

KINETICS OF HYDROGENOLYSIS OF  
LOW TEMPERATURE COAL TAR

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Abstract

The hydrogenolysis of a low temperature coal tar in a batch autoclave over a molybdenum trioxide catalyst yielded 77% gasoline at 475°C and 3000 psi pressure. The highest quality gasoline, containing 60% aromatics, was obtained in a yield of 47% at 450°C and a pressure of 2500 psi. Hydrogenolysis of tar proceeds through a mechanism involving a combination of simultaneous and consecutive cracking and hydrogenation reactions and the overall kinetics observed indicated that the formation of gasoline from tar is of first-order with an activation energy of 11.5 K cal./mole. Chemisorption of tar molecules on the catalyst surface appears to be the rate-determining step.

Introduction

Hydrogenolysis is a potential method for the treatment of low temperature tars, mainly to convert the whole tar or selected fractions to motor fuels. Most of the work reported was done in batch or continuous systems and the product distributions were investigated over different catalysts (Kalechits and Salimgareeva, 1956; Lang and Lacey, 1960; (Mrs.) Mirza, et al., 1965). Very few data are so far published on the kinetics of coal tar hydrogenolysis, though some work was reported on the kinetics of the hydrogenation of pure compounds present in tars (Wilson, et al., 1957; Owens and Amberg, 1962; Tarama, et al., 1963). In the present communication, the results of the hydrogenolysis of a low temperature tar in a batch autoclave over a molybdenum trioxide catalyst are reported. The influence of process variables on product distribution and an overall kinetic evaluation of the data are presented.

Experimental

Materials.

Low temperature tar (Table I) obtained from a high volatile bituminous coal by carbonization at 650°C was used as the feed material. Analar grade molybdenum trioxide with a surface area of 190 square meters per gram and -200 mesh size was used as the catalyst. Pure hydrogen was taken from a cylinder with a maximum pressure of 2300 psi.

### Equipment.

A 1-litre high pressure autoclave (Figure 1), provided with a magnetic drive stirrer of 1800 r.p.m., pressure and temperature control devices, liquid and gas sampling lines, and water quenching system was used for the experimental work.

### Experimental procedure.

In each experiment, 100 grams of tar and 5 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 hot pressure was adjusted to the experimental value. Pressure was maintained constant except in experiments conducted at pressures higher than 2000 psi where there was a reduction of about 100 psi during the course of the experiment. Experiments were conducted at different reaction times depending upon the reaction temperature (Table II). 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 and the autoclave opened. The product was transferred to a beaker, filtered to remove the catalyst, and the water was 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. The total oil product was washed with 10% sodium hydroxide and 20% sulfuric acid to remove tar acids and bases, respectively. The neutral oil was then distilled to get a gasoline fraction boiling up to 230°C, a middle oil fraction from 230° to 360°C and residue.

### Product analysis.

Tar acids and bases were estimated by extraction with 10% sodium hydroxide and 20% sulfuric acid, respectively. Hydrocarbon type analysis was done by the Fluorescent-Indicator-Adsorption method (ASTM, D-1319-65T). The hydrocarbon types in the neutral oil fraction from the feed were determined by washing with 20% sulfuric acid for olefins and a mixture of 70% concentrated sulfuric acid and 30% phosphorus pentoxide (ASTM, D-1019-62) for aromatics. The gas analysis was done by gas chromatography in the F.M. Model 720 dual column programmed temperature gas chromatograph.

### Results and Discussion

The liquid product from hydrogenolysis contained 1 to 3 c.c of water which might have been formed by the hydrogenation of tar acids. The gaseous product contained hydrogen sulfide and ammonia

which could not be quantitatively estimated. They might have been formed by the hydrogenation of heterocompounds containing sulfur and nitrogen.

#### Product distribution.

The yield of gasoline and gas increased linearly with temperature while the middle oil and residue decreased. Gasoline and gas were formed by the hydrogenolysis of middle oil and residue (Figure 2). The composition of gasoline (Figure 3) indicated that hydrogenation reactions took place under all temperature conditions at 3000 psi. The gasoline yield increased at different rates with pressure with a corresponding decrease in the yields of middle oil and residue (Figure 4). The rate of gasoline formation was high in the pressure range 500 to 1500 psi, slowing down in the range 1500 to 2500 psi and increasing again at higher pressures. The residue decreased rapidly but the gas yield remained almost constant in the range 500 to 1500 psi (Table III). Pressure does not seem to have a marked influence on cracking reactions in the range 500 to 1500 psi but the increase in gasoline yield may be due to the suppression of 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 its aromatic content. At higher pressures, complete hydrogenation of aromatics to the corresponding naphthenes takes place, thus increasing the gasoline yield and its saturated hydrocarbon content (Figure 5). High aromatic gasolines were formed in the pressure range 2000 to 2500 psi. A maximum yield of 77% of gasoline was obtained at 475°C and 3000 psi pressure but the highest quality product containing 60% aromatics was formed at 450°C and 2500 psi pressure in a yield of 47%.

#### Kinetics.

Equilibrium was reached at different time periods at different temperatures with respect to gasoline formation (Figure 6). Plot of  $\log \frac{a}{a-x}$  versus time (Figure 7), where "a" is the equilibrium conversion to gasoline, is linear and the hydrogenolysis reactions with respect to gasoline formation from tar are first-order. The first-order rate constant can thus be represented by equation 1.

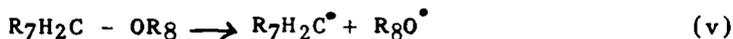
$$\frac{d(\text{Gasoline})}{dt} = k_g (\text{Tar}) \quad (1)$$

Where  $k_g$  is the rate constant for gasoline formation. The gasoline formation reactions follow true Arrhenius temperature dependence (Figure 8) and the rate constant can be represented by equation 2.

$$k_g = 1.0 \times 10^7 e^{11,500/RT} \text{ mints.}^{-1} \quad (2)$$

The enthalpy and entropy of activation calculated from Eyring's plot (Figure 9) are 10,500 cal./mole and -57.8 e.u., respectively.

The product distribution data indicated that the hydrogenolysis of low-temperature tar produces middle oil, gasoline, and gas by a mechanism involving a combination of simultaneous and consecutive cracking and hydrogenation reactions as can be represented by steps (i) to (xiii).



Where "R" represents a hydrocarbon radical or hydrogen atom. Step (i) represents dissociation of hydrogen molecules and the concentration of hydrogen atoms depends upon the dissociation equilibrium. Steps (ii) to (v) represent breakage of C-C, C-S, C-N, and C-O bonds present in the hydrocarbon and heteromolecules of tar and steps (vi) to (xiii) indicate hydrogenation reactions. The steps listed above are the principal reactions that are likely to occur during the hydrogenolysis of tar and indicate that the overall kinetics observed resulted from a sequence of this type. In the presence of an initial excess of hydrogen, there will be a preponderance of hydrogen atoms and the reactions between radicals and hydrogen atoms occur freely and rapidly. Steps (vi) to (xiii) are thus expected to be fast and cannot be rate-controlling. Any step involving hydrogen may limit the rate only when hydrogen concentration is very low. The cracking reactions taking place must be purely of a thermal nature and need higher activation energies than those obtained in the present work. Hence, steps (ii) to (v) cannot be rate-determining. It is well established that all the heterogeneous catalytic processes involve (1) diffusion of the reactants from the bulk phase to the catalyst surface, (2) adsorption of the

reactants on the catalyst surface, (3) reaction of the adsorbed molecules to form products, (4) desorption of the products, and (5) diffusion of the desorbed products from the catalyst surface to the bulk phase. The magnitude of the activation energy obtained will exclude steps 1, 4, and 5 from being rate-limiting. It was shown by the foregoing discussion that step 3 did not control the rate. Therefore, step 2, involving the adsorption of the reactants on the catalyst surface, must be rate-determining. Physical adsorption cannot occur at high temperatures used in this investigation. Hence, chemisorption of the tar molecules on the surface of the catalyst must be the rate-controlling step in the hydrogenolysis of tar.

#### Acknowledgement

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Table 1. Properties of low temperature tar

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Sp. gr., 25°C	1.0426
Sulfur, wt. %	0.9424
Nitrogen, wt. %	0.8213
Oxygen, wt. %	4.1
Carbon, wt. %	84.9
Hydrogen, wt. %	9.3
<u>Distillation data</u>	
I.B.P., °C	180
14 wt. %	230
50 wt. %	325
55 wt. %	345
Residue, wt. %	45.0
Hydrocarbon types in neutral fraction up to 345°C, vol. %	
Saturates	20.0
Olefins	15.0
Aromatics	65.0

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Table II. Effect of temperature on product distribution.  
Pressure, 3000 psi

Temperature, °C	350	375	400	425	450	475
Reaction time, hrs.	26	20	18	14	12	10
Product distribution, wt. %						
Gasoline	23	33	46	56	65	77
Middle oil	50	46	34.5	26	17.5	4
Gas	nil	1	2.5	3	4.5	6
Residue	27	20	17	15	13	13
Tar acids, vol. %	15	2	nil	-	-	-
Tar bases, vol. %	2	1	nil	-	-	-
Composition of gasoline, vol. %						
Saturates	71	73	74	79	80	82
Olefins	2	2	2	1	1	1
Aromatics	27	25	24	20	19	17



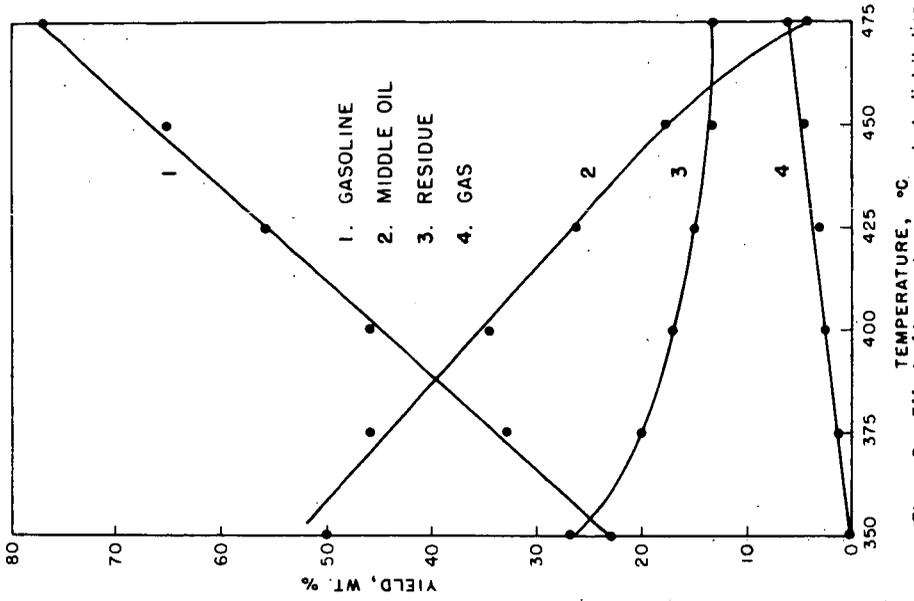


Figure 2. Effect of temperature on product distribution.

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

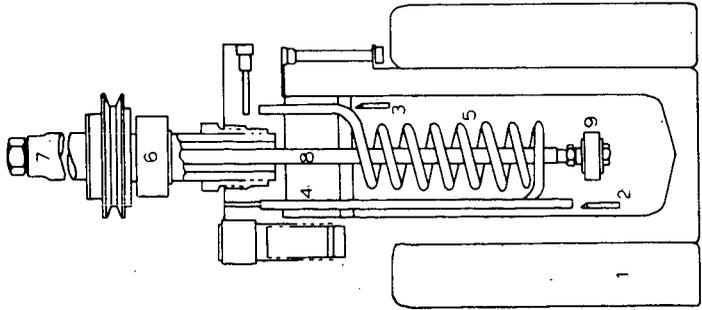


FIGURE 1. ASSEMBLY OF EQUIPMENT

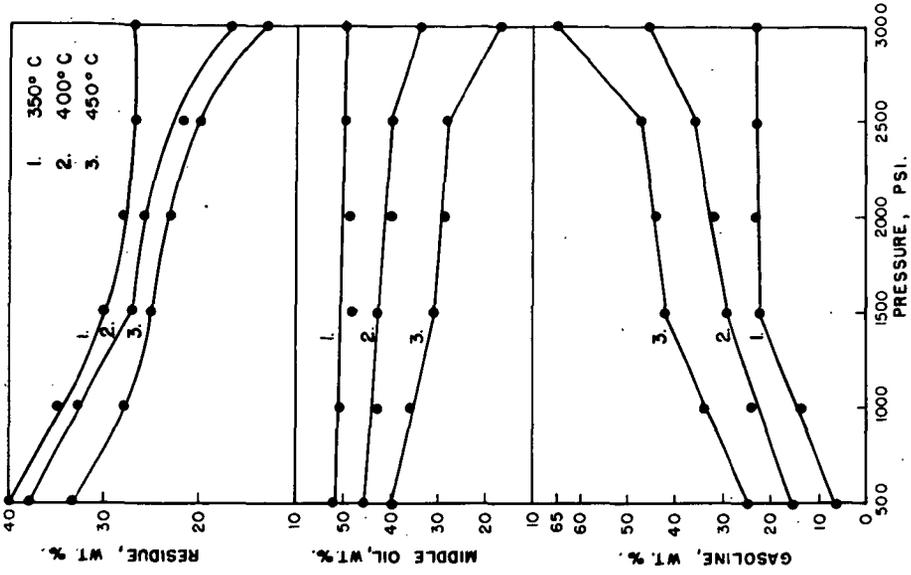


Figure 4. Effect of pressure on product distribution.

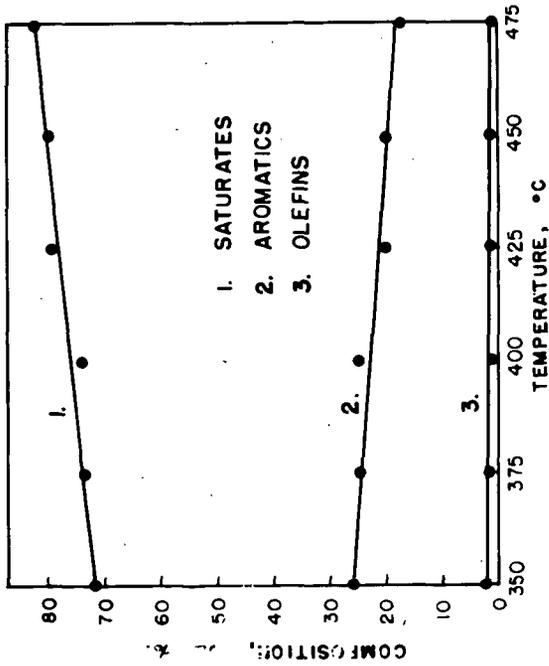


Figure 3. Effect of temperature on the composition of gasoline. pressure 3000psi.

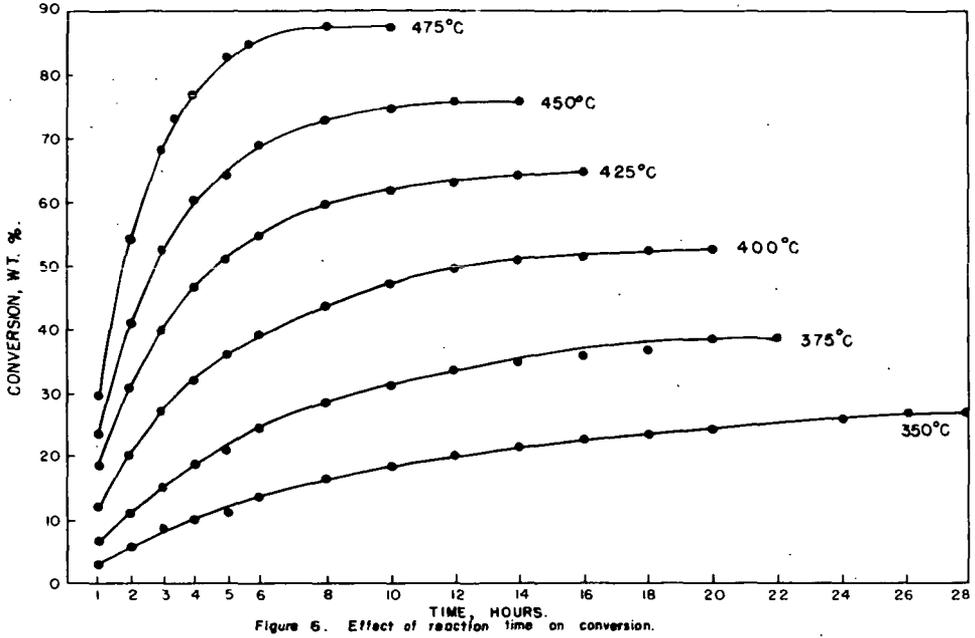


Figure 6. Effect of reaction time on conversion.

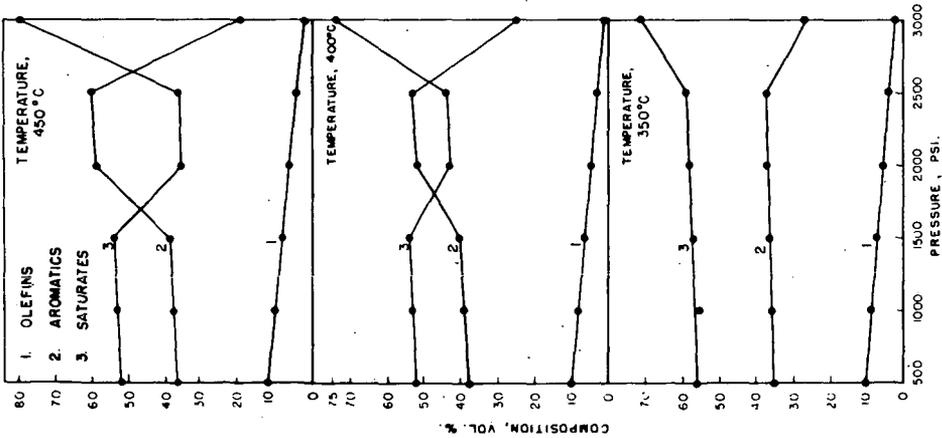


Figure 5. Effect of pressure on gasoline composition.

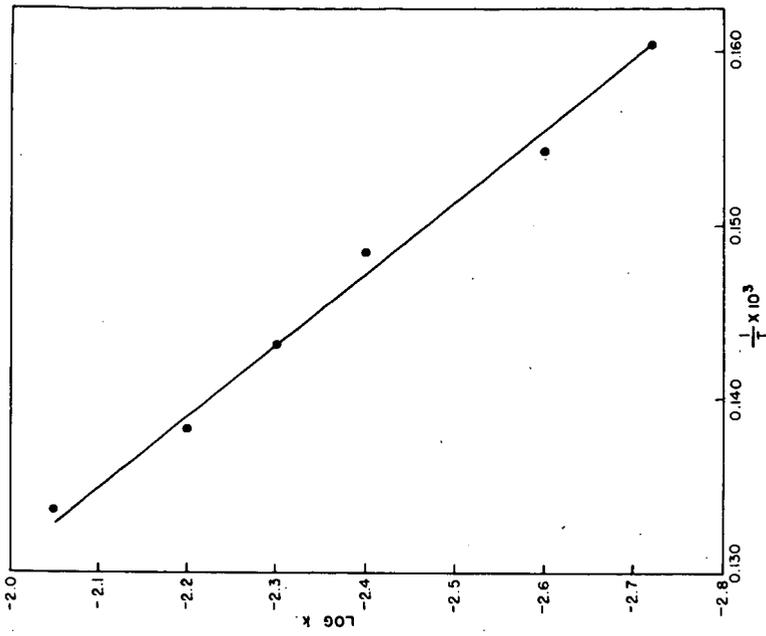


Figure 8. Arrhenius Plot.

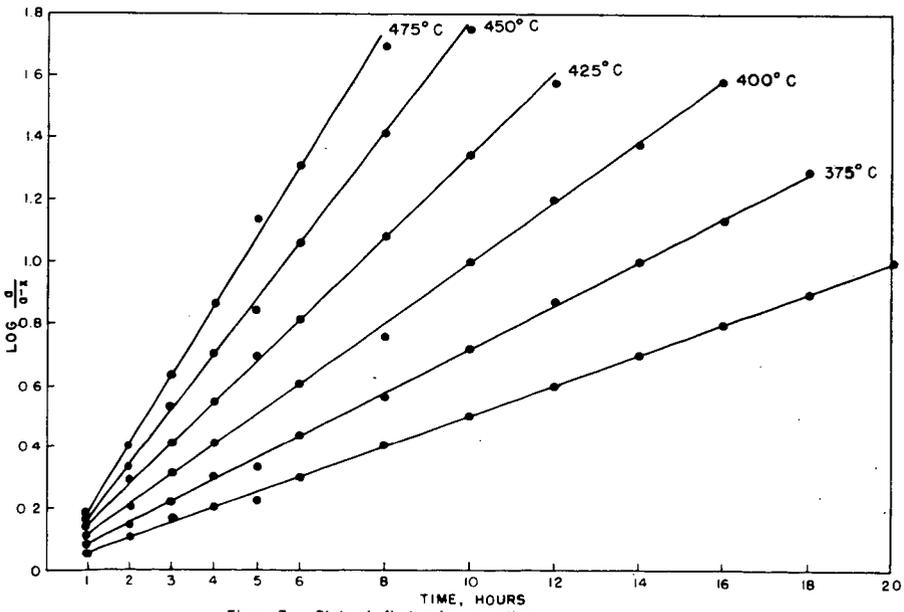


Figure 7. Plot of first-order equation.

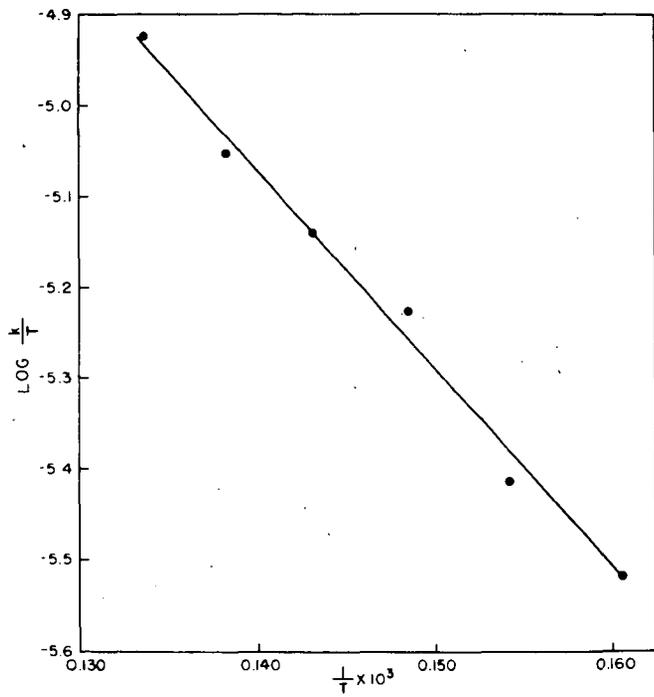


Figure 9. Absolute rate reaction plot.