



The separation of hydrocarbon isomers by extractive crystallization with thiourea  
by Patrick Joseph Gorton

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE  
in Chemical Engineering  
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**Abstract:**

Due to the similarity in their chemical structure, the separation of aromatic hydrocarbons, such as ethylbenzene, and the three isomeric xylenes (para, meta and ortho) was difficult to perform by conventional means. The development of a new technique to effect the separation of these types of compounds was desirable.

Previous research indicated the use of extractive crystallization with thiourea as a possible means of aromatic hydrocarbon separation. This investigation explored this process in further detail, optimizing some of the variables involved.

The extractive crystallization procedure involved contacting a solution of methanol and thiourea with the hydrocarbon feed mixture and with an inductor. The inductor was necessary for the formation of adducts with thiourea and the aromatic system. The resulting mixture was cooled whereupon adducted thiourea crystals were formed. Removal of the crystals by filtration and decomposition by steam stripping yielded an enriched product that was higher in concentration than the feed mixture.

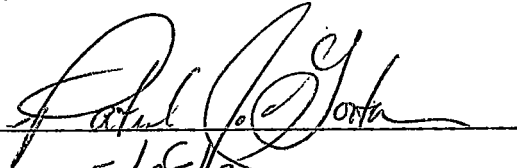
It was determined that methanol was the optimal solvent in terms of separation ability with the aromatic systems. The optimal ratio of solvent to thiourea was found to lie between 2.5 and 5.5 ml/g. Two inductors were studied in depth (1,2,4-trichlorobenzene and 1,1,2-trichlorotrifluoroethane). Equilibrium data was compiled using all possible aromatic combinations with the two inductors. It was shown that the extractive crystallization process compared well against distillation techniques and, in some cases, it far exceeded the ability of conventional distillation. Analyses of the effect of hydrocarbon feed and inductor amounts on separation were also performed.

In summary, it was determined that the process of extractive crystallization in conjunction with the separation of aromatic hydrocarbons was indeed feasible and in some cases, it was much desired over distillation techniques.

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THE SEPARATION OF HYDROCARBON ISOMERS BY  
EXTRACTIVE CRYSTALLIZATION WITH THIOUREA

by

PATRICK JOSEPH GORTON

A thesis submitted in partial fulfillment  
of the requirements for the degree


of

MASTER OF SCIENCE


in

Chemical Engineering

Approved:

  
Chairman, Graduate Committee

  
Head, Major Department

  
Graduate Dean

MONTANA STATE UNIVERSITY  
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## ABSTRACT

Due to the similarity in their chemical structure, the separation of aromatic hydrocarbons, such as ethylbenzene, and the three isomeric xylenes (para, meta and ortho) was difficult to perform by conventional means. The development of a new technique to effect the separation of these types of compounds was desirable.

Previous research indicated the use of extractive crystallization with thiourea as a possible means of aromatic hydrocarbon separation. This investigation explored this process in further detail, optimizing some of the variables involved.

The extractive crystallization procedure involved contacting a solution of methanol and thiourea with the hydrocarbon feed mixture and with an inductor. The inductor was necessary for the formation of adducts with thiourea and the aromatic system. The resulting mixture was cooled whereupon adducted thiourea crystals were formed. Removal of the crystals by filtration and decomposition by steam stripping yielded an enriched product that was higher in concentration than the feed mixture.

It was determined that methanol was the optimal solvent in terms of separation ability with the aromatic systems. The optimal ratio of solvent to thiourea was found to lie between 2.5 and 5.5 ml/g. Two inductors were studied in depth (1,2,4-trichlorobenzene and 1,1,2-trichlorotrifluoroethane). Equilibrium data was compiled using all possible aromatic combinations with the two inductors. It was shown that the extractive crystallization process compared well against distillation techniques and, in some cases, it far exceeded the ability of conventional distillation. Analyses of the effect of hydrocarbon feed and inductor amounts on separation were also performed.

In summary, it was determined that the process of extractive crystallization in conjunction with the separation of aromatic hydrocarbons was indeed feasible and in some cases, it was much desired over distillation techniques.

## INTRODUCTION

The people of the United States have become a society that demands a high standard of living, yet they deplore the current high costs of this standard. Today, as we are becoming more and more energy conscious, industry is faced with the monumental task to provide products at a lower cost to our energy reserve and to still maintain the standards that are set by society.

Within the framework of long-range industrial planning a large area of concern falls within the scope of separation and purification of hydrocarbons. This separation and purification is necessary for the production of synthetics; specifically, those necessary for synthetic rubber, fiber, and chemical plastics. Included in this class of products are the chemical intermediates needed for these materials. This involves the purification or production of isomeric xylenes and ethylbenzene.

Over 90% of the  $C_8$  isomers (1) used in the United States are obtained as a by-product stream from the petroleum reforming operation. A typical analysis of this mixed stream is shown in Table I. The remainder of the isomers produced come from coke-oven byproducts.



Ethylbenzene, the most widely used of the C<sub>8</sub> isomers, is used almost exclusively in the production of styrene from which polystyrene, polyesters and other plastics are manufactured.

The mixed xylenes are also highly in demand as paint and varnish solvents, as motor fuel octane boosters and as chemical intermediates in the plastics and film industry. The latter industry accounts for a major portion of the total use.

Synthetic fibers have been steadily increasing in world popularity. Recent figures show a yearly growth rate in this industry of over 25% (3). Polyesters, such as Dacron, depend on high purity p-xylene as a chemical intermediate. (99.2% p-xylene is converted to the necessary terephthalic acid used in the polyester fibers and films.)

The most plentiful of the mixed xylenes is used the least. M-xylene finds uses mainly as a gasoline blending agent and as a solvent. The meta-xylene is frequently left in the petroleum stream to be isomerized to other more essential xylenes. A small amount of the isomer is used in the production of isophthalic acid, a chemical intermediate in the manufacture of plasticizers, alkyd resins and other esters.

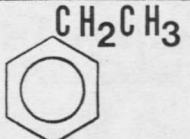

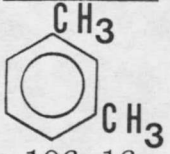
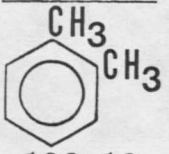
Essentially, all of the o-xylene isomer is consumed in the production of phthalic anhydride, which is used in dyes, plastics and plasticizers.

Since all of the processes mentioned so far need one specific isomer in relatively high purity, separation of the mixed petroleum stream is necessitated. Several general techniques have been developed for separation of these components; for example, fractional crystallization, extractive distillation and fractional distillation. However, in view of the chemical and physical similarities of the compounds, current research (2) shows that the separation of these isomers is often difficult and costly. In Table II, these similarities can be seen for ethylbenzene and for the three isomeric xylenes (ortho, para and meta).

Current methods of separation of p-xylene include fractional crystallization which removes ~65% of the xylene from the stream. This separation is due to p-xylene's high freezing point relative to the other components. Several other crystallization processes are given in the literature (1),(3). A new and novel approach to this separation, called the Parex process, has been developed by Universal Oil Products. The UOP process is thought to use potassium and barium substituted molecular sieves, which allows selective adsorption of the p-xylene



TABLE II. VARIOUS PROPERTIES OF XYLENES AND ETHYLBENZENE(8)

Structure	Ethylbenzene 	p-xylene 	m-xylene 	o-xylene 
Molecular Weight	106.16	106.16	106.16	106.16
Boiling Point °C(1 atm)	136.19	138.35	139.10	144.41
Freezing Point °C	-94.98	+13.26	-47.87	-25.18
Specific Gravity(20°C)	.8670	.8611	.8642	.8802
Vapor Pressure, mm Hg(20°C)	7.07	6.52	6.15	4.89

and absorbant (4).

Since o-xylene has a volatility sufficiently different from the other compounds conventional distillation techniques can be effectively used for separation, although large numbers of theoretical plates (100+) and high reflux ratios are still necessary. Extractive distillation has shown some improvements on the separation of a mixture consisting of ethylbenzene and p-xylene (2), but the question of economic feasibility in terms of large scale production remains unanswered.

Difficulty is also encountered with the separation of a stream of ethylbenzene and m-xylene; therefore about 91% of the ethylbenzene market is obtained through the alkylation of benzene with ethylene (5).

Since the method of separation accounts for the major portion of the bulk cost of a material, it appears that for use on a petroleum stream the development of a low cost, energy efficient separation technique would be advantageous. The savings incurred from such a process could, theoretically, be passed on to the consumer in the form of lower prices of synthetic products. This is exemplified by Table III, in which the projected demand of the  $C_8$  isomers for 1979 is shown.

It is on this basis that work was undertaken to investi-

TABLE III. COST AND DEMAND FOR C<sub>8</sub> HYDROCARBONS (9)

	<u>Ethylbenzene</u>	<u>p-xylene</u>	<u>m-xylene</u>	<u>o-xylene</u>
Current Cost(1978) \$/lb.	.13	.15	.22	.11
Projected 1979 Demand (millions of lbs)	8500	3500	--	1140
Projected 1979 Demand (billions of \$)	1.11	.53	--	.13

gate the use of extractive crystallization as a mode of C<sub>8</sub> hydrocarbon separation. Previously, this process showed promising results (6),(7) and it could become an important unit operation in the chemical industry.

## BACKGROUND

Extractive crystallization is defined in the literature as any process using urea or thiourea to form an adduct permitting selective separation of a particular molecule in a hydrocarbon mixture. The term was first introduced in 1957, by Elgin (10). Since that time, it has gained popularity as a means of separating close boiling hydrocarbon isomers, such as the dimethylbenzene compounds (7).

The actual kinetics of this process are not well understood, although similar formations of clathrates with Werner complexes have been well documented (11),(12). The major difference between these two processes is the formation itself. In extractive crystallization, the crystal formation can be likened to a two-dimensional channel structure in which the guest hydrocarbon is trapped by the host (the amide). Clathrates were found to be a three-dimensional cage-like structure held together by weak intramolecular bonds, such as hydrogen bonding or Van der Waals forces (13).

As mentioned previously, the exact mechanism for adduction is not well understood. Weak bonding, similar to that found in clathrates, is thought to hold the crystal intact.

Previous hypotheses suggest that the diameter of the channel places stringent limitations, structurally, on the cross-section of the guest ( $5.8 \pm 0.5$  Å by  $6.8 \pm 0.3$  Å). Thus, only those compounds that are both chemically and structurally compatible with the host form a stable adduct. The relative positioning of the guest within the adduct is not specified. Rather, the guest is allowed to position itself end to end with other molecules of the same type in the formation.

Of the amides found to exhibit this behavior of adduction, only thiourea allows the formation of stable adducts with branched-chain paraffins or naphthenic compounds. This behavior is thought to be due to the bulky sulfur atoms in the thiourea molecule (Figure 2) creating a larger diameter channel adduct. It also has been shown that adducts form with selenourea and tellurourea (14).

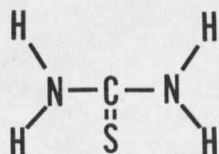


FIGURE 2. THIOUREA STRUCTURE

## RELATED RESEARCH

The accidental discovery of channel adducts of urea was made in Germany by M. F. Bengen in 1940. This information was relayed to the United States through several publications in the Technical Oil Mission Reel (15). Bengen filed and received a German patent in 1953 for these newly discovered adducts.

In 1947, using selective complex formations, Fetterly stumbled across the thiourea based adducts while attempting to improve octane ratings in gasoline. The adducts he found seemed to complement those found by Bengen, and were the basis for a series of U.S. patents awarded to Fetterly starting in 1950 (16).

Zimmerschied and other scientists (17) made one of the first systematic studies into the various capabilities of the channel adducts. These men substantiated the method described by Bengen as a process with significant possibilities in the separation of mixtures and purification of specific chemical compounds. Their investigation included a search of possible adduct formations of urea with linear aliphatic molecules such as the normal alcohols and the recovery of n-alkanes from petroleum sources.

Angla (18), working independently in 1949, reported that certain naphthenic and chlorocarbon compounds formed complexes.

with thiourea.

Redlich made a study (19) in 1950 concerning the thermodynamics of the channel adducts at equilibrium conditions. He showed that the equilibrium was established much as in a normal chemical reaction. His studies also showed that the system could be described by using Gibbs free energy relationships in conjunction with a chemical equilibrium equation.

Since the first patent was issued, several general improvements on the basic process have been made (20),(21). One of the improvements for the adducted phase was a washing method using a saturated aqueous solution of the amide. Other improvements in washing have also been described (22). The patent literature also report numerous process descriptions concerning improvements on a single stage crystallization system (23).

A patent was issued in 1956 (24) for a process involving the continuous fractionation of straight or branched chain hydrocarbons into two large fractions from a petroleum stream. No test results were given. Rather, only the apparatus and procedure were described. The process employed the movement of 25-100 mesh urea or thiourea through a horizontal column in which the urea contacts the feed stream countercurrently. This allowed two fractions to be removed, each enriched in a portion of the incoming petroleum stream. In another publication, the results



of a pilot plant using an extractive crystallization process for the separation of n-paraffins and n-olefins from a petroleum source have been reported (25).

Fuller published the findings of a "slurry promoter" which appeared to alter the thermodynamic equilibrium in such a way that a very small amount of the hydrocarbon remained in the non-adducted phase (26).

The widespread general use of adduct formation was implemented in the investigations of Newey (27) concerning the separation of a fatty acid mixture to produce high quality drying oils such as linseed oil, castor oil or soybean oil. Other uses reported in the literature (28) included stereospecific polymerization using urea complexes of certain monomers, fractionation and refinement of several types of oils including vegetable oil, liver oil and fish oil and also the manufacture of several explosives.

More current applications involved: improvements to the viscosity index of several lubricating oils (29), formation of adducts with bicyclic and tricyclic compounds, and separation of C<sub>14</sub>-C<sub>20</sub> hydrocarbons from shale oil fractions.

Several excellent reviews of the pertinent literature through 1970 have been published (28),(30),(31),(32),(33).

In their work, Chivate and Shah have reported numerous "misuses" of the term extractive crystallization (34). The confusion was in the understanding of the basic definition and kinetics of two similar operations, extractive crystallization and adductive crystallization.

Extractive crystallization, as reported by Chivate and Shah, was entirely a physical process in which the components of a mixture formed an eutectic mixture with a foreign agent, an "inductor". This formation shifted the normal eutectic point of the two components, hopefully, in a favorable direction. This yielded a ternary eutectic point in which one component was enriched over the other two components. Therefore, a separation occurred. It was obvious that the inductor played a very important role in this process. The use of different inductors yielded different equilibrium compositions.

Adductive crystallization, again as reported by Chivate and Shah, relied on the formation of a loose molecular bond with either the component or the inductor. The resulting compounds differed in chemical properties and, thus, behaved differently under a cooling stage. The exact mechanism of this process was not well understood, but it was thought that the formation of hydrogen bonds played the overwhelming role to facilitate separation.

It appeared that the previous definitions seemed to conflict with the original term extractive crystallization as defined by Elgin. Both terms defined by Chivate and Shah relied heavily on a difference in melting points, whereas Elgin's definition was based entirely on the formation of urea or thio-urea complexes. From this point forward, the term "extractive crystallization" will be based on the definition given by Elgin.

Presently, there is only one known industrial application of extractive crystallization. Urea is used in the petroleum industry to recover, essentially, all of the  $C_{14}$ 's and n-paraffins in a single stage adduction unit. It appears that further fractionation using extractive crystallization could be used to effectively separate the stream into a large variety of products. This possibility has never been explored to any great extent. This might be due to the economics of the process as it stood in the 1950's. At that time, the carbon chain length was preferred to vary by four to six carbon atoms to achieve a "good" separation of the fraction. In terms of economics, this large difference in length gave more conventional separation techniques the advantage.

In general, the petroleum and petrochemical industries have spent little research money on the separation of components

by an extractive crystallization process, especially for isomeric compounds. Instead, industry concentrated on the use of this technique for the separation of classes of compounds.

Since most industrial processes yielded a "cut" of closely related compounds, application of conventional separation operations were often costly because of the similarities of the components in the cut. This suggested that a better, more efficient separation technique had to be developed.

Recent research (6),(7),(35),(36) at Montana State by various researchers has shown the use of extractive crystallization with difficult separations was effective.

The systems that were studied included the hydrogenated monoterpenes, the trimethylpentanes,  $\beta$ -phellandrene (from a dipentene cut) and the  $C_8H_{10}$  aromatic isomers. A summary of this research is shown in Table IV. (The separation factor,  $\alpha$ , is analogous to relative volatility in distillation data.)

It should be noted here, the research performed in the  $C_8H_{10}$  isomer separation area was slightly modified from the previous research. Thiourea formed adducts with isoparaffin, naphthenic, and terpene hydrocarbons, but thiourea was non-adducting with aromatic hydrocarbons, unless certain adduct formers or inductors were included in the aromatic feed mixture. For the  $C_8H_{10}$  iso-

mers, the reported data in Table IV was obtained using carbon tetrachloride as the adduct former or inductor.

TABLE IV. RESULTS OF EXTRACTIVE CRYSTALLIZATION TECHNIQUE USED ON SELECTED HYDROCARBON MIXTURES(6),(7),(35),(36)

MIXTURE	SEPARATION FACTOR
	$\alpha_{1,2}$
1,1,4 trimethylcycloheptane/carane	8.2
cis p-menthane/trans p-menthane	2.7
trans pinane/cis pinane	2.7
$\beta$ -phellandrene/limonene/p-cymene	5.8
2,2,4 trimethylpentane/2,3,3- and 2,3,4-trimethylpentane	5.1
2,3,3 trimethylpentane/2,3,4 trimethylpentane	1.4
cis 1,2 dimethylcyclohexane/trans 1,2 dimethylcyclohexane	4.5(McCandless)*
cis 1,4 dimethylcyclohexane/trans 1,4 dimethylcyclohexane	4.5(McCandless)*
Ethylbenzene/m-xylene <sup>†</sup>	5.6
O-xylene/m-xylene <sup>†</sup>	4.5
Ethylbenzene/p-xylene <sup>†</sup>	2.8
O-xylene/p-xylene <sup>†</sup>	2.4
P-xylene/m-xylene <sup>†</sup>	1.7
Ethylbenzene/o-xylene <sup>†</sup>	1.2
<sup>†</sup> Carbon Tetrachloride used as inductor <span style="float: right;">* unpublished data</span>	

## RESEARCH OBJECTIVES

The objective of this investigation was to develop an extractive crystallization process for the separation of close boiling compounds. This objective involved the determination of several operating parameters for the system which included:

- (1) an optimal solvent for the thiourea
- (2) an optimal inductor for the system
- (3) determination of run time and temperature effect on the separation
- (4) determination of the effect of the ratio of solvent to thiourea on the separation
- (5) determination of the effect of the amount of hydrocarbon and inductor in the system
- (6) determination of equilibrium curves for the various systems studied.

## EXPERIMENTAL EQUIPMENT AND PROCEDURE

The methods of adduct formation have been well documented (31). The basic procedure used in this investigation is diagrammed in Figure 3. To facilitate the description of the procedure and equipment, a typical run will be described in detail. The actual procedure varied with varying parameters investigated. The reader is asked to refer to Figure 3 for further clarification.

Using gentle heating and agitation to encourage dissolution, a solution of thiourea was prepared in a 250-ml beaker by dissolving 20.0 grams of thiourea in 110 ml of methanol. A Cenco hotplate with a magnetic stirrer was employed for the solution preparation.

A mixture of 10 ml of 50 wt% ethylbenzene and 50 wt% p-xylene was added to 10 ml of  $\text{CCl}_4$  (inductor). This mixture, in turn, was added to the hot methanol/thiourea solution. The resulting mixture was cooled immediately in a chest type freezer ( $-20^\circ\text{C} \pm 2^\circ$ ) for a 24 hour period. No agitation of the mixture was used during the cool down period.

After this period of cooling, the crystals were filtered by using a Buchner type vacuum filter. The mother liquor (residue) was washed with ~150 ml of distilled water and allowed to phase



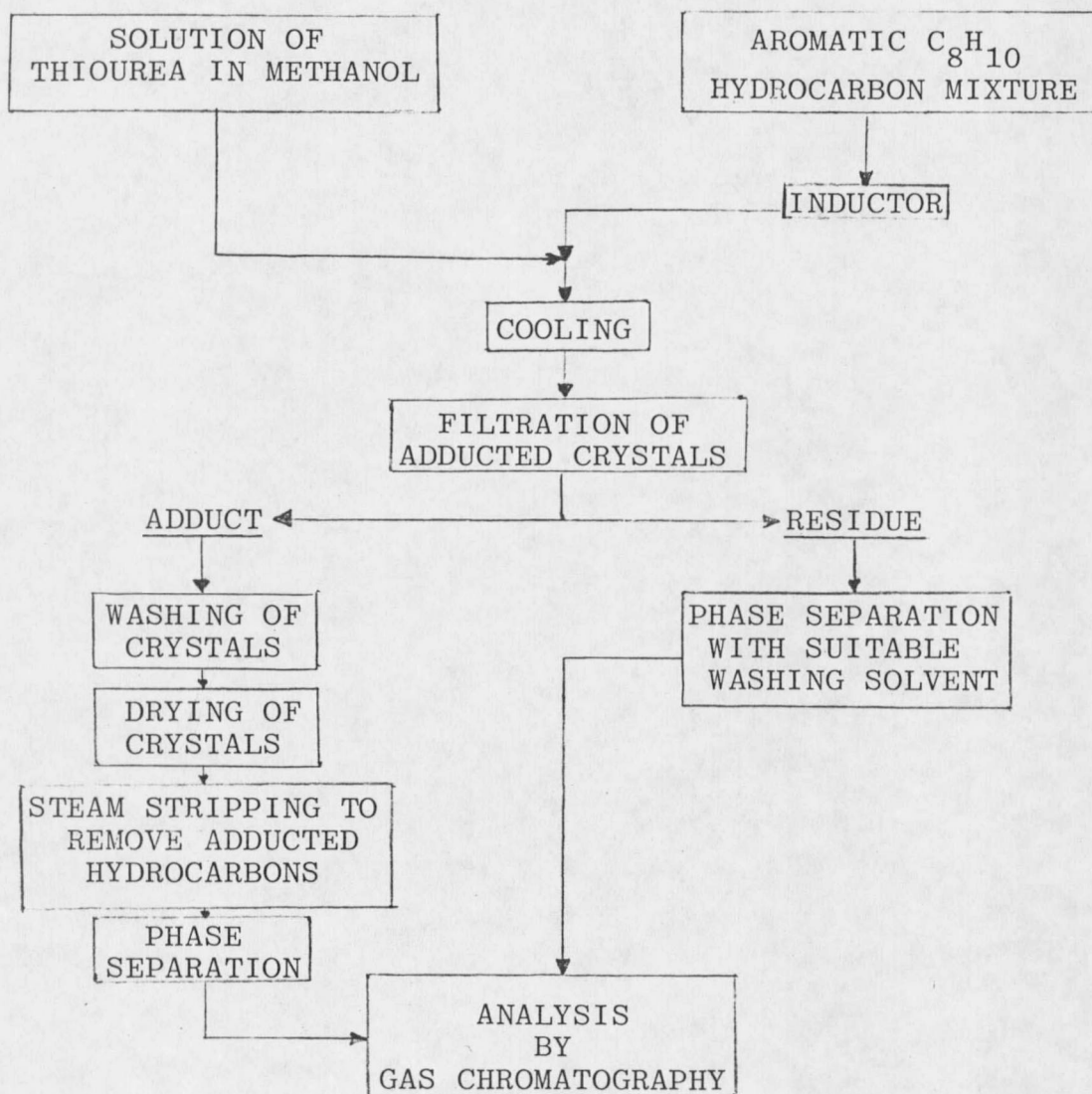


FIGURE 3. FLOWSHEET OF EXPERIMENTAL PROCEDURE

separate in a 250 ml separatory funnel. The resulting hydrocarbon phase was removed, weighed and analyzed using a gas chromatograph.

The adducted crystals were washed with ~50 ml of n-pentane in two successive washings, then the crystals were allowed to dry at room temperature for two hours. The removal of the adducted hydrocarbon was accomplished by contacting the crystals with a mixture of steam and hot water in the apparatus shown in Figure 4. The hydrocarbon phase was removed from the separatory funnel and was also analyzed using a gas chromatograph.

All run temperatures were measured using a J-28 Iron/Constantan thermocouple in conjunction with a Brown potentiometer. Cooling, during the runs made to investigate the effect of temperature, was accomplished using a Thermoelectric Stir-Kool cold plate(Model SK-12). The beaker was coated on the bottom with a light oil to improve heat transfer characteristics and the outer surface was insulated with a layer of insulation to maintain a constant solution temperature.

All chemical reagents used are listed according to grade and source in the Appendix.

During this investigation, analysis of the feedstocks and

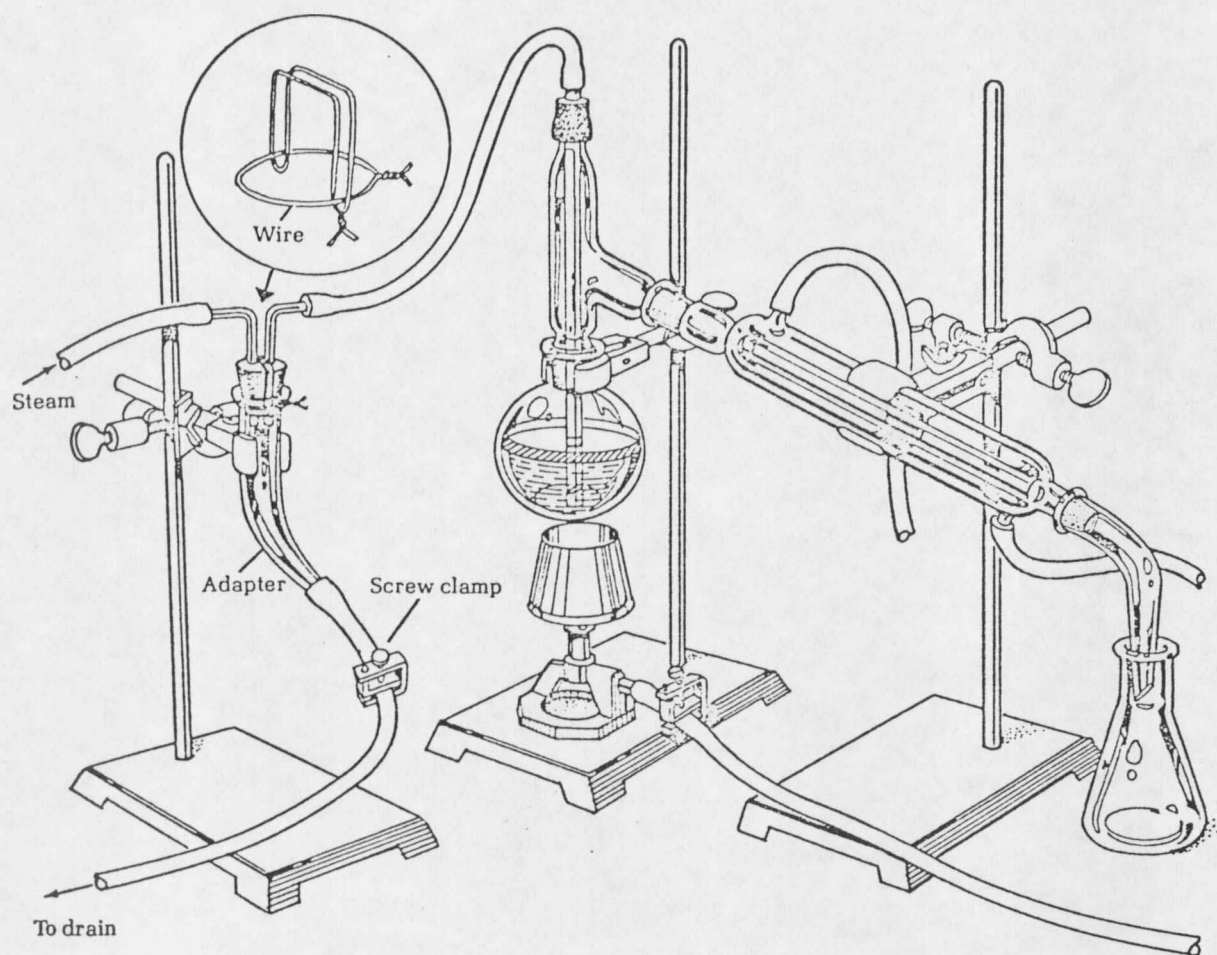


FIGURE 4. STEAM DISTILLATION APPARATUS

products obtained was performed using two gas chromatographs. An Aerograph Model 660 flame ionization gas chromatograph, with a Sargent Model SR strip-chart recorder and a Varian Model 1420 thermal conductivity gas chromatograph, with a Varian Model 9176 strip-chart recorder were both employed. The early portion of this research, that is the solvent study and preliminary inductor study, was performed using the Aerograph model. All subsequent work used the Varian for the analyses. The specifications and operating conditions for the two chromatographs are shown in Tables V and VI.

TABLE V. GC SPECIFICATIONS AND OPERATING PARAMETERS

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TYPE:	Aerograph Model 660 Flame Ionization
COLUMN:	1/8" OD x 10' copper tubing
PACKING:	5% Bentone 34 + 5% diisodecylphthalate on 60/80 mesh Chromosorb W
COLUMN TEMPERATURE:	75°C
INJECTOR TEMPERATURE:	220°C
DETECTOR TEMPERATURE:	115°C
SAMPLE SIZE:	.2 $\mu$ l
RETENTION TIME:	~13 mins(xylenes and ethylbenzene)

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TABLE VI. GC SPECIFICATIONS AND OPERATING PARAMETERS

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TYPE: Varian 1420 Thermal Conductivity(TC) dual column

COLUMN: 1/8" OD x 15' copper tubing

PACKING: 5% Bentone 34 + 5% diisodecylphthalate on 80/100 mesh High Performance Chromosorb W

COLUMN TEMPERATURE: 85°C(C<sub>8</sub>H<sub>10</sub> isomers and 1,1,2 trichloro-fluoroethane)  
150°C(1,2,4 trichlorobenzene)

INJECTOR TEMPERATURE: 190°C

TC DETECTOR TEMPERATURE: 200°C

TC DETECTOR CURRENT: 150 mA

CARRIER GAS FLOW RATE: ~30 cc/min (H<sub>2</sub>)

SAMPLE SIZE: 0.4 µl

RETENTION TIME: 1 min(1,1,2 trichlorotrifluoroethane)  
10 mins(Xylenes and ethylbenzene)  
14 mins(1,2,4 trichlorobenzene)

---

Both gas chromatographs gave consistent and comparable results.

Since the area under the output curve from the chromatograph was proportional to the weight percent of a particular component in the sample, a correlation curve had to be developed to determine the actual percent composition of the sample from the recorder output. These curves and the methods of calculation

are developed in the appendix for the various compounds analyzed.

## RESULTS AND DISCUSSION

The investigation of the problem previously stated was accomplished in several stages closely paralleling the research objectives. A univariant search scheme was employed throughout this investigation; that is one variable was altered and the others held constant to determine any effect of the one variable on the degree of separation.

Discussion of the data compiled in this investigation will be reported in the following subgroups:

- A) Methods of Analysis of Data
- B) Solvent Study
- C) Preliminary Inductor Study
- D) Effect of Run Time and Temperature
- E) Effect of Solvent to Thiourea Ratio
- F) Effect of the Amount of Feed and Inductor
- G) Equilibrium Curves for the  $C_8H_{10}$  Systems
- H) Summary

### Methods of Analysis of Data

Previous research performed at Montana State University (7) used two characteristic parameters in discussing separation ability of the extractive crystallization process. These parameters, al-

though mathematically related, gave important pieces of information not common to one parameter alone.

The first and most widely used separation index is defined below as the separation factor( $\alpha$ ).

$$\alpha_{1,2} = \frac{y_1}{1-y_1} \times \frac{1-x_1}{x_1}$$

$y_1$  = mole fraction of the species enriched in the adduct

$x_1$  = mole fraction of the same species in the residue

The separation factor is analogous to relative volatility in distillation work. The range of  $\alpha$  is from 1 (no separation) to  $\infty$ .

The second parameter used in analyzing this data was the extent of separation( $\xi$ ). This index gave a better indication of the actual quantitative amount of separation taking place. Rony (38) defined the extent of separation as:

$$\xi_{1,2} = \text{abs} \left( \frac{1}{1+K_1} - \frac{1}{1+K_2} \right)$$

$$K_1 = \frac{\text{moles of component 1 in residue}}{\text{moles of component 1 in adduct}}$$

$$K_2 = \frac{\text{moles of component 2 in residue}}{\text{moles of component 2 in adduct}}$$

The range for this parameter is from 0 (no separation) to 1 (com-



plete separation).

The advantage in using the extent of separation( $\xi$ ) over the separation factor( $\alpha$ ) was that for a given set of conditions (solvent/thiourea ratio, grams of feed, grams of inductor, run temperature and run time), there was one extent of separation possible.

It can be shown mathematically that:

$$\alpha_{1,2} = K_2/K_1$$

It was possible to obtain a system in which  $K_2=10$  and  $K_1=1$ , or  $\alpha=10$ . Equally, it would have been possible to obtain a system in which  $K_2=100$  and  $K_1=10$ , and in which  $\alpha$  would again have been equal to 10. Even though the separation factors were equivalent, the separation indices were not. ( $\xi$  for case 1 = .41 and  $\xi$  for case 2 = .08) Thus, the extent of separation accounted for the difference in these two cases and therefore gives a much improved separation parameter.

#### Solvent Study

The goal of any investigation of this type is the eventual application of the research to industrial scale work. Feedback was received from an industrial firm stressing the large-quantity material handling problems in relation to the solvent used in the extractive crystallization process. With this in mind, work was

carried out to investigate various possible solvents in order to achieve a good separation and yet decrease this material handling problem. This could be accomplished, possibly, by using a solvent with a higher boiling point than the  $C_8H_{10}$  isomers, i.e., greater than  $145^{\circ}C$ .

Fifteen solvents were investigated (Table IXb). Of these, eight showed some promising results. These are listed in Table VII with their respective boiling points and separation factors. The system used in this study was based on previous research (7), with the run conditions detailed in Table IXa.

TABLE VII. SOLVENT STUDY DATA

Solvent	Boiling Point ( $^{\circ}C$ )	$\alpha_{EB/PX}$
Methanol	64.7	3.28
n-Propanol	97.2	3.09
80/20 wt% mix of MeOH and Diethylene glycol		2.76
Ethylene glycol n-butyl ether	168.4	2.17
Ethylene glycol	197.6	2.02
Ethanol	78.5	1.68
Distilled Water	100.0	1.38
Benzyl alcohol	204.7	1.22

It appeared, for the solvents investigated, the higher boiling components tended to perform unsatisfactorily with the ethylbenzene/p-xylene system. Only one high boiling solvent

(>145°C) showed the ability for aromatic isomer separation. Therefore, since the separation factor appeared to decrease with an increase in the boiling point of the solvent, methanol was used throughout the remainder of this investigation as the solvent for the thiourea.

#### Preliminary Inductor Study

Previous research (7) with the  $C_8H_{10}$  isomers revealed they formed adducts with thiourea in the presence of a third component (the inductor). Several inductors have already been investigated, with most of the previous work based on the use of carbon tetrachloride.

Twelve inductors were examined in this research. These are detailed in Table Xb, with the run conditions shown in Table Xa. Two compounds were found to show consistent results with good separation factors. These were 1,2,4 trichlorobenzene ( $\alpha=3.26$ ) and 1,1,2 trichlorotrifluoroethane ( $\alpha=4.33$ ). Both of these inductors were comparable to the carbon tetrachloride system ( $\alpha=2.84$ ). The one major difference between the three inductors mentioned was in the selectivity of the adduct formation. Both 1,1,2 trichlorotrifluoroethane and carbon tetrachloride adducted the ethylbenzene molecule, preferably, while the 1,2,4 trichlorobenzene selected the p-xylene molecule. Since all other variables remained, essentially, constant during this study, the inductor was found to play a very

important role in the degree of separation and also in the selectivity of the adduct. Both 1,1,2 trichlorotrifluoroethane and 1,2,4-trichlorobenzene will be discussed in more depth within this paper.

#### Effect of Run Time and Temperature

Since a maximum separation ability for the various systems was desired, an optimal run time and temperature had to be determined. The first variable investigated was the effect of run time on an ethylbenzene/p-xylene system using 1,2,4 trichlorobenzene as the inductor. Two different run temperature ranges were used. Figure 5 shows a plot of run time versus the separation indices for a run temperature of  $-20^{\circ}\text{C} \pm 2$ . With an increase in run time both separation indices had a tendency to increase to a maximum level. This maximum level appeared to be reached at a run time greater than ten hours with the following average separation parameters: ( $\alpha=3.06$ ;  $\xi=.0228$ ). Figure 6 shows the same type of plot, except the run temperature was decreased to  $-14^{\circ}\text{C} \pm 2$ . The temperature decrease shifted this maximum separation index to a slightly lower level. To achieve the maximum level of separation required an extended run time ( $>15$  hours). The average separation parameters reported were  $\alpha=2.74$  and  $\xi=.0144$ .

The second variable investigated was the effect of run temperature on the separation. A plot of run temperature versus the

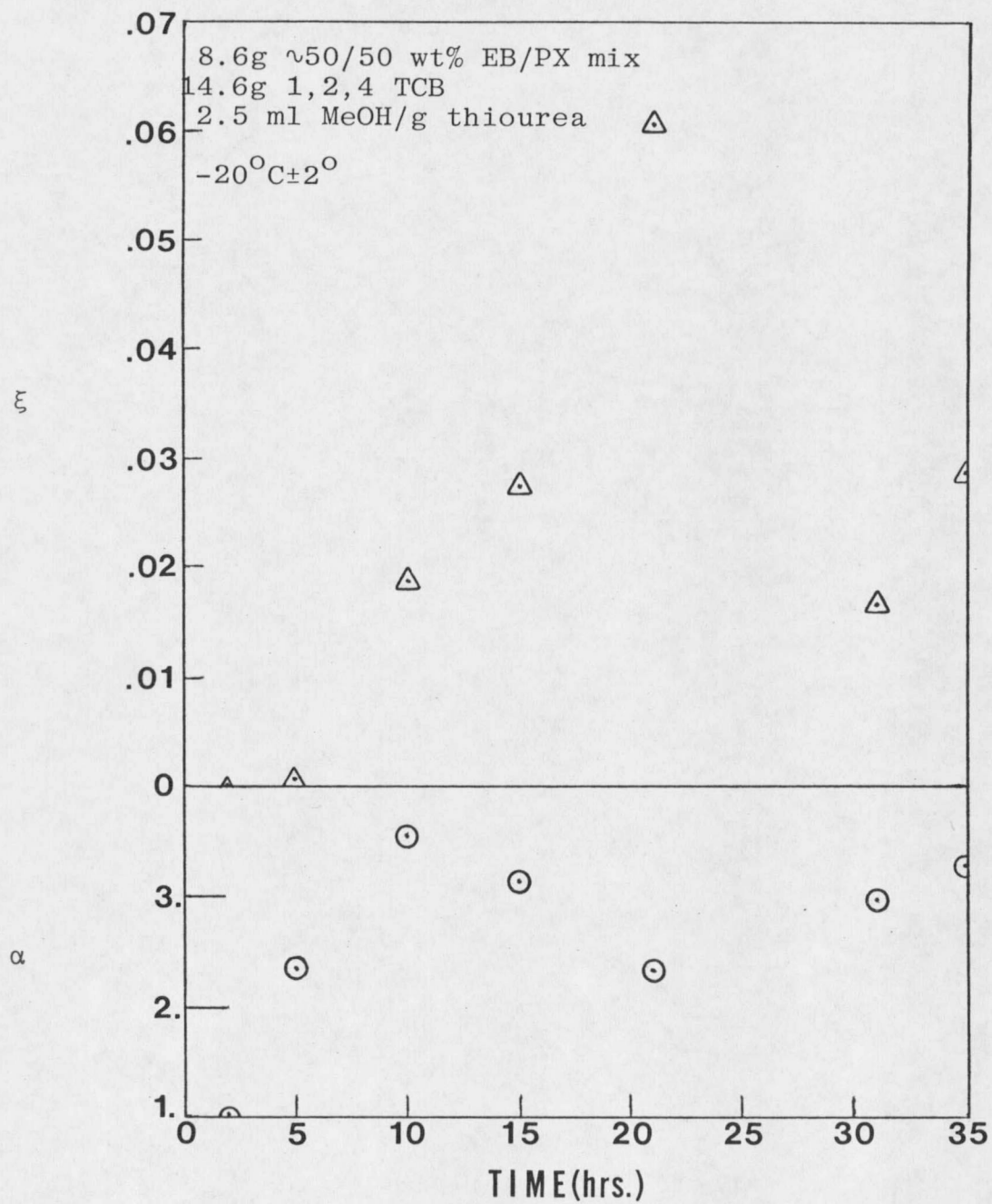


FIGURE 5. EFFECT OF RUN TIME ON SEPARATION

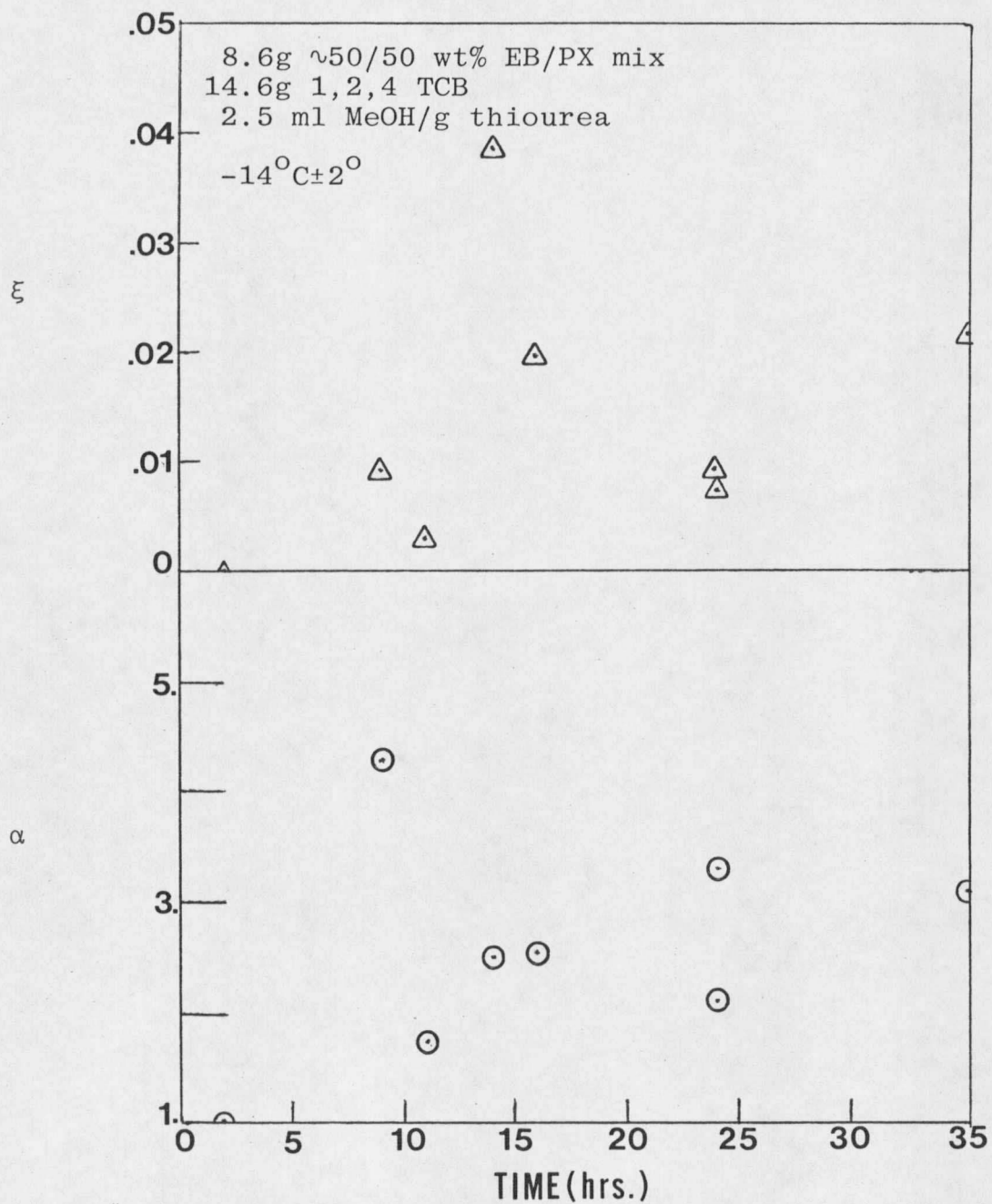


FIGURE 6. EFFECT OF RUN TIME ON SEPARATION

separation parameters is shown in Figure 7. Here again, the same solvent/inductor/feed system was used as in the previous analysis. The separation factor ( $\alpha$ ) was found to be much more sensitive to changes in temperature than the extent of separation ( $\xi$ ) was found to be. With the extent of separation quickly reaching an average value of .01, both indices increased with a decrease in run temperature. The run time used in this study was kept constant at 24 hours. (a complete summary of the experimental data and run conditions is detailed in Tables XI-a and b).

Based on the results from this study, further research was performed using a run time of 24 hours and a run temperature of  $-20^{\circ}\text{C} \pm 2^{\circ}$ .

#### Effect of Solvent to Thiourea Ratio

The amount of solvent for the ethylbenzene/p-xylene system was varied to determine the effect of the solvent to thiourea ratio. Figures 8 and 9 show the results of this study using 1,2,4 trichlorobenzene and 1,1,2 trichlorotrifluoroethane, respectively, as the inductors.

Figure 8 exhibits a maximum separation as the solvent to thiourea ratio was increased. The optimal point of operation

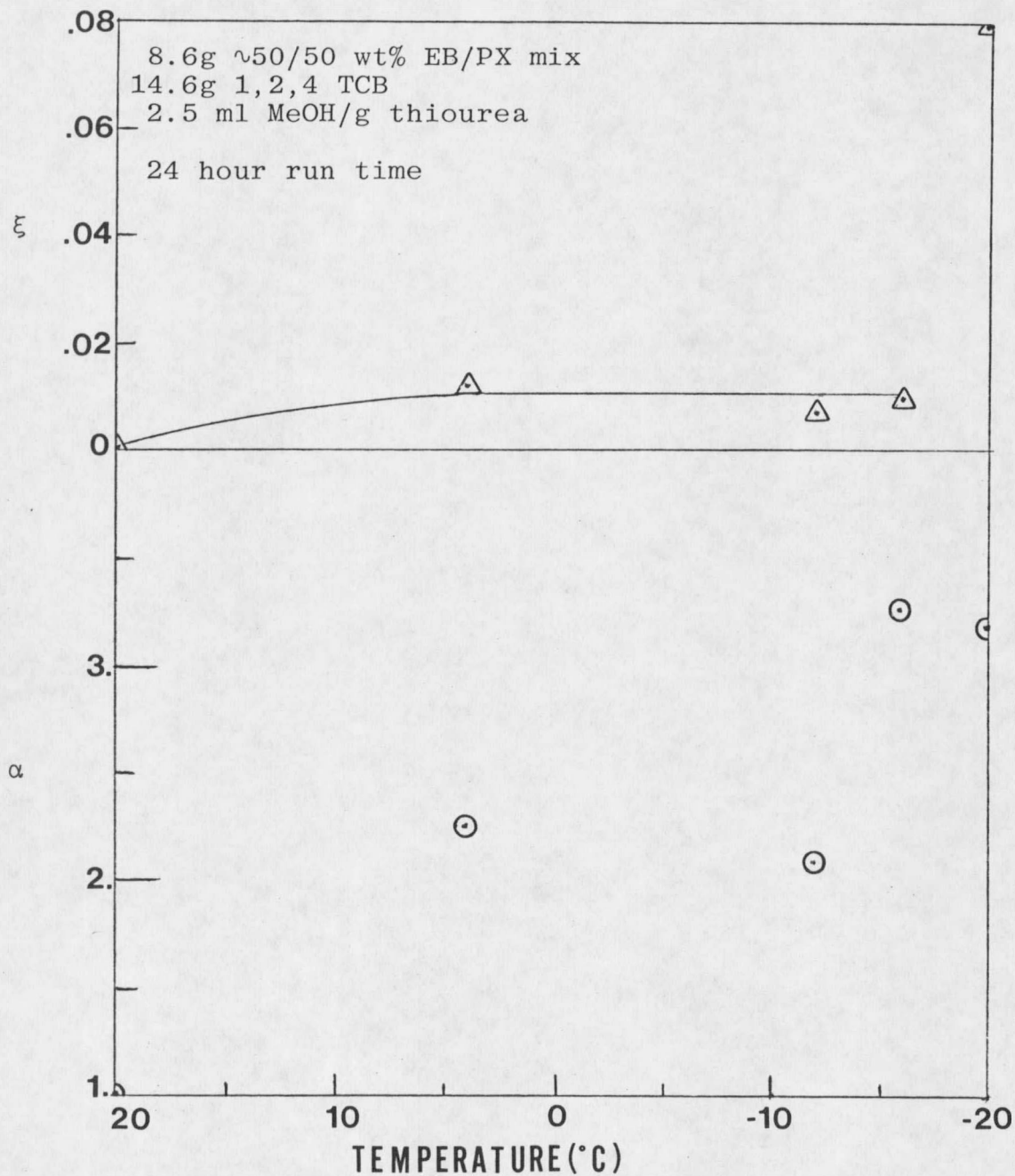


FIGURE 7. EFFECT OF RUN TEMPERATURE ON SEPARATION



appeared near 2.5 - 3.0 ml/g for the 1,2,4 trichlorobenzene system. For the 1,1,2 trichlorotrifluoroethane system, Figure 9 also shows a maximum point at a ratio of 5.5 ml/g .

As indicated previously, the extent of separation( $\xi$ ) was much less sensitive to changes in run conditions than was the separation factor ( $\alpha$ ). The occurrence of the maximum degree of separation was probably due to the increased difficulty in feed contact with the methanol/thiourea solution when the ratio was small, and to the lack of available thiourea molecules for ad-  
duction when the ratio was large.

Since both systems exhibited comparable results with this study, a solvent to thiourea ratio of 5.5 ml/g was used throughout the remaining research. This allowed consistent comparison with previous research (7). (a complete summary of this data is listed in Tables XII and XIII).

#### Effect of Amount of Feed and Inductor

Figure 10 shows the results of varying the hydrocarbon feed. Both 1,2,4 trichlorobenzene and 1,1,2 trichlorotrifluoroethane are reported on this plot. As expected, the use of 1,2,4 trichlorobenzene as an inductor exhibited a decrease in the degree of separation with an increase in feed quantity. The

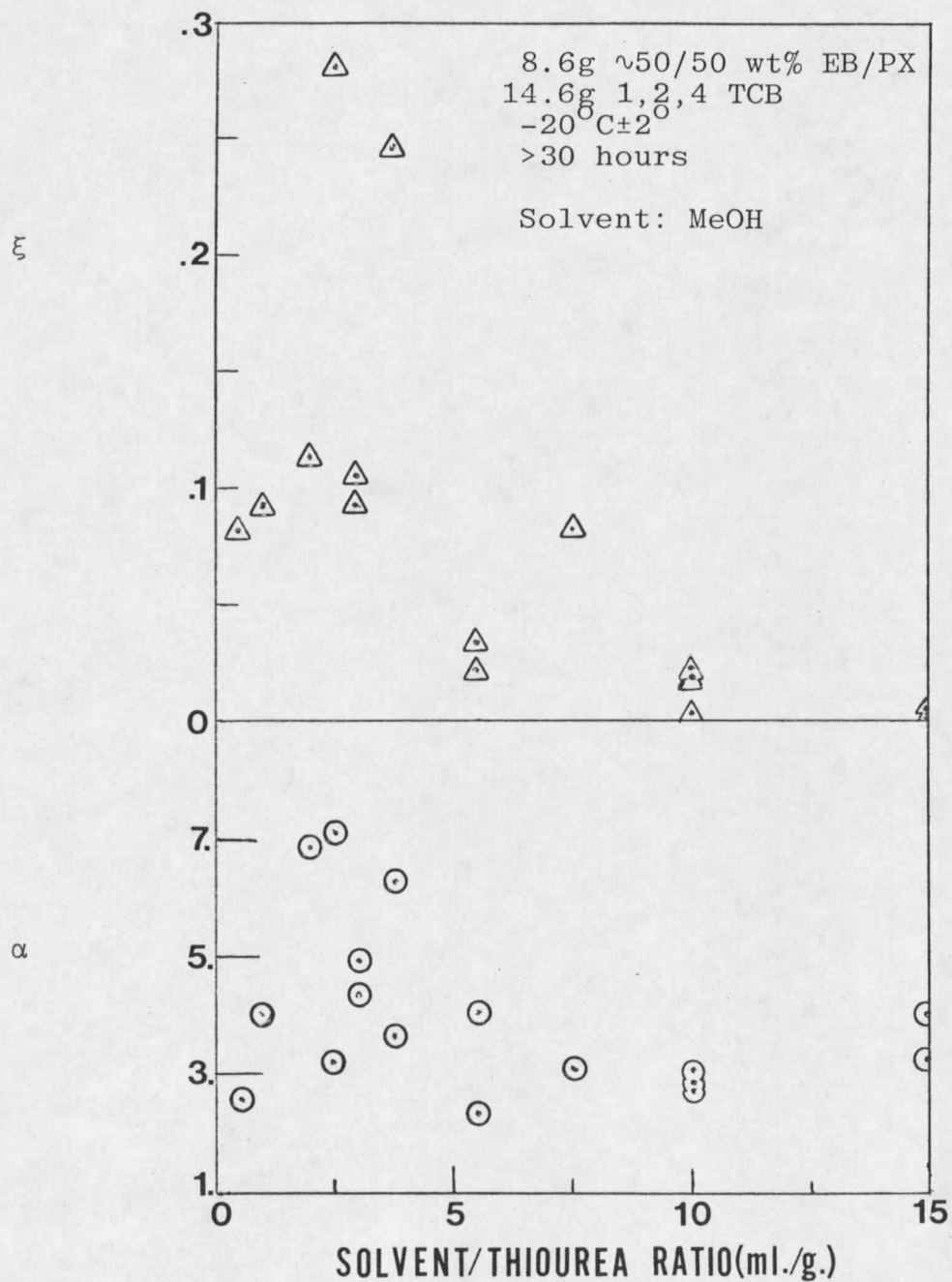


FIGURE 8. EFFECT OF SOLVENT/THIOUREA RATIO ON SEPARATION

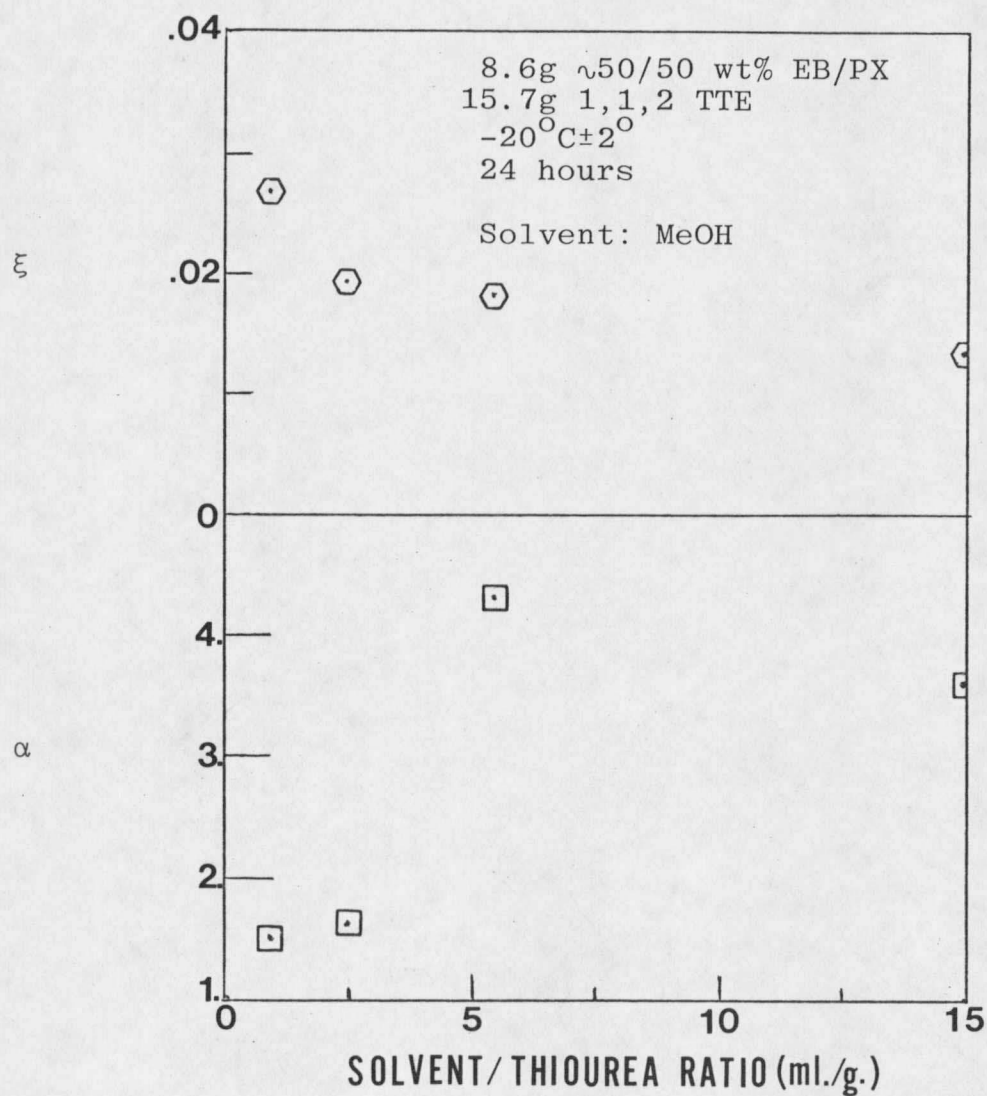


FIGURE 9. EFFECT OF SOLVENT/THIOUREA RATIO ON SEPARATION

effect was much more pronounced for the 1,2,4 trichlorobenzene system than for the 1,1,2 trichlorotrifluoroethane inductor. In fact, it can be seen from Figure 10 that as the hydrocarbon feed was increased, the use of 1,1,2 trichlorotrifluoroethane caused a slight increase in the degree of separation. The reason for this behavior must be explained by the internal workings of the inductor within the extractive crystallization process.

The effect of increasing the amount of inductor for both the 1,2,4 trichlorobenzene and the 1,1,2 trichlorotrifluoroethane systems is shown in Figure 11. Both systems exhibited an increased degree of separation with increased amounts of inductor. The 1,1,2 trichlorotrifluoroethane system had a more pronounced effect with the drop in extent of separation at an inductor level of 22 grams. This was, probably, due to the increased selectivity of the adduct toward the inductor itself. There appeared to be little improvement in the 1,2,4 trichlorobenzene system for quantities of inductor greater than 20 grams. (A complete summary of the experimental data for this study can be found in Tables XIV and XV).

#### Equilibrium Curves for $C_8H_{10}$ Systems

Variation of the feed composition resulted in a curve similar to an equilibrium curve as shown in Figure 12. The particular component that is reported, for example, p-xylene was

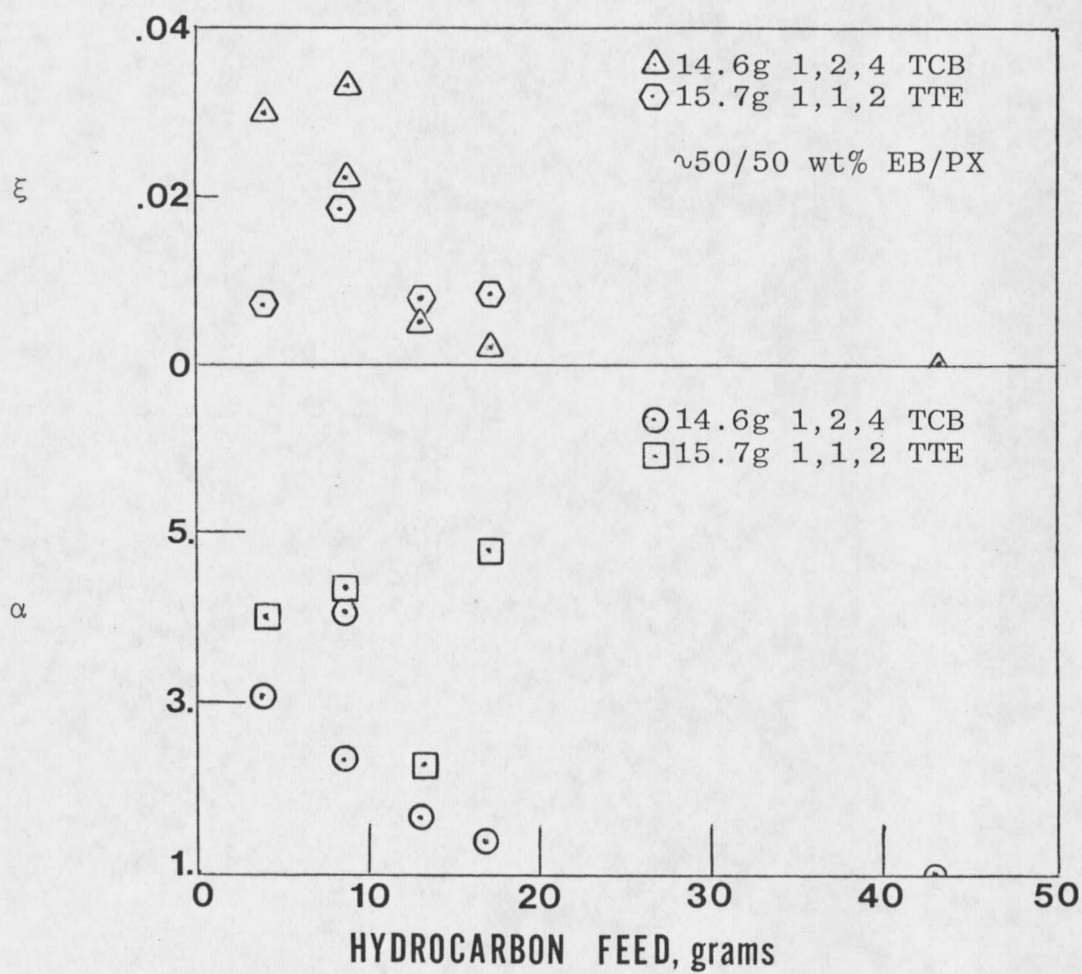


FIGURE 10. EFFECT OF FEED QUANTITY ON SEPARATION





















































































































































