective diffusivities obtained from this experiment

	Effective diffusivity (m^2/s)	
	Pulsed	Nonpulsed
Zone 1	$1.560*10^{-12}$	$1.531*10^{-12}$
Zone 2	$3.750*10^{-13}$	$2.210*10^{-13}$
Zone 3	$6.126*10^{-13}$	$2.210*10^{-13}$

Moreover, they found that the oil was extracted much more rapidly when the solvent was forced to flow through the flakes than when flakes were suspended where about 70% of the oil extracted easily in the packed extractor, while about 30% extracted easily in the nonpacked one.

Dursun Ali Sasmaz [1996] measured the diffusion coefficient of rapeseed oil. The experiment were carried out in a Gulbaran extractor diffuser with hexane as solvent. He

found that molecular diffusion is an important mechanism in the extraction of oil from seeds after the removal of surface oil by washing. The diffusion rate during solvent extraction of oil bearing seeds was explained with Fick's second law of unsteady state molecular diffusion. The result showed that the diffusion coefficient of rapeseed oil in hexane is $3.40*10^{-8}$ cm^2/s. And the oil concentration difference between the solid and liquid phase, which is the driving force for diffusion, depends on the solvent drain rate at the beginning of the process but becomes independent toward the end.

2.3.3 Effect of particle size

Nieh et al. [1991] investigated the effect of particle size on extraction by comparing the extraction rate of oil from either fine flour (smaller than 150 μm) or soybean flakes (about 0.25 mm.), in a column. This study determined that oil extraction from flakes, depended on contact time rather than volume of solvent. No matter what the flow rate was the same amount of oil was extracted in the same time period, whereas in the case of flour, flow rate increased as the amount of oil extracted per unit time increased. The limit on the rate of extraction of flakes was controlled by diffusion of the solvent into and out of the tissue. Furthermore, they found that particle size had an effect not only on the extraction rate, but also on the amount of oil extracted.

Abhay et al. [1983] studied that solid particle size controlled the rate of solvent extraction from rice bran in a percolator. It clearly showed that the time to reach 1% residual oil, an index of the extraction rate, decreased as the size of the pellets or surface area/g increased.

2.3.4 Effect of ratio of feed flow rate

Ghilddyat et al. [1991] examined the effect of feed rate of solvent on enzyme leaching in a pulsed flow column extractor for the recovery of amyloglucosidase. The results showed the leaching of the enzyme increased with the increase in the feed rate (5, 10 and 15 $ml*min^{-1}$) of the solvent up to 10 $ml*min^{-1}$, but it remained fairly constant with a further increase in the feed rate.

Nieh et al. [1991] also investigated the effect of feed flow rate on extraction from soybean flour. They found that flow rate increased the amount of oil extracted per unit time as shown in Figure 2.5.

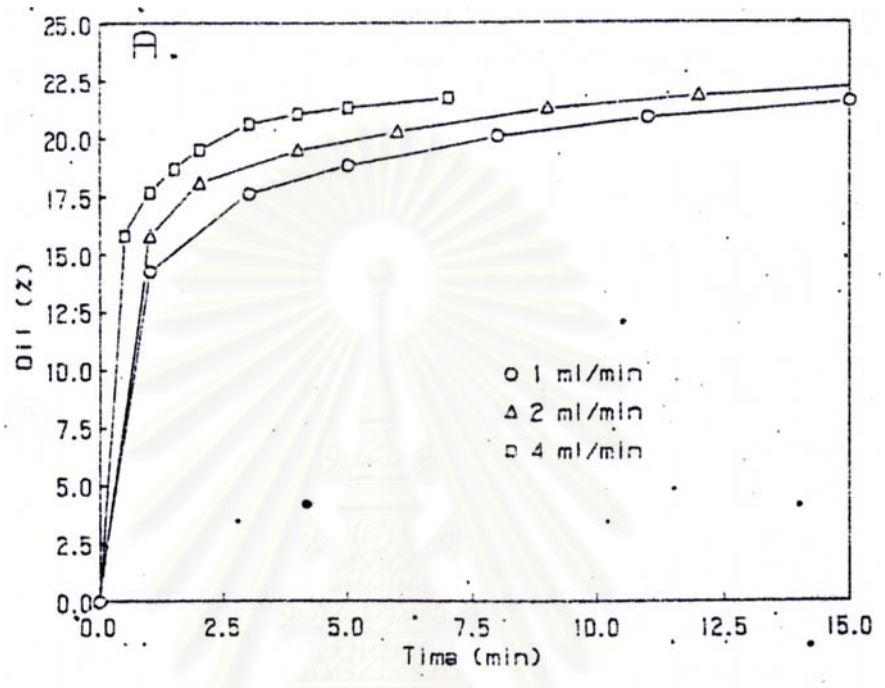


Figure 2.5 Oil extraction in a column at different solvent flow rates

2.3.5 Effect of ratio of solid to solvent

Ghilddyat et al. [1991] also studied the effect of ratio of solid to solvent on enzyme leaching in a pulsed flow column extractor for the recovery of amyloglucosidase by various ratio of dried bran mouldy (DMB): extract with in three different feed rates. The results identified that the leaching of the enzyme increase with the decrease in the ratio of DMB to extract at almost all the solvent feed rates studied. The feed rate of 10 ml*min-1 appeared to be the best when the ratio of DMB to extract is at 1:2 or 1:3 as presented in Figure 2.6.

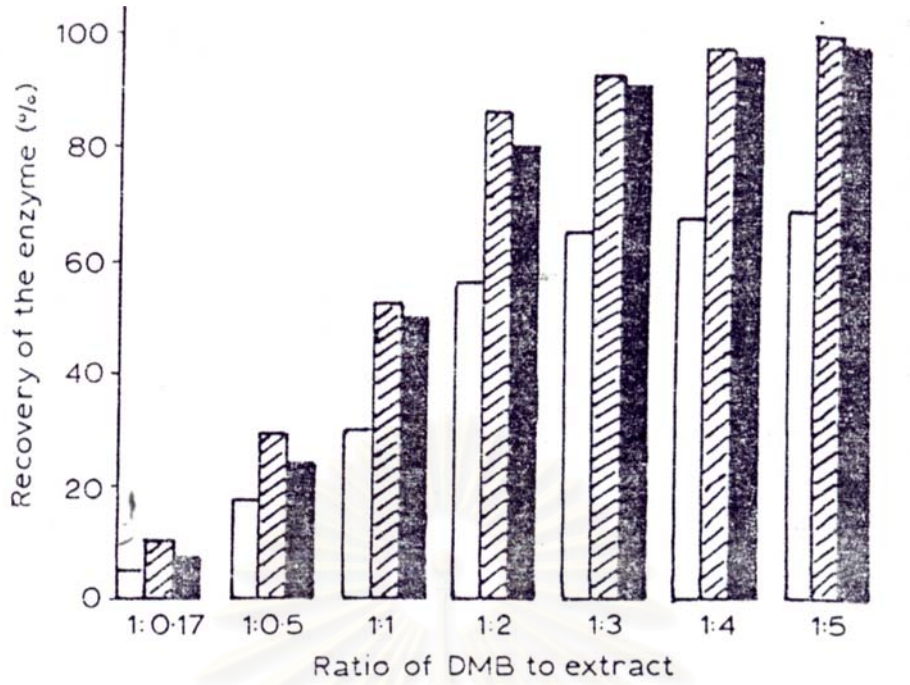


Figure 2.6 Effect of the feed flow rate of the solvent on enzyme leaching in a pulse plug flow extractor with respect to different DMB : extract ratios.

- ☐ 5 ml/min feed rate of the solvent,
- ▨ 10 ml/min feed rate of the solvent,
- ■ 15 ml/min feed rate of the solvent

CHAPTER 3

THEORY

3.1 Extraction of Drugs from Plant Material

3.1.1 Terms and Definitions

The extraction of drugs from plant material (Solid extraction) represents the separation of a solid from a solid, as solid components must be extracted from a solid substance. This type of extraction is generally known as solid-liquid extraction, as the solid drug is extracted with a liquid medium. The extraction is thus distinguished from liquid-liquid extraction, in which two liquids, the carrier phases, which are not miscible, represent the substance to be extracted (solvent extraction)

Further definitions are:

Menstruum = solvent or solvent mixture use for extraction

Miscella = solution containing extracted substances

Rinsing = dissolution of extractive substances out of disintegrated cells

Two processes run parallel with one another in the extraction of drugs as shown in Figure 3.1:

1 The rinsing of extractive substances out of disintegrated plant cells.

2 The dissolution or extraction of extractive substances out of intact plant cell by diffusion. This step requires the prior steeping and swelling of the drug plant material in order to increase permeability of the cell walls.

Many researchers have attempted to separately analyse the three stages

1 Penetration of the solvent into the plant cell and swelling of the cells

2 Dissolution of the extractive substances.

3 Diffusion of the dissolved extractive substances out of the plant cell.[List et al.; 1989]

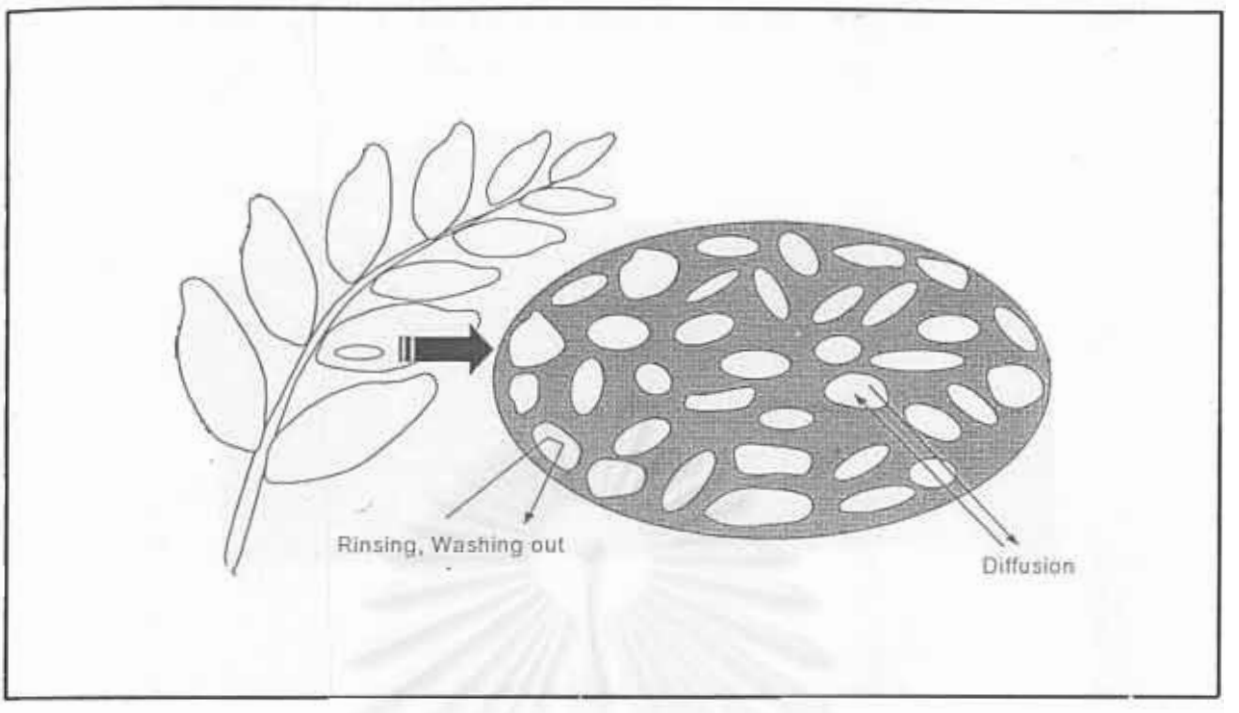


Figure 3.1 Process of Extraction

3.1.2 Convective diffusion

In many cases when a fluid is outside the solid, convective mass transfer is occurring at the surface

$$N_A = k_c(c_{L1} - c_{Li})$$

where k_c is a mass transfer coefficient

c_{L1} is the bulk fluid concentration

c_{Li} is the concentration in the fluid adjacent to the surface of the solid

The case for a mass transfer coefficient being present at the boundary is shown in figure 3.2) the concentration drop across the fluid is c_{L1}-c_{Li}. The concentration in the solid c_i at the surface is in equilibrium with c_{Li} and are related by

$$K = \frac{c_{Li}}{c_i}$$

where K is the equilibrium distribution coefficient. [Christi, 1995]

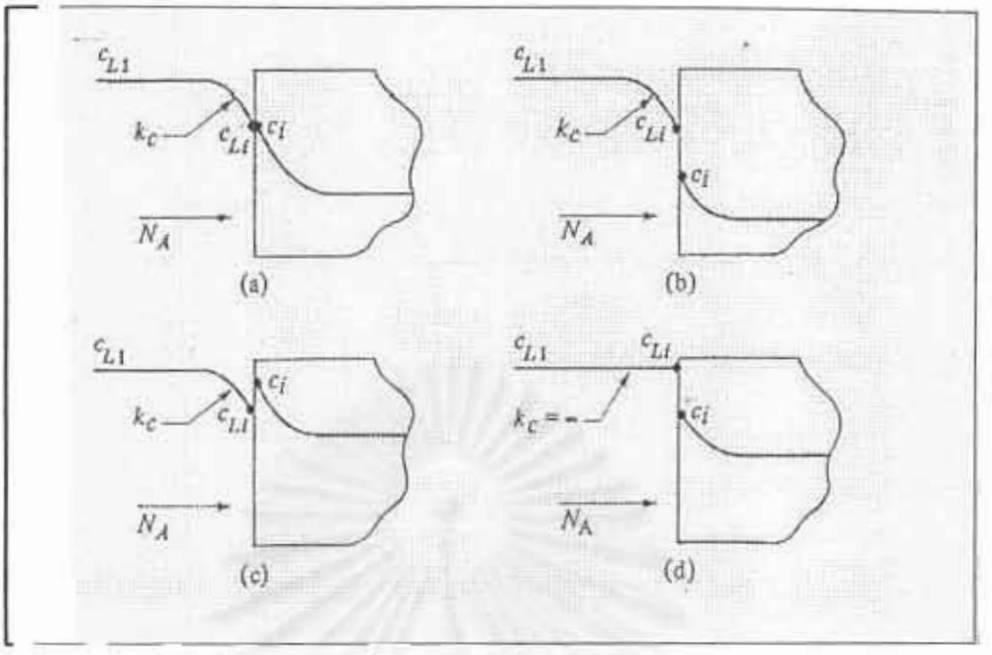


Figure 3.2 Interface condition for convective mass transfer and equilibrium distribution coefficient.

3.1.3 Molecular diffusion in solids

Even though rates of diffusion of gases, liquid and solids in solids are generally slower than rates in liquids and gases, mass transfer in solids is quite important in chemical and biological processing. Some examples are leaching of foods and of metal ores

We can broadly classify transport in solids into two types of diffusion: diffusion that can be considered to follow Fick's law and that does not depend primarily on the actual structure of the solid, and diffusion in porous solid where the actual structure and void channels are important. [Christi, 1995]

Fick's law diffusion

Diffusive transfer of solutes in solids is governed by Fick's First and Second Laws. Even though biological solids are not structurally homogeneous and diffusion occurs mainly in the fluid occluded within the solid, Fick's Laws will be express in terms of X. that is

$$J_z = -D_z \frac{\partial X}{\partial r}$$

Equation 3.3) treated the solid as a uniform homogeneous-like material. The porous solid has pores or interconnected voids in the solid which affect the diffusion so that the diffusion coefficient becomes equation 3.4). A cross section of such a typical porous solid is shown in Figure 3.3. [Christi, 1995]

$$D_{eff} = \frac{\varepsilon}{\tau} D_{AB}$$

where ε is the open void fraction and τ is the tortuosity.

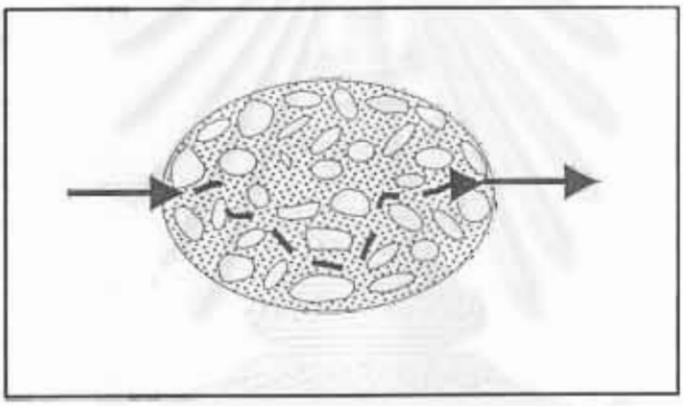


Figure 3.3 Sketch of a typical porous solid.

And the more frequently used Fick's Second Law expressed in a form that is valid for infinite slabs, infinite cylinders and sphere:

$$\frac{\partial X}{\partial r} \quad \frac{1}{r^{\nu-1}} \frac{\partial}{\partial r} (r^{\nu-1} D_z \frac{\partial X}{\partial r})$$

In solving Equation 3.3; it usually is assumed that $X = X_0$ for all r at $t = 0$, and that $\partial X/\partial r = 0$ at $r = 0$. Furthermore, since Bi is usually quite large except for certain heterogeneous extractions (including supercritical extractions), it is assumed

that $X = Y/M$ at r = a for t> 0. The most commonly used solutions for Equation 3.4) are exponential series which are expressed in general form by Equation 3.5):

$$X = Y = \sum_{i=0}^{\infty} C_i \exp(-q_i^2 \tau)$$

The q_i are functions of the boundary conditions and the C_i are functions of boundary conditions and initial conditions.

Table 3.1 Coefficients and Eigenvalues for Fick's Second Law solution for batch extractions in which a is constant and Bi is infinite

Solid shape	α	Equation for q_i	C_i
Infinite slab	Finite	$q_i = -$ [illegible]	[illegible]
	Infinite	$q_i = -$ [illegible]	$\frac{-}{2}$
Infinite cylinder	Finite	[illegible]	[illegible]
	Infinite		
Sphere	Finite	$q_i = -\frac{(3+\alpha q_i^2 \tan(q_i))}{3}$	[illegible]
	Infinite	$q_i = i\pi$	

Extraction processes are still today carried out with a great variety of methods and apparatus. The reasons for this diversity are

1 Large differences in the required quantity of extract

2. Great difference in starting material

3. The use of various menstrua

In addition to the actual extraction, further preparative stages such as the removal of ballast material, evaporation of the solvent in order to thicken

concentrate the extract, and drying are frequently necessary. Further purification and crystallization stages are also required to obtain pure substances from crude plant substances.

3.1.4 Extraction processes for drugs

Extraction processes for drugs can be divided into two major groups

1. Processes resulting in the establishment of a concentration equilibrium between solution and solid residue.

The extraction process comes to a halt when the distribution of the extractive substances between miscella and drug residue reaches the value K, when the concentration gradient between miscella and residue becomes zero.

The simplest case of this extraction process is simple maceration, the extraction of drug with a solvent with several daily shakings or stirrings at room temperature. Compared with other methods of extraction the intensity of movement during maceration is so low that we use the term stationary conditions. Kinetic maceration is carried out similarly at room temperature, the difference being that the material is kept in constant motion. For remaceration some solvent is added to the drug. After filtration the residue is extracted a second time with the remainder of the solvent and drug residue sqeezed out to express as much solvent as possible.

The position of the equilibrium here is determined both by the properties of the drug, such as type, quantity, moisture content and degree of communition, and by those of the solvent, such as selectivity and quantity. Although the degree of comminution of the drug does not affect the position of the concentration equilibrium, it is essential for the speed of establishment of the equilibrium.

The parameters affecting the establishment and position of the equilibrium are as follows:

Mixture ratio: The yield of extract decreases with constant quantity of solvent and increasing proportion of drug material.

Dissolution from disintegrated cells: Substances are dissolved out of disintegrated cells more rapidly than from intact cells. A greater degree of comminution of the drug plant material results in a larger proportion of disintegrated cells and hence in a more rapid establishment of the equilibrium. Finely divided drug material would

therefore in principle be preferred. So long as it does not make the subsequently necessary separating processes more difficult.

Steeping and swelling of drug plant material: This is very important for extraction, as it dilates the cell capillaries and hence increases diffusion. Extraction can be hindered or prevented altogether in medicinal plants containing a large amount of mucilage. Ideally, therefore, swelling should only be allowed to a certain extent to allow diffusion of the extractive substances without hindering extraction.

Diffusion from intact cells: The solvent must first diffuse into the intact cells before it can dissolve the extractive substances out. The substances to be extracted must be sufficiently soluble in the solvent to produce an increase in concentration of solution inside the cell so that equalization of concentration with the surrounding solvent can take place by diffusion.

Rate of establishment of equilibrium: This is decisive for total extraction time. In addition, the influences of particle size and degree of swelling of the drug plant material, the extraction temperature, the properties of the solvent such as viscosity and polarity, the type and intensity of movement of drug and solvent and any additives such as salts or surfactants all play a part here.

Temperature: Raising the temperature generally has the effect of shifting the extraction equilibrium towards dissolution.

pH value: The pH of the solvent influences the selectivity of extraction. The selectivity is related both to the qualitative and quantitative yield of extractable active substances and to the type and quantity of accompanying substances.

Interaction of dissolved constituents with insoluble support material of plants: Even with an optimum choice of solvent with regard to its selectivity for the substances to be extracted and its solubility there exists the possibility of adsorption of already dissolved constituents on to the support material of the drug plant. This adsorption was considered for the relatively low extract yield with increasing proportion of drug plant material in maceration.

Degree of lipophilicity: The chosen degree of lipophilicity is of great importance in the utilization of organic solvents or solvent mixtures. Any alternation will alter both the quantitative ratio of the extracted substances and the qualitative

composition of an extract. It is therefore necessary to check the composition of the extract again if the extraction agent is changed. This also applies to the interchange of similar solvents such as ethanol/methanol

2. Process in which the drug is extracted exhaustively.

Exhaustive extraction is defined as the complete removal of the desired extractive substances from the drug material. The skeletal material of the drug plant remains behind. The objective is a quantitative extraction, which can be achieved through various ways as illustrated in Figure 3.4.

In percolation, the drug plant material is exhaustively extracted by the solvent. Only the extraction consumes a large quantity of fresh solvent and takes a long time. Repercolation the drug is first solvent and then some of the percolate is used for exhaustive extraction by stagewise concentration in another percolator. Continuous countercurrent extraction is a process in which fresh drug plant material is brought into contract with loaded / changed solvent at the same time as fresh solvent is being brought into contact with already pre-extracted drug.

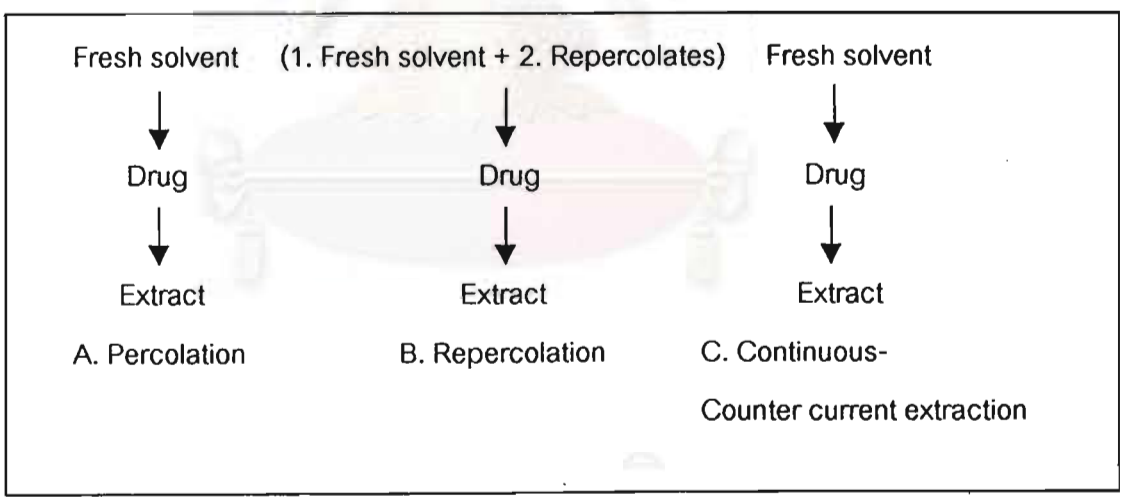


Figure 3.4 Exhaustive Extraction Procedure

Percolation and Repercolation

These authors [List et al.; 1987] worked out separate theories on the washout process, washing the extractive substances out of disintegrated cells of the drug plant and the diffusion process, which takes place during percolation.

The diffusion process is dependent parameters such as percolation rate, quantity of menstruum, diffusion constant of drug into menstruum and diffusion constant of menstruum into drug. The wash-out process is completed more rapidly than the diffusion process and hence after certain time pure diffusion prevails.

Countercurrent extraction

The starting material for the drug is put in the extraction apparatus, where first comes into contact with extraction solvent already containing extract. The further the starting material is moved into the extraction apparatus, the less concentrated is the extract in the solvent with which is coming into contact, until at the end of the apparatus it eventually meets fresh solvent. In this way complete extraction is possible with the correct choice of quantity and velocity of flow.

The theoretical relationships were first established for liquid-liquid countercurrent extraction and subsequently applied to solid-liquid countercurrent extraction.

Both streams of material continuously move against each other. This type of extraction is also called absolute countercurrent extraction.

In relative countercurrent extraction, the other hand, only one phase (as rule the extraction solvent) is in motion, the other phase (usually the solid) remains stationary. These definitions show that there is gradual transition between percolation and continuous countercurrent extraction. A battery of percolators may also be regarded as stationary solid phase against which solvent phase continuously flows. The various types of extraction are shown in Figure 3.5.

In discontinuous absolute countercurrent extraction the extraction solvent and the drug move against each other. In continuous relative countercurrent extraction only the liquid phase moves, whereas the drug material remains in the same vessel throughout the entire extraction. In continuous absolute countercurrent extraction both extraction solvent and drug material are in continual motion. A percolator battery operating on countercurrent therefore produces continuous relative counterflow extraction

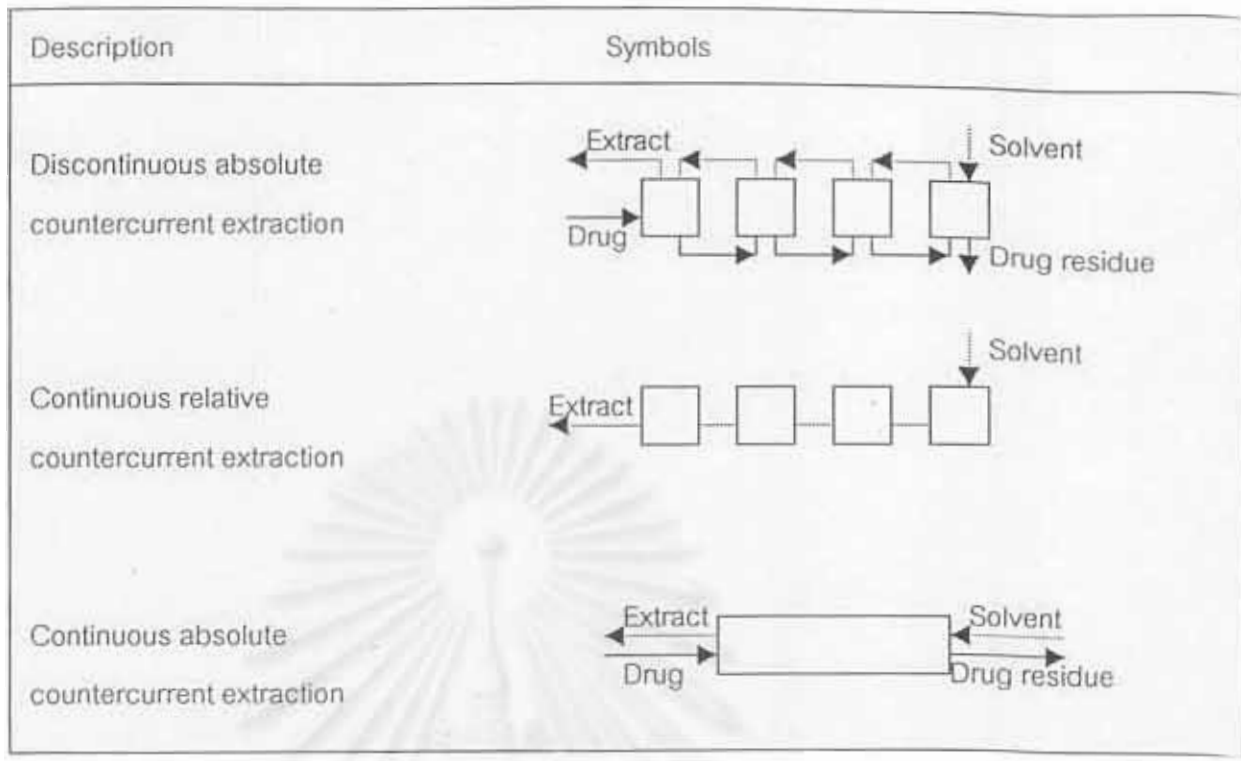


Figure 3.5 Countercurrent Extraction Procedures

Factors influencing the Rate of Extraction

The selection of the equipment for an extraction process will be influenced by several factors which are responsible for limiting extraction rate. Thus, if the diffusion of the solute through the porous structure solids is the controlling factor, the material should be of small size to decrease solute travel distance. On the other hand if diffusion of the surface from the particles to the bulk of the solution is sufficiently slow to control the process, a high degree of agitation of the fluid is called for.

Four important factors need to be considered as follows[Christi, 1995]

1. Particle size: The particle size influences the extraction rate in a number of ways. The smaller the size, the greater is the interfacial area and the higher the rate of transfer of material; further more, the smaller is the distant the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is impeded, and separation of the particles from the liquid and drainage of the solid residue is made more difficult. It is

generally desirable that the range of particle size should be small so that each particle requires approximately the same time for extraction and, in particular, the production of a large amounts of fine material should be avoided as it may wedge in the interstices of the larger particles and impede flow of the solvent.

2. Concentration gradient: The concentration gradient between that at the surface of solid and that in the bulk of the solution is also important. The solvent must be selective with respect to the solute to be extracted. It must also have a low enough viscosity to permit good circulation through the bed of solid. Countercurrent systems of extraction enable control to be exercised over the concentration gradient so that extraction can continue even when the concentration of solute in the solid is low. This facilitates more complete recovery of solute as compared with that attainable in single stage or multistage concurrent systems as shown in Figure 3.6.

3. Temperature: In most cases, the solubility of the material to be extracted increases with temperature to give a higher rate of extraction. Further more the diffusion coefficient will be expected to increase with rise in the temperature and this will also improve the rate. In some cases, the upper limit of temperature is determined by secondary considerations, such as the necessity of preventing enzyme reaction during the extraction of sugar sugar for example.

4. Agitation of the fluid: Agitation of the solvent is important as it increases the eddy diffusion and therefore increases the transfer of material from the surface of the particles to the bulk of the solution. Further, agitation of suspensions of fine particles prevents sedimentation and more effective use is made of the interfacial surface.

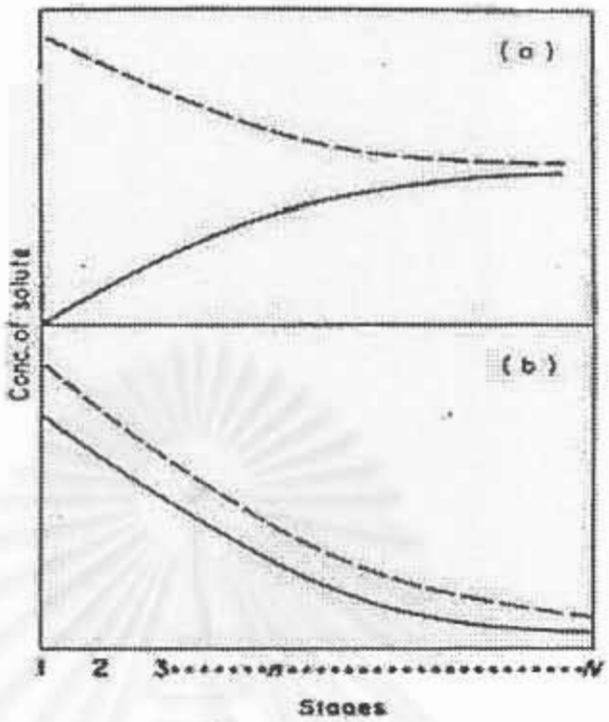


Figure 3.6 Graphical representation of concurrent and countercurrent extraction systems. (a) Concurrent system; (b) countercurrent system.

Solid; ————Solution.

3.1.5 Equipment for extraction of drug from plant materials [List et al.; 1989]

1.Equipment for maceration

The preparation of extracts is done by maceration in sealed vessels and then left to stand for 5 days with occasional shaking. This is now carried out only on a small scale. Maceration is carried out an industry scale mostly as kinetic maceration, which can also include regular renewal of the solvent (remaceration) or maceration at high temperature (digestion). Two groups of machines are available for kinetic maceration.

1.1 Machinery without stirrers

These include all machines, which bring about mixing of drug material and solvent as free fall mixers. Figure 3.7 summarizes the possible types of such machines. The extraction vessel is charged fully with drug material and an excess of

solvent. Then the solvent becomes enriched with crude extractive substances. After sufficient contact time the extract is drained off. The process can be repeated as many times as needed until the drug material has been exhaustively extracted

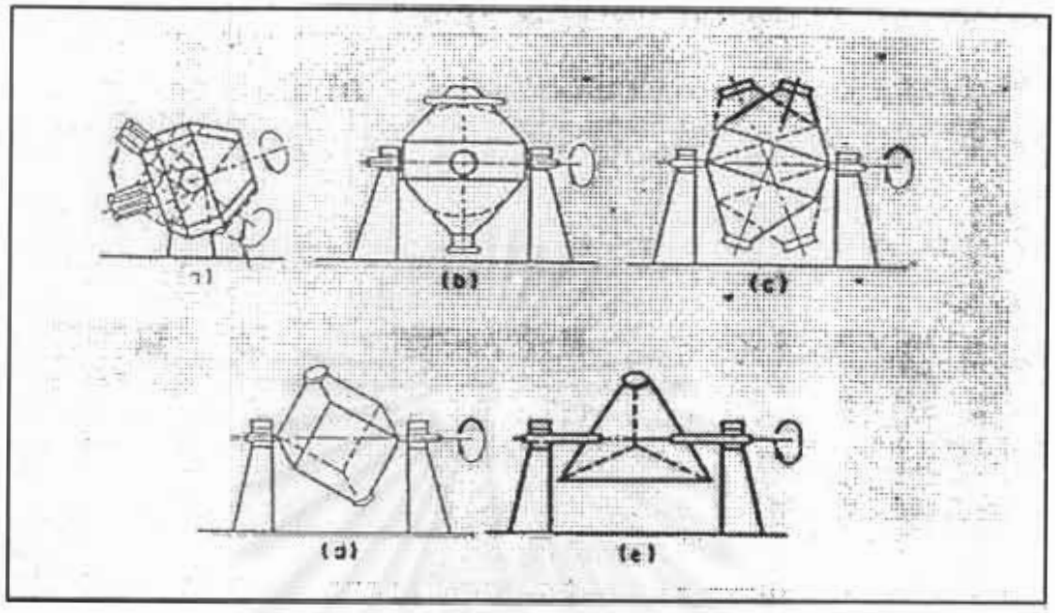


Figure 3.7 Various Mixers for Maceration: (a) mixing barrel, (b) twin cone mixer, (c) inclined twin cone mixer, (d) cubic mixer, (e) tetrahedral mixer

1.2 Stirring equipment

The efficiency of maceration can be improved by the use of stirring equipment, which produces a more rapid equalization of concentration. The stirrers should be of a design and dimension such that they guarantee homogeneous mixing of the entire contents of the container, Examples of suitable stirrers are the Z-blade or cross-beam and the intermix stirrers as illustrated in Figure 3.8.

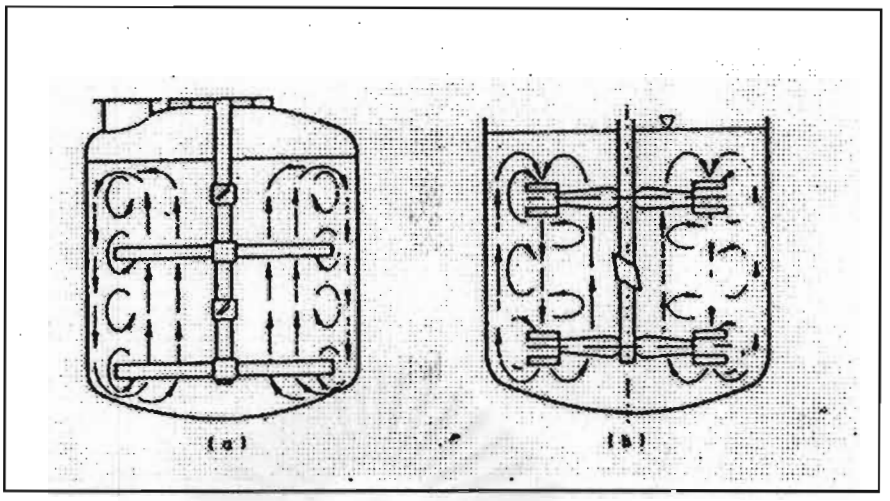


Figure 3.8 Stirrers for Extraction: (a) Cross-beam stirrer, (b) Intermig Stirrer.

2. Machinery for percolation equipment

Percolators used for this study are cylindrical or conical vessels at the bottom of which is a stopcock for regulating the outflow. Figure 3.9 shows the usual type of percolator. The comminuted material is first soaked with a quantity of solvent weighing 30% of the weight of drug material for 2 hours to make it swell before it is placed in the percolator. The degree of comminution of the drug should be such that a sufficient area of contact with the solvent is available, though on the other hand the material should be substantially free of powder to prevent clogging and the production of a cloudy miscella. The degree of comminution depends on the drug plant material, though for most of these a particle size of 1-3 mm is suitable for percolation. The preswollen drug material is then pressed lightly and evenly into a percolator in such a way as to prevent the formation of channels in which the solvent would preferably flow. The cake of drug material is covered with a filter paper, which is then weighted down with glass beads. The solvent is poured in with the stopcock open to force the air contained in the cake of drug material out at the bottom. As soon as the liquid begins to drip from the percolator the stopcock is closed and the drug material is left to macerate in the solvent for 24 hours. The extract is then allowed to drip out of the percolator while solvent is continually added at the top.

Semi-continuous operation using fresh solvent can be circumvented by using more than one percolator and percolates less rich in extract for treating new. The concept is repercolation and is the prelude to continuous countercurrent extraction, in which fresh drug is placed in contact with solvent already rich in solute and new solvent is added to partially extracted drug.

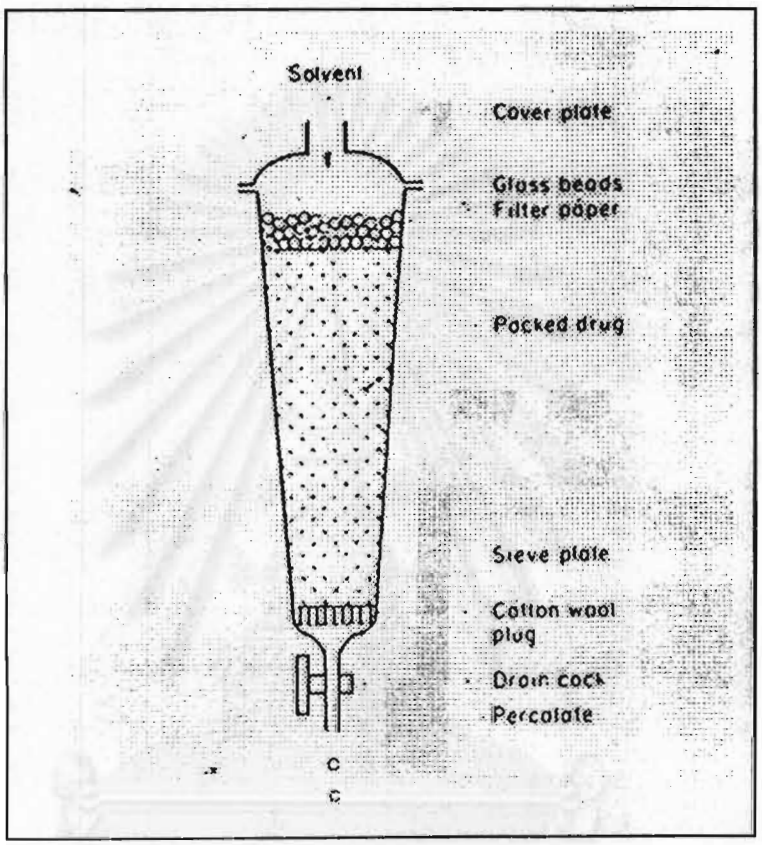


Figure 3.9 Parts of Percolator.

3. Countercurrent extraction equipment

3.1 Countercurrent screw extractor

The countercurrent screw extractor or helical extractor operates on the principle of continuous absolute countercurrent extraction, in which the drug material and the solvent are kept in continual motion in opposite directions to each other. Figure 3.10 shows a diagram of the apparatus.

The apparatus consists of a pressure resistant cylinder, a section of which can be heated or cooled, and inside which is a conveyor-screw. The drug

material is fed into the extractor through a hopper and is conveyed by the screw, with mixing and partial compaction, towards the discharge end of the cylinder. The solvent flows against the drug material from the discharge end.

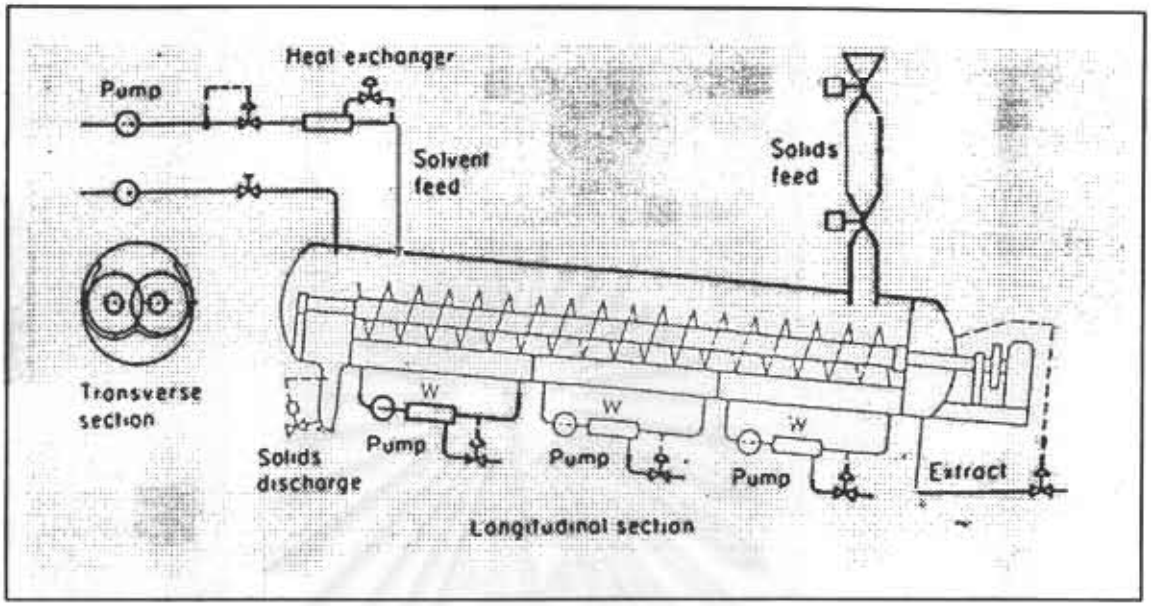


Figure 3.10 Countercurrent Screw Extractor

3.2 Carousel extractor

The carousel extractor works on the principle of continuous relative countercurrent extraction. It may also be regarded as a countercurrent operated percolation battery in which each chamber of the extractor represents a percolator. Figure 3.11 shows the principle.

The percolator is made up of 10 to 20 segments, on one or two planes that rotate. During the movement each chamber containing drug is washed by solvent, which comes from the underlying part and has a different concentration in each compartment. The carousel, which rotates clockwise is always loaded and unloaded at the same point. The exhausted drug at the end of the run is conveyed to the desolventizer. The carousel extractor is popular among pharmaceutical manufactures.

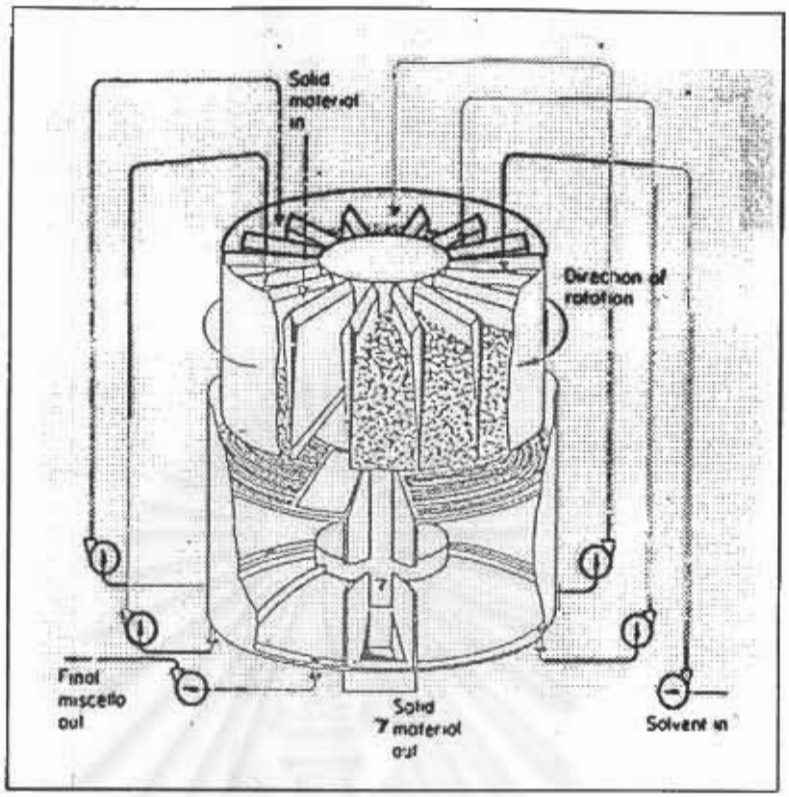


Figure 3.11 Principle of The Carousel Extractor.

3.3 Circulation extractor (U-extractor)

The U-extractor, like the carousel extractor, operates on the principle of continuous relative countercurrent extraction. In both cases the solvent floes against the drug material contained in fixed chambers. The difference lies in the arrangement of the chambers; whereas in the carousel extractor the chambers move horizontally, in the U-extractor the movement is in a vertical direction as illustrated in figure 3.12

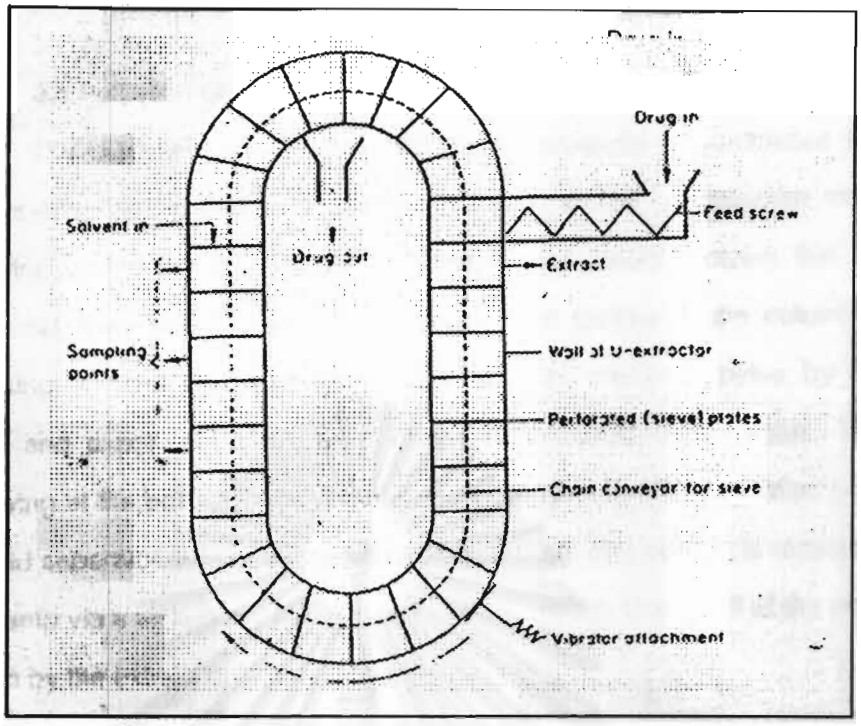


Figure 3.12 Circulation Extractor (U-extractor)

3.4 Hildebrandt conveyor-screw extractor

This apparatus operates on the same principle as the U-extractor. The design difference is that the helical screw instead of conveyor baskets transport the drug material in the U-extractor. Figure 3.13 shows a diagram of this apparatus.

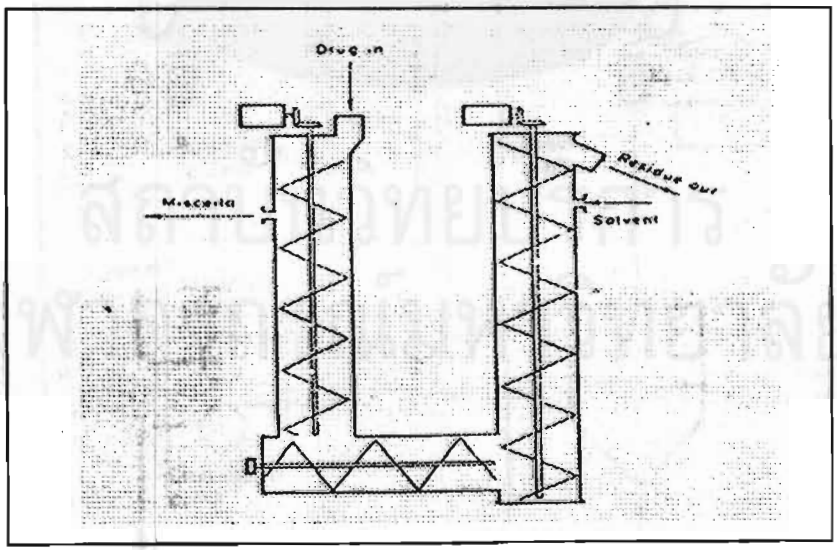


Figure 3.13 Hildebrandt conveyor-screw extractor.

3.5 Pulsation column

The pulsation column operates on the principle of continuous absolute countercurrent extraction as demonstrated in Figure 3.14. The comminuted material is fed into the top of the column through a funnel and a chute. Solvent fed in via a measuring pump flows upwards against it. Plates and buffles in the column ensure intensive mixing of solid and liquid. The liquid is also made to pulse by rhythmic compression and expansion of a gas reservoir in a pulsation apparatus. The solid particles arriving at the bottom of the column are conveyed by the circulation pump into the solid liquid separator, where the solid is separated off. The solvent is recycled to the circulation pump via a temporary storage tank. The extract is drawn off at the upper end of the column by the extract pump.

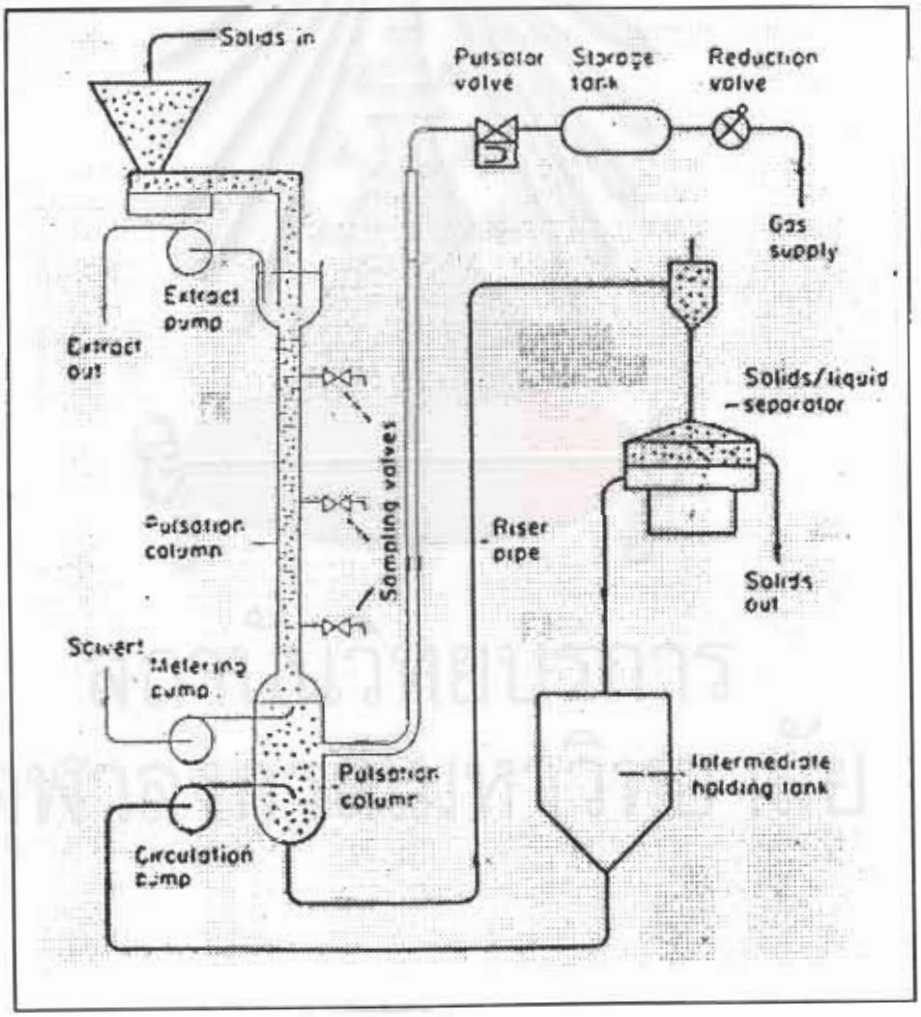


Figure 3.14 Pulsation Column

CHAPTER 4

EXPERIMENTS

This chapter describes the apparatus and experimental methods used for crude barakol extraction from *Cassia siamea* packed in a column extractor with 15% (V/V) ethanol solution as solvent.

4.1 Apparatus

The apparatus used are listed as follows.

- Peristatic pump model 505U of Watson Marlow, England.
- Centrifuge model Kubota 7820 of Kubota Corporation, Japan
- Mechanical stirrer model RW20ZMn of Ika laboratechnik, Germany
- High performance liquid chromatography (HPLC) model LC-3A from Shimadzu, Japan

  Detector model 4100 of LDC, Japan
- Blender model MX-T31GM from national, Japan
- Sieving apparatus
- Hot air oven model ULM500 from Memmert, Germany
- Column extractor as shown in Figure 4.1

4.2 Chemicals

The chemicals used are listed as followes.

- 95.5% (V/V) ethanol from Thai Alcohol, Thailand
- Dried ground *Cassia siamea* leaves
- Demineralized water
- Analytical grade ethanol from Carlo erba reagent

4.3 Experimental Methods

4.3.1 Preparation of starting material

Fresh *Cassia siamea* leaves obtained from Ratchaburi Province were purchased locally. After washing the leaves were dried in a hot air oven at 50 °C for 48 hours. The dried *Cassia siamea* leaves were then ground in a blender. A sieving apparatus was used to separate the ground dried *Cassia siamea* leaves. 100 gram of ground dried *Cassia siamea* leaves was placed into the top of a standard screen which contained 4 sieve mesh sizes: 20, 30, 40 and 50 mesh number. The sieving apparatus was then vibrated for 30 minutes. The standard for sieve as defined by the US standard was determined using the mean particle size of ground dried *Cassia siamea* leaves.

4.3.2 Study of the effect of temperature on decomposition of barakol

The purpose of this experiment was to study the effect of temperature on the decomposition of barakol. A tube containing extracted barakol was immersed into a temperature controlled waterbath set at 30, 40 and 50 Degree Celsius for 8 hours. The concentration of barakol in solution was analyzed using a high pressure liquid chromatograph. The difference of barakol concentration was the decomposition of crude barakol after heating for 8 hours.

4.3.3 The extraction of barakol in packed bed column without recycle.

The extraction of barakol was carried out in a column extractor of 29 mm i.d. and 30 cm height as shown in Figure 4.1. Before being loaded into the column extractor the *Cassia siamea* powder was prepared according to the following procedure. 30 gram of *Cassia siamea* powder was soaked with 30 ml of 15% (V/V) ethanol solution, for 15 minutes in order to completely preswell the *Cassia siamea* powder. The soaked Cassia siamea powder was gradually loaded into the column extractor and then moderately compressed by temper. Fresh solvent as 15% (V/V) ethanol was pumped through the bed at selected feed flow rates using the peristatic pump. The direction of solvent pumped into the column extractor was in an upward direction from the bottom as shown in Figure 4.2. The outlet miscella was sampled periodically. The experiment time was approximately 3 hours. At the end of the extraction, the ground *Cassia siamea* powder was submitted to a second

extraction in a stirred tank with 300 ml of fresh solvent to determine residual barakol in the solid. The extraction time used was 3 hours. The barakol concentration in 15%(V/V) ethanol was determined using a high performance liquid chromatograph (HPLC). The experiment was repeated using the same experimental procedure, except that the direction of flow was set downward as illustrated in Figure 4.3.

Bed porosity was determined by the replacement of a known density solution into the void space. 15% (V/V) ethanol solution was poured into the column extractor until the bed was full of solution. Then the volume of solution that was used to replace the void of bed was the value of porosity.

A study of the effect of the direction of feed solution was made (upward or downward direction). Particle size and feed flow rate were held constant throughout each experiment.

To study the effect of particle size on the barakol extraction, particle size was varied as 0.84, 0.59 and 0.42 mm, respectively whereas other parameters were constant throughout each experiment with feed flow rates of 18.44, 29.36 and 37.96 ml/min for an upward direction of feed solution 14.80, 23.68 and 30.88 ml/min for a downward direction of feed solution.

To study the effect of feed flow rate on barakol extraction, the following feed flow rates were used 18.44, 29.36 and 37.96 ml/min for the upward direction of feed solution and 14.80, 23.68 and 30.88 ml/min for the downward direction of feed solution whereas other parameters were constant throughout each experiment.

Table 4.1 Operating conditions of barakol extraction system for seeking suitable condition

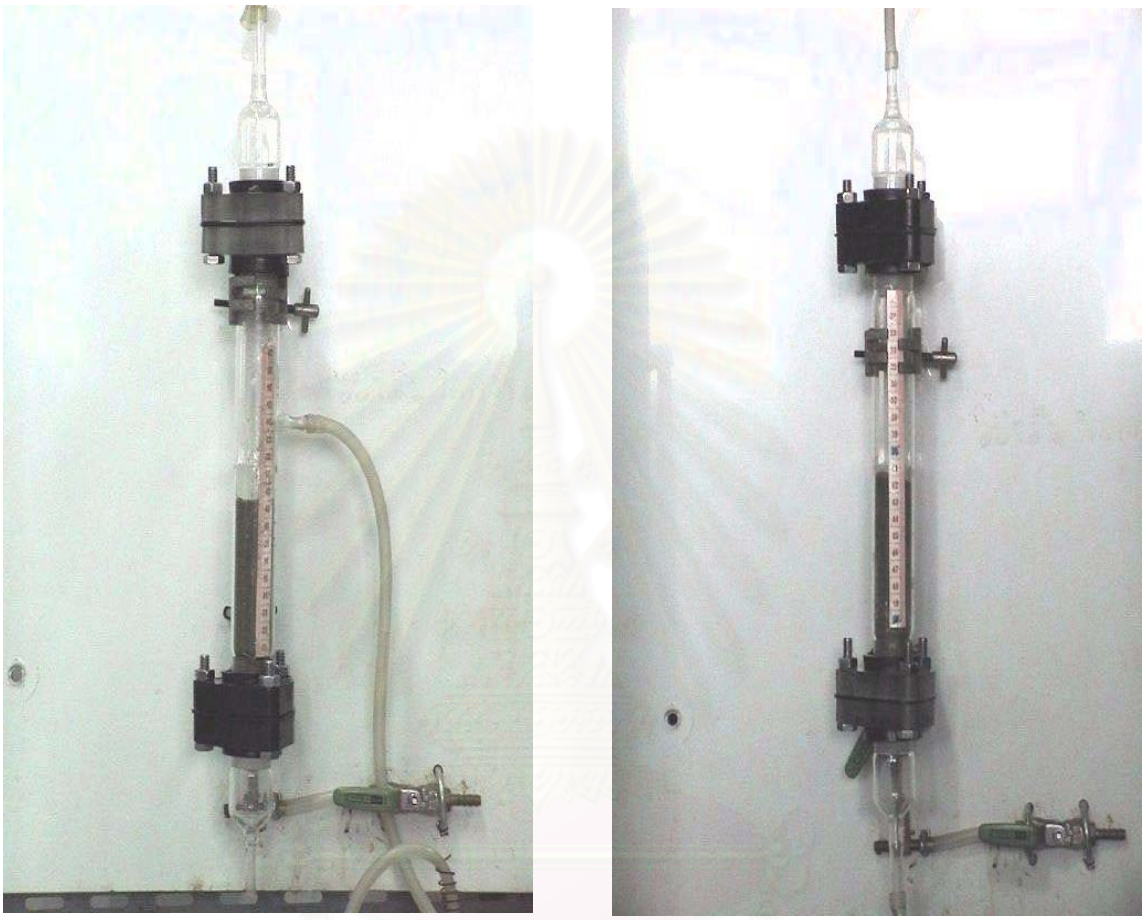
Particle size (mm.)	Direction of inlet	Feed flow rate (ml/min)
0.84	Upward	18.44, 29.36, 37.96
0.84	Downward	14.80, 23.68, 30.88
0.59	Upward	18.44, 29.36, 37.96
0.59	Downward	14.80, 23.68, 30.88
0.42	Upward	18.44, 29.36, 37.96
0.42	Downward	14.80, 23.68, 30.88

4.3.4 The extraction of barakol in packed bed column with recycle

The objective of this procedure is to study the effect of ratio of solid to solvent (W/V) on barakol extraction and compare the yield obtained from suitable conditions without recycle and with recycle. The operating condition of the crude barakol extraction obtained from the previous section were carried out at 37.96 ml/min of solvent flow rate, a 0.59 mm. particle size, and an upward flow direction. The procedure was the same as in section 4.3.2. The ratios of solid to solvent (W/V) were 1:33.33, 1:50 and 1:60, respectively. The barakol concentration of 15%(V/V) ethanol was determined by high performance liquid chromatograph (HPLC). Figure 4.3 shows the schematics of the barakol extraction with recycle.

4.3.5 Determination of product concentrations

Crude barakol was determined by high pressure liquid chromatograph (HPLC) using a Shimadzu model LC-3A chromatograph equipped with a LDC detector with UV 242nm. Separation took place in a 125mm* 4mm column packed with Linchrocart C_{18} and 48% MeOH in 0.05 M Sodium Acetate was used as mobile phase. The data obtained from a recorder integrator showed a retention time of 5 minutes for barakol.



(a) (b)

Figure 4.1 Column extractor (a) upward direction of feed solution, (b) downward direction of feed solution

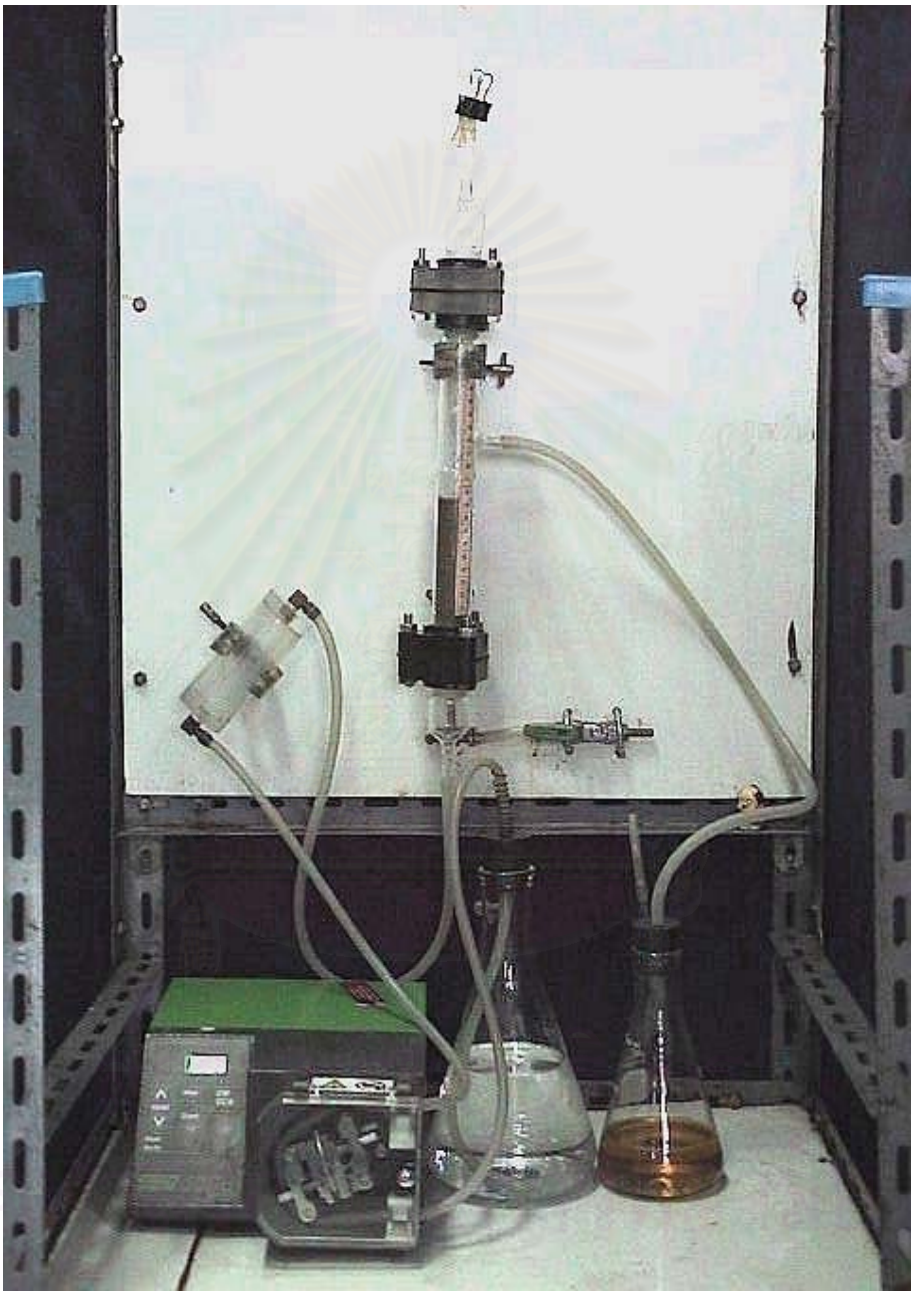


Figure 4.2 Picture of the upward direction of feed solution.

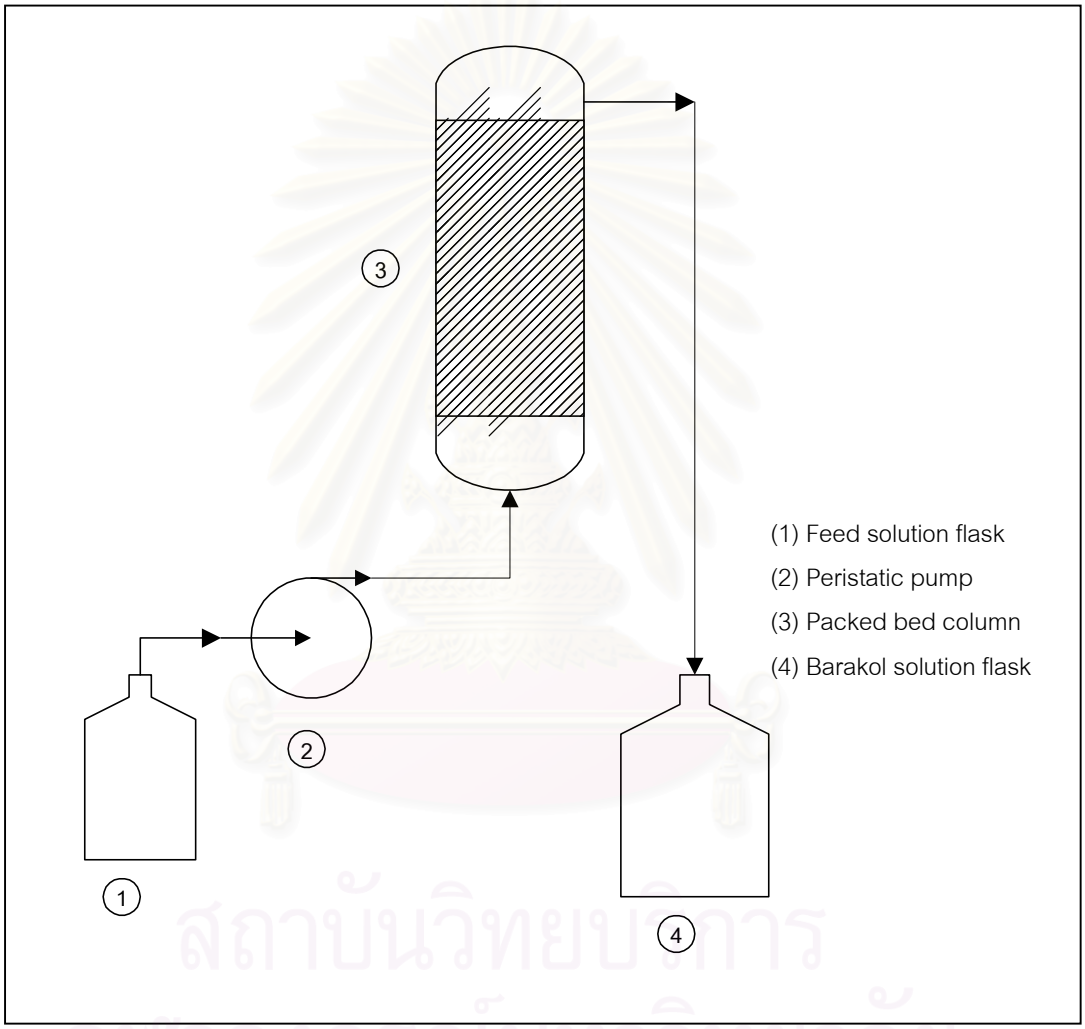


Figure 4.3 The schematic diagram for the upward direction of feed solution.

Figure 4.4 Picture of the downward direction of feed solution.

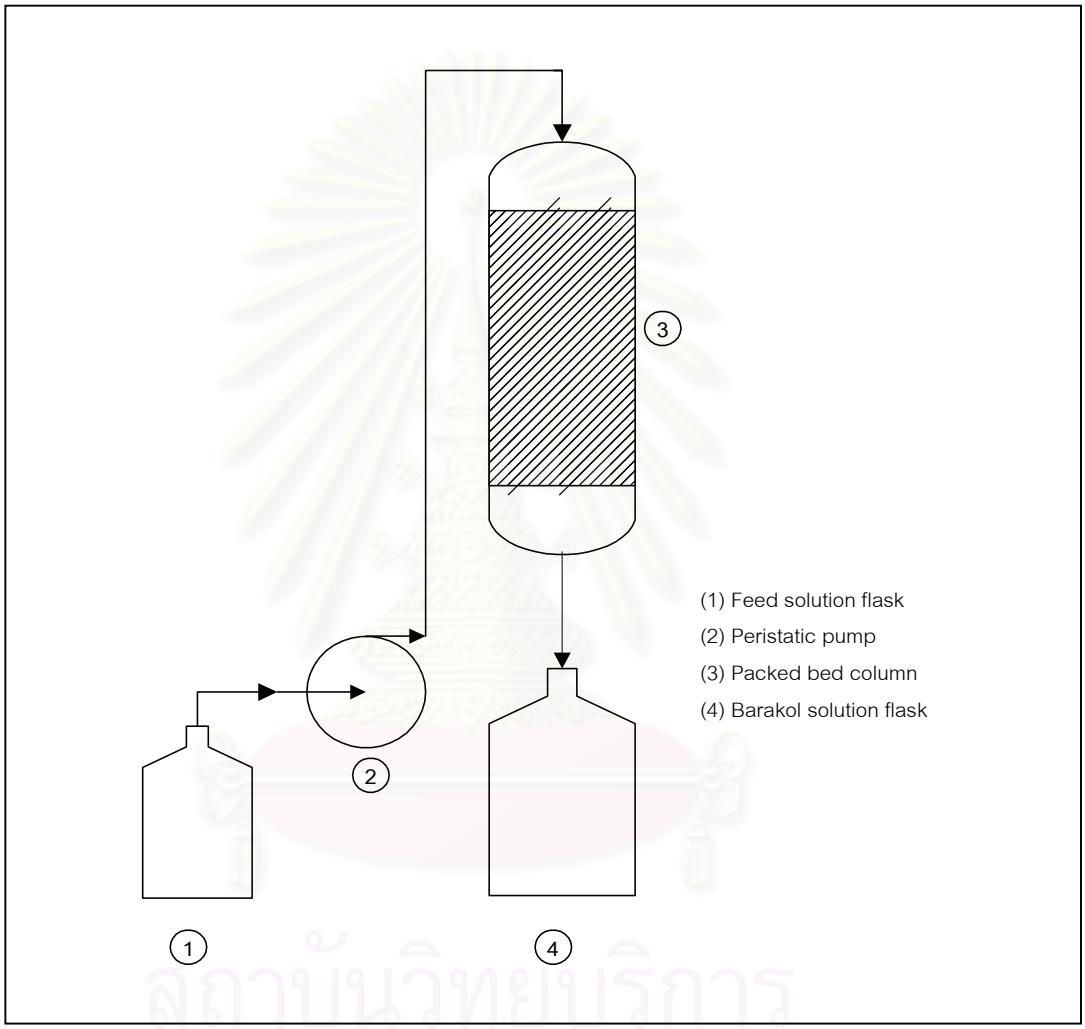


Figure 4.5 The schematic diagram for the downward direction of feed solution;

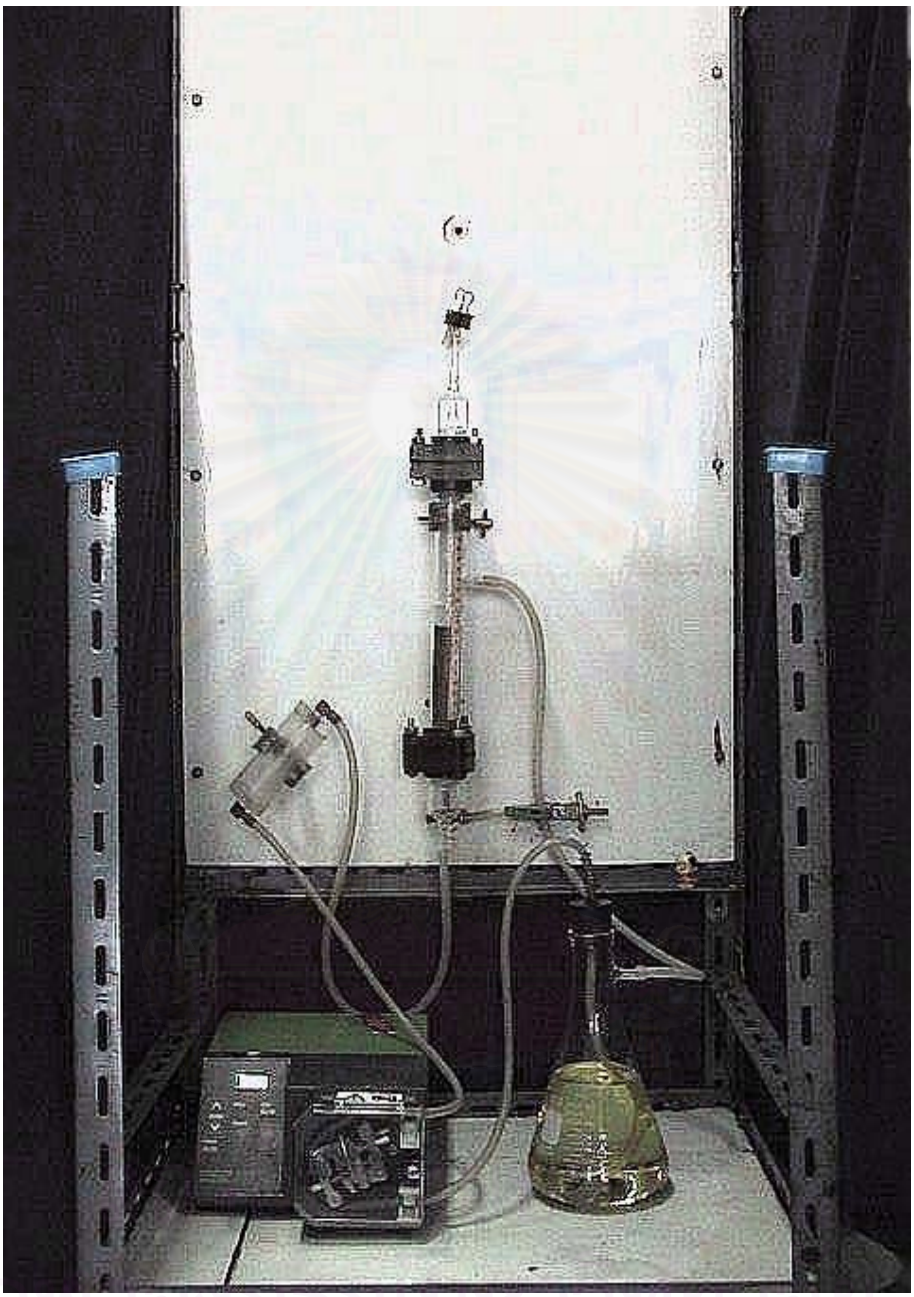


Figure 4.6 Picture of the barakol extraction with recycle.

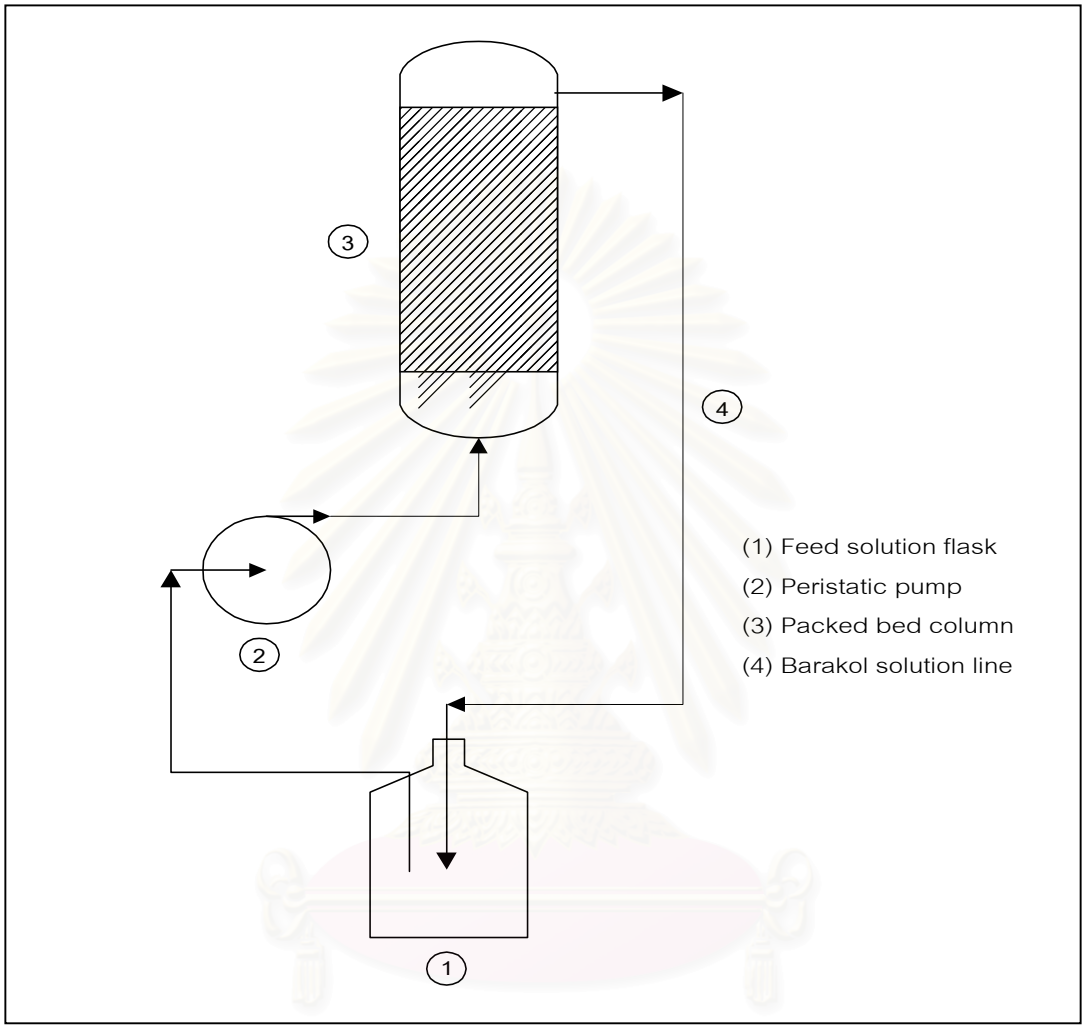


Figure 4.7 The schematic diagram for the barakol extraction with recycle

CHAPTER 5

RESULTS AND DISCUSSION

This chapter presents the experimental results and a discussion dealing with the parameters which affect the extraction of crude barakol.

5.1 Effect of temperature on the decomposition of crude barakol

The study of the effect of temperature on the decomposition of crude barakol took place by immersing crude barakol solution tubes into constant temperature water baths set at 30, 40 and 50 degree Celsius for 8 hours. The concentration of barakol in the solution was analyzed using a high performance liquid chromatograph (HPLC) as described in Appendix A. The difference of barakol concentration between the initial and final stages is the decomposition value of crude barakol after exposure to water at three different temperatures for 8 hours. As shown in Figure 5.1 the concentration of crude barakol declined for almost all temperatures studied. The percent of decomposition of crude barakol increased with increasing temperature as presented in Table 5.1 Similar results were reported by Atthanatho [1999] and Tangsrisamruang [1997] for studies of the effect of temperatures on the decomposition of crude barakol. Atthanatho [1999] who carried out experiments at 30, 35 and 40 degree Celsius for 8 hours found percentages of decomposition of crude barakol to be 0.60, 6.71 and 8.49, respectively. Tangsrisamruang [1997] who carried out experiments at 30, 40 and 50 degree Celsius for 48 hours showed a percent of decomposition of crude barakol of 1.2, 29.3 and 46.3, respectively.

Table 5.1 percent of decomposition of crude barakol

Temperature (°C)	%Decomposition		
	This work[a]	Atthanatho [1999][a]	Tangsrisamruang [1997][b]
30	0.06	0.06	1.2
35	-	6.71	-
40	2.14	8.49	29.3
50	11.21	-	46.3

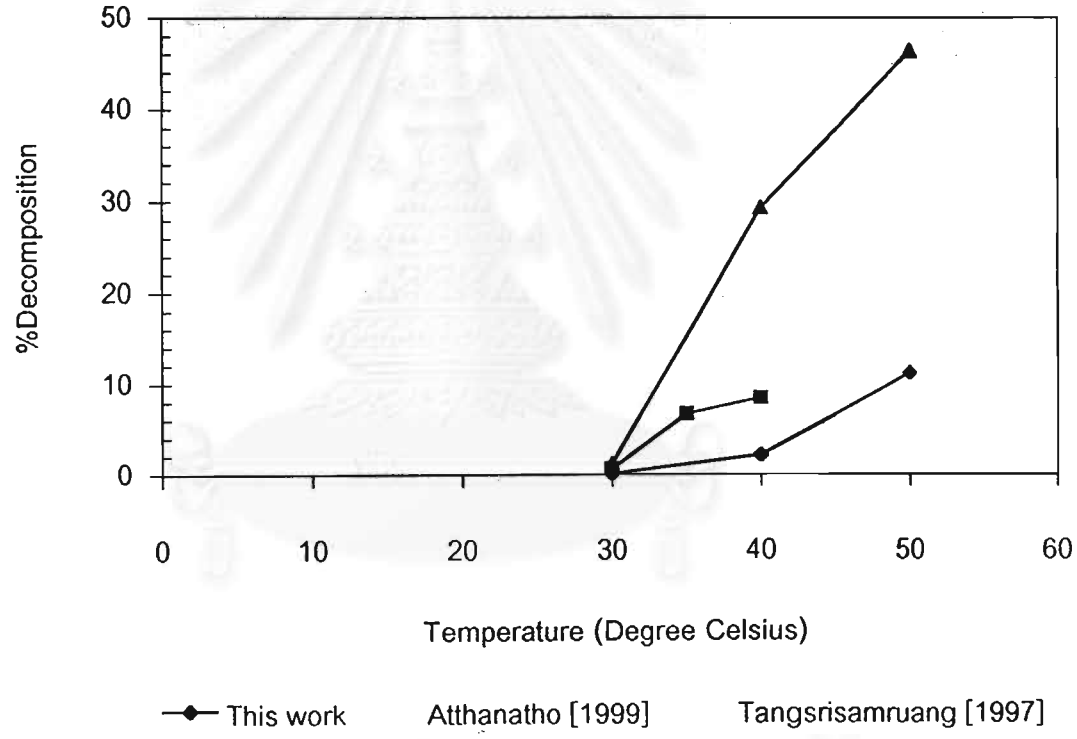


Figure 5.1 Effect of temperature on decomposition of barakol

immersing crude barakol solution tubes into constant temperature water bath for 8 hours

[b]. immersing crude barakol solution tubes into constant temperature water bath for 48 hours

5.2 Effect of direction of feed solution

In order to examine the effect of direction of feed solution this study used particle sizes of 0.84, 0.59 and 0.42 mm. and speeds of the peristaltic pump of 3, 5 and 7 rpm with both upward and downward directions undertaken using the same internal diameter of silicone tube.

In the experiments conducted the values of the entrance feed flow rates in both directions were not the same despite the fact the peristaltic pump revolutions per minute were the same. This means that although the same mechanical energy was added to the fluid for both directions of flow the difference in flow rate can most probably be attributed to different frictional resistances. In the downward flow direction case the flow rate of solvent was lower than in the upward flow direction case despite the fact that the rpm of the peristaltic pump was identical as shown in Table 5.2.

Table 5.2 The feed flow rate of upward and downward direction of solution

Speed of pump (rpm)	Feed flow rate (ml/min)	
	Upward direction	Downward direction
3	18.44	14.80
5	29.36	23.68
7	37.96	30.88

Furthermore extraction of barakol was less in the case of the downward flow direction; this finding is not surprising as less solvent passes through the bed if the downward flow direction is selected under the same peristaltic pump rpm. There are two parts of the equipment that can have different frictional resistances depending on the flow direction. In the case of the downward flow direction the tubing connecting the peristaltic pump and the top of the packed bed column is longer than in the case of the upward flow direction where the entrance of the feed solvent is located at the bottom of the packed bed column. The other part is the flow resistance within the packed bed itself. In the case of the downward flow direction it has been observed that the solid is compacted by the downward flow to a certain extent. In the case of

the upward flow direction it has been observed that the bed expands to a certain extent. A cause of bed expansion may be explained by the swelling property of the natural material. From the experiment, it was found that *Cassia siamea* powder starts swelling within 15 minutes of the extraction as shown in Figure 5.2. The difference between the bed heights in both flow direction is very noticeable and is in the neighborhood of 1 cm. As the bed is compressed by the pressure of the downward flow of liquid the void area in the bed becomes smaller resulting in higher resistance to flow. This flow resistance phenomena within the compressed bed is believed to be the reason for the lower rates of flow for the downward flow direction case. It is not believed that the added friction within open tubes between the pump and the packed bed are important enough to cause the difference in flow rates observed between the upward and downward flow directions. Ghildyal et al [1991] did studies of extraction of amylo-glucosidase from packed bed of bran mouldy and found also a difference in resistance in the bed as the bed became more compact as a function of time after start of the extraction and flow of solvent in the downward direction.

From the reasons as mentioned in the previous paragraph, the entrance feed flow rate for the upward direction of feed solution was higher than the downward direction of feed solution. And the upward direction of flow yielded a barakol extraction yield which was superior than in the downward case as shown in Figure 5.3.

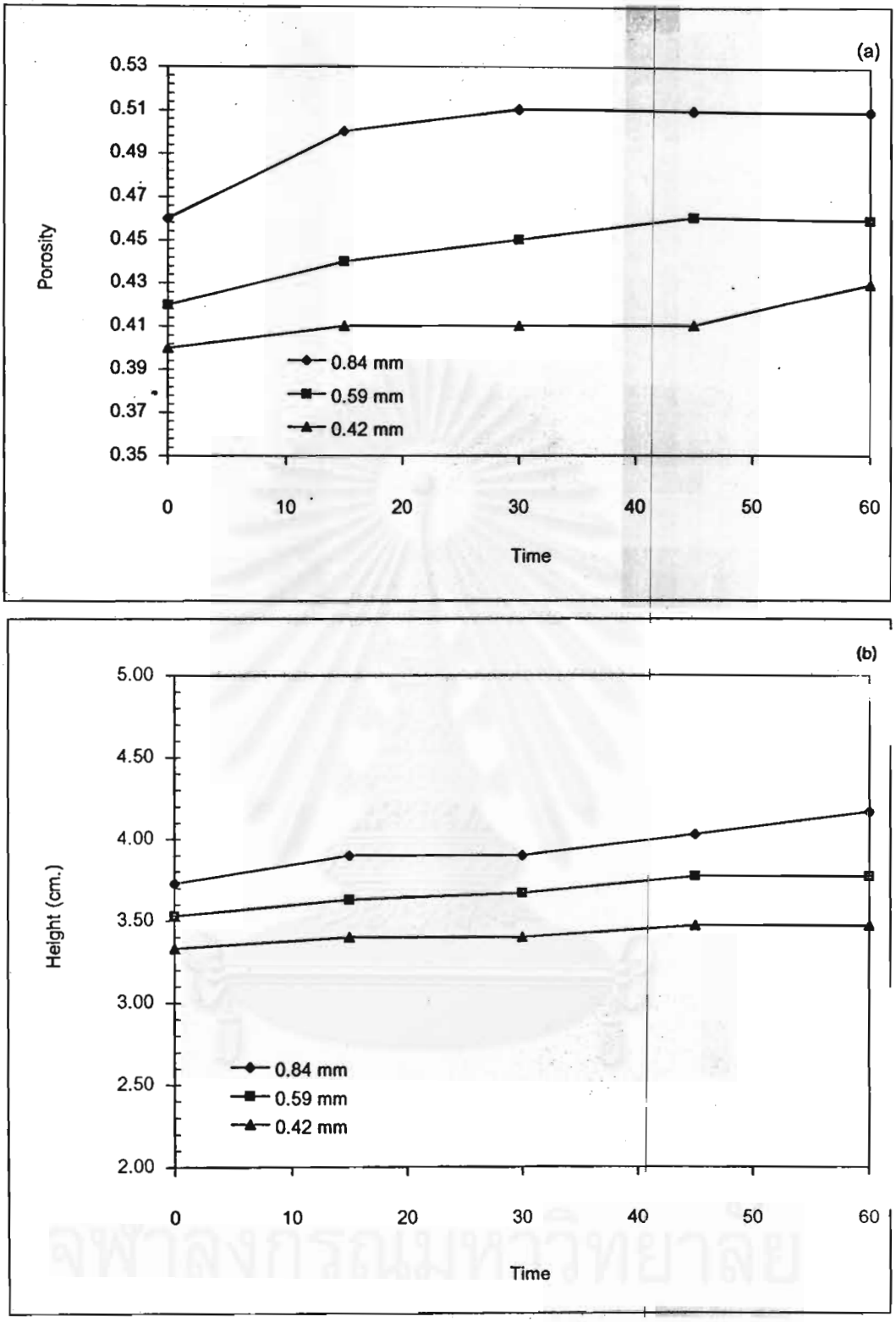


Figure 5.2 Effect of swelling property of *Cassia siamea* powder on the bed

(a) Bed porosity

(b) Bed expansion

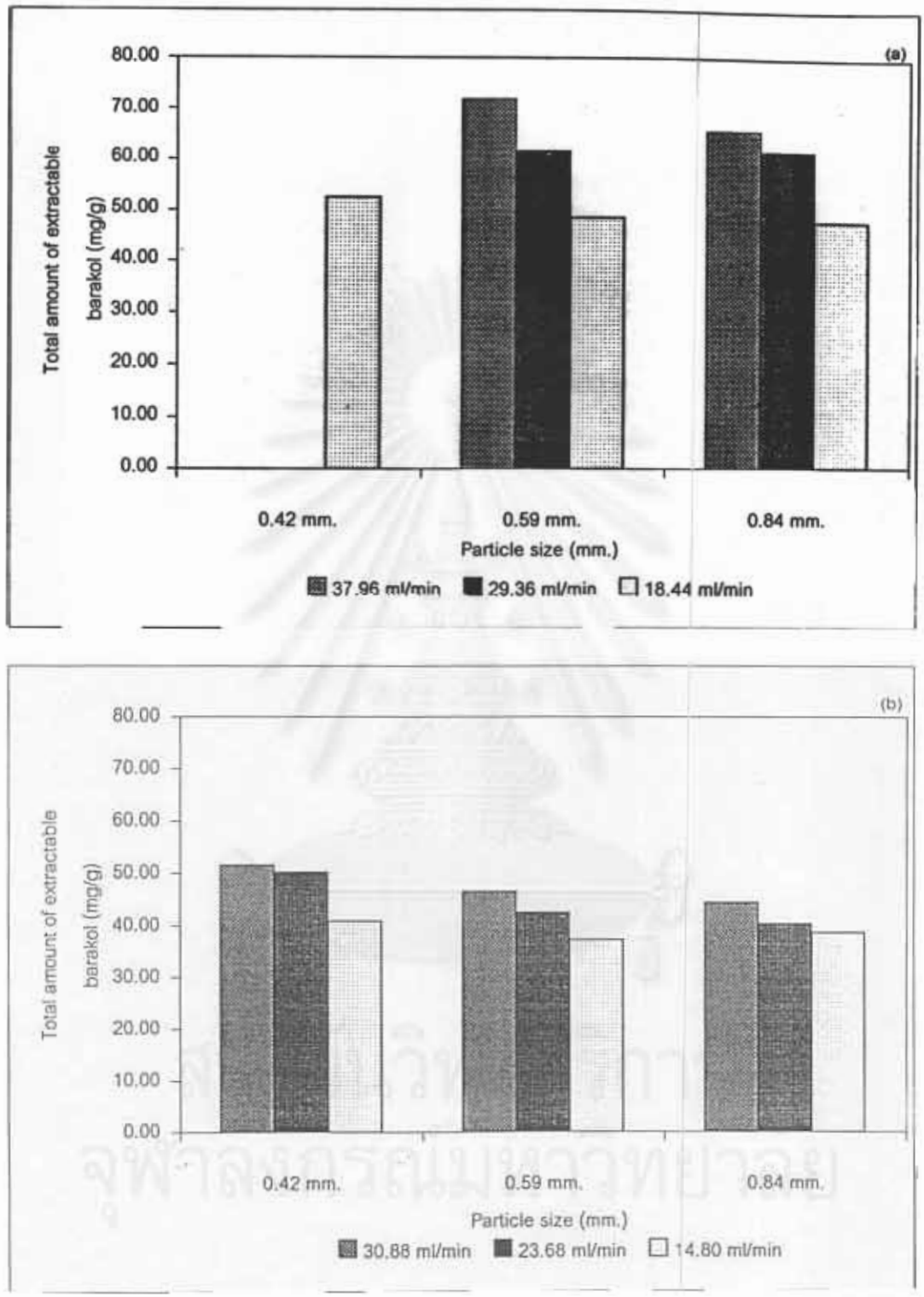


Figure 5.3 The total amount of extractable barakol during extraction time.

(a) an upward direction of feed flow rate

(b) a downward direction of feed flow rate

5.3 Effect of particle size and feed flow rate on the barakol extraction

In order to study the effect of particle size on barakol extraction a series of experiments like the previous section were undertaken except that the particle size of 0.42 mm. was not tested at feed flow rates of 37.80 and 28.64 ml/min.

From the experimental results it can be concluded that the extraction of barakol from *Cassia siamea* may be separated into two periods. A first period where a major portion of barakol is extracted by simple washing from or near the surface of the solid to the solvent. As a result the plot of the amount of extractable barakol as a function of time sharply rises as shown in Figures 5.4 and 5.5. It is believed that the controlling mechnism is convection. In the second period the remaining barakol is extracted from a diffusional process from within the solid to the solvent and becomes significant after the washing stage is complete [George et al; 1986]. The slope the curve in this period remains fairly constant over time. It is believed that in this second period the controlling mechanism is internal diffusion.

The decrease in particle size increases the amount of extractable barakol. Although, if too fine a size is used, the bed behaved as a fluidized bed. As a result, particles with a size of 0.42 mm. were not tested at feed flow rates of 29.36 and 37.96 ml/min. The best operating condition where the highest total amount of extractable barakol was obtained was a packed bed extractor with a 0.59 mm. particle size and a 37.96 ml/min feed flow rate with an upward direction of feed solution. The amount of extractable barakol for that best case was 71.80 mg/g of dried *Cassia siamea* powder.

The effect of particle size on the initial rate of barakol extraction is illustrated in Figure 5.6. It is found that the increase of particle size reduces the initial rate of barakol extraction for both cases of direction of flow. This situation may be explained by the fact that a decrease of particle size increases surface area of mass transfer. The experimental results are shown in Table 5.3.

Table 5.3 The initial rate of barakol extraction for each conditions in 15 minutes.

Particle size (mm)	Initial rate of barakol extraction (mg/(g*min)) (15 minutes)					
	Upward direction of solution			Downward direction of solution		
	37.96 ml/min	29.36 ml/min	18.44 ml/min	30.88 ml/min	23.68 ml/min	14.80 ml/min
0.42	-	-	1.65	2.30	1.66	1.14
0.59	2.79	2.18	1.22	1.78	1.32	1.02
0.84	1.94	1.07	0.74	1.49	1.26	1.03

Figures 5.7 (a) and (b) illustrate the effect of particle size on the total amount of barakol extraction with the upward and downward direction of feed solution, respectively. It was found that for both the upward and downward directions of flow, the total amount of extractable barakol increased with decreasing particle size. The controlling mechanism of the barakol extraction until the end of the extraction time is internal diffusion as presented by the following diffusion equation. [Sionero et al.; 1996]

$$\frac{\partial c}{\partial t} = D_{AB} \frac{\partial^2 c}{\partial x^2}$$

Cassia siamea are biological materials which have cellular structures, pores and interconnected voids which affect the diffusion so that the diffusion coefficient equation 5.1) may be rewritten as equation 5.2) as mentioned in theory. [Christi, 1995]

$$\frac{\partial c}{\partial t} = D_{eff} \frac{\partial^2 c}{\partial x^2}$$

this transient diffusion equation can be solved only for known rigid particle geometry as illustrated in section 5.7. The solution to the diffusion equation is [Ali Sasmaz, 1996]

$$\frac{c - c_s}{c_0 - c_s} = \alpha \exp\left(\frac{-B \cdot D_{eff}}{x^2}\right)t \qquad 5.3)$$

where α and B are constants

c is the concentration

c_0 is the initial homogeneous solute concentration in the particle

c_s is the barakol concentration of solution

Equation 5.3) indicates that the decreasing distance of solvent penetration increased the total amount of extractable barakol. Furthermore the decrease of particle size also enhances surface area of mass transfer. Our experimental results are in accordance with those of other researchers. Nieh et al. [1991] studied the effect of particle size on extraction by comparing the extraction rate of oil from either fine flour soybean or soybean flakes, and showed that oil extraction from flakes depended on contact time rather than volume of solvent because the limit on the rate of extraction of flakes is believed to be controlled by diffusion. Besides, Abhay et al. [1983] also concluded that in his studies solid particle size control the rate of oil extraction. The experimental results in this study clearly show that time to reach 1% residual oil decreases as the size of the pellets decreases or surface area/g increases. For the downward direction of feed solution at a feed flow rate of 14.80 ml/min, the total amount of barakol extracted from a 0.59 mm. particle size bed was smaller than the total amount of barakol extracted from a 0.84 mm. particle size bed. This situation may be described by the complexity of the structure of natural products. The total amounts of extractable barakol for each condition are shown in Table 5.4.

Table 5.4 The total amount of extractable barakol for each conditions.

Particle size (mm.)	Total amount of extractable barakol (mg/g)					
	Upward direction of solution			Downward direction of solution		
	37.96 ml/min	29.36 ml/min	18.44 ml/min	30.88 ml/min	23.68 ml/min	14.80 ml/min
0.42	-	-	52.47	51.54	50.20	40.88
0.59	71.80	61.65	48.53	46.52	42.55	37.31
0.84	65.52	61.50	47.64	44.43	40.39	38.71

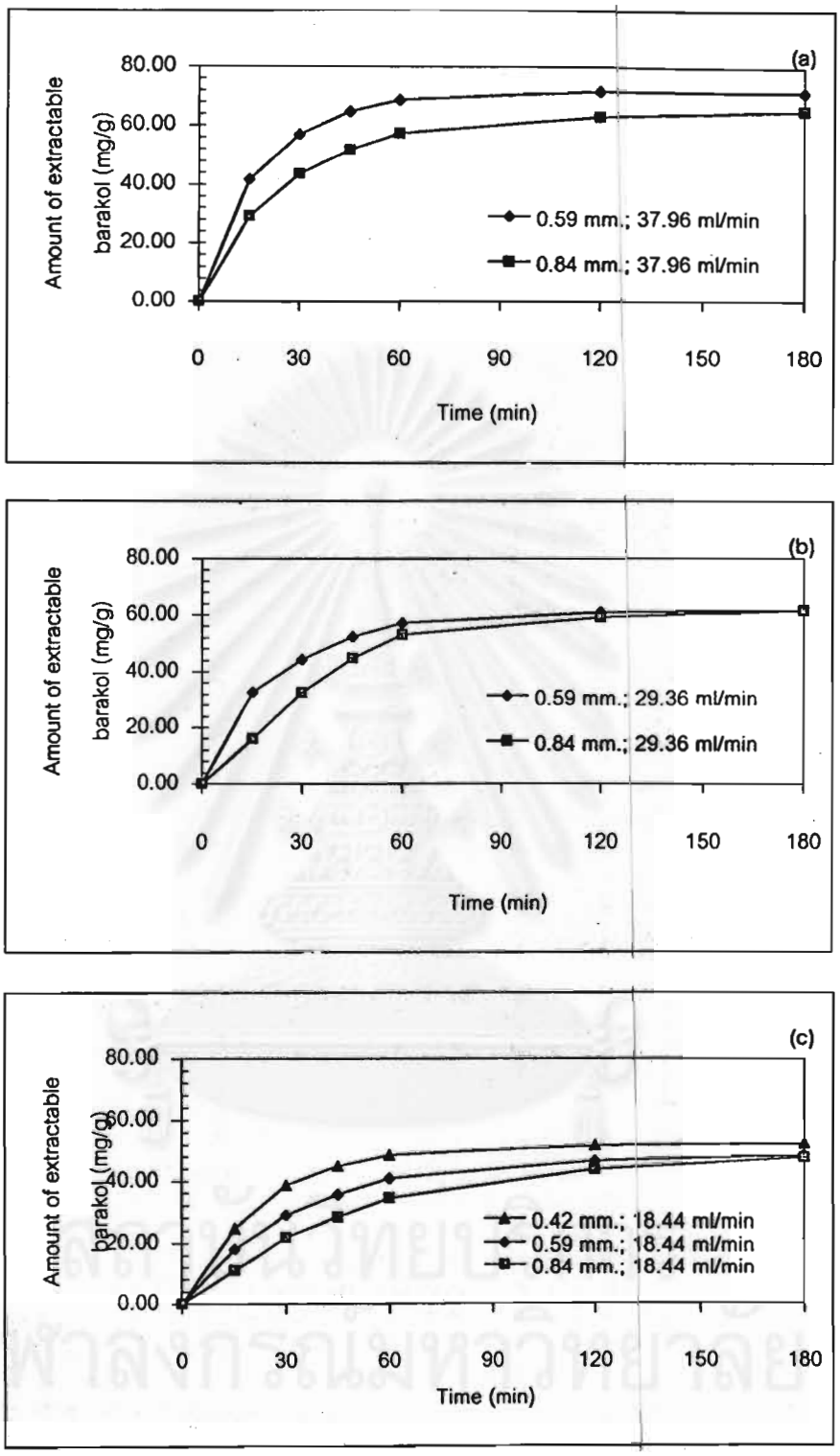


Figure 5.4 The extraction curve of barakol with various feed flow rates (a) 37.96 ml/min, (b) 28.96 ml/min and (c) 18.44 ml/min for the upward direction of flow at room temperature.

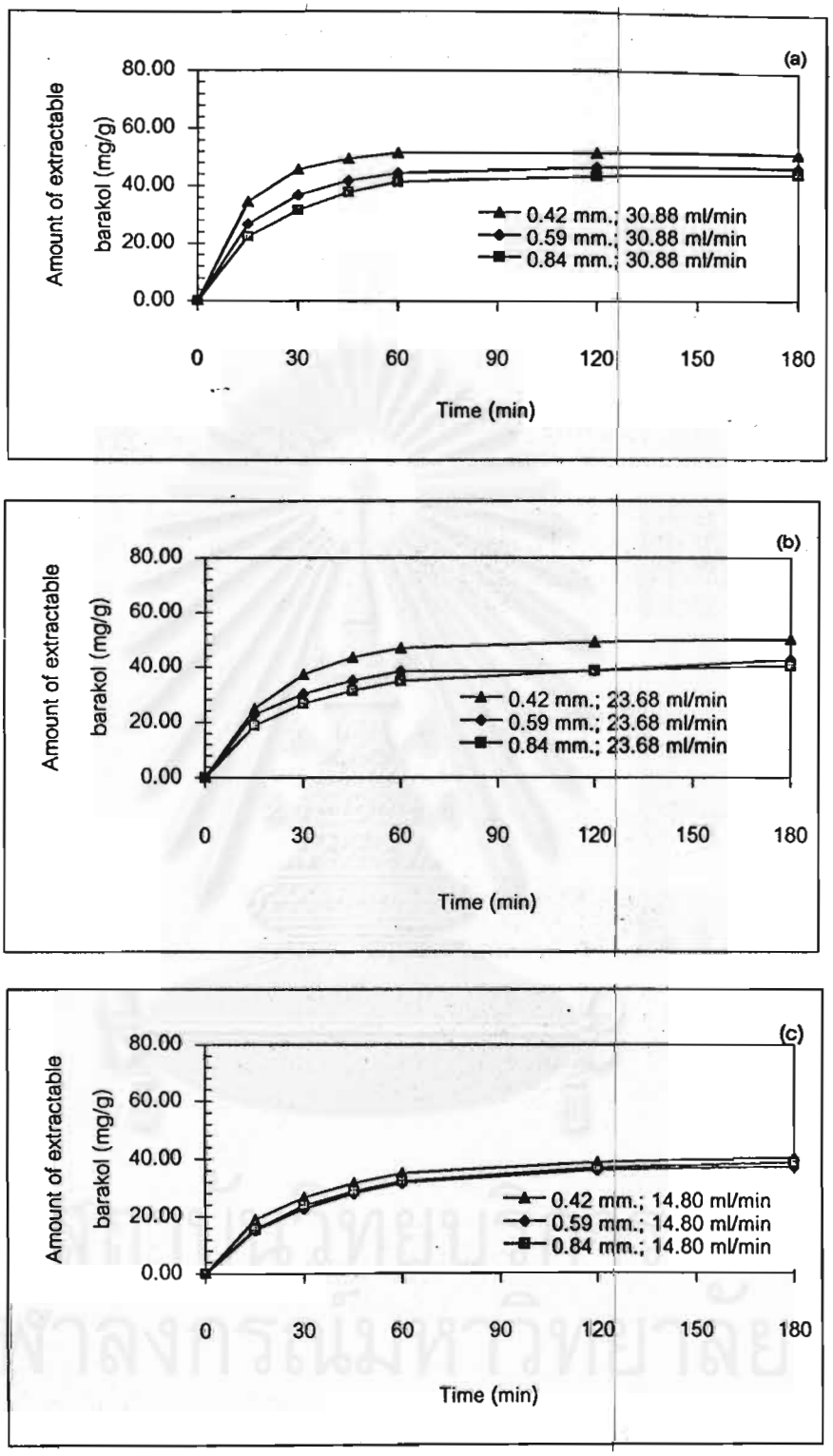
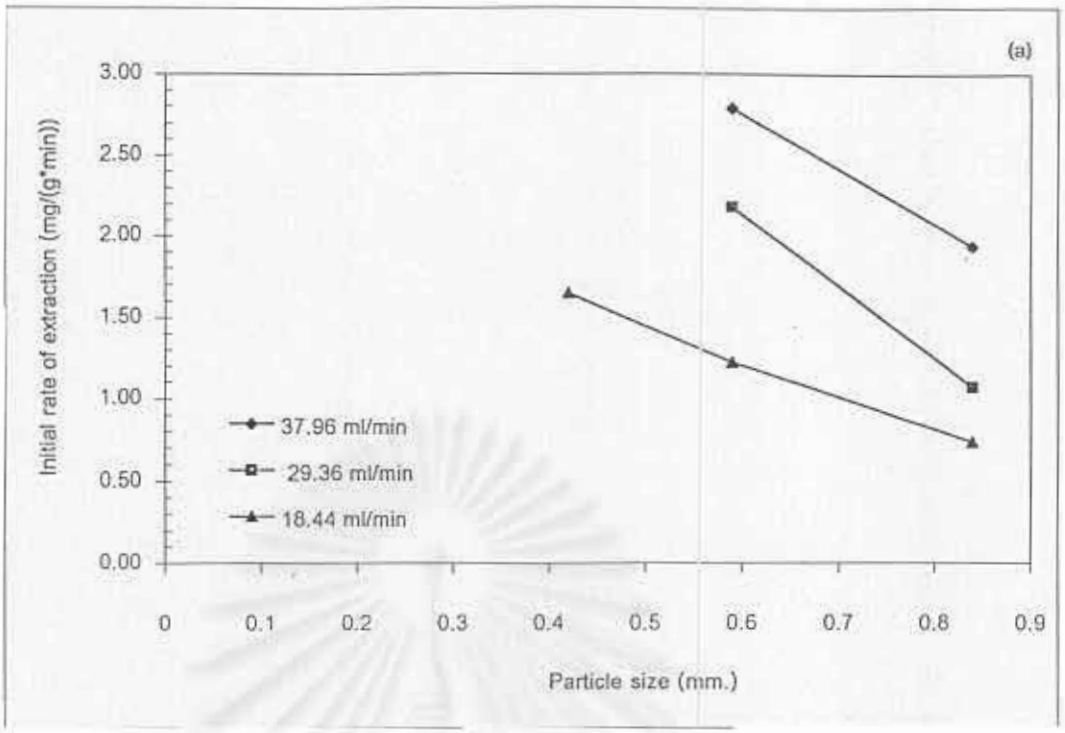


Figure 5.5 The extraction curve of barakol with various feed flow rates (a) 30.88 ml/min, (b) 23.68 ml/min and (c) 14.80 ml/min for the downward direction of flow at room temperature.



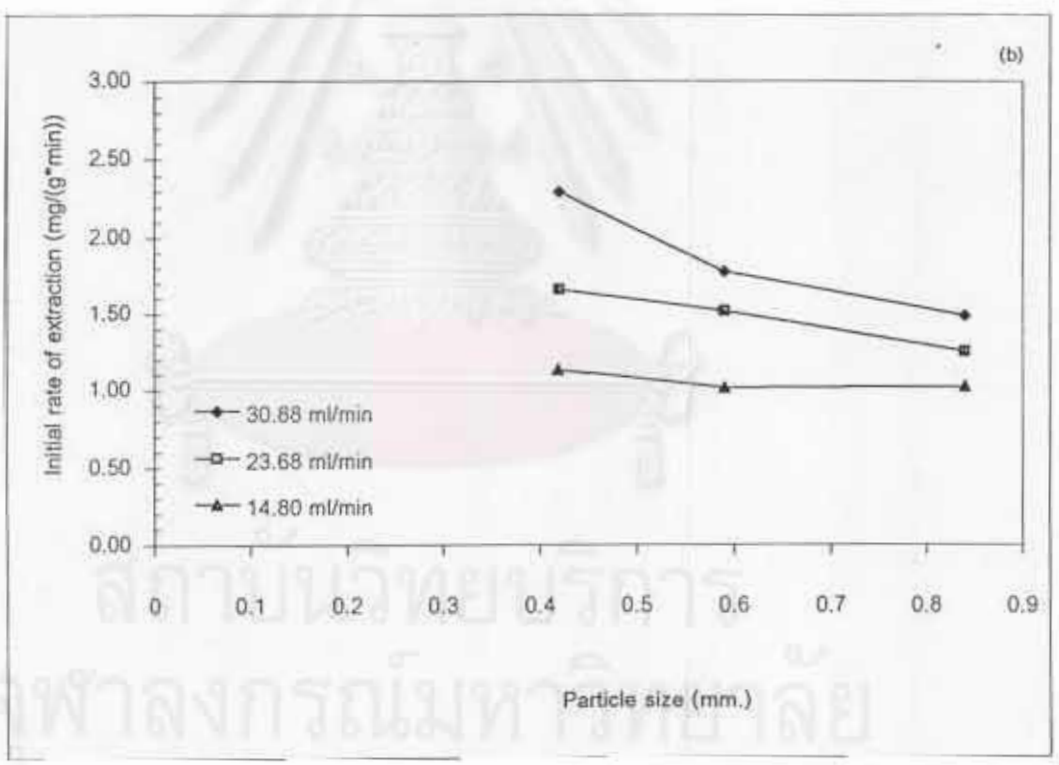


Figure 5.6 Effect of particle size on initial rate of barakol extraction at room temperature

(a) an upward direction of feed flow rate

(b) a downward direction of feed flow rate

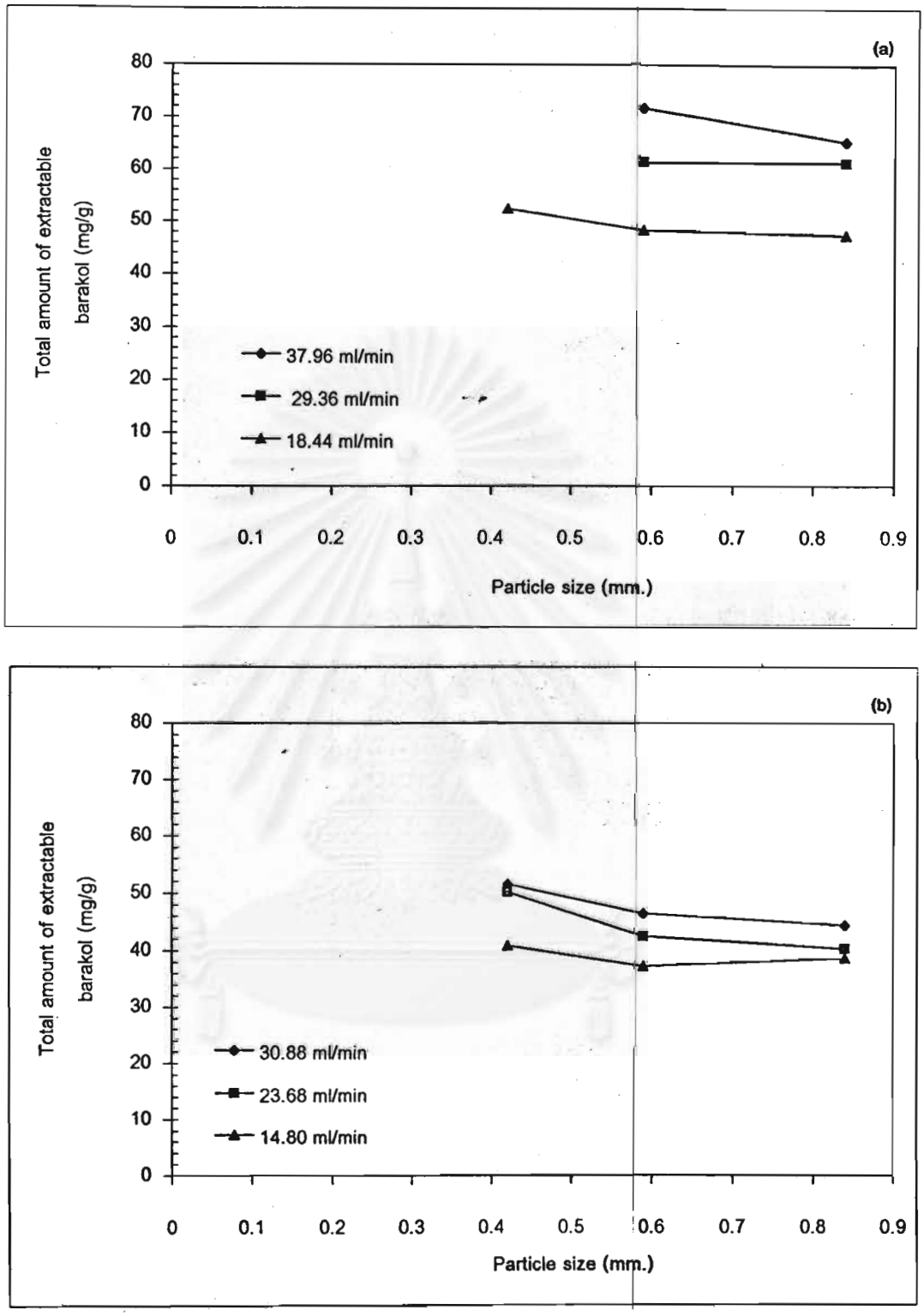


Figure 5.7 Effect of particle size on total amount of barakol extraction at room temperature

(a) an upward direction of feed flow rate

and (b) a downward direction of feed flow rate

When a fluid flowing outside a solid surface in forced convective motion increases the major part of barakol which is removed by convection. After about 60 minutes into the extraction, the remaining barakol is extracted by diffusion of barakol within the solid to the solvent as shown in Figure 5.8 and 5.9. Consequently, the increase of feed flow rate in the diffusion process is not essential.

The effect of feed flow rate on initial rate of barakol extraction is shown in Figure 5.10. The experiments indicate that feed flow rate affects the initial rate of barakol extraction for both directions of feed solution. The increase of feed flow rate increases the initial rate of barakol extraction. This phenomenon may be described by convective mass transfer. When a fluid is flowing outside a solid surface in forced convection motion, the rate of convective mass transfer from the surface to the fluid is followed by [Christi, 1995]

$$N_A = k_c(c_{AS} \quad c_A) \qquad 5.5)$$

where k_c is a mass transfer coefficient in m/s.

c_A is the bulk fluidd concentration.

c_{AS} is the concentration in the fluid next to the surface of the solid or concentration of the saturated solution in contact with the particles.

This mass transfer coefficient is a function of the system geometry, fluid properies and flow velocies. From equation 5.5), the driving force is the difference of concentration between the bulk fluid and solid surface. As velocity of feed solution increases, the concentration difference is higher. Moreover the increase of velocity of feed solution decreases the film resistance around solid particles. Similar results were reported by Nieh et al. [1991] while studying the effect of feed flow rate on oil extraction from soybean flour. The results showed that increasing flow rate increased the amount of oil extracted. In the other words, the extraction was depended on the volume of solvent.

Figures 5.11 (a) and (b) show plots between the total amount of barakol extracted for both directions of feed solution. The data indicates that when the feed flow rate increases, the total amount of extractable barakol increases. From Figure 5.11(a), there are no differences

between initial rates of extraction between particle sizes of 0.59 and 0.84 mm. at low feed flow rates. The reason may be that in this situation is that at low feed flow rates, film resistance controls barakol extraction. With an increase of feed flow rate, there is difference in the total amount of extractable barakol between particle size of 0.59 and 0.84 mm. due to the effect of particle size.

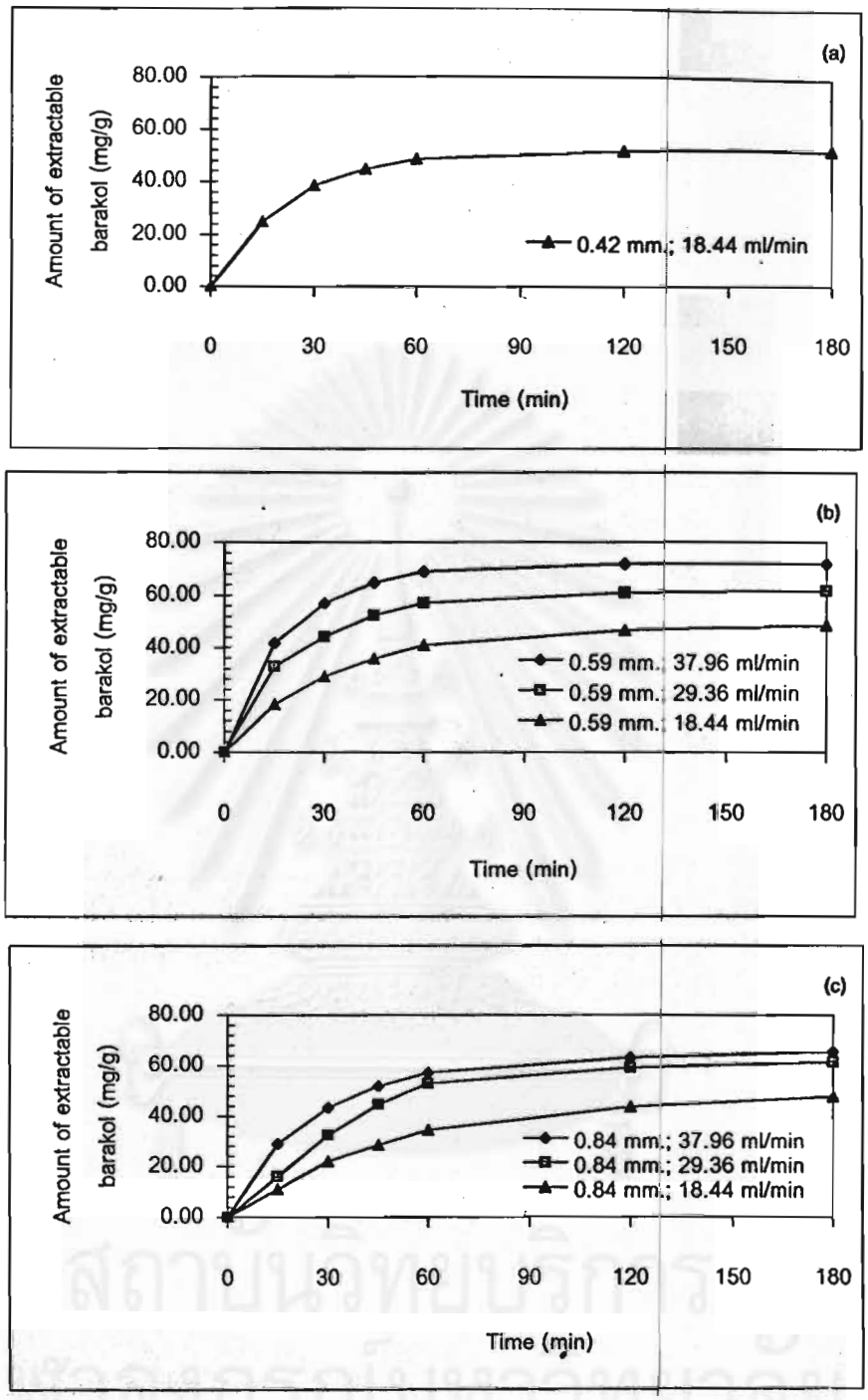


Figure 5.8 The extraction curve of barakol with various particle size (a) 0.42 mm (b) 0.59 mm (c) 0.84 for the upward direction of flow at room temperature.

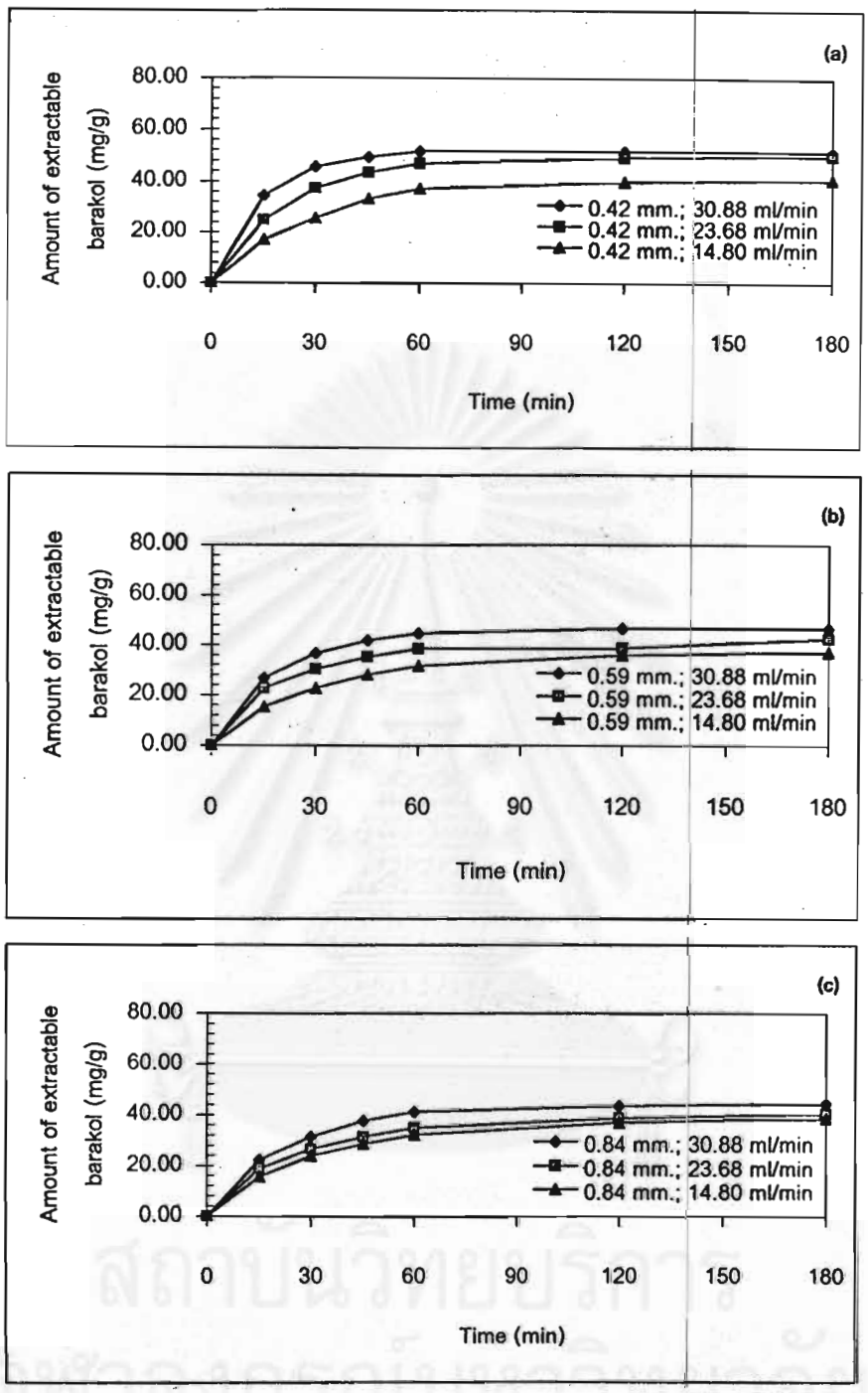


Figure 5.9 The extraction curve of barakol with various feed flow rates (a) 0.42 mm (b) 0.59 mm and (c) 0.84 mm for the downward direction of flow at room temperature.

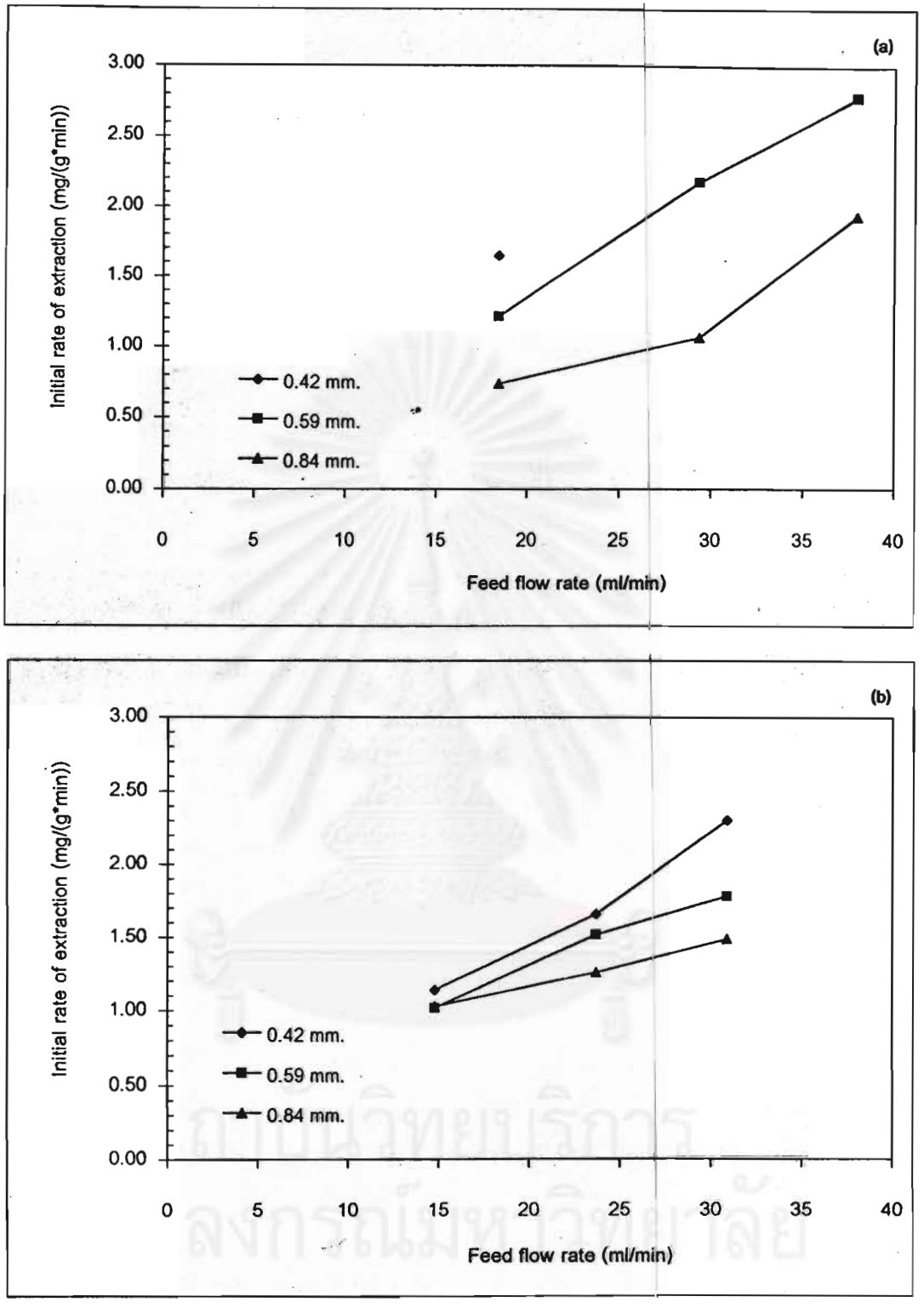


Figure 5.10 Effect of feed flow rate on initial rate of barakol extraction at room temperature

(a) upward direction of feed flow rate

(b) downward direction of feed flow rate

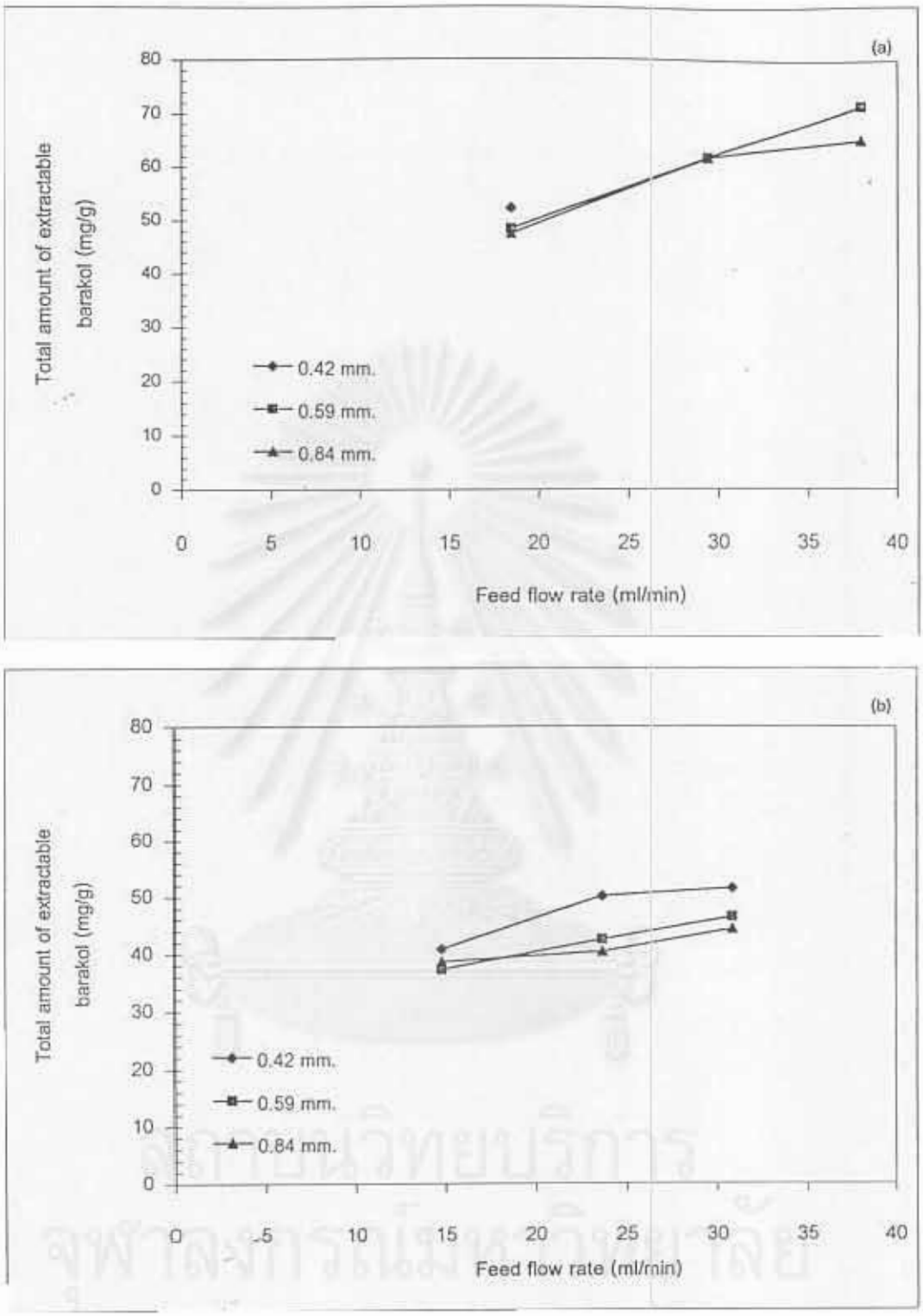


Figure 5.11 Effect of feed flow rate on total amount of barakol extraction at room temperature

(a) upward direction of feed flow rate

(b) downward direction of feed flow rate

5.4 Effect of ratio of solid to solvent (W/V) on barakol extraction

To study the effect of solid to solvent (W/V) ratio on barakol extraction a series of experiments with a feed flow rate of 37.96 ml/min and a particle size of 0.59 mm. with a recycle of feed solution were undertaken at three ratios of solid to solvent (W/V) of 1:33.33, 1:50 and 1:60 (W/V).

Figure 5.12 presents the barakol extraction curve at various solid to solvent ratios (W/V). From Figure 5.12 it was found that the barakol extraction process might stop after 180 minutes. The amount of barakol extraction at 180 minutes were 38.02, 43.49 and 56.75 mg/g of dried *Cassia siamea* powder respectively for this set of conditions. This phenomenon may be described that the bulk concentration and the concentration of extractive substance at surface are clearly equilibrium values. The total amount of extractable barakol during extraction time is shown in Figure 5.13. The total amount of extractable barakol were 37.35, 45.11 and 56.27 mg/g of dried *Cassia siamea* powder, respectively. It was found that the total amount of extractable barakol during the extraction time increased with a reduction in the ratio of solid to solvent. In other words, the volume of solvent increased whereas the weight of solid was constant. It can be described that increasing volume flow rate of feed solution extended concentration equilibrium. In other words, the concentration between bulk of the liquid and the surface of solid was high enough to allow extraction to continue. Until the concentration gradient between bulk and solid becomes zero, the content of extractable substance remains almost constant.

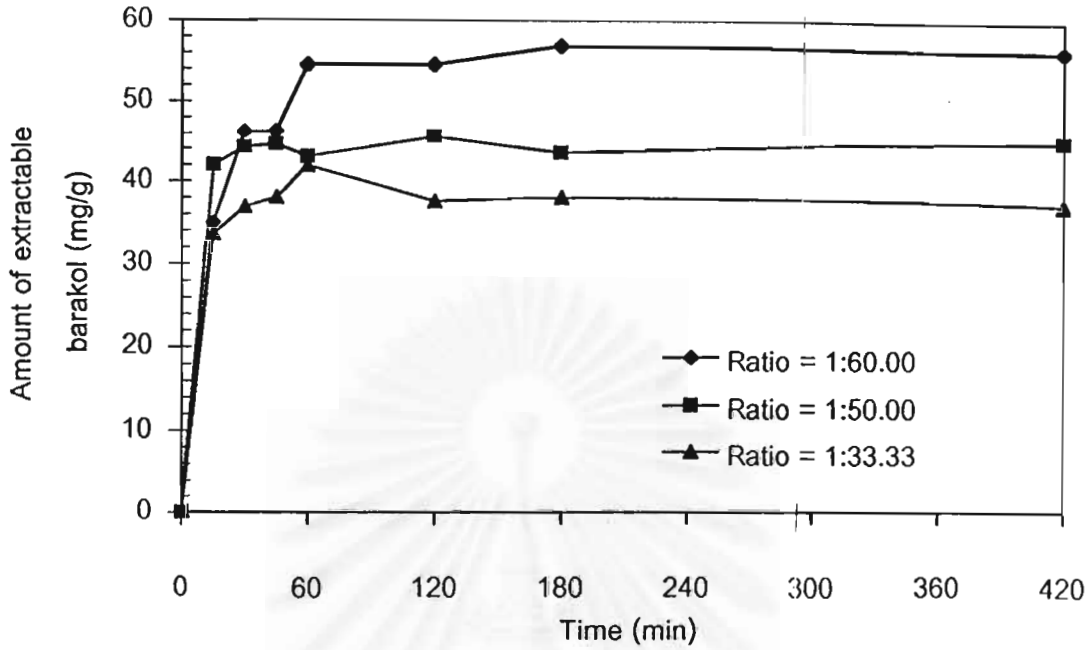


Figure 5.12 Extraction curve of barakol at feed flow rate of 37.96 ml/min and particle size of 0.59 mm. with recycle system

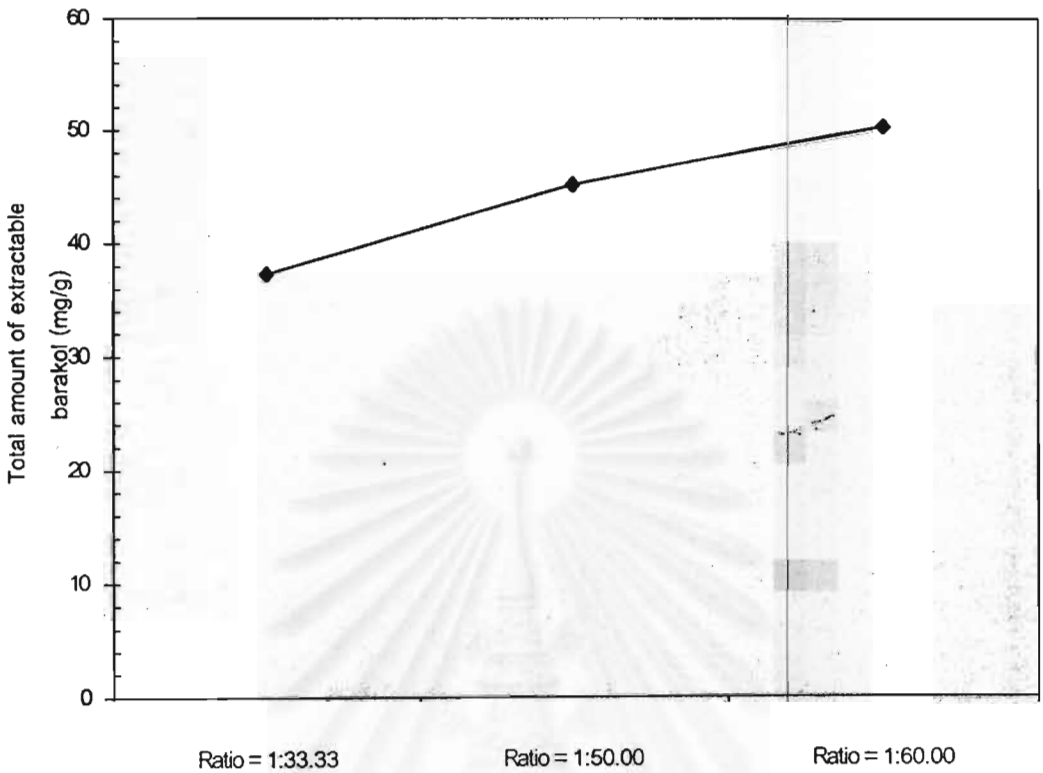


Figure 5.13 Effect of solid to solvent ratio (W/V) on content of extractable barakol during extraction time

5.5 Comparison between barakol extraction yield with recycle and without recycle

To compare the yield of barakol extraction with and without recycle this study was carried out at 37.96 ml/min of solvent flow rate with a particle size 0.59 mm. both with and without recycle at three solid to solvent ratios.

Figure 5.14 shows the total amount of extractable barakol. It is clearly shown that the barakol extraction without recycle gives a higher total amount of extractable barakol. Fresh solvent contacted the surface of solid during extraction time in the case of extraction without recycle. As a result, in that case the concentration gradient was higher than extraction with recycle during which the concentration gradient declines continuously during extraction time. Thus, extraction time with recycle was extended to obtain comparable yields from extraction without recycle. Consequently, this extraction consumes higher energy than extraction without recycle. Nevertheless, extraction without recycle uses higher volumes of solvent than extraction with recycle.

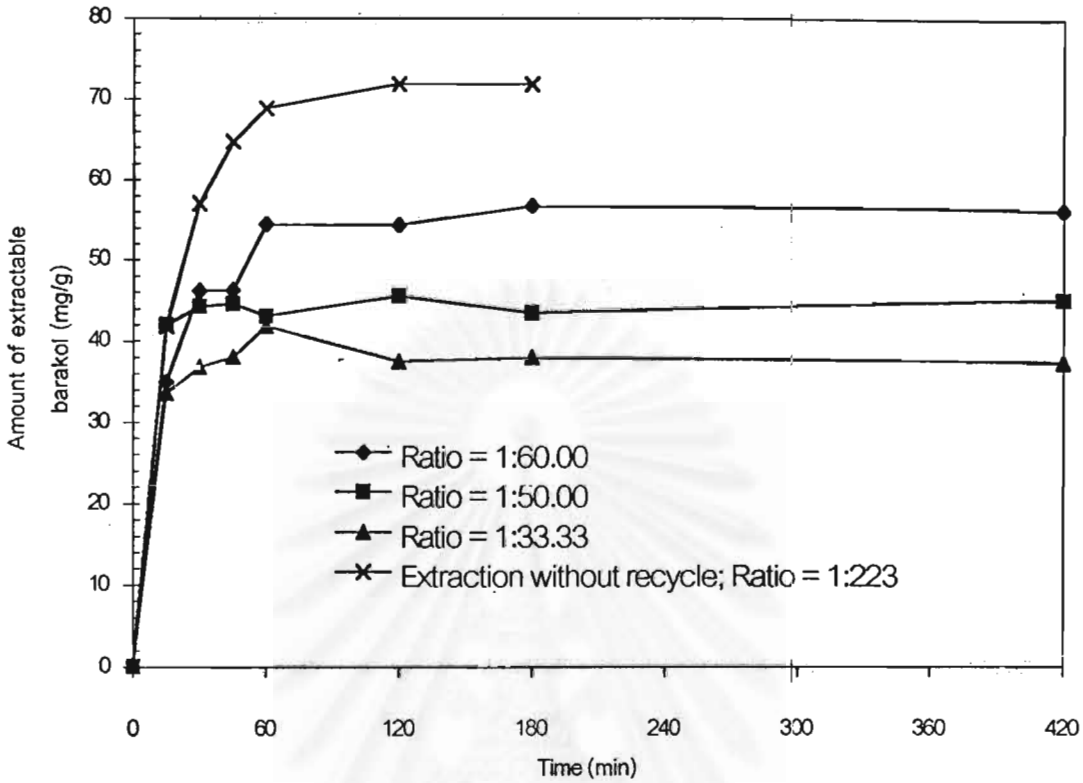


Figure 5.14 Comparison of yield of barakol extraction between extraction with recycle and without recycle

5.6 Determination of the mass transfer coefficient of barakol in 15%(V/V) ethanol solution

From Figures 5.4 and 5.5, it is believed that the controlling mechanism of the first period of barakol extraction is convection. Thus the determination of the mass transfer coefficient of barakol was performed using the convective mass transfer as illustrated in Equation 5.5)

$$N_A = V\frac{dc_A}{dt} = k_c(c_{AS} - c_A)$$

The time t taken for the concentration of the solution to rise from its initial value c_{A0} to value c_A is found by integration, on the assumption that both b and a remain constant.

$$\ln\frac{c_{AS} - c_{A0}}{c_{AS} \quad c} = \frac{k\ a}{Vb}t$$

If pure solvent is used initially, $c_{A0}=0$

and where k : a overall mass transfer coefficient (min^{-1})

c_A the concentration of A in the solution at time t (g/cm^3)

c_{AS} : the concentration of the saturated solution in contact with the particles (g/cm^3)

a : surface area of particles (cm^2)

b : the effective thickness of the liquid film surrounding the particles (cm)

V : total volume of solution (cm^3)

The relationship between $\ln\frac{c_{AS}}{c_{AS} \quad c}$ and time was plotted to determine the slope of the curve in order to calculate the mass transfer coefficient according to Equation 5.6) as illustrated in Figure 5.15

$$\text{Slope} = \frac{ka}{Vb}$$

Experimentally, the values of a and b are difficult to measure. Therefore the value of the mass transfer coefficient includes the values a and b. Figure 5.16 shows calculated mass transfer coefficients. The mass transfer coefficient of barakol extraction for all size of particle is illustrated in Table 5.5. It clearly shows that an increase of feed flow rate increases the mass transfer coefficient. Our experiment results are in accordance with the results of Christi [1995] that the mass transfer coefficient is a function of the system geometry, fluid properties and feed velocies.

Table 5.5 The calculated mass transfer coefficient for an upward direction of feed solution

Upward direction		
Particle size (mm.)	Slope of linear from Figure 1	Mass transfer coefficient (cm/min)
Feed flow rate = 18.44 ml/min		
0.84	0.0143	*3.56*
0.59	0.0166	*4.38*
0.42	0.0236	*6.07*
Feed flow rate = 29.36 ml/min		
0.84	0.0105	*4.07*
0.59	0.0267	*11.24*
0.42	-	-
Feed flow rate = 37.96 ml/min		
0.84	0.0235	*13.14*
0.59	0.0271	*14.88*
0.42	-	-

Table 5.5 The calculated mass transfer coefficient for a downward direction of feed solution

Downward direction		
Particle size (mm.)	Slope of linear from Figure 1	Mass transfer coefficient (cm/min)
Feed flow rate = 14.80 ml/min		
0.84	0.0211	*4.59*
0.59	0.0269	*5.76*
0.42	0.0217	*4.45*
Feed flow rate = 23.68 ml/min		
0.84	0.0261	*9.31*
0.59	0.0255	*8.61*
0.42	0.0248	*8.44*
Feed flow rate = 30.88 ml/min		
0.84	0.0240	*10.63*
0.59	0.0259	*11.15*
0.42	0.0279	*12.62*

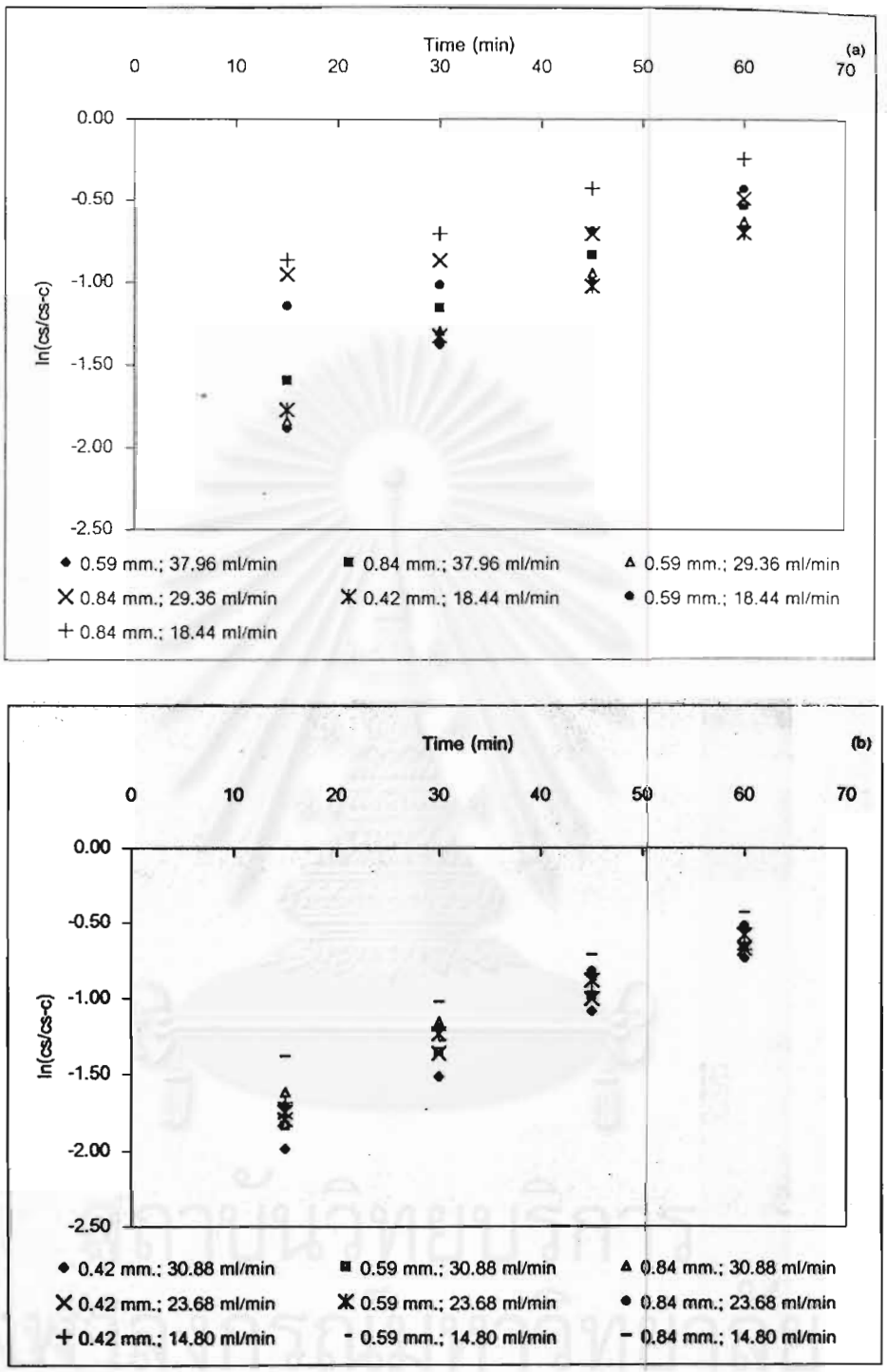


Figure 5.15 Plot of linearized data according to Equation 5.7 (a) an upward direction of flow and (b) a downward direction of flow

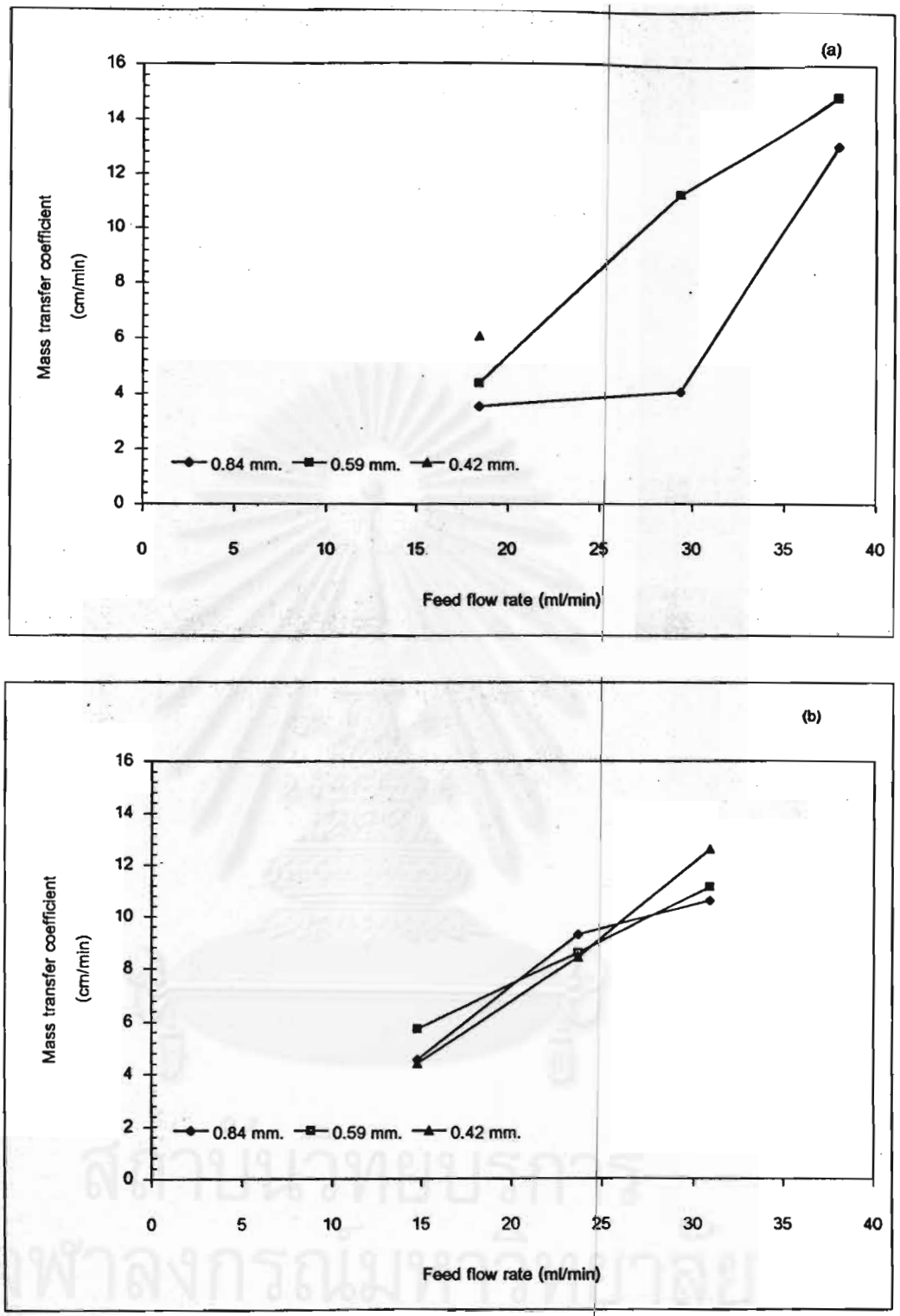


Figure 5.16 Calculated mass transfer coefficient for barakol extraction at room temperature for (a) an upward direction of flow and (b) a downward direction of flow

5.7 Determination of effective diffusivity of barakol in 15%(V/V) ethanol

Extraction from food and pharmaceutical product is controlled by internal diffusion according to Schwartzberg et al. [1982] and Sionero et al. [1996] who pointed out that the mechanism of polyphenol extraction from sunflower press cake, into a 96%(V/V) ethanol solvent, in a semicontinuous pulsed-flow-immersion extractor and in a conventional immersion extractor depends to a large degree on internal diffusion.

Barakol extraction from *Cassia siamea* leaves is believed to be controlled by internal diffusion as solid internal structure contains pores, or interconnected void space. For this situation, the void are filled with solvent as 15%(V/V) ethanol, the concentration of barakol at boundary $\pm l; c = 0$ and at $-l < x < +l; c = c_A$. The barakol diffusing through the solvent in the void volume takes a tortuous path determined by the tortuosity factor τ, as presented in section 5.3.

The determination of effective diffusivity of barakol extraction which is controlled by internal diffusion was performed using the diffusion equation [Sionero et al.; 1996]

$$D_{eff}\frac{\partial^2 C}{\partial^2 x} = \frac{\partial C}{\partial t} \qquad 5.8)$$

It can be assumed that the process is the same as that for an arbitrary meal laminate.

Where D_{eff} = effective diffusivity = $\frac{\varepsilon}{\tau} D_{AB}$

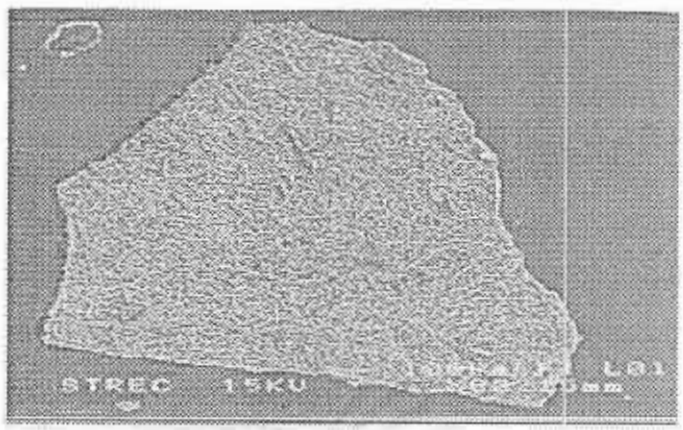
C = barakol concentration in the laminate (mg/g inert solid)

Boundary conditions employed are:

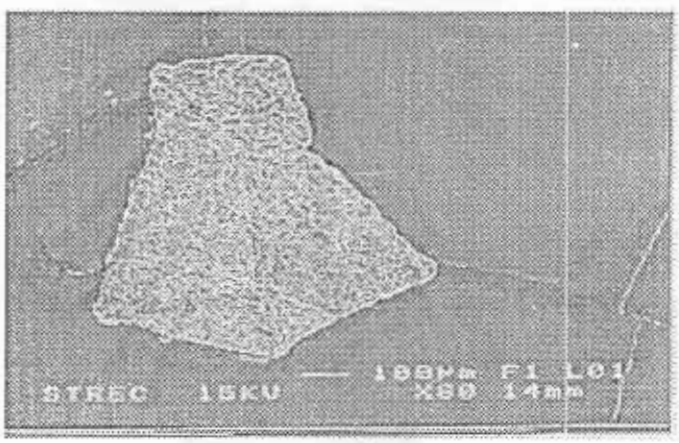
$C = 0 \qquad X = \pm l \qquad t \geq 0$

$C = C_0 \qquad -l < X < l \qquad t = 0$, with $2l$ being the laminate thickness as shown in Figure 5.16.

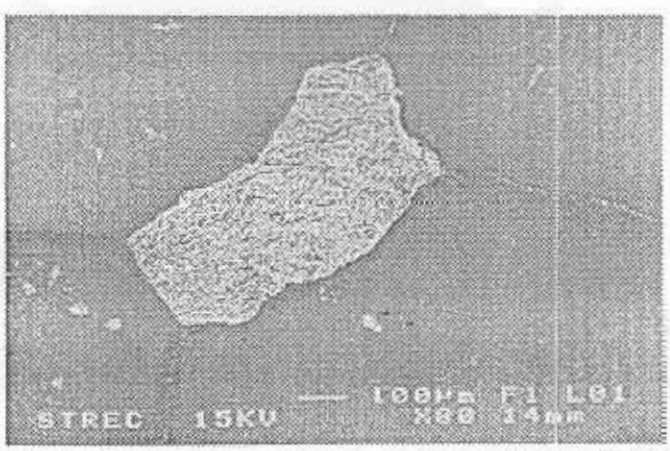
the solution of equation 5.8) can be obtained using by the method of separation of variables to obtain equation 5.6)



(a)



(b)



(c)

Figure 5.17 SEM study of *Cassia siamea* powder at various mean particle size (a) 0.84 mm (b) 0.59 mm and (c) 0.42 mm

$$\gamma = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\cdot e^{-\left(\frac{(2n+1)^2\pi^2 D_{eff}\cdot t}{4l^2}\right)}$$

Where $\gamma = \frac{c}{c_0}$ = the fraction of unextracted barakol

It is generally assumed that for Fourier number $\left(\frac{\pi^2 D_{eff}}{4l^2}\right) >> 0.1$ only the first term of the series becomes significant. When this condition is attained, the effective diffusivity can be calculated by plotting $\ln(Y)$ against time (t). A linear behavior must be observed, according to

$$\ln(\gamma) \quad \ln\left(\frac{8}{\pi^2}\right) \quad \frac{\pi^2 D_{eff}}{4l^2}\cdot t \qquad 5.10)$$

In Figures 5.17 and 5.18, the residual barakol content vs. extraction time was plotted. It was found discovered that the residual barakol content is reduced with increasing time. In the first period, unextractable barakol fraction greatly declines and in the final period, the curves of extractable barakol fraction remains constant in all cases.

The relationship between $\ln(\gamma)$ and time (t) were plotted to determine the slope of the curve in order to calculate the effective diffusivity according to equation 5.11) as shown in Figures 5.19

$$slope \quad \frac{\pi^2 D_{eff}}{4l^2}$$

Theoretically the effective diffusivities should be constant for a specific substance at a constant temperature. The temperature for these experiments was room temperature so that the effective diffusivities should be approximately constant. The effective diffusivity for barakol extraction for all size of particle was illustrated in Table 5.6 and the average effective diffusivity of barakol in 15% ethanol solution (V/V) was $8.16*10^{-11}$ m^2/s.

Table 5.6 The calculated effective diffusivities for an upward direction of feed solution

Upward direction		
Particle size (mm.)	Slope of linear from Figure 5.19	Effective diffusivity (m^2/s)
Feed flow rate = 18.44 ml/min		
0.84	-0.0191	$7.17*10^{-11}$
0.59	-0.0203	$7.62*10^{-11}$
0.42	-0.0259	$9.72*10^{-11}$
Feed flow rate = 29.36 ml/min		
0.84	-0.0263	$9.88*10^{-11}$
0.59	-0.0210	$7.88*10^{-11}$
0.42	-	-
Feed flow rate = 37.96 ml/min		
0.84	-0.0207	$7.77*10^{-11}$
0.59	-0.0178	$6.68*10^{-11}$
0.42	-	-

Table 5.6 The calculated effective diffusivities for a downward direction of feed solution

Downward direction		
Particle size (mm.)	Slope of linear from Figure 5.19	Effective diffusivity (m^2/s)
Feed flow rate = 14.80 ml/min		
0.84	-0.0214	$8.03*10^{-11}$
0.59	-0.0248	$9.31*10^{-11}$
0.42	-0.0234	$8.78*10^{-11}$
Feed flow rate = 23.68 ml/min		
0.84	-0.0213	$8.00*10^{-11}$
0.59	-0.0249	$9.35*10^{-11}$
0.42	-0.0218	$8.19*10^{-11}$
Feed flow rate = 30.88 ml/min		
0.84	-0.0154	$5.78*10^{-11}$
0.59	-	-
0.42	-	-

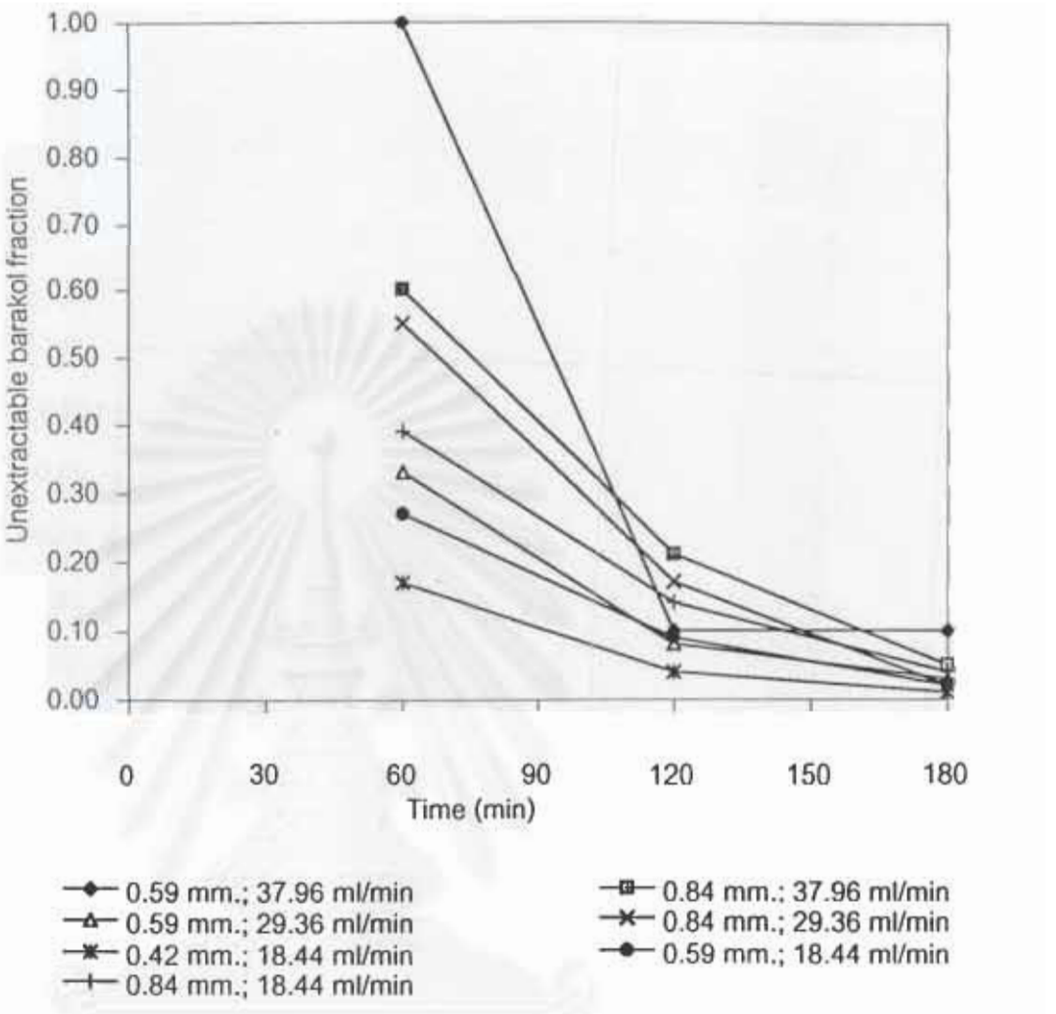


Figure 5.18 Residual content of barakol in the inert solid with an upward direction of flow

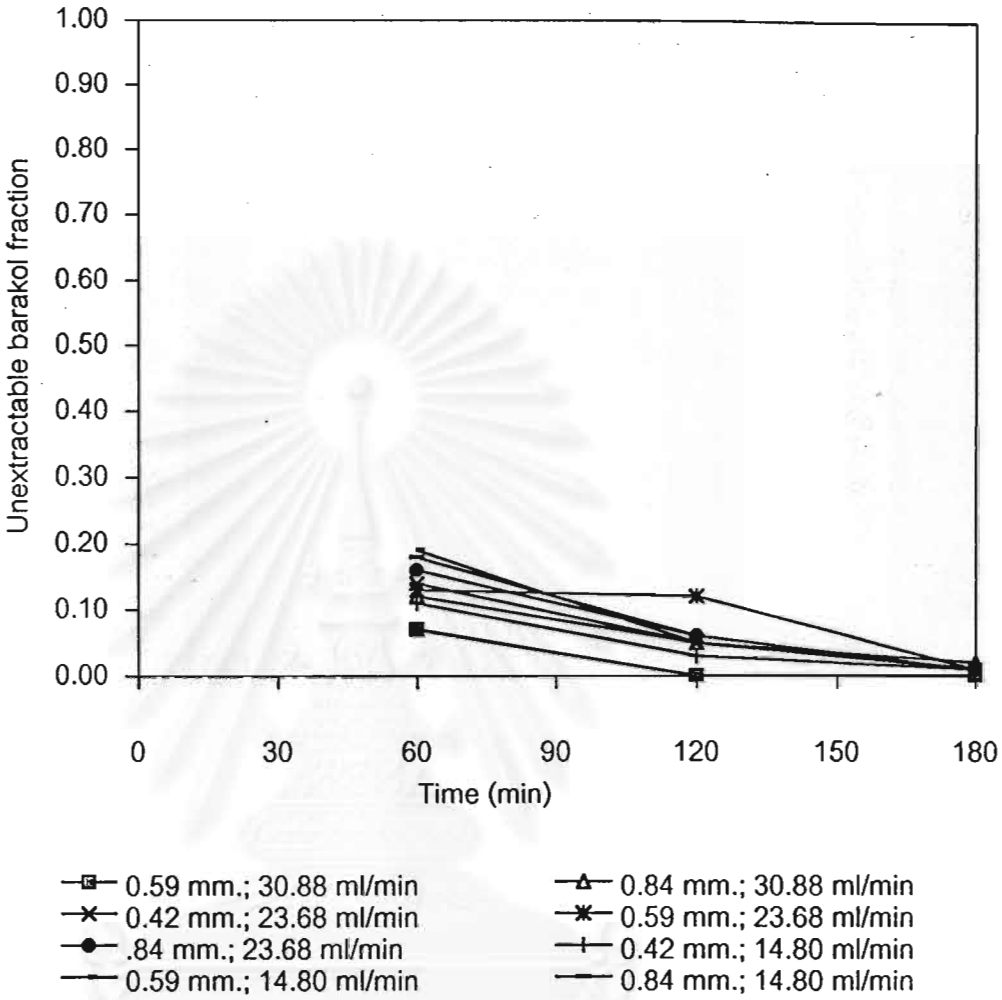


Figure 5.19 Residual content of barakol in the inert solid with a downward direction of flow

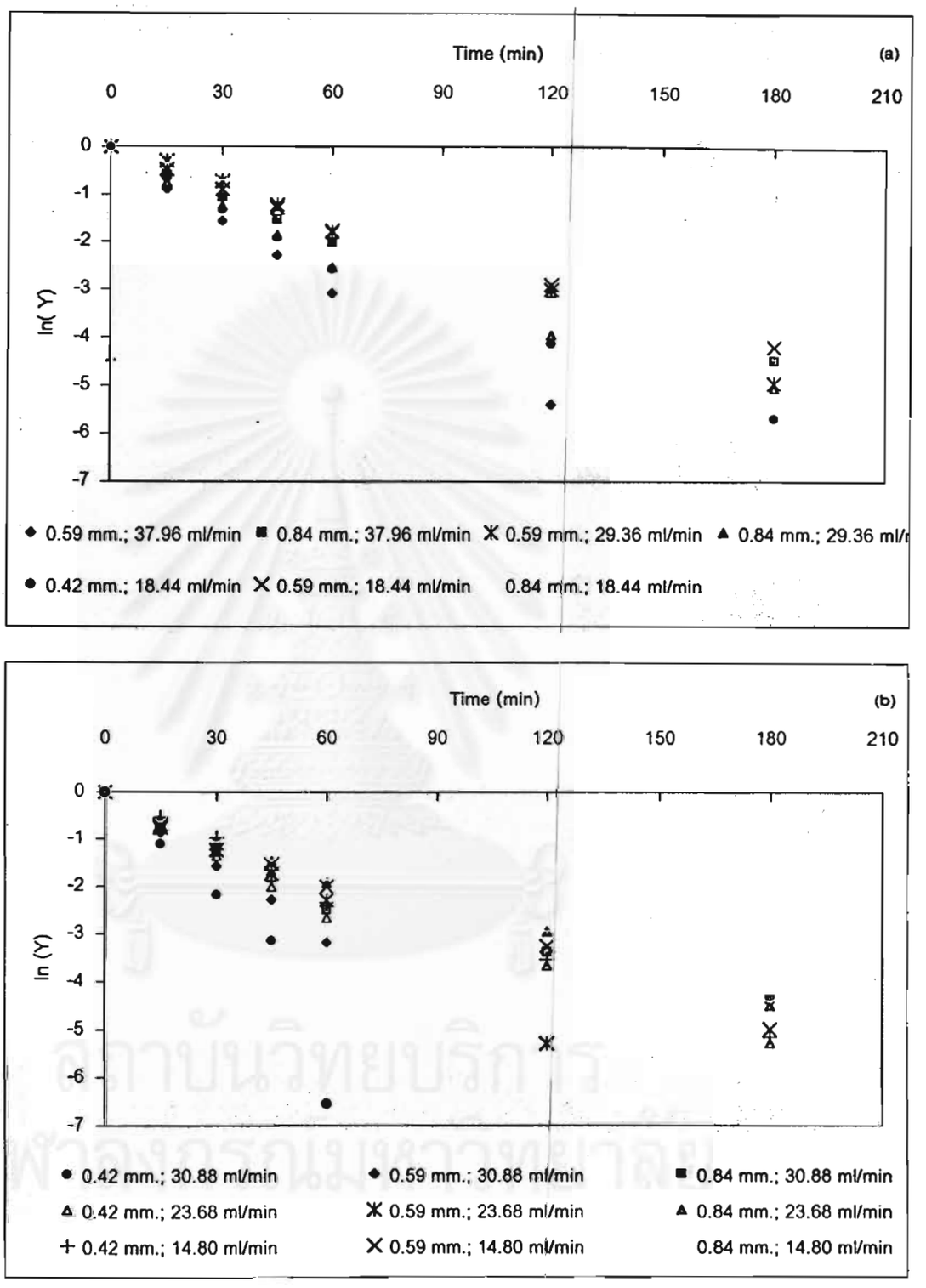


Figure 5.20 Plot of linearized data according to Equation 5.8 for barakol extraction (a) an upward direction of flow and (b) a downward direction of flow

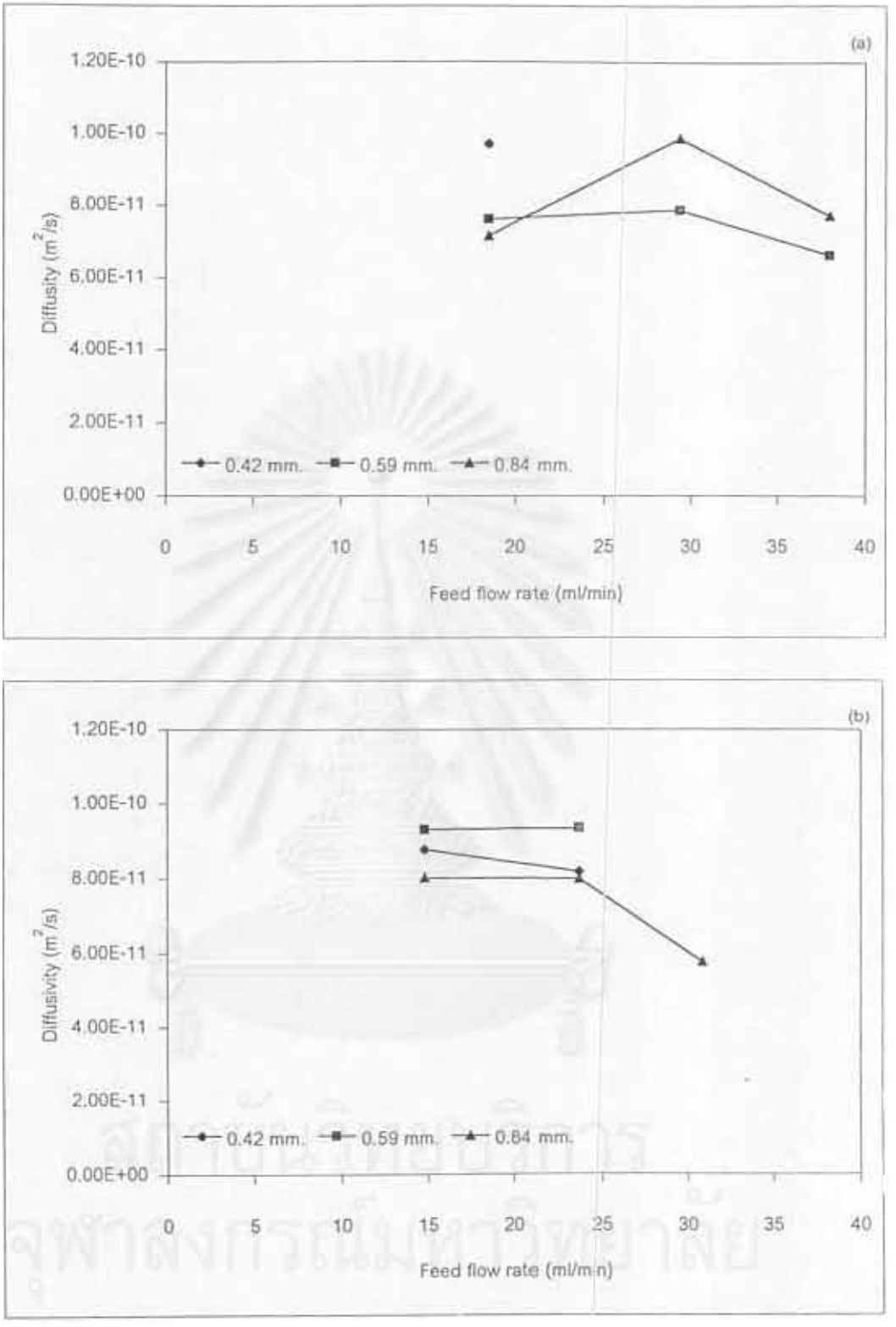


Figure 5.21 Calculated effective diffusivity for barakol extraction at room temperature for (a) an upward direction of flow and (b) a downward direction of flow

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This chapter presents the conclusions of this study and the recommendations.

6.1 Conclusions

1. At room temperature, the percentage of decompositiion of crude barakol was nil, but at temperatures over 40 °C, the percentage of decomposition of crude barakol increases dramatically.
2. In this study, the most suitable conditions for barakol extraction in a packed bed extractor was found to be the extraction from particles with an average size of 0.59 mm and a solvent flow rate of 37.96 ml/min. The total amount of extractable barakol was 71.80 mg/ g of dried *Cassia siamea* leaves. For this particular experiment an upward direction of feed solution was used.
3. It is believed that the controlling mechanism of the first period of barakol extraction was convection, during which a major part of barakol is removed by simple washing out of barakol from the solid surface to the solvent. The second phase of the extraction, which occurs after about 60 minutes into the extraction, is believed to be controlled by internal diffusion; the remaining barakol is extracted by diffusion of barakol within the solid to the solvent.
4. The reduction of particle size enhances the surface area for extraction and it is believed that the initial rate of barakol extraction increases with decreased particle size. Total amount of extractable barakol also increases with decreased particle size.
5. The increase of feed flow rate of solvent increases the initial rate of extraction of extractable barakol. Total amount of extractable barakol also increased with increases flow rate of solvent.
6. The total amount of extractable barakol increases with a decrease in the ratio of weight of solid per volume of solvent. The ratio of solid to solvent which

gives the highest extracted barakol was found to be 1:60, beyond this ratio the amount of extracted barakol is not significant.

7. The yield of barakol from extraction without recycle was higher than with a recycle stream. This is understandable however there is a cost associated with recovery of barakol from the solvent.
8. The mass transfer coefficient was found to be a function of feed flow rate. The experiments indicate that the mass transfer coefficient increases with increasing feed flow rate.
9. The average effective diffusivities of barakol in 15% ethanol solution was $8.16*10^{-11}$ m^2/s.

6.2 Recommendations

1. The set of optimum conditions for the extraction of barakol found in this study can be used for future extraction scale-ups.
2. A set of optimum conditions for the extraction of barakol could be developed for continuous extraction by having a no-recycle system for 30 minutes followed by a recycle system for the remainder of the experiment.

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APPENDICES

APPENDIX A

LIQUID-LIQUID CHROMATOGRAPHY

A-1 THE BASIC CHROMATOGRAPHIC PROCESS AND CLASSES OF CHROMATOGRAPHY

Chromatography has been classically defined as a process in which separation of substances is achieved by distributing them between two phases, a **mobile phase** and a **stationary phase**. The solute molecules will only migrate through the column while they are in the mobile phase; whereas when they are distributed in the stationary phase they will remain at rest. Thus, the more they are distributed in the mobile phase (the smaller the distribution coefficient with respect to the stationary phase), the faster they will migrate through the chromatographic system. Conversely, solutes that are mostly distributed in the stationary phase (the distribution coefficient of the solute with respect to the stationary phase is large) will be retained longer in the chromatographic system and thus move more slowly through it.

It should be clearly understood that chromatography is solely a separation process. The chromatographic system accepts a mixture of substances and retains them to different extents so that, ideally, they are eluted as individual components from the system. However, if the efluent from the chromatographic system is monitored by an appropriate detection device which responds to solute mass or concentration, the quantity of each component present in the original mixture can be determined, thus producing an analysis. The determination, however, can only be obtained with the aid of the detector; the chromatographic system can only achieve a separation.

The phases that are employed in the chromatographic system may take any of the three physical forms that are feasible. The mobile phase can be a gas or a liquid, the stationary phase can be a supported liquid or solid. Indeed, the physical form of the phases employed in the chromatographic system is used as a basis for the classification of the types of chromatography. As shown in Figure A-1, chromatography can be divided into two primary classes based on the physical nature of the mobile phase. In gas chromatography (GC) and liquid chromatography (LC) the mobile phases are a gas and liquid, respectively. Two further classes of chromatography arise from varying the physical nature of the

stationary phase. Employing a solid as the stationary phase gives rise to gas-solid chromatography (GSC) and liquid-solid chromatography (LSC). Conversely, employing a liquid as the stationary phase (usually contained on a suitable inactive support) gives rise to gas-liquid chromatography (GLC) and liquid-liquid chromatography (LLC).

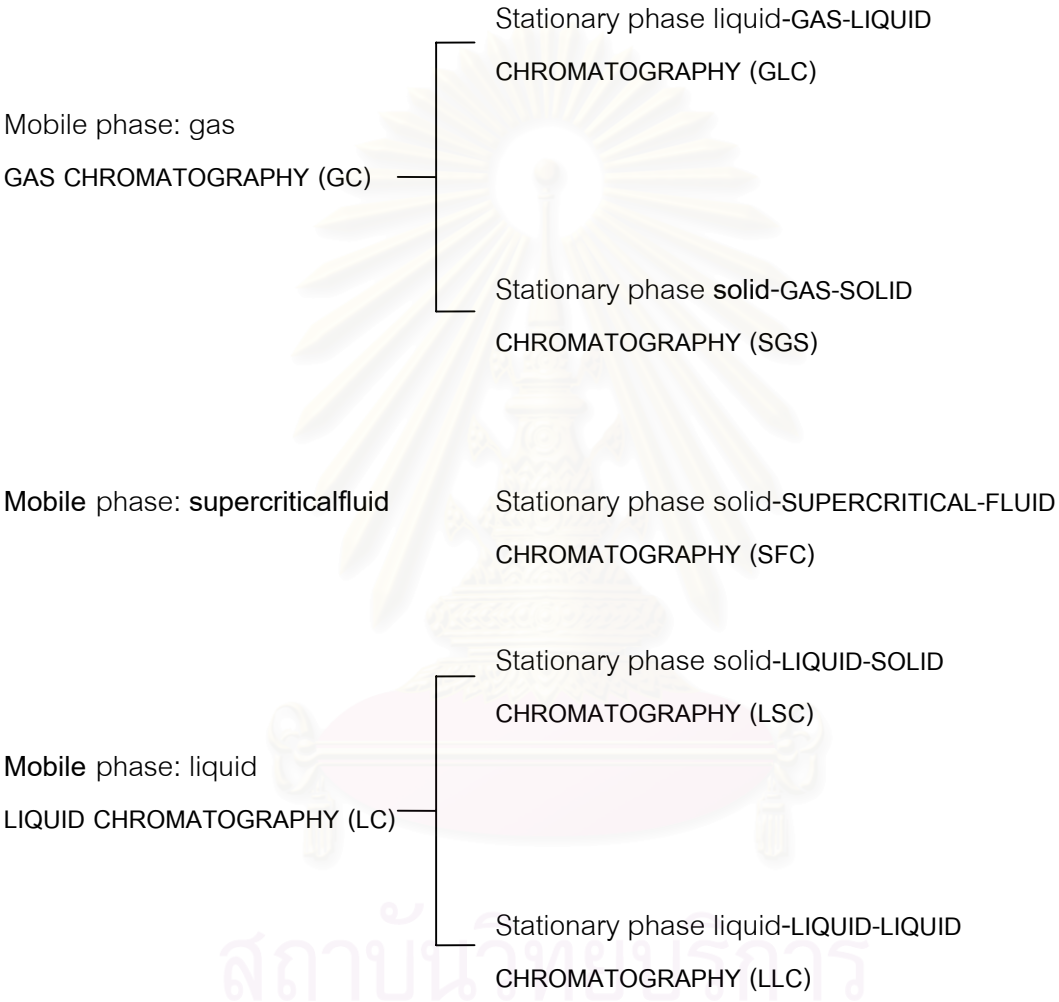

Figure A-1: Types of column chromatography. The type of mobile phase provides the chief basis for classification and the type of stationary phase a secondary basis. The names of the classes are given in uppercase letters and their standard acronyms in parentheses.

High-performance liquid chromatography, or liquid chromatography (LC) as it is more simply called, has developed into one of the premier analytical techniques. Its development came after gas chromatography. Liquid chromatography is similar to GC both in common underlying principles and basic instrumentation. Its unique characteristics arise from the distinctive properties of liquids-values of diffusion, viscosity, polarizability, and acidity are orders of magnitude different for liquids than for gases. As a consequence, in LC the mobile as well as the stationary phase can be used for differential interaction with the components of mixtures. The differences also greatly affect the design and construction of modules for LC. The situation can be summarized by stating that while the underlying principles of chromatography are similar for the two techniques, the manner in which they are reduced to practice follows very different lines. Or to put it more generally, LC is truly complementary to GC.

The modular layout of a liquid chromatograph is shown in Figure A-2. As the liquid phase is pumped to the column, a sample is introduced by an injection system just before the column. The mobile phase containing a thin plug of sample enters a narrow, cylindrical packed chromatographic column. As the plug moves through the column, sample components are separated, and on emerging, their presence is sensed by a detector. Processing modules establish the chromatogram of the sample, allowing the solutes to be tentatively identified on the basis of elution times (or elution volumes). The amount of each is determined from the height or area of its peak in the chromatogram.

To plan a separation by LC, the user must select both a type of column and a mobile phase appropriate to the analyses in the samples at hand. In addition, the user must identify a chromatographic system that will maintain the sharpness of analyse bands as a sample moves through the column to the detector. Both of these aspects will be taken up in the following sections on the types of LC and the basic modules and systems aspects of a liquid chromatograph.

LIQUID CHROMATOGRAPHIC SEPARATION OF COMPOUNDS

Separation in LC is achieved by means of differences in the interactions of the analytes with both the mobile and stationary phases. The mobile phase must be chosen to ensure solubility of the sample solutes. For the stationary phase, micro-particulate silica

(bare or chemically modified) is used almost universally because its high surface area accentuates the differences in solute stationary-phase interactions. The use of a stationary phase that interacts strongly with solutes relative to solute mobile-phase interactions will result in very long retention times, a situation which is not analytically useful. Hence, the stationary phase must be selected so as to provide weak to moderate solute interactions relative to those in the mobile phase. As a consequence, the nature of the sample governs the type of LC selected; the stronger interactions should occur in the mobile phase to ensure sample solubility and ready elution, while the stationary phase should be responsive to more subtle differences among the solutes. For example, polar neutral compounds are usually better analyzed using a polar mobile phase together with a nonpolar stationary phase that distinguishes subtle differences in the dispersive character of the solutes.

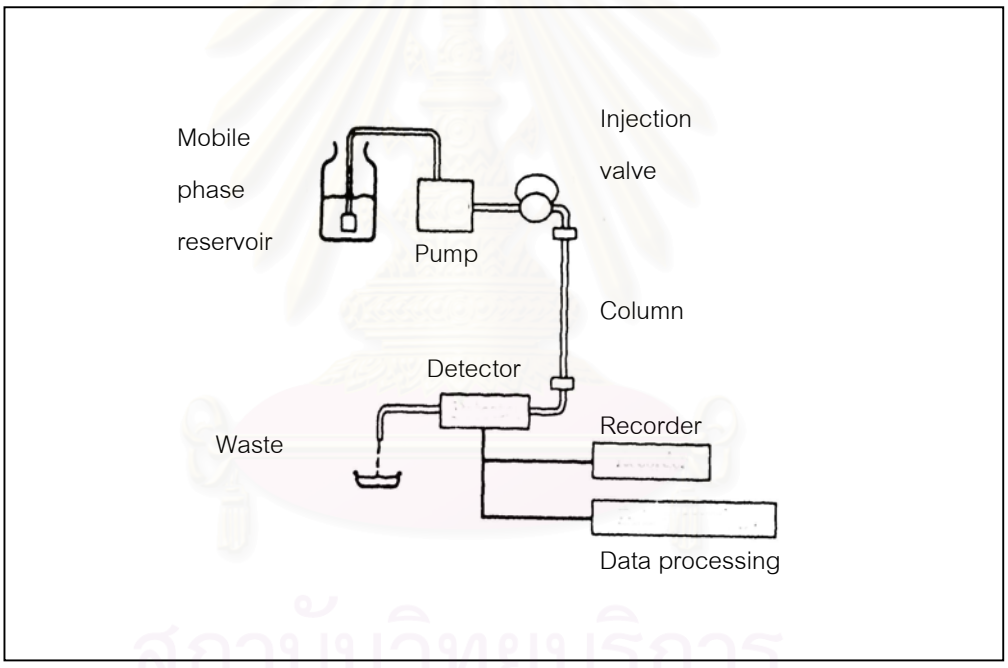

Figure A-2: Schematic diagram of the liquid chromatographic system

ANALYTICAL MEASUREMENTS

The process of identifying and determining analyses by LC begins with the choice of a type of chromatography and continues with the selection of an appropriate mobile phase-stationary phase combination.

Quantitative measurements require the determination of the response of the analytical system, that is, the slope of the plot of output signal (peak height or peak area)

against the amount of solute injected. This procedure is typically carried out using standards made up in the mobile phase. A similar procedure, but with the standards made up in the sample provides additional confirmation of peak retention time matching. The minimum detectable concentration or limit of detection is the concentration corresponding to a signal twice the baseline noise or better, three times the standard deviation of the noise, as has recently been recommended.

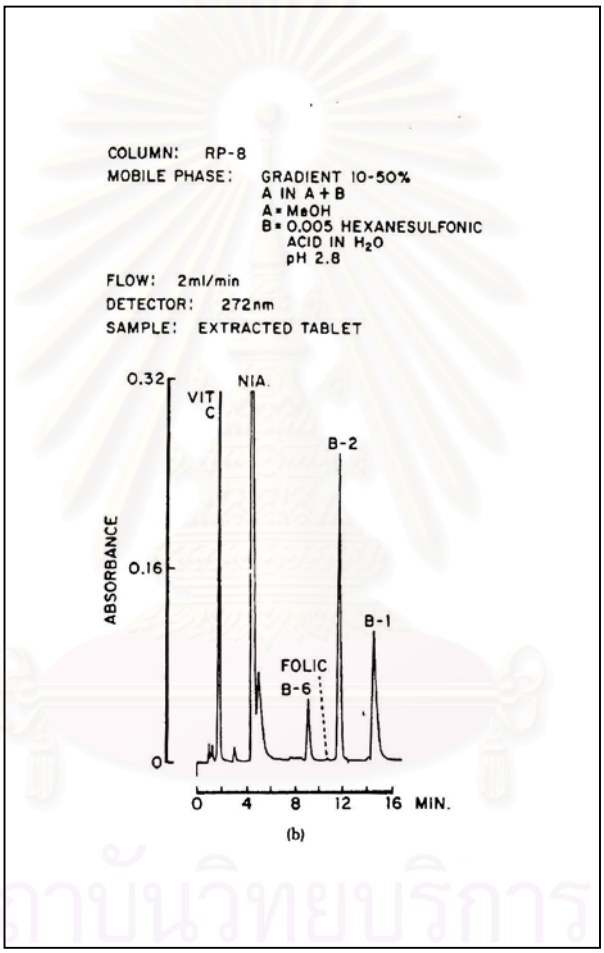

Figure A-3: Chromatogram of water-soluble vitamins on RP-8 column (C8 bonded-phase silica). Separation of tablet extract.

APPENDIX B
SOLUTION OF THE DIFFUSION EQUATION

The determination of the effective diffusivity of barakol extraction which is controlled by internal diffusion was performed starting from the diffusion equation [Sionero et al.; 1996]

$$D_{eff}\frac{\partial^2 C}{\partial^2 x}=\frac{\partial C}{\partial t} \qquad \text{B\_1)}$$

It can be assumed that the process is applicable for an arbitrary meal laminate.

Where D_{eff} = effective diffusivity = $\frac{\varepsilon}{\tau}D_{AB}$

c = barakol concentration as a function of x

C = average barakol concentration in the laminate (mg/g inert solid)

The following boundary conditions are used:

$c = 0 \qquad x = \pm l \qquad t \geq 0$

$c = C_0 \qquad -l < x < l \qquad t = 0$, with $2l$ being the laminate thickness.

The solution of equation B_1) using the method separation variables is as follows

If we write

$$C = X(x)T(t)$$

We find that

$$\frac{1}{X}\frac{d^2X}{dx^2}=\frac{1}{D_{eff}T}\frac{dT}{dt} \qquad \text{B\_2)}$$

The left hand side of B_2) is wholly a function of x while the right hand side is wholly a function of t. Therefore this is only possible if both term are exactly equal to a constant. The solution of the resulting ordinary differential equations yield

$$T = K_1 e^{-a^2 D_{eff} t} \qquad a^2 \neq 0 \qquad \text{B\_3)}$$

$$X = K_2 \cos ax + K_3 \sin ax \qquad a^2 \neq 0 \qquad \text{B\_4)}$$

$$T = K_4 \qquad a^2 = 0 \qquad \text{B\_5)}$$

$$X = K_5 + K_6 x \qquad a^2 = 0 \qquad \text{B\_6)}$$

The general form of the solution is as follows

$$C = K_7 + K_8 x + (e^{-a^2 D_{eff} t})(K_9 \cos ax + K_{10} \sin ax) \qquad \text{B\_7)}$$

We use the boundary conditions to evaluate some constants.

$$C = Ae^{-a^2 D_{eff} t}\cos ax \qquad \text{B\_8)}$$

When $a = \frac{\pi}{l}(2n+1)$

Therefore equation B_8) becomes

$$C = Ae^{-\frac{\pi^2}{l^2}(2n+1)D_{eff}t}\cos\frac{\pi}{l}(2n+1)x \qquad \text{B\_9)}$$

In order to calculate A we revert to the following statement

$$C = \sum_{n=0}^{n=\infty} A_n\left[e^{-\frac{\pi^2}{l^2}(2n+1)^2 D_{eff}t}\cos\frac{\pi}{l}(2n+1)x\right] \qquad \text{B\_10)}$$

The determination of A_n takes some mathematical manipulations to obtain equation

$$A_n = (-1)^n\frac{4}{\pi(2n+1)} \qquad \text{B\_11)}$$

so that

$$C = \frac{4}{\pi}\sum_{n=0}^{n=\infty}\frac{(-1)^n}{2n+1}e^{-\frac{(2n+1)^2\pi^2 D_{eff}t}{l^2}}\cos\frac{(2n+1)\pi x}{l} \qquad \text{B\_12)}$$

From boundary condition $-l < x < l$ with constant initial concentration C_0, changing the original B_12) to the mid –point of the slab and replacing $\frac{l}{2}$ by l gives

$$C = \frac{4C_0}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)}e^{-\left(\frac{(2n+1)^2\pi^2 D_{eff}t}{4l^2}\right)}\cos\frac{(2n+1)\pi x}{2l} \qquad \text{B\_13)}$$

Some numerical results for this problem can be solved to obtain the average concentration c_{av} in the slab at time t is

$$C_{av} = \frac{8C_0}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{-\left(\frac{(2n+1)^2\pi^2 D_{eff}t}{4l^2}\right)} \qquad \text{B\_14)}$$

Where $Y = \frac{C_{av}}{C_0}$

$$Y = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}e^{-\left(\frac{(2n+1)^2\pi^2 D_{eff}t}{4l^2}\right)} \qquad \text{B\_15)}$$

APPENDIX C

STANDARD CURVE OF BARAKOL SOLUTION

Standard barakol solution preparation

1. 0.0005 g of standard barakol dissolved in 10 ml 15% (V/V) ethanol.
2. Mix well and dilute standard barakol from Item 1 by sucking 4 ml., 2 ml. and 1 ml. of Item 1 with pipettes into 10 ml volumetric flasks, respectively.
3. Adjust volume to 10 ml with 15% (V/V) ethanol foe each known concentration solution.
4. The known concentration solutions are analysed by HPLC
5. Read peak area from chromatogram and plot graph between peak area and known concentration solution.

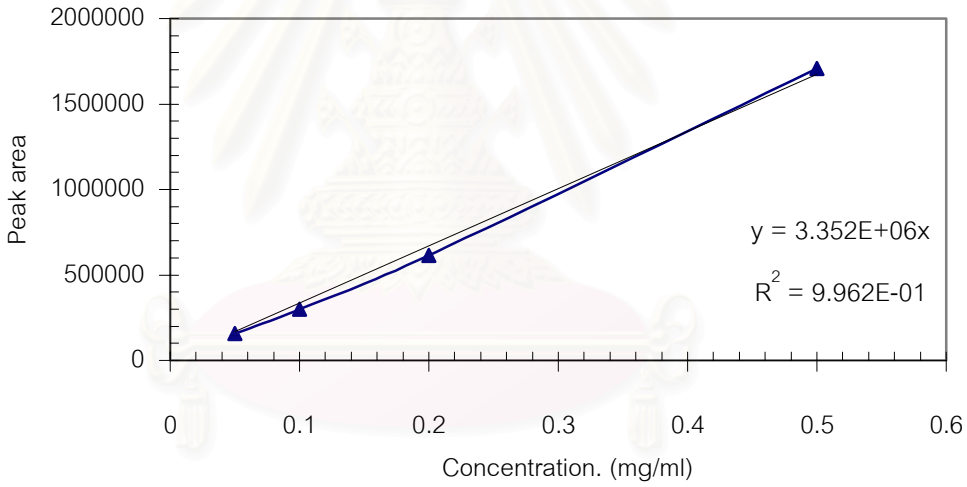

Figure C-1: Standard curve of barakol solution

APEENDIX D

EXPERIMENTAL DATA

Table D-1: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.84 mm

Feed flow rate = 14.80 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
728003	15	2.17	214	15.49	0.61	-0.49
384377	30	1.15	218	23.83	0.40	-0.91
227645	45	0.68	216	28.72	0.28	-1.28
157828	60	0.47	222	32.20	0.19	-1.66
53021	120	0.16	887	36.88	0.07	-2.61
20601	180	0.06	895	38.71	0.03	-3.60
18221	240	0.05	300			
			2952			

Table D-2: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.59 mm

Feed flow rate = 14.80 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
1153671	15	3.44	184	21.11	0.53	-0.64
449398	30	1.34	220	30.94	0.31	-1.17
219851	45	0.66	228	35.93	0.20	-1.61
155963	60	0.47	225	39.42	0.12	-2.10
40532	120	0.12	902	43.06	0.04	-3.20
14427	180	0.04	897	44.34	0.01	-4.40
9220	240	0.03	300			
			2956			

Table D-3: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.42 mm

Feed flow rate = 14.80 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
782216	15	2.91	176	17.08	0.58	-0.54
327373	30	1.22	214	25.77	0.37	-0.98
278456	45	1.04	215	33.19	0.19	-1.65
148255	60	0.55	215	37.14	0.10	-2.34
24108	120	0.09	927	39.92	0.03	-3.53
8272	180	0.03	942	40.88	0.01	-5.14
6458	-	0.02	300			
			2689			

Table D-4: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.84 mm

Feed flow rate = 23.68 ml/min

No Recycle

Area	Time	concentration (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
593462	15	1.77	320	18.89	0.54	-0.62
215320	30	0.64	365	26.70	0.35	-1.06
127634	45	0.38	370	31.40	0.23	-1.46
93142	60	0.28	372	34.85	0.15	-1.92
25515	120	0.08	1517	38.70	0.05	-2.94
11522	180	0.03	1482	40.39	0.01	-4.48
15512	-	0.05	300			
			4426			

Table D-5: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.59 mm

Feed flow rate = 23.68 ml/min

No Recycle

Area	Time	concentration (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
728455	15	2.06	332	22.80	0.47	-0.76
233924	30	0.66	338	30.26	0.29	-1.23
153566	45	0.43	339	35.16	0.18	-1.73
99767	60	0.28	342	38.38	0.10	-2.28
2847	120	0.01	1398	38.76	0.09	-2.37
28505	180	0.08	1411	42.55	0.01	-5.27
7797	-	0.02	300			
			4160			

Table D-6: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.42 mm

Feed flow rate = 23.68 ml/min

No Recycle

Area	Time	concentration (mg/ml)	Vol	content ($mg_{barako}l/g_{powder}$)	unextractable fraction	ln(Y)
659457	15	2.45	305	24.95	0.51	-0.68
287244	30	1.07	348	37.35	0.26	-1.35
143542	45	0.53	352	43.61	0.14	-2.00
74610	60	0.28	357	46.92	0.07	-2.66
12189	120	0.05	1479	49.15	0.03	-3.65
5779	180	0.02	1459	50.20	0.01	-5.26
7020	-	0.03	300			
			4300			

Table D-7: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.84 mm

Feed flow rate = 30.88 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
442657	15	1.56	430	22.40	0.50	-0.69
175227	30	0.62	445	31.57	0.30	-1.21
113670	45	0.40	460	37.72	0.16	-1.82
69356	60	0.24	437	41.29	0.08	-2.49
10154	120	0.04	1825	43.47	0.03	-3.37
5370	180	0.02	1530	44.43	0.01	-4.34
16649	-	0.06	300			
			5127			

Table D-8: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.59 mm

Feed flow rate = 30.88 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
541430	15	1.91	420	26.76	0.42	-0.86
192878	30	0.68	439	36.72	0.21	-1.56
98847	45	0.35	428	41.70	0.10	-2.27
55692	60	0.20	435	44.55	0.04	-3.16
9490	120	0.03	1772	46.52	0.00	-
0	180	0.00	1776	46.52	0.00	-
0	-	0.00	300			
			5270			

Table D-9: Experimental data of barakol extraction

Condition : Downward direction

Size = 0.42 mm

Feed flow rate = 30.88 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
808760	15	2.29	452	34.47	0.33	-1.10
272407	30	0.77	438	45.72	0.11	-2.17
84758	45	0.24	457	49.37	0.04	-3.13
49904	60	0.14	462	51.54	0.00	-6.55
0	120	0.00	1821	51.54	0.00	-6.55
0	180	0.00	1922	51.54	0.00	-6.55
2597	-	0.01	300			
			5552			

Table D-10: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.84 mm

Feed flow rate = 18.44 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
396871	15	1.54	215	11.04	0.78	-0.25
321102	30	1.25	264.5	22.03	0.55	-0.60
190945	45	0.74	259	28.43	0.42	-0.86
182018	60	0.71	259	34.53	0.30	-1.21
66580	120	0.26	1065	43.70	0.11	-2.21
28654	180	0.11	1062	47.64	0.03	-3.51
37804	-	0.15	300			
			3124.5			

Table D-11: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.59 mm

Feed flow rate = 18.44 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
517291	15	2.40	229	18.34	0.63	-0.47
251390	30	1.17	276	29.09	0.41	-0.89
154055	45	0.72	278	35.72	0.28	-1.29
120873	60	0.56	273	40.83	0.17	-1.76
33060	120	0.15	1117	46.54	0.06	-2.89
12935	180	0.06	994	48.53	0.01	-4.20
15842	-	0.07	300			
			3167			

Table D-12: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.42 mm

Feed flow rate = 18.44 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
702695	15	3.26	228	24.81	0.53	-0.64
312143	30	1.45	286	38.63	0.27	-1.32
169705	45	0.79	236	44.83	0.15	-1.91
87799	60	0.41	279	48.62	0.08	-2.57
18040	120	0.08	1137	51.80	0.02	-4.13
3753	180	0.02	1152	52.47	0.00	-5.68
3882	-	0.02	300			
			3318			

Table D-13: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.84 mm

Feed flow rate = 29.36 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
301749	15	1.40	342	15.98	0.74	-0.30
268578	30	1.25	400	32.61	0.47	-0.75
197055	45	0.92	400	44.82	0.28	-1.29
128583	60	0.60	409	52.96	0.15	-1.93
28990	120	0.13	1388	59.19	0.04	-3.11
10677	180	0.05	1395	61.50	0.01	-4.93
9671	-	0.04	300			
			4334			

Table D-14: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.59 mm

Feed flow rate = 29.36 ml/min

No Recycle

Area	Time	Conc. (mg/ml)	Vol	Conc. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
558246	15	2.59	379	32.76	0.47	-0.75
173927	30	0.81	429	44.31	0.29	-1.25
119736	45	0.56	433	52.34	0.16	-1.85
69732	60	0.32	443	57.12	0.08	-2.53
13883	120	0.06	1737	60.86	0.02	-3.95
2890	180	0.01	1777	61.65	0.01	-5.05
8602	-	0.04	300			
			5198			

Table D-15: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.84 mm

Feed flow rate = 37.96 ml/min

No Recycle

Area	Time	Concentration. (mg/ml)	Vol	Content. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
517806	15	1.69	517	29.11	0.56	-0.58
231551	30	0.76	574	43.56	0.34	-1.07
136801	45	0.45	562	51.92	0.22	-1.53
85645	60	0.28	583	57.35	0.13	-2.01
23190	120	0.08	2320	63.20	0.05	-3.07
9305	180	0.03	2291	65.52	0.01	-4.48
22968	-	0.07	300			
			6847			

Table D-16: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.59 mm

Feed flow rate = 37.96 ml/min

No Recycle

Area	Time	Conc. (mg/ml)	Vol	Conc. ($mg_{barakol}/g_{powder}$)	unextractable fraction	ln(Y)
525502	15	2.44	514	41.82	0.42	-0.87
175520	30	0.82	559	57.01	0.21	-1.57
88608	45	0.41	563	64.74	0.10	-2.29
46658	60	0.22	561	68.79	0.04	-3.10
8609	120	0.04	2255	71.80	0.00	-5.73
0	180	0.00	2239	71.80	0.00	-5.73
7165	-	0.02	300			
			6691			

Table D-17: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.59 mm

Feed flow rate = 37.96 ml/min

Solid to solvent ratio (W/V) = 30 g : 1000 =1 :33.33

Recycle

Area	Time	Concentration (mg/ml)	Content ($mg_{barakol}/g_{powder}$)
322398	15	1.01	33.54
354049	30	1.10	36.83
294485	45	0.92	30.63
365610	60	1.14	38.03
402339	120	1.26	41.85
360724	180	1.13	37.52
365505	300	1.14	38.02
359070	420	1.12	37.35
245531	540	0.77	25.54

Table D-18: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.59 mm

Feed flow rate = 37.96 ml/min

Solid to solvent ratio (W/V) = 30 g : 1500 =1 : 50

Recycle

Area	Time	Concentration (mg/ml)	Content ($mg_{barakol}/g_{powder}$)
216318	15	0.84	41.98
227698	30	0.88	44.19
210446	45	0.82	40.84
229826	60	0.89	44.61
221578	120	0.86	43.01
234827	180	0.91	45.58
224056	300	0.87	43.49
232445	420	0.90	45.11

Table D-19: Experimental data of barakol extraction

Condition : Upward direction

Size = 0.59 mm

Feed flow rate = 37.96 ml/min

Solid to solvent ratio (W/V) = 30 g : 1800 =1 : 60

Recycle

Area	Time	Concentration (mg/ml)	Content ($mg_{barakol}/g_{powder}$)
150128	15	0.58	34.97
198392	30	0.77	46.21
193390	45	0.75	45.04
198542	60	0.77	46.24
233786	120	0.91	54.45
233633	180	0.91	54.41
243659	300	0.95	56.75
215853	420	0.84	50.27

VITA

Miss Geerati Somwattana was born on 2 May, 1975 in Saraburi, Thailand. She received a Bachelor's Degree of Science in Chemical Technology from the Faculty of Science, Chulalongkorn University in 1996. After then she subsequently completed the requirements for a Master's Degree in Chemical Engineering at the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in 2001.