

## KINETICS OF HYDROCRACKING OF LOW TEMPERATURE COAL TAR

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### Abstract

The results of hydrocracking of a low temperature coal tar in a batch autoclave over a catalyst containing sulphides of nickel and tungsten, supported on silica-alumina, indicated that gasoline can be obtained in a yield of 77% at 500°C and 3000 psi pressure. The highest quality product, containing 60% aromatics and 13% isoparaffins, was obtained at 450°C and 2000 psi but in a lower yield of 60%. Most of the sulfur, nitrogen, and oxygen present in the tar were removed. The gasoline formation, desulphurization, and denitrogenation reactions were all found to be of first-order with activation energies of 17,000, 14,500, and 15,000 calories per mole respectively. Linear relationships were found between rate constants for gasoline formation ( $k_g$ ), desulphurization ( $k_s$ ), and denitrogenation ( $k_n$ ) as can be represented by the following equations:

$$k_g = 1.1371 k_s - 0.1278$$

$$k_g = 2.11 k_n - 0.0669$$

$$k_n = 0.5397 k_s - 0.0837$$

Hydrocracking reactions involving the breakage of chemical bonds on the catalyst surface are rate-determining.

### Introduction

Hydrocracking has been investigated in recent years as a potential method for upgrading coal-derived liquids. The work reported so far is very much limited and the fundamental aspects of such processing are not well understood. Much of the earlier work was carried out in connection with the coal hydrogenation processes (Gordon, 1935, 1940, and 1947 and Pier, 1949) where a two-stage reaction was used in which the first stage liquified the coal and the second converted the resulting heavy distillates to gasoline by catalytic hydrocracking. Carpenter, et al (1963) reported the results of hydrocracking a lignite tar in a continuous fixed bed reactor over cobalt-molybdate and zinc chromite catalysts for producing gasoline. A maximum yield of 59% of gasoline was obtained at 477°C and 3000 psi pressure. Rutkowski

(1965) studied the influence of temperature, pressure, hydrogen-oil ratio, diluents, and catalysts on the hydrocracking of low temperature tars and reported minimum coke yields using tetralin and cyclohexane as diluents. Katsobashvili and Elbert (1966) reported a yield of 83.8% saleable products when a tar distillate boiling from 230° to 360°C was hydrocracked in a continuous fixed bed reactor at 500° to 550°C and 50 atmospheres under recycle conditions. The economic feasibility of producing gasoline from coal by the H-coal process, wherein the heavy oil produced in the first stage was hydrocracked in a subsequent stage, was demonstrated by the results published by Alpert, et al (1966). Zielke, et al (1966) investigated the suitability of zinc halide catalysts for hydrocracking coal extracts for the production of gasoline. The results indicated that a maximum yield of 68% of gasoline could be obtained at 427°C, 4200 psi pressure and 60 minutes reaction time. In the present communication, the results of hydrocracking of a low temperature coal tar in a batch autoclave over a catalyst containing sulphides of nickel and tungsten, supported on silica-alumina, are described. The influence of temperature and pressure on product distribution and kinetic evaluation of the data are presented.

### Experimental

#### Materials.

Low temperature tar from a high volatile bituminous coal from Utah was prepared by carbonization at 550°C in a laboratory oven. The light oil boiling up to 200°C was separated from tar by distillation (Table I). The catalyst (commercial) contained 6% nickel and 19% tungsten, both as sulphides; supported on silica-alumina and had a surface area of 212 sq. meters per gram and size of -200 mesh. 5-A molecular sieves were of chromatographic grade.

#### Equipment.

A 1-litre high pressure autoclave with a magnetic drive stirrer, pressure and temperature control devices, liquid and gas sampling lines, and water quenching system (Figure 1) and hydrogen cylinders with maximum pressure of 2300 psi were used.

#### Procedure for hydrocracking experiments.

In each experiment 100 c.c of tar and 10 grams of the catalyst were used. The equipment was evacuated to remove most of the air, filled with hydrogen and heated to the desired temperature. The temperature rose to 300°C in 21 minutes and 500°C in 28 minutes. The reaction time was taken from the start of heating the equipment. When the reaction temperature was reached, the pressure was adjusted to the experimental value and maintained constant throughout except in experiments conducted at pressures higher than 2000 psi where there was a reduction in pressure of about 200 to 300 psi during

the course of the experiment. Experiments were conducted at different reaction times and 4 gas samples were taken out during each experiment. At the end of the reaction time, heating was stopped and the product was quenched rapidly by circulating water in the cooling coil immersed in it. It took 1 to 2 minutes to cool the product down to 250°C and 15 minutes to atmospheric temperature. The pressure was then released slowly and the autoclave opened. The product was transferred to a beaker, filtered to remove the catalyst, and the water separated to get the total oil product. The mechanical losses were found to be less than 1%. The yield of the product was taken as 100% and 100 minus the volume of the total oil product was taken as percent conversion to gas. A few c.c of the total oil product were used for sulfur and nitrogen analysis and the remainder was washed with 10% sodium hydroxide and 20% sulphuric acid to remove tar acids and bases respectively. The neutral oil was then distilled into a gasoline fraction boiling up to 200°C, a diesel oil fraction boiling from 200° to 360°C and residue. The volume of each fraction in c.c obtained from the total oil product was taken as volume percent conversion to that particular fraction.

#### Product analysis.

Sulfur was determined by the bomb method and nitrogen by the C-H-N chromatographic analyzer, F.M. Model 185. Tar acids and bases were estimated by extraction with 10% sodium hydroxide and 20% sulphuric acid respectively. Hydrocarbon-type analysis was done by the Fluorescent-Indicator-Adsorption method (ASTM, D1319-65T). For the estimation of naphthenes and isoparaffins, the saturated hydrocarbon portion was first separated from the mixture by sulphonation with a mixture of 70% concentrated sulphuric acid and 30% phosphorus pentoxide (ASTM, D1019-62). The naphthenes were estimated by the refractivity intercept method (ASTM, D1840-64). The N-paraffin content was determined by adsorption over 5-A molecular sieves in a glass column of 0.5-inch diameter and 1.5-foot length. The isoparaffins were obtained by the difference. The diesel index was calculated from API gravity and aniline point. The gas analysis was done by gas chromatography in the F.M. Model 720 dual column programmed temperature gas chromatograph.

#### Results and Discussion

##### Product distribution.

The yield of gasoline and gas and the iso-normal ratio in butanes increased with temperature whereas the diesel oil decreased while the residue remained almost the same (Figure 2). Tar acids and bases were removed completely along with most of the sulfur and nitrogen at 450°C and 1500 psi pressure (Table II). Isomerization increases with cracking and the gas yield and iso-normal ratio in butanes are qualitative indications of the extent of cracking reactions taking place leading to the formation of gasoline. A

pressure of 1500 psi is sufficient to suppress coke-forming reactions and the gasoline is formed mainly by the cracking of the diesel oil, thereby affecting the quantity and quality of the latter. The composition of gasoline obtained at different temperatures remains almost the same and the aromatics of the gasoline are mainly formed by the dealkylation of alkylbenzenes, hydrocracking of hydroaromatics, and hydroremoval of sulfur, oxygen, and nitrogen compounds.

The gasoline yield increased at different rates with pressure (Figure 3). The rate of gasoline formation was high in the pressure range 1000 to 1500 psi, slowing down in the range 1500 to 2500 psi, and increasing again at higher pressures. The residue decreased rapidly in the range 1000 to 1500 psi but the decrease was small at higher pressures. On the other hand, the gas yield and iso-normal ratio in butanes remained almost constant up to a pressure of 1500 psi and increased at higher pressures (Figure 4). Pressure does not have a marked influence on cracking reactions in the range 1000 to 1500 psi but the increase in the yield of gasoline is due to the suppression of the coke-forming reactions. In the range 2000 to 2500 psi, partial hydrogenation of aromatics to hydroaromatics takes place followed by the cracking of the latter which increases the yield of gasoline and the aromatic content (Figures 5 to 7). At higher pressures complete hydrogenation of aromatics to naphthenes takes place and increases the gasoline yield. The naphthenes in the gasoline increase with a corresponding decrease in the aromatics. Isomerization increases with pressure and temperature. High aromatic gasolines were obtained in the pressure range 1750 to 2500 psi (Table III). A maximum yield of 77% of gasoline was obtained at 500°C and 3000 psi pressure but the highest quality product containing 60% aromatics and 13% isoparaffins was formed at 450°C and 2000 psi pressure which can compare well with the premium grade gasoline from petroleum (Table IV).

### Kinetics

Equilibrium was reached at different time periods at different temperatures with respect to gasoline formation but the conversion was 100% in the case of sulfur and nitrogen removal (Figures 8 to 10). The sulfur and nitrogen removal reactions are not governed by thermodynamic limitations but are limited only by kinetic factors under the experimental conditions employed. Plots of  $\log \frac{a}{a-x}$  versus time (Figures 11 to 13), where "a" is the equilibrium conversion in case of gasoline and initial concentration in case of sulfur and nitrogen, are linear and the hydrocracking reactions with respect to gasoline formation and removal of sulfur and nitrogen are all first-order. The first-order rate constants are thus represented by equations 1 to 3.

$$\frac{d(\text{Gasoline})}{dt} = k_g \cdot (\text{Tar}) \quad (1)$$

$$-\frac{d(\text{Sulfur})}{dt} = k_s (\text{Sulfur}) \quad (2)$$

$$-\frac{d(\text{Nitrogen})}{dt} = k_n (\text{Nitrogen}) \quad (3)$$

where " $k_g$ ," " $k_s$ ," and " $k_n$ " are rate constants for gasoline formation and removal of sulfur and nitrogen respectively. There was no change in the concentration of hydrogen in the system during the course of the reaction since the hydrogen pressure was maintained constant throughout. Hydrogen atoms may be involved in the rate-determining step but their concentration constitutes one of the constant factors in the rate constant term and does not show up in the rate equation. However, hydrogen actually takes part in the hydrocracking reactions and, hence, the reactions are considered pseudo-first-order

The hydrocracking reactions under study follow true Arrhenius temperature dependence (Figure 14) and the rate constants can be represented by equations 4 to 6.

$$k_g = 0.1567 \times 10^6 e^{-17,600/RT} \text{ hrs.}^{-1} \quad (4)$$

$$k_s = 0.2134 \times 10^5 e^{-14,500/RT} \text{ hrs.}^{-1} \quad (5)$$

$$k_n = 0.4738 \times 10^5 e^{-15,900/RT} \text{ hrs.}^{-1} \quad (6)$$

The following values of enthalpies and entropies of activation were calculated by the Eyring equation plotting  $\log k'/T$  versus  $\frac{1}{T}$  (Figure 15).

$$\Delta H_g = 16,200 \text{ cal/mole, } \Delta S_g = -43.5 \text{ e.u.}$$

$$\Delta H_s = 12,200 \text{ cal/mole, } \Delta S_s = -44.9 \text{ e.u.}$$

$$\Delta H_n = 14,900 \text{ cal/mole, } \Delta S_n = -45.9 \text{ e.u.}$$

Linear relationship was found between  $k_g$ ,  $k_s$ , and  $k_n$  (Figure 16) and can be represented by equations 7 to 9

$$k_g = 1.1371 k_s - 0.1278 \quad (7)$$

$$k_s = 2.1100 k_n - 0.0669 \quad (8)$$

$$k_n = 0.5397 k_s - 0.0837 \quad (9)$$

A major part of the gasoline is expected to be formed by the cracking of hydrocarbons, but a minor part comes from the decomposition of some of the sulfur, oxygen, and nitrogen compounds. The yield of gasoline thus depends, to some extent, on the removal of sulfur and nitrogen and this may result in some sort of interrelationship between  $k_g$ ,  $k_s$ , and  $k_n$ . The dissociation energies of the C-C, C-S, and C-N bonds may also have some influence on the above relationship, especially between  $k_s$  and  $k_n$ . However, the results presented in this paper do not throw much light on the effect of other temperature and pressure conditions and equations 7 to 9 are not considered to be having much quantitative significance at this stage.

The energies and enthalpies of activation indicate that chemical reactions but not physical processes are rate-controlling. The probable chemical reactions occurring during hydrocracking are cracking, isomerization, hydrogenation, polymerization, condensation, and dehydrogenation, all taking place on the catalyst surface. Under the experimental conditions employed, polymerization, condensation, and dehydrogenation are very much suppressed and may be eliminated. It has been established by Weisz and Prater (1957) and Keulemans and Voge (1959) that reactions occurring on acidic sites of the dual-functional catalyst, like the one used in this investigation, are rate-determining which eliminates the possibility of hydrogenation reactions to be rate-limiting. Hence, cracking reactions involving the breakage of chemical bonds and the isomerization reactions, wherein skeletal rearrangement of carbonium ions takes place, must be rate-limiting. It is known that in catalytic hydrocracking, cracking precedes isomerization and only the isomerization of the cracked fragments occurs without any change of the uncracked material (Flinn, et al., 1960, and Archibald, et al., 1960). An excess of branched isomers than can be predicted by thermodynamic equilibrium are also formed; the latter can only happen if the isomerization of the cracked fragments can occur very rapidly and leave the catalyst surface without appreciable readsorption. Therefore, the isomerization is believed to be very rapid and cannot be rate-controlling. Hence, the cracking reactions, involving the breakage of chemical bonds on the catalyst surface, are rate-determining.

#### Acknowledgment

The research work reported in this paper was sponsored by the U. S. Office of Coal Research and the University of Utah.

Table I. Properties of Feed Material

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|   |        |
|---|--------|
| Sp. gr. (25°C)  | 0.9942 |
| Tar acids, vol. % of feed   | 30.0   |
| Tar bases, wt. % of feed  | 3.5    |
| Sulfur, wt. % of feed   | 0.6984 |
| Nitrogen, wt. % of feed   | 0.4018 |
| Distillation data   |        |
| I.B.P., °C.   | 200    |
| 50% distillate  | 298°C  |
| Pitch point   | 360°C  |
| Residue, vol. % of feed   | 30.0   |
| Hydrocarbon types in neutral<br>fraction 200 <sup>o</sup> to 360 <sup>o</sup> C, vol. % |        |
| Saturates   | 32.0   |
| Olefins   | 19.0   |
| Aromatics   | 49.0   |

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Table II. Influence of Temperature on Product Distribution  
(Pressure, 1500 psi)

| Temp. (°C.)                     | 400    | 425    | 450    | 475    | 500    |
|---------------------------------|--------|--------|--------|--------|--------|
| Reaction Time, hrs.             | 13     | 12     | 10     | 8      | 5      |
| Yield, vol. % of feed           |        |        |        |        |        |
| Gasoline                        | 45.0   | 51.0   | 56.0   | 61.0   | 64.0   |
| Diesel oil                      | 35.0   | 29.0   | 24.0   | 20.0   | 16.0   |
| Tar acids                       | 2.0    | 1.0    | -      | -      | -      |
| Tar bases                       | 1.0    | 0.5    | -      | -      | -      |
| Residue                         | 12.0   | 12.0   | 13.0   | 11.5   | 12.0   |
| Gas (including losses)          | 4.5    | 6.5    | 7.0    | 7.5    | 8.0    |
| Sulfur, wt. % of feed           | 0.0489 | 0.0210 | 0.014  | 0.0135 | 0.0136 |
| Nitrogen, wt. % of feed         | 0.0924 | 0.0442 | 0.0321 | 0.0201 | 0.0163 |
| Composition of gasoline, vol. % |        |        |        |        |        |
| Aromatics                       | 33.5   | 35.0   | 34.0   | 32.0   | 33.0   |
| Naphthenes                      | 10.0   | 9.0    | 10.5   | 10.0   | 10.0   |
| Olefins                         | 2.0    | 3.0    | 2.0    | 2.0    | 4.0    |
| Isoparaffins                    | 25.5   | 26.0   | 26.0   | 27.0   | 25.0   |
| N-paraffins                     | 29.0   | 27.0   | 27.5   | 29.0   | 28.0   |
| Diesel index of diesel oil      | 40.0   | 37.5   | 34.0   | 31.0   | 28.0   |
| <u>Isobutane</u>                |        |        |        |        |        |
| N-butane                        | 1.0    | 1.25   | 1.45   | 1.51   | 1.75   |

Table III. Influence of Pressure on Yield and Composition of Gasoline

| Yield and Hydrocarbon Types, Vol. % | Temperature, °C. | Pressure, psi. |      |      |      |      |      |      |      |      |
|-------------------------------------|------------------|----------------|------|------|------|------|------|------|------|------|
|                                     |                  | 1000           | 1250 | 1500 | 1750 | 2000 | 2250 | 2500 | 2750 | 3000 |
| Yield                               | 400              | 15.0           | 36.0 | 45.0 | 48.0 | 50.0 | 54.0 | 58.0 | 63.0 | 68.0 |
| Aromatics                           |                  | 33.5           | 36.0 | 33.5 | 46.0 | 50.0 | 46.5 | 40.0 | 33.5 | 28.0 |
| Naphthenes                          |                  | 10.0           | 9.5  | 10.0 | 10.5 | 10.0 | 18.5 | 24.0 | 28.5 | 31.0 |
| Olefins                             |                  | 5.5            | 3.0  | 2.0  | 1.5  | 2.0  | 3.5  | 2.5  | 4.0  | 3.5  |
| Isoparaffins                        |                  | 24.0           | 24.0 | 25.5 | 19.0 | 20.0 | 18.5 | 19.0 | 20.5 | 25.5 |
| N-paraffins                         | 27.0             | 27.5           | 29.0 | 23.0 | 18.0 | 13.0 | 14.5 | 13.5 | 12.0 |      |
| Yield                               | 450              | 36.0           | 49.0 | 56.0 | 58.0 | 60.0 | 62.0 | 66.0 | 69.0 | 73.0 |
| Aromatics                           |                  | 36.0           | 32.5 | 34.0 | 44.0 | 60.0 | 56.0 | 47.0 | 39.0 | 33.0 |
| Naphthenes                          |                  | 11.0           | 10.0 | 10.5 | 12.0 | 12.5 | 15.0 | 23.0 | 29.0 | 35.0 |
| Olefins                             |                  | 3.0            | 3.5  | 2.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  | 1.0  |
| Isoparaffins                        |                  | 23.5           | 26.5 | 26.0 | 21.0 | 13.0 | 14.0 | 15.5 | 19.0 | 22.0 |
| N-paraffins                         | 26.5             | 27.5           | 27.5 | 22.0 | 14.0 | 14.0 | 13.5 | 12.0 | 9.0  |      |
| Yield                               | 500              | 44.0           | 54.0 | 64.0 | 66.0 | 68.0 | 69.0 | 71.0 | 74.0 | 77.0 |
| Aromatics                           |                  | 36.5           | 33.0 | 33.0 | 44.0 | 50.0 | 49.0 | 41.0 | 32.5 | 26.0 |
| Naphthenes                          |                  | 11.5           | 10.0 | 10.0 | 11.0 | 12.5 | 13.0 | 19.0 | 25.5 | 34.0 |
| Olefins                             |                  | 4.0            | 5.0  | 4.0  | 4.5  | 3.0  | 4.5  | 2.0  | 3.0  | 2.0  |
| Isoparaffins                        |                  | 23.0           | 25.0 | 25.0 | 19.5 | 17.5 | 17.0 | 21.0 | 23.5 | 26.0 |
| N-paraffins                         | 25.0             | 27.0           | 28.0 | 21.0 | 17.0 | 16.5 | 17.0 | 15.5 | 12.0 |      |

Table IV. Comparison of Yield and Composition of Gasolines  
 (Gasoline 1 at 450°C, 2000 psi, 10 hours and Gasoline 2  
 at 500°C, 3000 psi, and 5 hours, both from Tar)

| Yield, vol. % of feed<br>Hydrocarbon composition,<br>vol. % | Gasoline |      | Regular<br>grade<br>gasoline<br>from<br>petroleum | Premium<br>grade<br>gasoline<br>from<br>petroleum |
|---|----------|------|---|---|
|   | 1        | 2    | petroleum   | petroleum   |
| Aromatics   | 60.0     | 77.0 | -   | -   |
| Naphthenes  | 60.0     | 26.0 | 33.0  | 34.0  |
| Olefins   | 12.5     | 34.0 | 18.0  | 12.0  |
| Isoparaffins  | 1.0      | 2.0  | 11.0  | 14.0  |
| N-paraffins   | 13.0     | 26.0 | 22.0  | 28.0  |
|   | 14.0     | 12.0 | 16.0  | 12.0  |

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- 1 CERAMIC FURNACE
- 2 LIQUID SAMPLING TUBE
- 3 GAS SAMPLING TUBE
- 4 THERMOWELL
- 5 COOLING COIL
- 6 COOLING JACKET
- 7 MAGNETIC DRIVE ASSEMBLY
- 8 SHAFT
- 9 IMPELLER

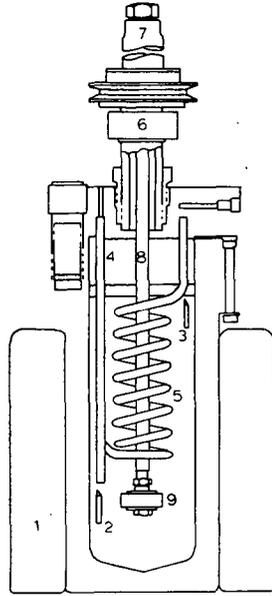


Figure 1. Assembly of equipment

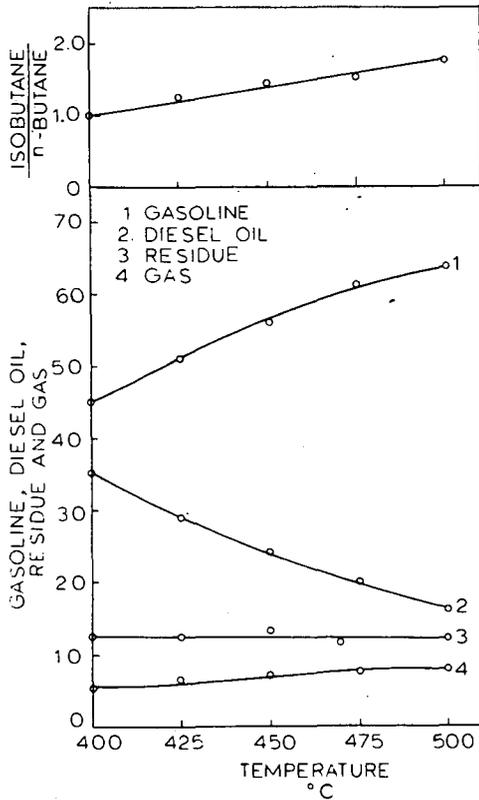


Figure 2. Effect of temperature on product distribution  
 Pressure, 1500 psi.  
 Reaction time, 13 hrs. at 400°C., 12 hrs. at 425°C.,  
 10 hrs. at 450°C., 8 hrs. at 475°C.,  
 5 hrs. at 500°C.

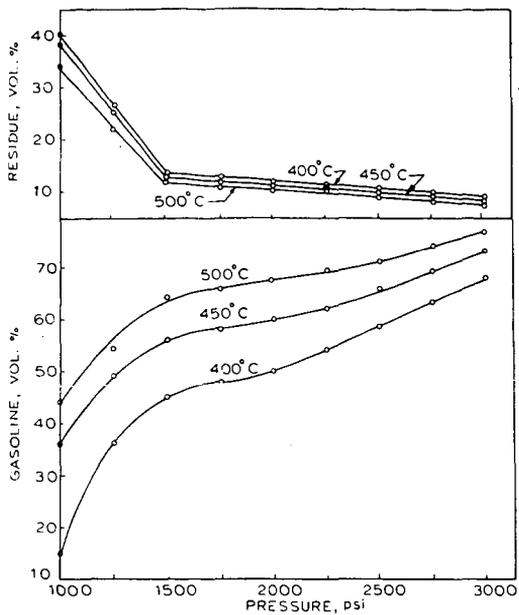


Figure 3. Effect of pressure on product distribution  
 Reaction time, 13 hrs. at 400°C.  
 10 hrs. at 450°C.  
 5 hrs. at 500°C.

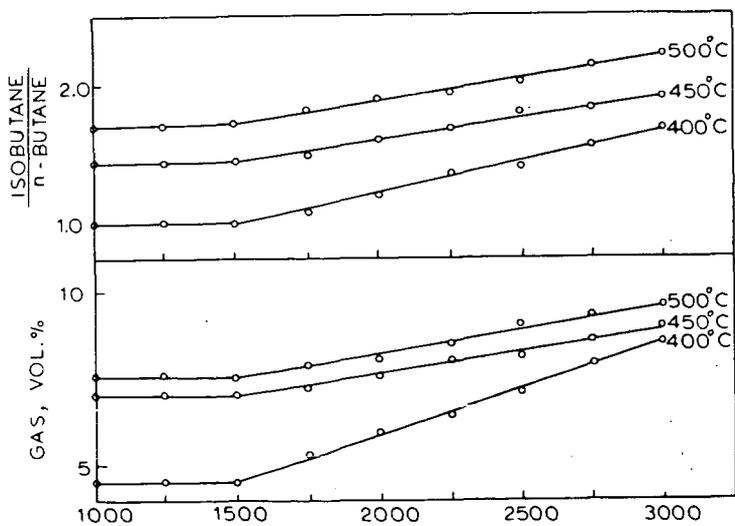


Figure 4. Effect of pressure on product distribution

Reaction time, 13 hrs. at 400 C  
 10 hrs. at 450 C  
 5 hrs. at 500 C

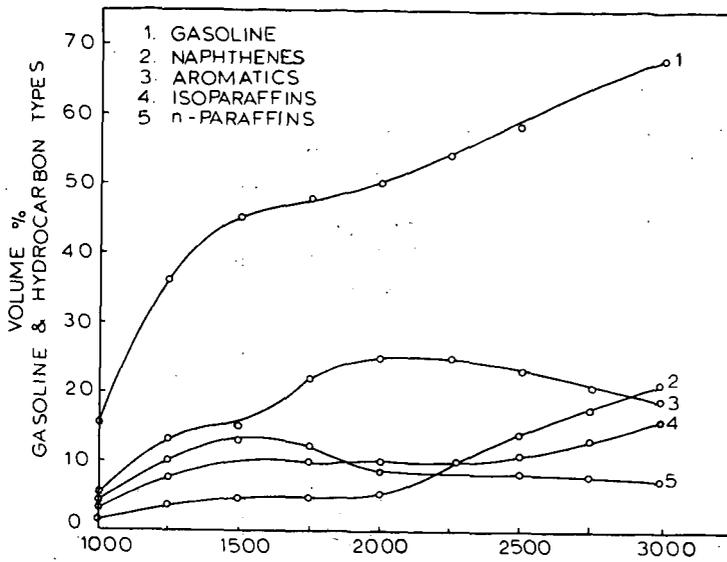


Figure 5. Effect of pressure on the yield of gasoline and hydrocarbon types - Temperature, 400 C

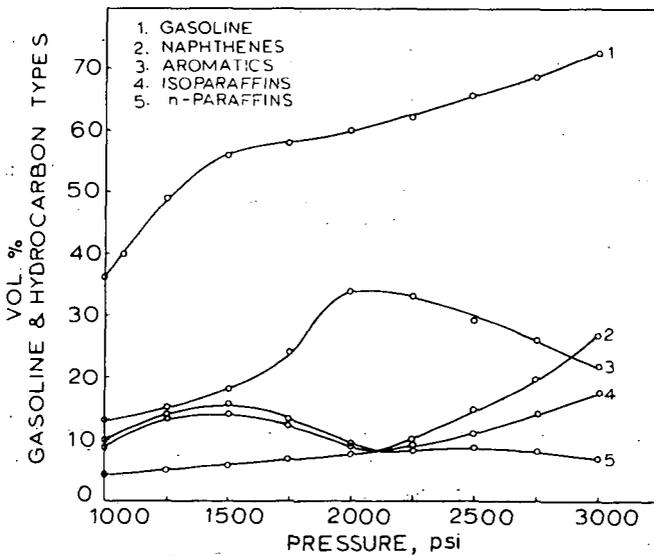


Figure 6. Effect of pressure on the yield of gasoline and hydrocarbon types - Temperature, 450 C

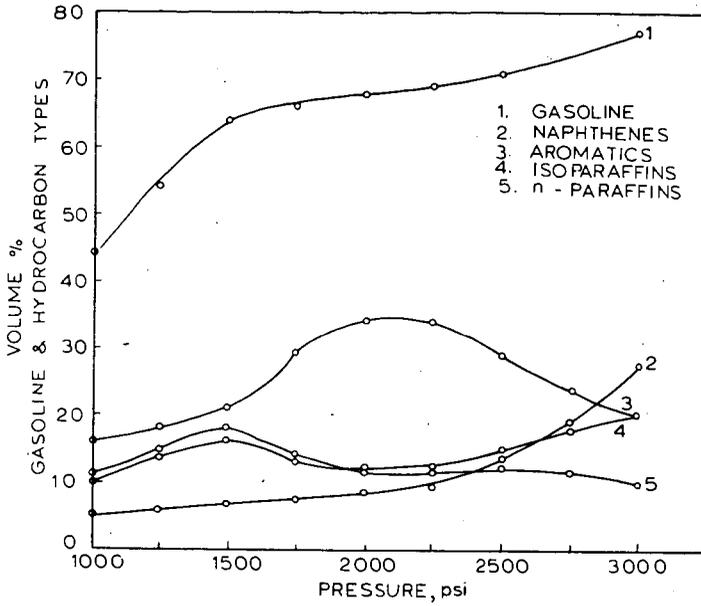


Figure 7. Effect of pressure on the yield of gasoline and hydrocarbon types - Temperature, 500 C

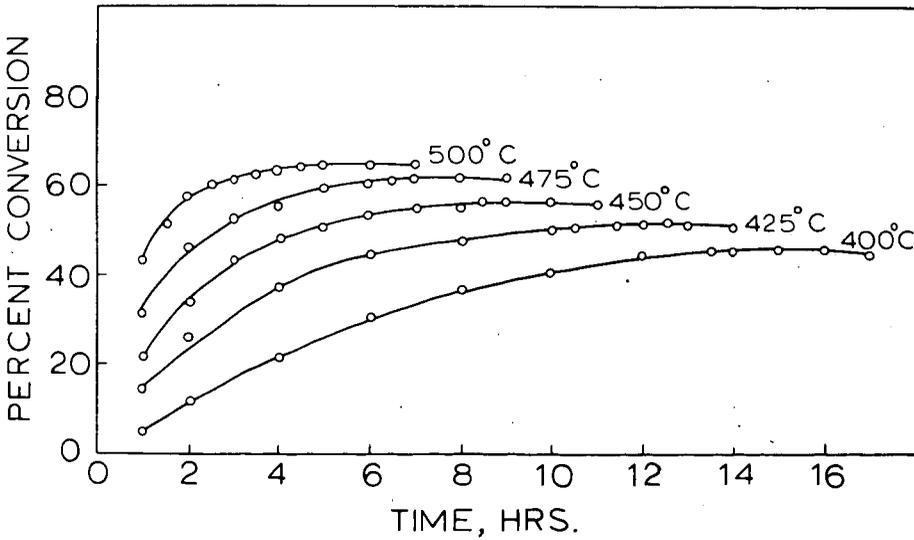


Figure 8. Effect of reaction time on gasoline formation  
Pressure, 1500 psi

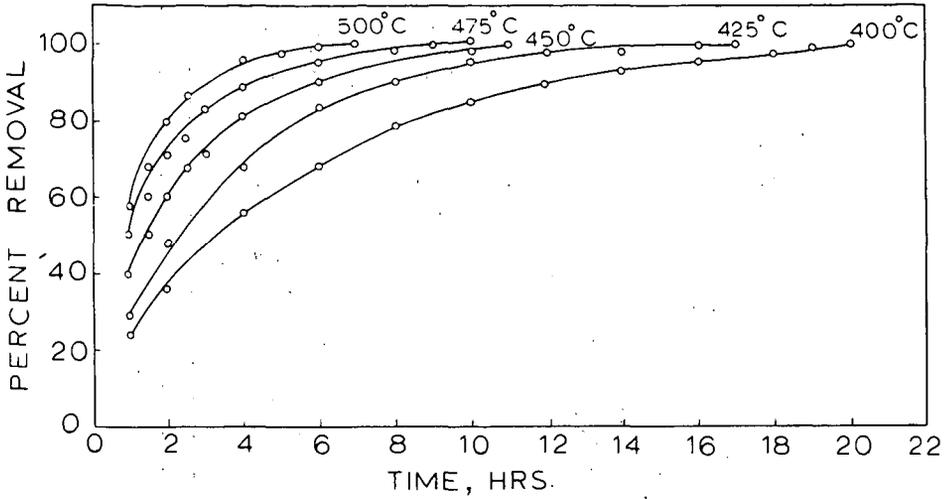


Figure 9. Effect of reaction time on desulphurization  
Pressure, 1500 psi.

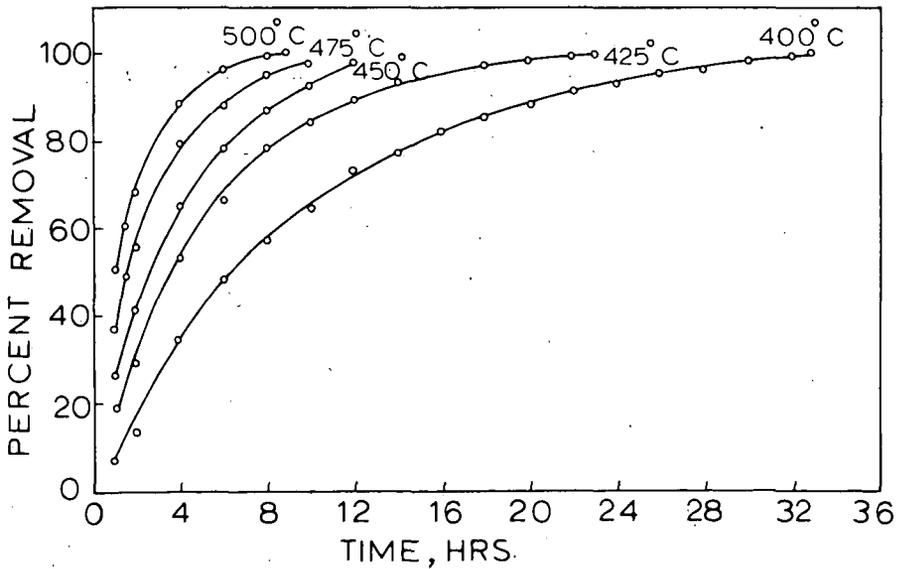


Figure 10. Effect of reaction time on denitrogenation  
Pressure, 1500 psi

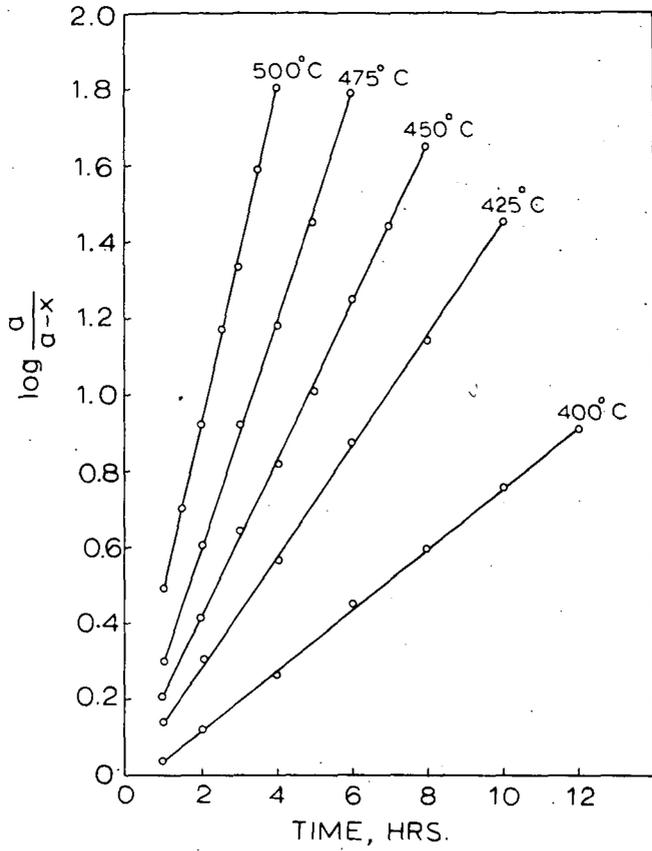


Figure 11. Plot of first-order equation for gasoline formation

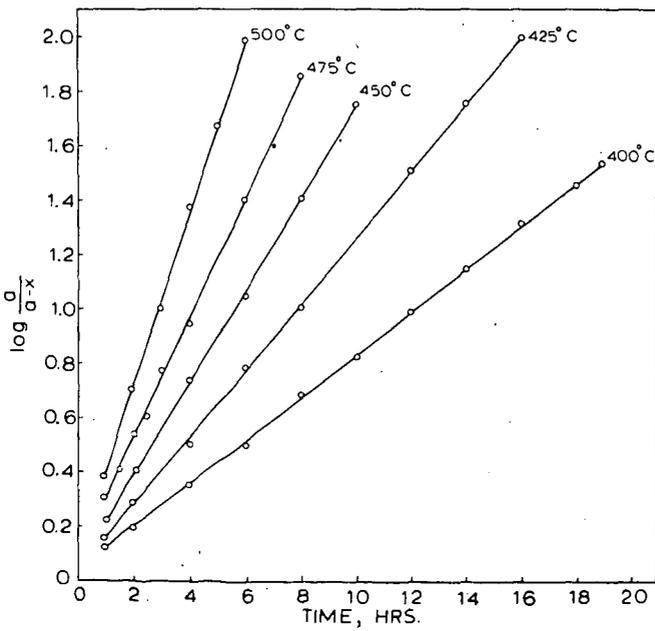


Figure 12. Plot of first-order equation for desulphurization.

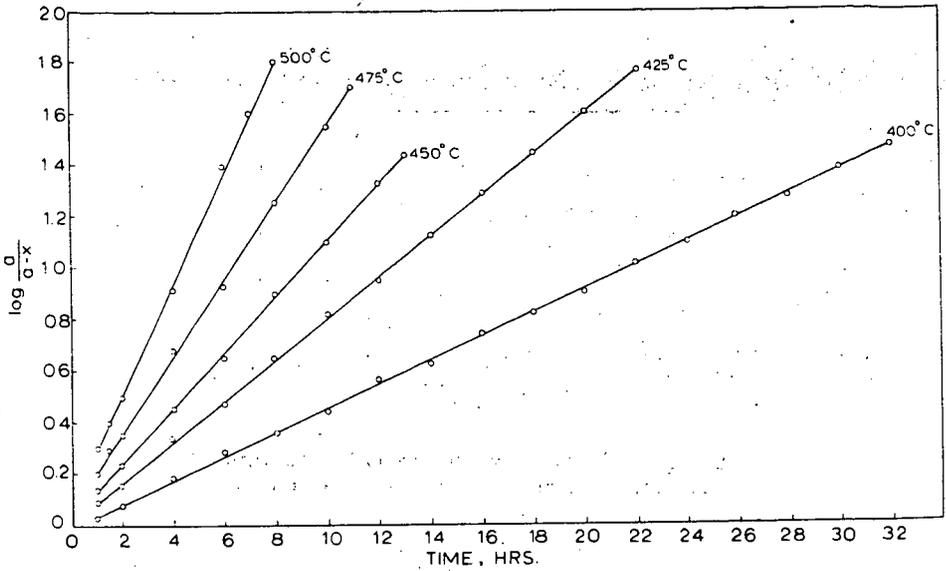


Figure 13. Plot of first-order equation for denitrogenation

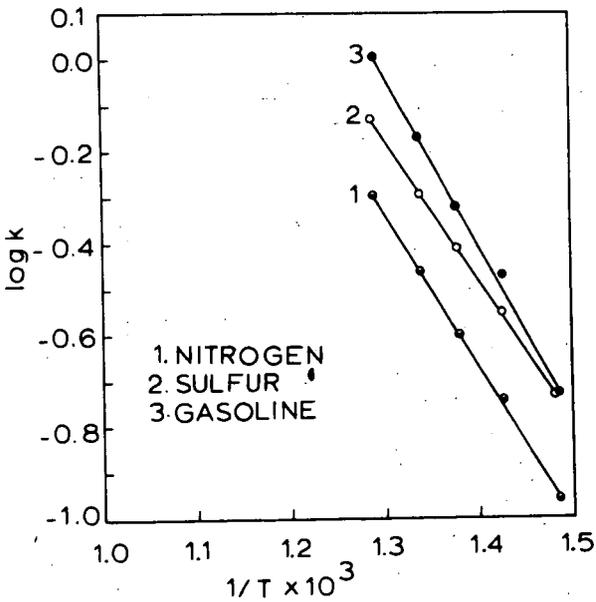


Figure 14. Arrhenius plot for gasoline formation, desulphurization and denitrogenation

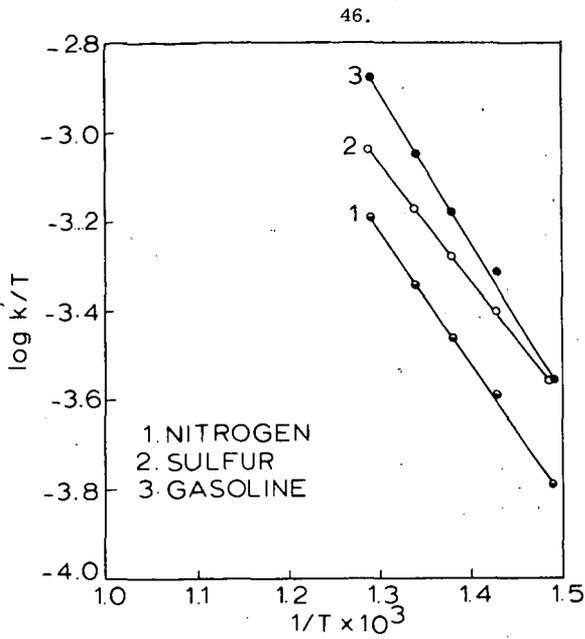


Figure 15. Eyring plot for gasoline formation, desulfurization and denitrogenation.

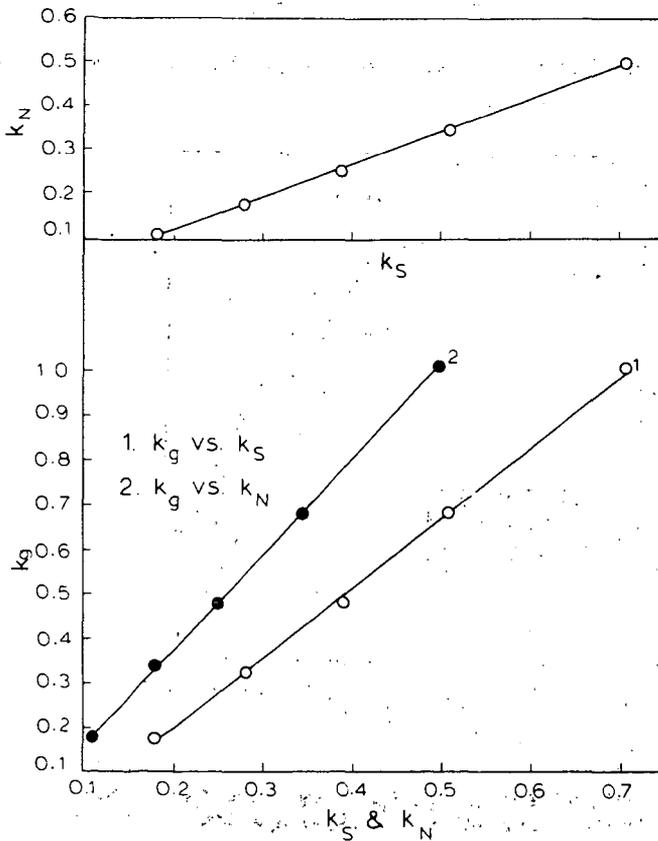


Figure 16. Relationship between rate constants  
Pressure, 1500 psi.  
Temperature, 400°, 425°, 450°, 475° and 500°C.