

HYDROTREATING OF SRC I PRODUCT - OPTIMIZATION
OF PROCESS VARIABLE SPACE

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INTRODUCTION

In the Solvent Refined Coal Process, coal is dissolved in a coal-derived solvent to produce a filterable liquid. This is accomplished by means of a mild liquid phase hydrogenation of the coal. The liquid is separated from the insoluble minerals and unreacted organic matter by filtration. The solvent is recovered for recycle by vacuum distillation, and the SRC is obtained as a black shiny solid at room temperature. Some of the sulfur present in the coal is removed in the form of hydrogen sulfide gas.

The present sulfur standards (0.97 percent sulfur in SRC) are being met by conventional SRC processing. New Source Performance Standards (NSPS) recently proposed by the Environmental Protection Agency (EPA) would require a sulfur content of 0.5 to 0.6 percent in SRC for most coals. The proposed NSPS could be met using the conventional SRC process with the application of severe operating conditions (e.g., a reaction temperature of 450°C, a H₂ pressure of 2,000 psig or 13.9 MPa and a long reaction time of 30 to 60 minutes. This would result in an unreasonably high hydrogen consumption and operating cost. Therefore, a modification of the conventional SRC process is necessary to meet the proposed NSPS with minimum hydrogen requirements.

For the coal studied here, a bituminous Western Kentucky #9/14 coal, dissolution of the coal has been shown to occur very rapidly, requiring less than 30 minutes to liquefy most of the coal (~90 percent). However, a relatively long reaction time (120 min.) is required to reduce its sulfur level low enough to meet even the current standards (1). A new short residence time two-stage SRC type process has been suggested by Auburn University (2) for solvent refining this coal. This process has been shown to have the potential of producing a low-sulfur solid SRC product that meets the proposed NSPS. It involves the dissolution of the coal (first stage) in the presence of an inexpensive mineral additive, and then subsequent hydrotreating of the filtered liquid from the first stage in the presence of a presulfided Co-Mo-Al catalyst.

The objective of the present work is to evaluate the effect of a wide range of process or reaction variables--reaction temperature, hydrogen partial pressure, catalyst loading, and reaction time--on hydrodesulfurization and hydrogenation of filtered liquid product (coal-derived liquid) obtained from the coal dissolution stage in the presence of a commercial presulfided Co-Mo-Al catalyst. The selectivity for desulfurization over hydrogenation (Se) is used to rate the effectiveness of the above mentioned process variables. Se is defined as the fraction of sulfur removal per unit (g) of hydrogen consumed, that is,

$$Se = \frac{S_f - S_o}{\frac{S_o}{H_2 \text{ Used, g}}}$$

where Se: Selectivity,
 S_o: Original sulfur content of the coal liquids, and
 S_f: Sulfur content of the hydrotreated coal liquids.

The purpose of this study is to identify a set of operating conditions for hydrotreating reactions at which maximum selectivity is attained for a specified sulfur content of the solid SRC product.

There are many different types of search routines used to locate optimum operating conditions. One approach is to make a large number of runs at different combinations of temperature, reaction time, hydrogen partial pressure, and catalyst amount, and then run a multivariable computer search routine (like the Hooke-Jeeves method or Powell method). A second approach is to formulate a mathematical model from the experimental results and then use an analytical search method to locate the optimum. The formulation of a mathematical model is not an easy task, and in many cases, this is the most critical step. Sometimes it is impossible to formulate a mathematical model for the system, as in the case of the system studied here, and an experimental search must be performed.

The experimental strategy used here is to perform a series of small experiments instead of a single comprehensive experiment. A univariate search was made in which only one variable was changed at a time. The information obtained in the earlier experiments performed during the univariate search was used to plan subsequent experiments. By doing so, the results were available quickly, and the experimental error was checked and minimized during the course of experimentation.

In the first step of the univariate search a series of experiments were performed in which base values were used for the initial hydrogen partial pressure, reaction time and reaction temperature, and only the amount of catalyst used was varied. The amount of catalyst which yielded the best performance (i.e. maximum selectivity) and best satisfied practical constraints was selected. In the next step a series of experiments was performed in which the selected amount of catalyst was used, base values were used for temperature and time, and only the initial hydrogen partial pressure was varied. An initial hydrogen partial pressure was selected as was done for the amount of catalyst in the first step.

The dependence of selectivity (Se) on the reaction time and temperature was modeled using empirical expressions for desulfurization and hydrogen consumption kinetics. The same values selected for initial hydrogen partial pressure and amount of catalyst in the first two steps of the univariate search were used in determining these kinetic expressions. The final step of the search procedure was to perform a series of experiments mapping the region close to the above determine optimum conditions for verification.

EXPERIMENTAL

Reagents and Materials

Light recycle oil (LRO) and Western Kentucky #9/14 coal were obtained from the Wilsonville SRC Pilot Plant, operated by Southern Company Services, Inc. The

LRO contains 0.26% sulfur, and the Western Kentucky #9/14 coal is analyzed to be 67% C, 4.9% H, 3.10% S, and 12 % mineral matter. The coal was dried overnight at 100°C and 25 inches Hg vacuum before use.

The coal liquid is obtained by reacting Ky #9/14 coal-LRO slurry for 60 minutes at 410°C in an autoclave reactor under 2000 psig (13.9 MPa) hydrogen pressure. The product from the autoclave is collected and filtered using Watman #51 filter paper to remove the mineral matter and undissolved coal. The liquid product is saved and used for further hydrotreating studies. The analysis of the filtered product from the coal dissolution step is given in Table I.

Co-Mo-Al is a commercial catalyst from Laporte Industries, Inc. (Comox 451). The catalyst was ground and screened to -325 mesh before use. Presulfided Co-Mo-Al was prepared by collecting the solid residue after reaction of creosote oil (S = 0.64 percent) with Co-Mo-Al in the autoclave reactor. The sulfur content of the presulfided Co-Mo-Al was 2.76%.

Hydrogen gas cylinders (6000 psi grade) were supplied by Linde.

Equipment

A commercial 300 ml magnedrive autoclave (Autoclave Engineers) reactor was used for all reaction studies and has been previously described (3-6). Varian gas chromatographs (Model 920 and 1800) were used for analysis of gas samples and products from the hydrotreating reactions. A LECO sulfur determinator (Model 532) was used for analysis of sulfur in the products.

Procedure

One hundred grams of coal liquid was combined with a predetermined amount of presulfided Co-Mo-Al catalyst and charged to the autoclave. Reaction temperature for the runs varied from 360 to 435°C, depending on the run. A stirring setting of 1000 rpm was used, and the initial total pressure was varied from 1500 (10.4 MPa) to 2500 (17.3 MPa) psig. The heat-up rate was about 12 to 20°C/min, thus requiring a total heat-up time of about 20-25 min. After a specified reaction time, a gas sample was taken; the autoclave was cooled to below 100°C, and the reaction products were collected. The filtered liquid product was vacuum distilled under <1.0 mm Hg pressure to recover the process solvent added prior to the reaction. The 270°C + fraction obtained by vacuum distillation was defined as the solvent refined coal (SRC). A sulfur analysis was performed on each fraction.

The conversion of SRC to oil and gases is defined as

$$\text{SRC Conversion, \%} = \frac{(\text{Amount of SRC})_{\text{original liquid}} - (\text{Amount of SRC})_{\text{hydrotreated liquid}}}{(\text{Amount of SRC})_{\text{original liquid}}}$$

and is used as a constraint.

RESULTS AND DISCUSSION

Effect of Catalyst Loading

The effect of the amount of Co-Mo-Al catalyst present in the hydrotreating reaction is tabulated in Table II. It was observed that increasing the amount of Co-Mo-Al from 1 g to 15 g increases the sulfur removal by 52 percent, increases hydrogen consumption by 87 percent, and increases SRC conversion from 16 to 24 percent. Figure 1 shows the variation of selectivity versus the amount of catalyst used while keeping the other reaction variables constant. It can be seen that the maximum selectivity resulted when

10 g of Co-Mo-Al was used. However, the variation in selectivity for the different amounts of catalyst used was insignificant, that is, within the range of experimental error (standard deviation is only 3 percent). The change in SRC conversion to oil and gases, as shown in Table II, was also within the range of experimental error (standard deviation is less than 8 percent). The use of 1 g of Co-Mo-Al gave the lowest amount of SRC conversion (~ 16 percent). From the shape of the selectivity versus amount of Co-Mo-Al catalyst used curve (Figure 1), it appears that hydrodesulfurization is favored over hydrogenation in the range in which 1 g to 10 g of catalyst were used. However, increasing the Co-Mo-Al amount beyond 10 g tends to favor hydrogenation and a decrease in selectivity was observed. Thus 10 g of Co-Mo-Al was used throughout the remainder of the study. A search in the vicinity close to where maximum selectivity occurs (10 g of Co-Mo-Al) was not done because the insensitivity of selectivity and SRC conversion to the amount of catalyst used.

Effect of Pressure

Table III shows the effect of the initial hydrogen partial pressure on selectivity, sulfur removal, hydrogen consumption, and SRC conversion. It was observed that increasing the initial hydrogen partial pressure by 1500 psig (10.4 MPa) decreased the selectivity by 72 percent, increased hydrogen consumption by a factor of 2.6, enhanced sulfur removal by a factor of 1.9, and did not affect SRC conversion appreciably. For initial hydrogen pressures of 1500, 2000, and 2500 psig, the variation of selectivity was within the range of experimental error. Use of a 1000 psig hydrogen pressure gave the maximum selectivity. However, at 1000 psig the sulfur requirements set by the proposed NSPS (0.5 to 0.6 percent SRC sulfur) were not met (SRC sulfur content at 1000 psig is 0.66%). The use of a 2000 psig hydrogen partial pressure gave a slightly higher selectivity than was obtained with either 1500 or 2500 psig, and a sufficient amount of sulfur was removed. Therefore, a hydrogen pressure of 2000 psig was chosen for further studies.

Effect of Reaction Time and Temperature

The amount of catalyst (10 g of Co-Mo-Al in 100 g of coal liquids) and the initial hydrogen partial pressure (2000 psig) determined above were used to study the effect of reaction time and temperature. Hydrodesulfurization and hydrogen consumption kinetics were determined, as outlined in the following paragraphs.

In order to determine the rate equation for hydrodesulfurization, a semi-logarithmic plot of the total sulfur content with time was made (Figure 2). The plot indicated two independent first-order reactions with greatly different rate constants. This is in agreement with the findings of Gates et al. (7) and Pitts (3). A procedure similar to that of Pitts (3) was used to describe the hydrodesulfurization kinetics. The rate expression is given below

$$S_{\text{Total}} = S_{10} \text{ EXP } [-K_{10} \text{ EXP } (-\Delta E_1/RT) t] + S_{20} \text{ EXP } [-K_{20} \text{ EXP } (-\Delta E_2/RT) t]$$

The empirical parameters S_{10} , S_{20} , K_{10} , K_{20} , ΔE_1 , and ΔE_2 were determined by a numerical search routine. Figure 3 compares the theoretical curves with the experimental data and represents a satisfactory curve fit.

The amount of hydrogen gas present in the reactor was plotted against reaction time on a semi-logarithmic scale (Figure 4). This plot gave a straight line indicating a first-order rate expression. Pitts (3) also suggested a first-order rate expression

for hydrogen consumption. A procedure similar to that of Pitts (3) was used. The hydrogen consumption rate expression is given by

$$\frac{H_g}{H_{g0}} = \text{EXP} [-K_0 \text{EXP} (-\Delta E/RT)t]$$

A numerical search routine was applied to determine the value of K_0 and ΔE . Figure 4 compares the theoretical curve with the experimental data and represents a satisfactory curve fit. The total sulfur content and SRC sulfur content for hydro-treated product were plotted (Figure 5), and a linear relationship was shown to exist between them.

The rate expression for hydrodesulfurization and hydrogenation described above were used to compute selectivity. The optimum process conditions for different SRC sulfur contents (specifically, 0.6, 0.5, and 0.4 percent) were determined. The optimization procedure used is illustrated below for a specified SRC content of 0.5% or a total sulfur content of 0.23% (see Figure 5).

The variation of the calculated total sulfur values versus reaction time and reaction temperature was plotted (Figure 6). A dashed line was drawn at a total sulfur level of 0.23 percent; the region above this line was labelled as being infeasible because, for a total sulfur content higher than 0.23 percent, the SRC content was more than 0.5 percent. So, the feasible region of search was that below the dashed line. The computed values of selectivity versus reaction time and temperature was plotted (Figure 7).

The maximum selectivity for each temperature was found to be located on the dashed curve shown in Figure 7, that is, at the boundary. The maximum selectivity values for each temperature were compared (Table IV). The highest temperature and the shortest reaction time used gave the maximum selectivity. The conversion of SRC to oil with reaction time and temperature were plotted also for comparison purposes (Figure 8). As shown in Table IV, the highest temperature and the shortest reaction time resulted in the lowest amount of conversion of SRC to oil. Similar analyses were performed for different SRC sulfur contents, and for each case, the highest temperature and the shortest reaction time gave the maximum selectivity and the lowest SRC conversion. A summary of the optimum reaction conditions obtained for different sulfur levels is given in Table V.

The optimization study discussed above suggests the use of a high temperature and a short-reaction time. Because of the heat-up and cool-down time limitations of the autoclaves used, this study was limited to reaction temperatures $\leq 435^\circ\text{C}$. Verification studies at higher temperatures ($>435^\circ\text{C}$) are ongoing using micro-reactors. The present study should be supported by complementary catalyst aging studies to determine the maximum temperature limit below which serve deactivation and aging does not occur.

CONCLUSIONS

The proposed NSPS can be met by hydrotreating the coal liquids obtained by filtering the product from the coal dissolution stage. The desulfurization kinetics can be presented by two parallel first-order rate expression, and hydrogen consumption kinetics can be presented by a first-order rate expression. A linear relationship exists between total sulfur content and SRC sulfur content of the hydrotreated product. For

the Western Kentucky bituminous #9/14 coal studied here, the maximum selectivity and lowest SRC conversion to oil for a fixed SRC sulfur content are obtained using the highest reaction temperature (435°C) and the shortest reaction time (≈ 7 min.).

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REFERENCES

1. Garg, D., Ph.D. Dissertation, Auburn University, Auburn, Alabama (1979).
2. Garg, D., Tarrer, A. R., Guin, J. A., Lee, J. M., and Curtis, C., Fuel Processing Technology, 2, 189-208 (1979).
3. Pitts, W. S., M.S. Thesis, Auburn University, Auburn, Alabama (1976).
4. Guin, J. A., Tarrer, A. R., Prather, J. W., Johnson, J. R., and Lee, J. M., Ind. Eng. Chem. Process Des. Dev. 17(2), 118 (1978).
5. Lee, J. M., Van Brackle, H. F., Lo, Y. L., and Tarrer, A. R., Am. Chem. Soc. Div. Fuel Chem., prepr., 22(6), 120 (1977).
6. Lee, J. M., Van Brackle, H. F., Lo, Y. L., Tarrer, A. R., and Guin, J. A., Symposium of the 84th National ALChE Meeting, Atlanta, GA, Feb. 26 - March 1, 1978 (516).
7. Gates, B. C., J. R. Katzer, J. H. Olson, H. Kwart, and A. B. Stiles, Quarterly Progress Report, Prepared for U.S. Dept. of Energy, No. EX-76-C-01-2028, (December 2, 1976 - March 20, 1977).

Table I. Analysis of the Liquid Product Used in Hydrotreating Stage

Distillation Product Distribution, %	
Distillate (Oil)	61.6
SRC	38.4
Sulfur Distribution, %	
Distillate (Oil)	0.21
SRC	0.97
TOTAL LIQUID	0.54
TetraIn/Naphthalene Ratio	
Distillate is performed under <1 mm Hg pressure	0.24
Distillate: 270°C - fraction of vacuum distillation	
SRC: 270°C + fraction of vacuum distillation	

Table II. Effect of Catalyst Amount on Hydrotreating of Kentucky #9/14 Coal Liquid
 Coal Liquid = 100 g, Time = 30 min., T = 410°C, P = 2000 psi (13.9 MPa)H₂, 1000 RPM, Reactor - Autoclave

Amount of Catalyst	1.0	5.0	10.0	15.0
H ₂ Used, g	0.11	0.17	0.18	0.21
Total Sulfur S _f , %	0.36	0.22	0.20	0.17
$S_e = \frac{S_o - S_f}{S_o}$	2.8	3.3	3.4	3.2
H ₂ Used, g				
SRC Conversion, %	16	21	22	24
S _o = 0.54%				

Table III. Effect of Hydrogen Partial Pressure on Hydrotreating of Kentucky #9/14 Coal Liquid
 Coal Liquid = 100 g, Co-Mo-Al = 10 g, T = 410°C, 1000 RPM, Reaction Time = 30 min., Reactor - Autoclave

Pressure, Psig H ₂	1000	1500	2000	2500
H ₂ Used, g	0.08	0.13	0.18	0.22
Total Sulfur S _f , %	0.35	0.30	0.20	0.19
SRC Sulfur, %	0.66	0.57	0.49	0.45
$S_e = \frac{S_o - S_f}{S_o}$	4.1	3.3	3.4	2.9
H ₂ Used, g				
SRC Conversion, %	22	19	22	21

Table IV. Maximum Selectivity at Different Reaction Conditions Meeting 0.5% SRC Sulfur Content

Temp., °C	Time, Min.	Se	Standard Deviation in Se, %	SCR Conversion, % (Estimated from Fig. 8)
370	114	2.50	6.3	>20.0
385	62	2.80	7.5	>20.0
400	38	3.20	7.2	---
410	27	3.5	7.2	20.5
420	20	3.70	7.0	--
435	13	3.85	7.3	19.5

Table V. Summary of Operating Conditions for Various Maximum SRC Sulfur Contents

SRC Sulfur, %	Total Sulfur, %	Temperature, °C	Time, Min.	Se
0.6	0.29	435	7	5.40
0.5	0.23	435	13	3.85
0.4	0.17	435	21	2.80

Figure 1. Effect of Amount of Catalyst (Co-Mo-Al) on Selectivity

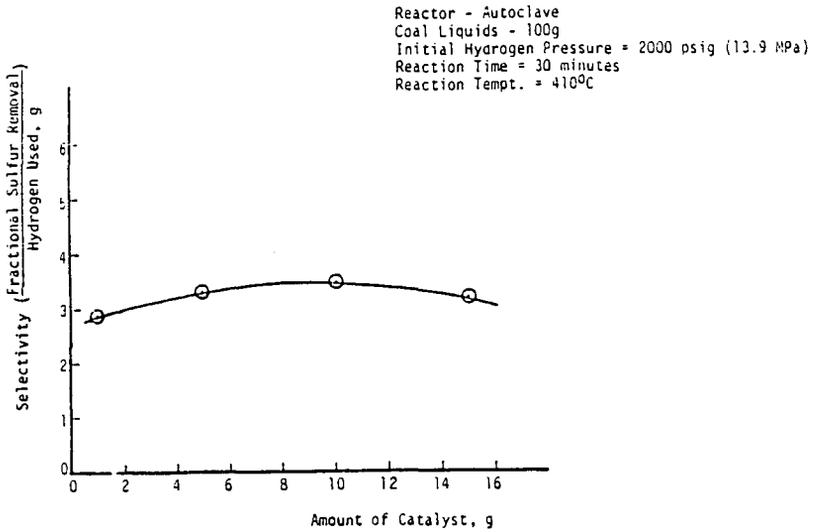


Figure 2. Semi-Log Plot of Total Sulfur (%) vs. Time for Hydrotreating Reaction in The Presence of Co-Mo-Al

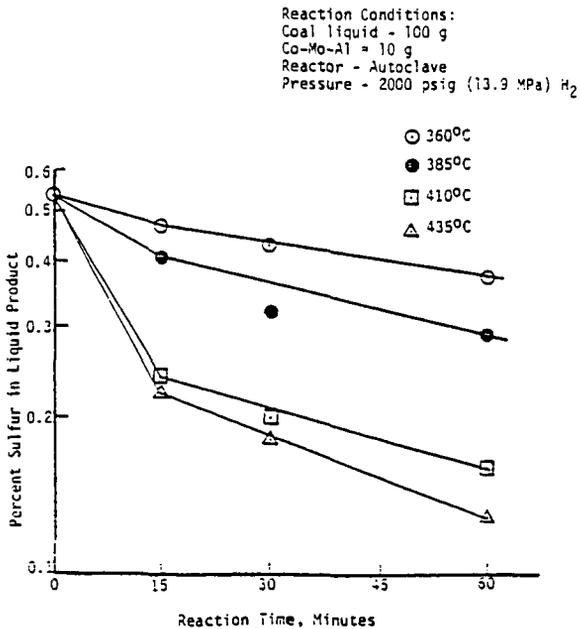


Figure 3. Effect of Hydrotreating Reaction Time on Total Sulfur Content

Reaction Conditions: See Figure 2

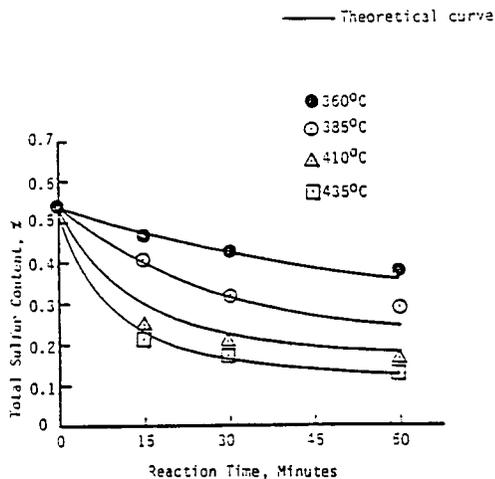


Figure 4. Semi-Log Plot of H_g/H_{g0} vs. Time for Hydrotreating Reaction in the Presence of Co-Mo-Al

Reaction Conditions: See Figure 2
 H_g = amount of hydrogen (g) in the reactor at any time
 H_{g0} = amount of hydrogen (g) initially charged to the reactor

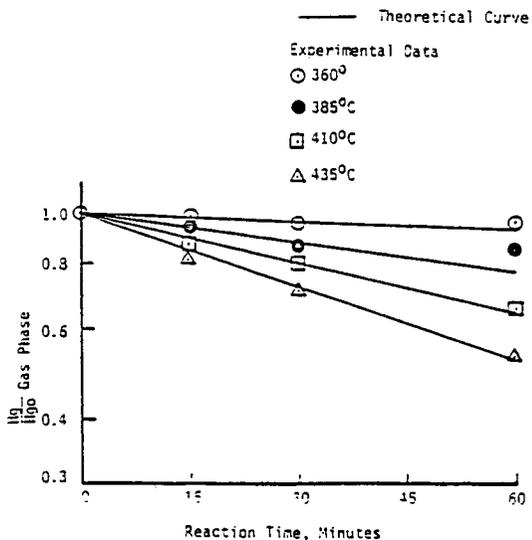


Figure 5. Relationship Between Hydrotreated Total Sulfur Content (%) and SRC Content (%)

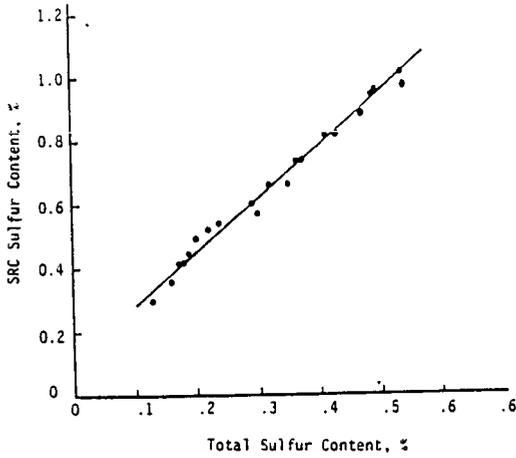


Figure 6. Variation of Total Sulfur Content with Reaction Time and Temperature for Hydrotreating Reaction

SRC Sulfur = 0.50%
 Total Liquid Sulfur = 0.23%

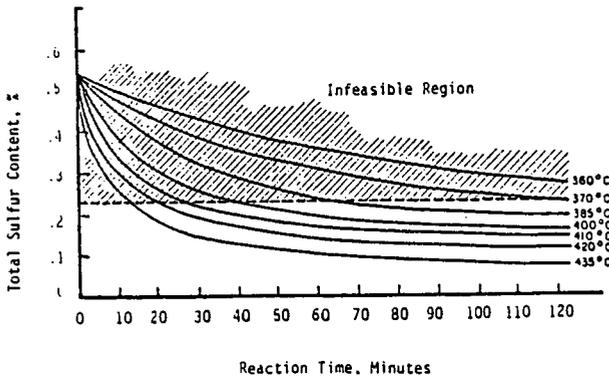


Figure 7. Variation of Selectivity with Reaction Time and Temperature for Hydrotreating Reaction

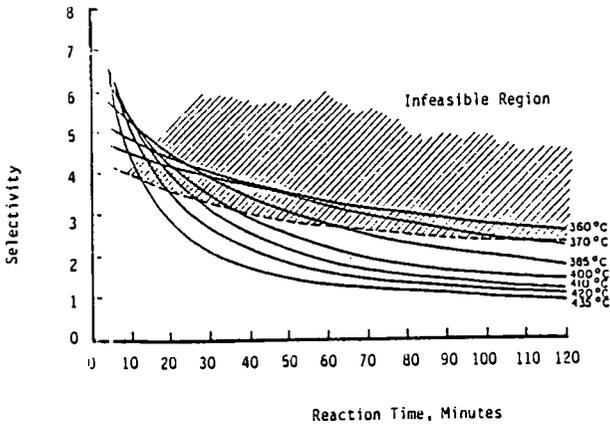


Figure 8. Conversion of SRC with Hydrotreating Reaction Time and Temperature

