STATISTICAL INVESTIGATION OF THE HYDRODENITRIFICATION OF 2,6 - LUTIDINE

by

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ABSTRACT

The development and analysis of a $1/4 \times 2^5$ experimental design used in a study of the hydrodenitrification of 2,6-lutidine is described within the context of the actual problem. Standard analysis techniques are modified to accomodate the multiple observations available in the data. A simple technique is developed to order treatment combinations in fractional 2^n factorial experiments for analysis by Yates technique.

Catalyst, 2,6-lutidine flow, temperature, pressure, and reactor residence time were all found to be significant variables. The conversion to reaction products was found to proceed via catalytic reaction while noncatalytic reaction was not significant. The very important discovery was made that hydrogen to lutidine feed ratio is very highly significant in conversion to the intermediate reaction product while being insignificant in conversion to end reaction products.

CONTENTS

ACKNOWLEDGMENTS

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Dedicated to

Carol and Russell, who have paid a higher price than they realize so this might be accomplished.

INTRODUCTION

The necessity of developing the experimental design described here arose in the initial investigation of the hydrodenitrogenation of shale oil. This dissertation covers the development and analysis of the design in the context of the actual problem being faced. The problem was to determine which effects of the five controllable process variables significantly influence the hydrodenitrogenation of 2,6-lutidine in a gas-phase, continuous-flow, stirred-tank reactor. The experimental design was also the first step in the appraisal of the usefulness of this approach to studying complex catalytic gas phase reactions.

General Background

The current shortage of satisfactory hydrocarbon fuels has focused attention on shale oil once again. The high nitrogen content of this fuel presents a definite problem because it poisons many refining catalysts[19] and it promotes instability in fuel products[31]. Petroleum crude oils generally have a much lower nitrogen content than does shale oil[3]. As a result, there are very few refineries with sufficient nitrogen removal capacity to process raw shale oil[2] and there is a lack of information concerning denitrification of hydrocarbons. Catalytic hydrogenation (hydrodenitrification) is the prime candidate for accomplishing the necessary nitrogen removal[8].

2,6-Lutidine

The nitrogen content in shale oil consists mostly of alkylated pyridine homologs and similar heterocyclic hydrocarbons[40]. 2,6-lutidine is characteristic of these compounds and has been idenitified in shale oil[35]. This and its availability made it the candidate for this study.

Catalyst

A nickel-molydenum catalyst was selected because such catalysts are preferred for hydrorefining of gasoline and naphtha containing nitrogen[37]. Aero HDS-9 catalyst manufactured by American Cyanimide Company was specifically chosen because the HDS series catalysts are already widely accepted[1]. The catalyst is activated with hydrogen sulfide and hydrogen prior to use in accordance with recommended practice[38].

Reactor

A continuous-flow, stirred-tank reactor was selected and developed for this study because it has a unique and useful property; the composition of the product leaving the reactor is the same as the composition throughout the bulk phase in the reactor and over the catalyst. Solid catalyst pellets are suspended in paddle-baskets (see fig. 1) which also serve to stir the bulk phase. Reactants are fed into the reactor continuously and products continuously drawn off at the reaction pressure and temperature during the experimental run. This reactor concept for laboratory analysis was developed at Notre Dame University where it was used to study the catalytic oxidation of carbon monoxide at atmospheric pressure[36].

This type of reactor has also been used in studying the hydrocracking of butane[34], and in studies of the methanation step in the Hygas coal gasification process[32]. No references were found concerning the use of the Carberry Reactor, as it has been christened in the literature, under the conditions used in this investigation.

DEVELOPMENT OF THE EXPERIMENTAL DESIGN

Experimental design is an important consideration in any investigation. In this situation, there were several factors which make the use of an efficient experimental design a virtual necessity.

Necessity for Experimental Design

Catalytic hydrogenation is, in fact, a complex combination of reactions. This mutltiplies the number of reaction products, and greatly complicates the analysis of the experimental results. A usable basis for preliminary estimates of the reaction parameters was not available.

The reaction products were analyzed by gas chromatography. Even though this is a proven and widely used technique, there was only scant information available to serve as a basis for determining the chromatograph operating conditions and for the design of the liquid partition columns. This meant that the only practical way to develop the analysis scheme for the reaction products was to make experimental runs.

The reactor used was a modified version of a batch hydrogenation reaction apparatus. Certain parts of the modification were subject to considerable wear. It was necessary to use severe operating pressures and temperatures, and corrosive reactants. All this made it necessary to minimize the total elapsed time of operation for the reactor.

Each experimental run was arduous and far from routine. The continuous, attended time of operation for each run ranged

from 12 hours to 17 hours with an additional four to ten hours required for preparation and equipment maintenance; each run also required at least four hours to complete the chromatographic analysis of the reaction products.

The feed components for the reaction were only available in limited quantity because of their expense.

Indeed, use of an efficient experimental design is the only practical way to assure gaining useful information in such circumstances.

Variables

There were five basic process variables which, from engineering considerations, could influence the reaction under study:

1. The amount of catalyst in the reactor.
2. The temperature of the bulk phase in the reactor.
3. The pressure in the reactor.
4. The hydrogen feed rate.
5. The 2,6-lutidine feed rate.

The ranges over which these parameters were varied in the experiment were determined by engineering considerations subject to the operating limitations of the equipment, and are discussed in Appendix E.

Catalyst: The amount of catalyst in the reactor influences the degree of reaction; the more catalyst there is, the more catalytic surface area is available on which reaction can occur, generally speaking. This does not, however, imply that this variable can be excluded from the experimental design because its participation in the reaction is already

known. Temperature and concentration gradients within catalyst pellets, surface adsorptive effects, and transport of reactants and products within the catalyst pellets, among other effects, all can produce considerable variations in the reaction process.

Temperature: The primary influence of temperature is expected to be manifested in the rate at which the reaction occurs. The basic expression for the rate of reaction is[17]:

$$r = k \prod_{i=1}^{n} (C_i^{a_i}) \qquad (1)$$

where r = rate of reaction
k = reaction velocity constant
C_i = concentration of reactant i
a_i = order of reaction with respect to the reactant i
n = number of reactants.

The term "reaction velocity constant" is an unfortunate choice for describing the proportionality factor (k) since it is not a constant at all but a function of temperature as expressed in the Arrhenius equation[18]:

$$k = k_o \, e^{-E/RT} \qquad (2)$$

where k = reaction velocity constant
k_o = frequency factor or preexponential (a constant)
E = activation energy (a constant)
R = the gas constant
T = temperature of reaction

The temperature on the catalyst surface where the actual reaction occurs is strongly influenced by the bulk phase temperature in the reactor. Since the reaction temperature on the catalyst surface cannot be directly controlled or measured, the bulk phase temperature is the parameter which is controlled.

The second important influence of temperature is its effect on the concentration of the reactants and products in the reactor. Since this is a gas phase reaction, this can be visualized by considering the ideal gas law[20]:

$$PV = \frac{m\,RT}{M.W.} \qquad (3)$$

where P = pressure
V = volume
m = mass of gas
M.W. = molecular weight of the gas
R = the gas constant
T = temperature

The expression for concentration using the ideal gas law then is:

$$\text{concentration} = \frac{m}{V\,(M.W.)} = \frac{P}{RT} \qquad (4)$$

So, generally speaking, concentration decreases as temperature increases.

Pressure: The primary effect of pressure is its effect on concentration of the reactants and products as can be seen from equation (4) above. Pressure can also affect the rate of side reactions which deactivate catalysts by deposition of coke on the catalyst surface, and adsorption on the catalyst.

Hydrogen Feed Rate: Hydrogen is one of the primary reactants. The rate at which it enters the reactor affects both its concentration in the reactor and the residence time in the reactor, that is the amount of time the reactants are exposed to the catalyst. It also affects the extent of nitrogen removal since the reaction is expected to take place in a series of steps:

2,6-lutidine + hydrogen → 2,6-dimethylpiperdine

2,6-dimethylpiperidine + hydrogen → 1-methylhexylamine

1-methylhexylamine + hydrogen → ammonia + heptane

Each of these steps is a reaction competing for the available hydrogen. Variation of the ratio of hydrogen to lutidine in the reactor feed thus becomes an important factor in determining which reaction step controls the degree of conversion to the end product.

2,6-Lutidine Feed Rate: 2,6-lutidine is the second primary reactant. The basic effects of variation in its flow rate are seen in concentrations in the reactor and the residence time in the reactor.

Experimental Design Selection

The goal was to identify significant effects and to obtain some indication of the operating characteristics of the experiment. Some variation of the 2^n factorial design was then appropriate; such designs are most effecient in such cases, especially when it is desireable to minimize the experimental effort. Indeed, even one complete replicate of a 2^5 factorial experiment would entail 32 experimental runs to study all effects and interactions of the five process variables. This was well beyond the limits of the available resources. Some fractional replication of a 2^5 design then was the most feasible alternative.

Terminology: The terminology used in this dissertation corresponds to that commonly used in discussing factorial designs. A readable discussion of such designs and the terminology involved is provided by Davies[10].

One term deserves specific attention because of its frequent use: interaction effect which cannot be distinguished from each other in the statistical analysis are referred to as an alias group.

Interaction Effects: In developing experimental designs it is very useful to attempt to predict how each interaction will manifest itself in the experiment. Table 1 in Appendix B is an attempt to qualitatively characterize the variable interactions. It represents a balance of the expected impact associated with the explaination given for each interaction against the likelihood that the interaction would be significant. The likelihood that an interaction will be significant decreases as the number of variables in the interaction increases. The complexity of the problem being faced and the lack of a priori detailed knowledge about the experiment make this an intuitive evaluation at best. Table 15 in Appendix E shows the symbols used to refer to the five process variables in interactions and treatment combinations, and illustrates that use.

Conventional Design: A $1/4 \times 2^5$ design is the smallest design in which five factors can be investigated. The most common choice is a $1/4 \times 2^5$ design with two three factor interactions as defining contrasts since this avoids confounding primary effects with each other. This is particularly useful when primary effects are the only effects that are likely to be significant.

The approach taken in this study did not use such a design because the engineering considerations indicated that certain third order interactions could be significant, and the execution of a $1/4 \times 2^5$ design as one block of the $1/2 \times 2^5$ design described below was desirable.

1/2 Replicate of a 2^5 Experiment: The key element in designing fractional replications is the defining contrast[11]. The rather obvious choice in this case is the conventional one, the fifth order interaction[12] (CTPHL). This allows estimation of all the primary effects and all the second order interactions. In this particular case, even potentially significant higher order interactions can be estimated since they are confounded with second order interactions that are expected to be insignificant. Table 2 in Appendix B shows the $1/2 \times 2^5$ design for this situation[24]. The 16 experimental runs required in this design could be conducted within the available resources, but it was still desirable to attempt the acquisition of useable information in fewer than 16 runs. To that end, it was decided to divide the 16 runs into two blocks. The principal block could be executed as $1/4 \times 2^5$ experiment; and, if the results were not conclusive, the second block of experiments could then be performed with the assurance of conclusive results being available. The choice of the confounding interaction to divide the experiment into two blocks was determined by the following $1/4 \times 2^5$ design.

1/4 Replicate of a 2^5 Experiment: Again, the choice of the defining contrasts determine the design. CTPHL was the defining contrast in the parent $1/2 \times 2^5$ design. This left one arbitrary choice of a defining contrast to be made since the last one would be developed from those already chosen[25]. Since the choice of CTPHL was imposed, one of the defining contrasts would have to be either a primary effect or a two factor interaction.

If a two factor interaction was chosen, two primary effects would be confounded. Of those possible, TL and HL emerged as prime candidates. Their effects were expected to be neglible. Their selection would result in an acceptable three factor interaction as the remaining defining contrast. The resulting confounded primary effects were thought to be acceptable. Table 3 and 4 in Appendix B show the designs that would result from the choice of TL and HL respectively.

If a primary effect was selected as a defining contrast, information about that effect would be completely lost. Of the primary effects, only L was acceptable since it was certain to be included in subsequent investigation. Table 5 in Appendix B shows the resulting design.

From these three alternatives, TL was selected. Choice of HL would have resulted in confounding three potentially significant effects with other primary effects. Choice of L would have eliminated any possible indication of the significance of that effect. This also made TL the confounding interaction for dividing the treatment combinations of the $1/2 \times 2^5$ experiment

into two blocks as shown in Table 2 in Appendix B. The techniques described by Johnson and Leone[26] were used to develop the design.

ANALYSIS OF THE EXPERIMENT

There were two basic aspects in the analysis of this experiment: first, the collection and reduction of the data; second, the statistical analysis. Neither of these was straightforward.

Data Description

Since the reaction actually consisted of a series of reactions, each of the intermediate reaction products was expected to be present in the reactor outlet stream along with the products of numerous side reactions. Using the chromatograms, the response for each individual component in the reactor product stream was determined relative to the 2,6-lutidine remaining in the stream; such relative response is an indication of the concentration of each component in the product stream. These relative responses then constitute the data used in this experiment. It is worthwhile to consider the intermediate reaction products in addition to the end product since information can then be obtained concerning rate controlling steps and the relative rates of reaction for each step in the reaction series. Only two of the expected products could be clearly identified on the chromatograms; they were n-heptane (the end product), and 2,6-dimethylpiperidine. For some engineering purposes, it is useful to consider conversion per gram of catalyst. Therefore, the data is analyzed both on a total response basis and on the basis of response per gram of catalyst.

For each experimental run, that is each treatment combination, three liquid samples were collected and analyzed by gas chromatography, giving three observations at each treatment combination. The difficulty in making an experimental run lay in preparation and start-up of the apparatus. Once reaction conditions were reached, the collection of additional samples came at a relatively small cost. It is obviously, then, beneficial to collect as much data at each set of conditions as might be useful in avoiding the cost of additional runs. This procedure was also necessary to provide data for subsequent engineering analysis not included here. It also facilitates an estimate, with several degrees of freedom, of the error variance from within the experiment itself; that is, indeed, valuable[13].

Statistical Techniques

The statistical analysis problem, then is that of a $1/4 \times 2^5$ experiment in three replications. The calculation of the effect totals was performed using both Yates technique and a table of algebraic signs developed from Johnson and Leone[28] in order to provide some verification of the validity of the resulting effect totals.

The tacit assumption seemingly made by several authors[4,14,21,27,33] is that fractional 2^n factorial designs will occur only in single replication. The analysis for this problem can, however, be developed from the more general case of multiple replications of a full factorial design.

Multiple Observations: In order to incorporate the three observations at each treatment combination into the calculations of treatment sum of squares, the sum of the observations at each treatment combination are used[28] instead of individual observations as the first numerical column for both Yates technique and algebraic sign table calculations. The total effects, average effects, and mean squares are then calculated in the usual way[23]. The average effects and mean squares are then divided by three[15], the number of observations at each treatment combination.

The total sum of squares in this problem was treated in two parts: the treatment sum of squares, and the error (residual) sum of squares[22]. There are 3 x 8 = 24 degrees of freedom in the experiment. Eight of these are used in estimation of the seven effects and the mean. This leaves 16 degrees of freedom for the error estimate. So, the residual sum of squares is found by subtracting the treatment sum of squares from the total sum of squares and dividing the result by 16[15].

Treatment Sum of Squares by Algebraic Sign Table: Table 6 in Appendix C is an algebraic sign table developed from that found in Johnson and Leone; they also describe the construction and use of such a table[28]. Table 6 was constructed by deleting from Johnson and Leone's table the entries for treatment combinations which do not appear in the design used here. Then, since the effects in an alias group will all have the same sign for each of the treatment combinations, the sign entry need be made only once for each group; thus reducing the table to the format in Table 6.

The use of Table 6 is best explained by an example. The effect total for effect C is found by summing the effects using their associated sign from row "C" of the table: C = -(1) + cp + ch - ph - tl + ctpl + cthl -tphl. The effect total for each of the effects is calculated in this fashion. The average effect and the effect mean square are then calculated from the resulting effect totals. Appendix C includes the calculations using this approach for the data in this experiment.

Treatment Sum of Squares by Yates Technique: The mechanics of calculating the effect totals in this experiment are the same as in complete replications. The difference in this problem is the technique used to order the treatment combinations and their associated data values at the start of the analysis. Explainations concerning the analysis of 1/2 replications were found[5,30], and the technique described below used here was developed from them.

If the experiment had only three factors, the eight treatment combinations would be a complete replicate, and the ordering of the treatment combinations would be straightforward. So, ignore two of the letters in the treatment combinations, temporarily, to reduce the experiment to a 2^3 factorial. Each of the defining contrasts must contain at least one of the ignored letters. Since CTPHL includes all the possible letters, both letters will appear in it. So, the obvious course is to choose one letter from each of the two remaining defining contrasts. For example, suppose t and p are chosen to be ignored. List the treatment combinations

in the experiment, and underline the letters to be ignored. Then, ignoring the underlined letters, arrange the list in the usual way[6]:

Defining Contrasts CTPHL, TL, CPH

Principal Block		Yates Ordered List
(1)		(1)
cp		cp
ch	rearrange to	ph
ph		ch
tphl		tl
cthl		ctpl
ctpl		tphl
tl		cthl

The usual Yates technique of summing and differencing[29] is then applied to the Yates ordered list to calculate the effect totals. The only essential rule is that each defining contrast must be "represented" among the ignored letters[30]. If this is not followed, one treatment combination is ignored in the list, and the analysis is therefore inoperative.

The technique described above was developed because the technique of deleting and restoring letters[5,30] becomes cumbersome and complex for designs using fractional replications smaller than 1/2. The technique is used in Appendix D to analyze the experimental data. A different set of letters is ignored in each analysis case. The results agree with those calculated using the algebraic sign table technique described above.

RESULTS DISCUSSION

The effects mean squares were tested by use of the F test[7] to determine if the hypothesis that there are no differences between the effects was valid. The results are summarized in Table 17 in Appendix E.

F Ratio Inferences

Generally speaking, the F ratios corroborate the expectations developed in the planning of the experiment. This in itself is valuable since it validates the equipment and analysis designs as well as the general experimental approach. This validation was the second major objective in conducting the experiment.

The catalyst effect (C) was significant in all cases. Its variation between analysis on a total catalyst basis and a unit weight basis was expected, but the variation warrants attention in subsequent engineering analysis since there are apparent differences between the values for n-heptane and for 2,6-dimethylpiperidine.

The temperature-lutidine flow effect (T,L) is significant in all four cases, as expected.

The F ratio values for the hydrogen parameter (H) provide, probably, the most important information in the entire experiment. The preponderance of its F ratio values for 2,6-dimethlypiperidine and the lack of significant values for n-heptane probably point to the rate controlling step in the reaction sequence. Had the statistical analysis been performed only on the n-heptane this information would have been obsured.

The pressure effect (P) is significant in all cases, but there is a notable difference between the analysis on a catalyst unit weight basis and a total catalyst basis. This is probably associated with the reaction mechanism.

The residence time parameter (PHL) is significant, though not for n-heptane calculated on a unit catalyst weight basis; this is probably also a result of the reaction mechanism.

The catalytic reaction effect (CHL) is significant in all cases indicating that the use of this experimental approach is useful from the engineering viewpoint. If this were not the case, the entire body of engineering thinking regarding the experiment would be grossly suspect.

The hydrogen-lutidine interaction (HL) is not significant. This infers that noncatalytic reaction is not significant, which, in turn, implies that blank runs without catalyst are not required to isolate catalytic effects in the reaction.

Remarks on Statistics

The most important aspect of the design used was the recognition that multiple replications were available, and the resultant modification of the standard fractional factorial design analysis. Had the least significant effects been used to estimate the residual mean square, as is usually the case[16], the general conclusions could have been very similar, except that, in several instances, effects would not be considered

significant since their F ratio values would not exceed the critical values. The residual mean square calculated using the three replications exceeds the least significant effect in all cases by a factor of approximately 10, except the case of 2,6-dimethlypiperidine on a total catalyst basis, where the factor is about 10,000. F ratio values calculated using the least significant effect, in that case, lead to conclusions that are very inconsistant with the other cases. This could lead the experimenter to ignore some of the data or to pursue a completely unfruitful course in his engineering analysis.

A larger experiment, such as a $1/2 \times 2^5$, would probably resolve any controversy concerning the signifance of the various effects. However, since the results seem to generally agree with the expectations for the experiment, additional experimental effort is probably better spent pursuing other goals.

The experimental runs made for this experiment served not only to supply the data included here, but also to shake-down the equipment and procedure. As a result, during the course of the experiment, various needed repairs and equipment modifications were made, and the expertise of the operator improved significantly. Since the runs were made in a randomized sequence, it is assumed that the effects of these changes do not detract from the significance of the results.

The design used was probably the most productive one available. In light of the results obtained, a cursory

examination of the alternate designs (Tables 4, 5) seems to indicate that they could have produced results that would be satisfactory, but not as conclusive as those obtained here. The use of $1/4 \times 2^5$ designs having two four factor interactions as defining contrasts would have been unsatisfactory since three of the significant effects would have been confounded with other significant effects, and all of the two factor interactions would be confounded with other two factor interactions (except the one lost as the third defining contrast). Use of $1/4 \times 2^5$ designs with two three factor interactions as defining contrast could have been used, but the information on the lack of noncatalytic reaction as well as the two significant third order effects could have been lost.

General Observations

The following remarks, general though they may be, are worth considering because they deal with very basic factors which determine success or failure of attempts to employ experimental design, and are directly applicable to this investigation.

Even though the a priori knowledge about the reaction and equipment behavior was indeed meager, the experiment was rather successful. The expectations for the experiment were developed through thorough application of very basic engineering knowledge, the kind of knowledge that is available in most situations. It is also noteworthy that the experiment could be greatly reduced in size via application of such

elemental engineering without restricting the scope of the study. In fact, the experimental design produced very significant information over and above the basic engineering data. It also facilitates an assessment of the confidence that can be placed in the results.

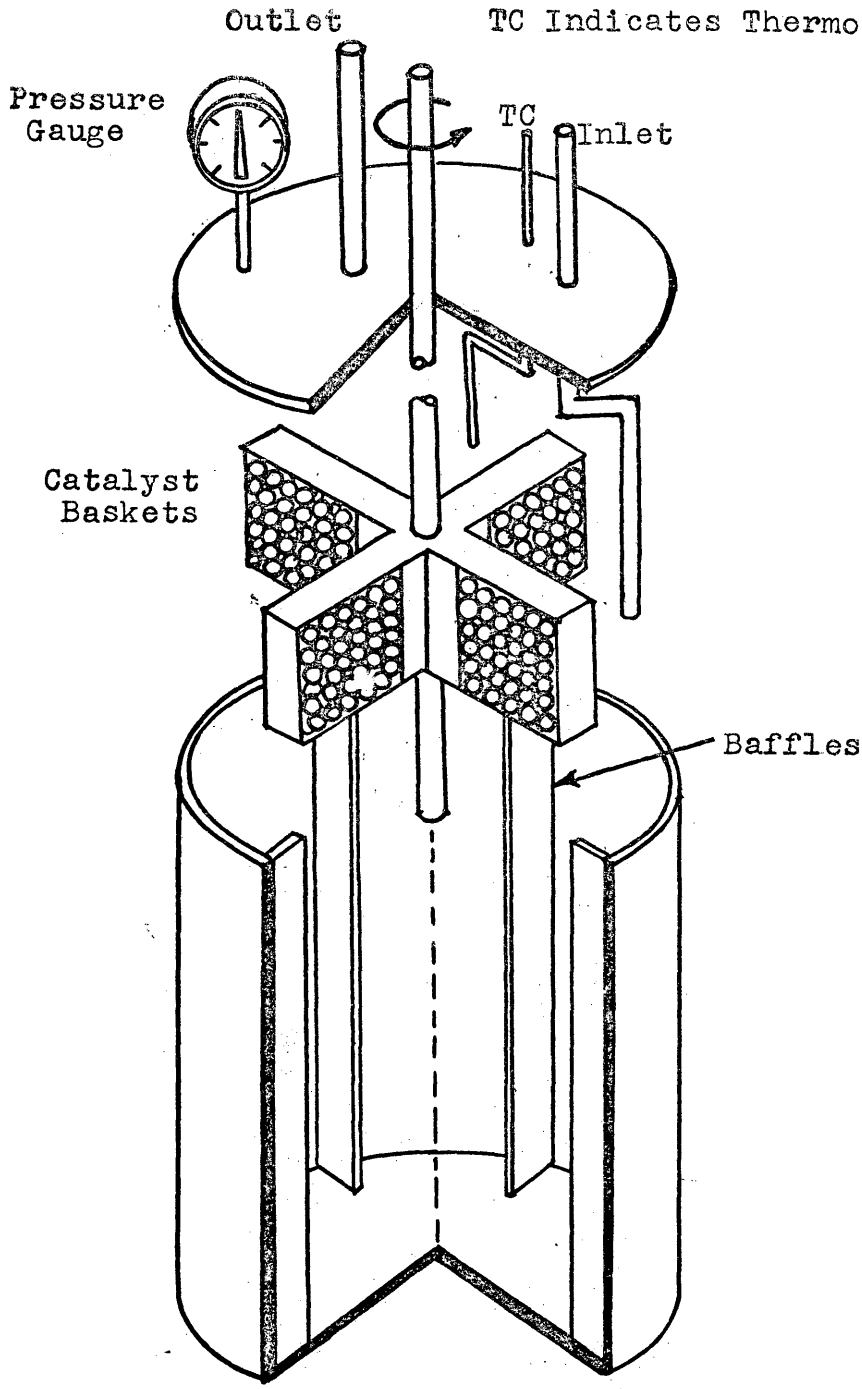
The use of experimental design, even in the earliest stage of the experiment, produced useful data, thus reducing the number of runs significantly while assuring achievement of definitive results. With the exception of runs in which mechanical failures negated the collection of data, all the experimental runs produced useable data.

The tendency to force data into standard analysis schemes is common. In this case, one might be tempted to average the three observations at each set of conditions and then perform the standard analysis, rather than adopting the somewhat unorthodox tact of treating the data as a fractional factorial experiment in three replications. The averaging, though it produces a better estimate of the value of each point, supresses useful information. The principle at work here might be stated thus: analyze data at the most basic level possible since each level of calculational operation extracts its price in useful information.

APPENDIX A

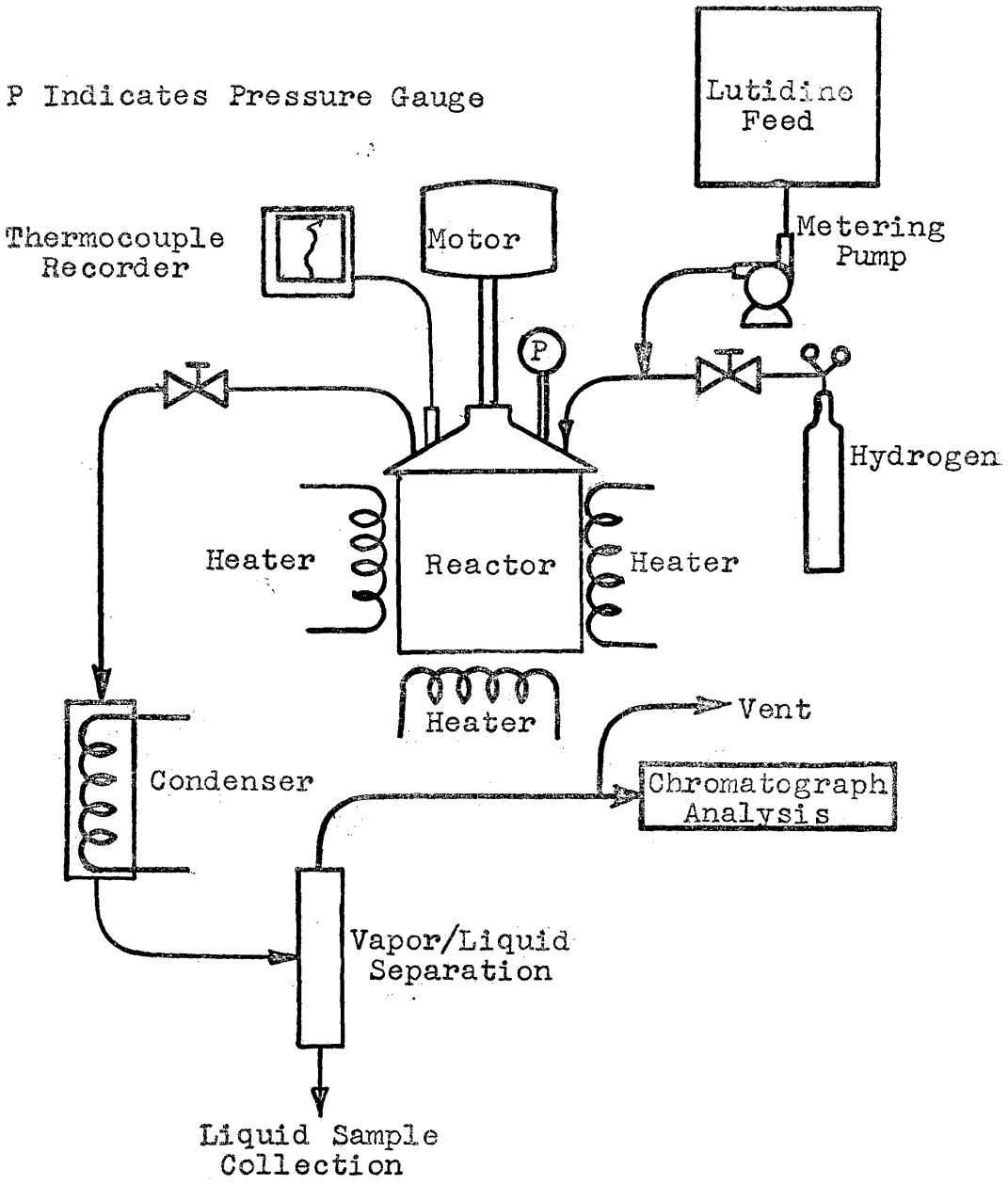
PROCESS FLOW SCHEME

The general flow scheme is shown in figure 2. The hydrogen is fed under pressure through a metering valve into the reactor. The lutidine is fed as a liquid by a metering pump, and vaporizes in the inlet line in the reactor. Temperature in the reactor is measured by a thermocouple; pressure is measured by a pressure gauge. The reaction products leave the reactor through a metering valve which is used to regulate the pressure in the reactor. The product stream passes through a condenser. Then the liquid portion of the stream is separated, measured, and collected subsequent analysis by gas chromatography. The vapor stream is analyzed by gas chromatography and vented.



REACTOR SCHEMATIC

Figure 1.



PROCESS FLOW SCHEMATIC
Figure 2.

APPENDIX B

Table 1

Interactions Characterization

Interaction Symbol	Plausible Explaination	Expected* Influence
CT	Change in Catalyst Activity	weak
CP	Inhibition of Catalyst Deactivation	fair
TP	none	none
CTP	Inhibition of Catalyst Deactivation	weak
CH	Catalyst-Hydrogen Reaction	weak
TH	Hydrogen Concentration	weak
CTH	Catalyst-Hydrogen Reaction	none
PH	Hydrogen Concentration	fair
CPH	Hydrogen Adsorption	weak
TPH	Hydrogen Concentration	weak
CTPH	Hydrogen-Catalyst Reaction	none
CL	Catalytic-Lutidine Reaction	weak
TL	Non-Catalytic Lutidine Reaction	none
CTL	Catalytic Lutidine Reaction	weak
PL	Lutidine Concentration	fair
CPL	Lutidine Adsorption	weak
TPL	Lutidine Concentration	weak
CTPL	Lutidine Adsorption	none
HL	Non-Catalytic Reaction	none
CHL	Catalytic Reaction	strong
THL	Non-Catalytic Reaction	weak
CTHL	Catalytic Reaction	fair
PHL	Residence Time	strong
CPHL	Catalytic Reaction	none
TPHL	Non-Catalytic Reaction	weak
CTPHL	none	none

* Strong: an impact equal to that of a primary effects.

Fair: a lesser impact.

Weak: a barely discernable impact.

Table 2

$\underline{1/2 \times 2^5}$ Experiment

CTPHL is the Defining Contrast

Effect	Aliases	Treatment Combinations	
I	CTPHL	TL is the Confounding Interation	
C	TPHL	Block 1	Block 2
T	CPHL		
P	CTHL	(1)	ctph
H	CTPL	tphl	cphl
CT	PHL	cthl	ct
TP	CHL	ctpl	cl
TH	CPL	cp	tp
L	CTPH	ch	th
CP	THL	tl	pl
CH	PHL	ph	hl
CL	TPH		
TL	CPH		
PH	CTL		
PL	CTH		
HL	CTP		

See table 15 for definition of the symbols.

Underlined effects could be expected to be significant.

Table 3

$\underline{1/4 \times 2^5}$ Experiment

Defining Contrasts are CTPHL, TL, CPH

Effect	Aliases			Principal Block
I	CTPHL	TL	CPH	(1)
C	TPHL	CTL	PH*	cp
T	CPHL	L	TCPH	ch
H	CTPL	THL	CP*	ph
P	CTHL*	TPL	CH	tphl
CT	PHL	CL	TPH	cthl
TP	CHL	PL*	CTH	ctpl
TH	CPL	HL	CTP	tl

Underlined effects were expected to be significant.

* denotes effects that could be significant.

See Table 15 for definition of the symbols.

Table 4

$1/4 \times 2^5$ Experiment

Defining Contrasts are CTPHL, CTP, HL

Effect	Aliases		
I	CTPHL	HL	CTP
C	TPHL	CHL	TP
T	CPHL	THL	CP
H	CTPL	L	CTPH
P	CTHL	PHL	CT
CH	TPL	CL	TPH
TH	CPL	TL	CPH
PH	CTL	PL	CTH

Table 5

$1/4 \times 2^5$ Experiment

Defining Contrasts are CTPHL, L, CTPH

Effect	Aliases		
I	CTPHL	L	CTPH
C	TPHL	CL	TPH
P	CTHL	PL	CTH
H	CTPL	HL	CTP
T	CTPHL	TL	CPH
CP	THL	CPL	TH
CH	TPL	CHL	TP
PH	CTL	PHL	CT

See Table 15 for definition of the symbols.

Underlined effects could be expected to be significant.

APPENDIX C

Table 6

Algebraic Sign Table for Calculating

Effect Mean Squares From Treatment Combinations

				Treatment Combinations							
Effect	Aliases			(1)	cp	ch	ph	tl	ctpl	cthl	tphl
I	CTPHL	TL	CPH	+	+	+	+	+	+	+	+
C	TPHL	CTL	PH	-	+	+	-	-	+	+	-
T	CPHL	L	CTPH	-	-	-	-	+	+	+	+
CT	PHL	CL	TPH	+	-	-	+	-	+	+	-
P	CTHL	TPL	CH	-	+	-	+	-	+	-	+
TP	CHL	PL	CTH	+	-	+	-	-	+	-	+
H	CTPL	THL	CP	-	-	+	+	-	-	+	+
TH	CPL	HL	CTP	+	+	-	-	-	-	+	+

Developed from Johnson and Leone[28].

Table 7

Analysis Using Sign Table for n-Heptane Chromatographic Relative Response Data

Treatment Combination	Relative Response
(1)	0.008107
cp	0.000779
ch	0.026449
ph	0.006914
tl	0.112546
ctpl	0.060816
cthl	0.183850
tphl	0.007362

Effect Total (1)	Average Effect (2)=(1)/12	Mean Square (3)=(1)x(1)/24	Effect *	F Ratio (4)=(3)/Error
0.406824	0.033902		I	-
0.136965	0.011414	0.00078165	C	16.67
0.322326	0.026860	0.00432891	T	92.33
0.112552	0.009379	0.00052783	CT	11.26
-0.255080	-0.021257	0.00271108	P	57.82
-0.201356	-0.016780	0.00168934	TP	36.03
0.042328	0.003527	0.00007465	H	1.59
-0.006628	-0.000552	0.00000183	TH	0.04

Treatment Sum of Squares = 0.01011528

* Only first column of alias list shown.

Total Sum of Squares = 0.01086545
Residual Sum of Squares = 0.00075017

Residual Sum of Squares = 0.00075017/16=0.00004689
(Error Estimate)

Table 8

Analysis Using Sign Table for n-Heptane

Relative Chromatographic Response per Gram of Catalyst

Treatment Combination	Relative Response
(1)	0.000811
cp	0.000060
ch	0.002035
ph	0.000691
tl	0.011255
ctpl	0.014142
cthl	0.004678
tphl	0.000736

Effect Total (1)	Average Effect (2)=(1)/12	Mean Square (3)=(1)x(1)/24	Effect *	(4)=(3)/Error
0.034408	0.002867		I	-
0.007422	0.000619	0.00000230	C	4.95
0.027215	0.002268	0.00003086	T	66.58
0.006237	0.000520	0.00000162	CT	3.50
-0.022076	-0.001840	0.00002031	P	43.81
-0.017889	-0.001491	0.00001333	TP	28.77
0.000801	0.000067	0.00000003	H	0.06
-0.002910	-0.000242	0.00000035	TH	0.76

Treatment Sum of Squares = 0.00006880

* Only first column of alias list shown.

Total Sum of Squares = 0.00007621
Residual Sum of Squares = 0.00000741

Residual Mean Square = 0.00000741/16 = 0.00000046
(Error Estimate)

Table 9

Analysis Using Sign Table for 2,6-Dimethylpiperidine

Relative Chromatographic Response Data

Treatment Combination	Relative Response
(1)	0.227512
cp	0.139408
ch	0.327832
ph	0.398510
tl	0.178799
ctpl	0.043029
cthl	0.338384
tphl	0.243476

Effect Total (1)	Average Effect (2)=(1)/12	Mean Square (3)=(1)x(1)/24	Effect	F Ratio (4)=(3)/Error
1.896951	0.158079		I	-
-0.199644	-0.016637	0.00166074	C	13.11
-0.289575	-0.024131	0.00349389	T	27.58
0.117920	0.009827	0.00057938	CT	4.57
-0.248105	-0.020675	0.00256484	P	20.24
-0.213254	-0.017771	0.00189488	TP	14.96
0.719454	0.059954	0.02156725	H	170.23
0.000610	0.000051	0.00000002	TH	0.00

Treatment Sum of Squares = 0.03176101

* Only first column of alias list shown.

Total Sum of Squares = 0.03378818
Residual Sum of Squares = 0.00202717

Residaul Mean Square = 0.00202717/16 = 0.00012670
(Error Estimate)

Table 10

Analysis Using Sign Table for 2,6-Dimethylpiperidine

Relative Chromatographic Response per Gram of Catalyst Data

Treatment Combination	Relative Response
(1)	0.022751
cp	0.010724
ch	0.025218
ph	0.039851
tl	0.017880
ctpl	0.003310
cthl	0.026030
tphl	0.024348

Effect Total	Average Effect (2)=(1)/12	Mean Square (3)=(1)x(1)/24	Effect	F Ratio (4)=(3)/Error
0.170111	0.014176		I	-
-0.039549	-0.003296	0.00006517	C	13.11
-0.026977	-0.002248	0.00003032	T	27.58
0.013773	0.001148	0.00000790	CT	4.57
-0.013646	-0.001137	0.00000776	P	20.24
-0.018858	-0.001571	0.00001482	TP	14.96
0.060781	0.005065	0.00015393	H	170.23
-0.002407	-0.000201	0.00000024	TH	0.00

Treatment Sum of Squares = 0.00028015

* Only first column of alias list shown.

Total Sum of Squares = 0.00029677
Residual Sum of Squares = 0.00001662

Residual Mean Square = 0.00001662/16=0.00000104
(Error Estimate)

APPENDIX D

Table 11

Yates Analysis of n-Heptane

Relative Response Data

Treatment Combination	Relative Response	(1)	(2)	Effect Total (3)
(1)	0.008107	0.008886	0.042249	0.406824
cp	0.000779	0.033363	0.364575	-0.255080
ch	0.026449	0.173362	-0.026862	0.042328
ph	0.006914	0.191212	-0.228218	-0.136965
th	0.112546	-0.007328	0.024478	0.322326
ctpl	0.060816	-0.019534	0.017850	-0.201356
cthl	0.183850	-0.051730	-0.012207	-0.006628
tphl	0.007362	-0.176488	-0.124759	-0.112552

Effect Total (3)	Average Effect (4)=(3)/12	Mean Square (5)=(3)x(3)/24	Effect *
0.406824	0.033902		I
-0.255080	-0.033902	0.00271108	P
0.42328	0.003527	0.00007465	H
-0.136965	-0.011414	0.00078165	C
0.322326	0.026860	0.00432891	T
-0.201356	-0.016780	0.00168934	TP
-0.006628	-0.000552	0.00000183	TH
-0.112552	-0.009379	0.00052783	CT
Treatment Sum of Squares =		0.01011529	

* Only the first Column of the alias List is shown.

Table 12

Yates Analysis of n-Heptane

Relative Response per Gram of Catalyst

Treatment Combination	Relative Response	(1)	(2)	(3)	Effect Total
(1)	0.000811	0.002845	0.003597	0.034408	
ch	0.002035	0.000751	0.030811	0.000801	
cp	0.000060	0.025397	0.001855	-0.022076	
ph	0.000691	0.005414	-0.001054	-0.007422	
tl	0.011255	0.001224	-0.002094	0.027215	
cthl	0.014142	0.000632	-0.019983	-0.002910	
ctpl	0.004678	0.002888	-0.000592	-0.017889	
tphl	0.000736	-0.003942	-0.006830	-0.006237	

Effect Total (3)	Average Effect (4)=(3)/12	Mean Square (5)=(3)x(3)/24	Effect *
0.034408	0.002867		I
0.000801	0.000067	0.00000003	H
-0.022076	-0.001840	0.00002031	P
-0.007422	-0.000619	0.00000230	C
0.027215	0.002268	0.00003086	T
-0.002910	-0.000242	0.00000035	TH
-0.017889	-0.001491	0.00001333	TP
-0.006237	-0.000520	0.00000162	CT

Treatment Sum of Squares=0.00006880

* Only first column of Alias List shown.

Table 13

Yates Analysis of 2,6-Dimethylpiperidine

Relative Response

Treatment Combination	Relative Response	(1)	(2)	Effect Total (3)
(1)	0.022751	0.047969	0.098544	0.170111
ch	0.025218	0.050575	0.071567	-0.039549
ph	0.039851	0.043910	-0.026661	-0.013646
cp	0.010724	0.027657	-0.012888	-0.060781
tl	0.017880	0.002467	0.002606	-0.026977
cthl	0.026030	-0.029127	-0.016252	0.013773
tphl	0.024348	0.008150	-0.031594	-0.018858
ctpl	0.003310	-0.021032	-0.029187	0.002407

Effect Total (3)	Average Effect (4)=(3)/12	Mean Square (5)=(3)x(3)/24	Effect *
0.170111	0.014176		I
-0.039549	-0.003296	0.00006517	C
-0.013646	-0.001137	0.00000776	P
-0.060781	-0.005065	0.00015393	H
-0.026977	-0.002248	0.00003032	T
0.013773	0.001148	0.00000790	CT
-0.018858	-0.001571	0.00001482	TP
0.002407	0.000201	0.00000024	TH

Treatment Sum of Squares 0.00028014

* Only first Column of alias list shown.

Table 14

Yates Analysis of 2,6-Dimethlypiperidine

Relative Response per Gram of Catalyst

Treatment Combination	Relative Response	(1)	(2)	Effect Total (3)
(1)	0.227512	0.366920	1.093263	1.096951
cp	0.139408	0.726342	0.803688	-0.199644
ph	0.398510	0.221828	-0.158782	0.719454
ch	0.327832	0.581860	-0.040862	0.248105
tl	0.178799	-0.088104	0.359422	-0.289575
ctpl	0.043029	-0.070678	0.360032	0.117920
tphl	0.243476	-0.35771	0.017426	0.000610
cthl	0.338384	0.094909	0.230680	0.213254

Effect Total (3)	Average Effect (4)=(3)/12	Mean Square (5)=(3)x(3)/24	Effect *
1.896951	0.158079	0.00000000	I
-0.199644	-0.016637	0.00166074	C
0.719454	0.059954	0.00256725	H
0.248105	0.020675	0.00256484	P
-0.289575	-0.024131	0.00349389	T
0.117920	0.009827	0.00057938	CT
0.000610	0.000051	0.00000002	TH
0.213254	0.017771	0.00189488	TP

Treatment Sum of Squares =0.03176101

* Only first column of alias list shown.

APPENDEX E

VARIABLE SETTINGS

The variable settings are summarized in Table 15. Tolerance on variable settings represented the approximate range within which the variables could be controlled.

The lower temperature setting of 600° F is the lower limit used in hydrotreating reactors. The upper temperature setting of 650° F is the recommended upper temperature limit for the Teflon seals in the reactor.

The pressure setting of 750 psia and 600 psia encompass the pressure range used in many hydrorefining processing using the Aero HDS-9 catalyst.

The lutidine to catalyst flow ratios of 4.0 and 3.0 were determined in consultation with a technical representative of American Cyanimide Company[39].

The hydrogen to lutidine feed ratio was set after considering the possible hydrogen consumption in the reaction. The ratio of 3:1 would furnish enough hydrogen to completely hydrogenate the lutidine ring producing the 2,6-dimethyl-piperidine intermediate, if the reaction were stopped at that stage. The 5:1 ratio furnished enough hydrogen to convert the lutidine completely to n-heptane if the reaction went to completion.

The catalyst levels of 10 gm and 13 gm were chosen in order to keep flow rates within the capacity of the equipment, while holding reactant consumption rates to a reasonable level.

Table 15

Process Variables

Symbol*	Variable Description	High Level (+)	Low Level (-)
C,c	Amount of Catalyst in the Reactor	13.000 gm	10.000 gm
T,t	Reaction Bulk Phase Temperature	650° F ±10° F	600° F ±10° F
P,p	Reaction Pressure	750 psia ±20 psia	600 psia ±20 psia
H,h	Hydrogen to Lutidine Molar Feed Ratio	5:1 ±0.05	3:1 ±0.05
L,l	Lutidine to Catalyst Volmetric Hourly Feed Rate (Liquid Hourly Space Velocity)	4.0 ±0.05	3.0 ±0.05

* Capitol Letters represent variable effects in alias an effects lists; small letters represent the high level variable setting in treatment lists and experimental blocks.

Interaction Labeling Illustration

The interaction effect of temperature and pressure is denoted by TP. The interaction of catalyst, lutidine flow rate, and pressure is referred to as CPL.

Treatment Combination Labeling Illustration

The experimental run made under conditions of

750 psia	(+)
600° F	(-)
13 gms. of catalyst	(+)
3:1 hydrogen feed ratio	(-)
3.0 lutidine space velocity	(-)

is referred to as cp.

Table 16

Relative Chromatographic Response Data

for n-Heptane and 2,6-Dimethylpiperidine

Treatment Combination	n-Heptane		2,6-Dimethylpiperidine	
	Total	per gm of Catalyst	Total	per gm of Catalyst
	.001513	.000151	.060336	.006034
(1)	.002541	.000254	.080278	.008028
	.004053	.000405	.086898	.008690
Sum =	.008107	.000811	.227512	.022751
	.000074	.000006	.037890	.002915
cp	.000244	.000019	.049741	.003826
	.000461	.000035	.051777	.004983
Sum =	.000779	.000060	.139408	.010724
	.008836	.000680	.105477	.008114
ch	.007749	.000596	.107973	.008306
	.009864	.000759	.114382	.009798
Sum =	.026449	.002035	.327832	.025218
	.002688	.000269	.146942	.014694
ph	.002049	.000205	.133946	.133995
	.002177	.000218	.117622	.011762
Sum =	.006914	.000691	.398510	.039851
	.052419	.005242	.051318	.005132
tl	.044054	.004405	.058218	.005822
	.016074	.001607	.069263	.006926
Sum =	.112546	.011254	.178799	.017880
	.019386	.001491	.015157	.001166
ctpl	.020649	.001588	.013107	.001008
	.020782	.001599	.014765	.001136
Sum =	.060816	.004678	.043029	.003310
	.058927	.004533	.117239	.009184
cthl	.064602	.004969	.129384	.009953
	.060321	.004640	.091761	.007014
Sum =	.183850	.014142	.338384	.026030
	.003185	.000319	.091222	.009122
tphl	.002463	.000246	.077348	.007735
	.001714	.000171	.074906	.007491
Sum =	.007362	.000736	.243476	.024328

Round off error occurs in some of the sums since digits beyond the sixth decimal place are omitted.

Table 17

F Ratio Summary

Effect	Aliases			F Ratios n-Heptane Total	n-Heptane per gm of Cat.	2,6-Dimethyl-piperidine Total	2,6-Dimethyl-piperidine per gm. of Cat.
I	CTPHL	TL	CPH	-	-	-	-
C	TPHL	CTL	PH	16.67*	4.95+	13.11#	62.74*
T	CPHL	L	TCPH	92.33*	66.58*	27.58*	29.19*
H	CTPL	THL	CP	1.59	0.06	170.23*	148.19*
P	CTHL	TPL	CH	57.82*	43.81*	20.24*	7.47@
CT	PHL	CL	TPH	11.26#	3.50	4.57+	7.61@
TP	CHL	PL	CTH	36.03	28.77*	14.96#	14.26#
TH	CPL	HL	CTP	0.04	0.76	0.00	0.23

Critical F Values[9]

F (1,16,0.999) = 16.12*

F (1,16,0.99) = 8.53#

F (1,16,0.975) = 6.12@

F (1,16,0.95) = 4.49+

Underlined effects are most likely to be significant from engineering considerations.

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