

## HYDROGENATION/DEHYDROGENATION OF MULTICYCLIC COMPOUNDS USING ATTM AS CATALYST PRECURSOR

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### Introduction

Coal liquefaction can be considered a viable technical alternative for production of advanced fuels if the coal macromolecule can be broken up into low molecular weight fragments and hydrogenated to decrease the concentration of aromatics in the final product. Previous studies have shown that the initial breakdown of coal can be achieved using various catalysts and various conditions. However, if the final product is to be a very high quality distillate, the coal liquids still need further hydrotreatment if they are to be satisfactory. One way to improve the quality is to add another step to the liquefaction process. This would employ a very active catalyst to hydrogenate the products from the first liquefaction stage. However if operating costs are to be kept to a minimum, it would be advantageous to hydrogenate the coal fragments as they are being released during the first stage of liquefaction. Burgess has shown that ammonium tetrathiomolybdate (ATTM) can be used as a catalyst precursor in a process for conversion of coal to a "proto-jet fuel" [1]. Coal conversion up to 95% were observed but the products were aromatic and contained some phenols.

Various temperature strategies have been formulated for coal liquefaction. The majority of these strategies are concerned with the depolymerisation of coal and the avoiding of retrogressive reactions. Another important aspect of temperature strategies is the thermodynamic behavior of released coal fragments. With careful 'fine tuning' of the reaction conditions, it could be possible to have advantageous thermodynamics in the system along with reasonably fast kinetics of depolymerisation of the coal macromolecule. Basically, a trade-off between kinetics and thermodynamics is possible.

Model compound studies can be used to understand the fundamental behavior of coal fragments during coal liquefaction and coal liquids upgrading. The literature on hydrogenation of model compounds is vast and has been recently reviewed by Girgis [2].

For the past several years we and our colleagues have been investigating the hydrogenation and dehydrogenation chemistry of a variety of polycyclic compounds. This work has aimed at investigating some of the fundamental chemical processes involved in various aspects of fuel utilization. The compounds investigated have included decalin and tetralin [3], anthracene [4], phenanthrene [5, 6], pyrene [6, 7] and chrysene [6].

This paper will discuss the hydrogenation and dehydrogenation behavior of naphthalene and pyrene. Kinetic and thermodynamic parameters will be calculated from product distribution trends. From these parameters it should be possible to outline a possible reaction strategy that allows all these compounds to remain in their hydroaromatic states during a coal liquefaction operation.

### Experimental

All reactions were carried out in 25ml microautoclave reactors (made of type 316 stainless steel). In all runs, 3±0.01g naphthalene or pyrene (Aldrich, 99%, used as received) and 0.075±0.005g ammonium tetrathiomolybdate (Aldrich, used as received) were weighed into the reactor. The reactor was then evacuated and pressurized with hydrogen to 7MPa. Heating was accomplished by lowering the reactor into a fluidized sand bath preheated to the desired temperature. After a measured reaction time, the reactor was quenched to room temperature by immersing it in a cold water bath. The products from the reaction were removed from the reactor using THF. The THF was removed by rotary evaporation and the product was weighed. It was found that in all cases the weight of the products equaled the weight of the original compound before reaction. The products were dissolved in acetone and analysed using a Perkin-Elmer 8500GC.

In order to determine the dehydrogenation behavior of the hydrogenated pyrenes, the products from pyrene hydrogenated at 350°C and 60 minutes, 400°C and 80 minutes, and 450°C and 40 minutes, were catalytically dehydrogenated under N<sub>2</sub>. This was accomplished using the same reactors as in the hydrogenation step. The products from the three hydrogenations listed above were weighed into the reactor along with a 1wt% (metal) loading of ATTm. The reactor was pressurized with approx. 3MPa N<sub>2</sub> and immersed in a sand bath at the desired temperature and for the desired reaction time. After this time, the reactor was quenched as before, and the products were removed using THF. The products were analysed using GC as before. The dehydrogenation behavior of tetralin was investigated in a similar way to the hydrogenated pyrenes.

### Results and discussion

#### 1. Naphthalene

##### Thermodynamics.

Figure 1 shows the product distributions of naphthalene hydrogenation at 350, 400 and 450°C for various reaction times up to 3hrs. In all cases only tetralin was detected as a

hydrogenation product of naphthalene. No decalin was observed. Cracking/isomerisation products of tetralin were observed at 450°C, but total concentration did not exceed 5wt%. At 450°C, conversion of naphthalene to tetralin reaches a maximum at 51%. At 400°C, conversion is 62% and at 350°C the reaction does not reach equilibrium, but after 3hrs conversion is 72% (to calculate  $K_p$  for 350°C reaction, extrapolation used to assume 95% conversion). Figure 2 shows how the product distribution at equilibrium varies with temperature. From these equilibrium compositions,  $K_p$  values were calculated as below:

$$K_p = \frac{[\text{tetralin}]_{\text{eq}}}{[\text{naphthalene}]_{\text{eq}} [\text{H}_2 \text{ pressure}]^2}$$

Table 1 reports the  $K_p$  values for naphthalene hydrogenation. As expected,  $K_p$  decreases with increasing temperature. This is because thermodynamics controls the extent of the reaction as the temperature increases.

The variation in  $K_p$  with temperature can be used to find the enthalpy of the reaction. This is done using the van't Hoff isochore equation:

$$d \ln K_p/dT = \Delta H/RT^2$$

A van't Hoff plot gives a value of -32 kcal/mol. This is in agreement with values given in the literature (-29-32 kcal/mol) [8, 9].

### Kinetics.

#### *1. Reversible reaction kinetics*

This can be modeled as a first order process with an effective rate constant equal to the sum of the forward and reverse rate constants:

$$-dC_A/dt = k_f C_A P H_2^n - k_r C_N$$

where  $C_A$  = concentration aromatic at time  $t$ ,  $C_N$  = concentration hydroaromatic at time  $t$ ,  $k_f$  = forward rate constant and  $k_r$  = reverse rate constant.

On integration, the following expression is derived:

$$\ln C_A - C_{Ae} / C_{A0} - C_{Ae} = -(k_f + k_r) t$$

where  $C_{A0}$  is the initial aromatic concentration and  $C_{Ae}$  is the equilibrium aromatics concentration.

#### *2. Irreversible reaction kinetics.*

If equilibrium effects are negligible, a simple pseudo-first order kinetic model can be used to obtain the forward rate constant:

$$\ln C_A / C_{A0} = -k_f t$$

If values of the above equation are plotted upto the time where equilibrium effects the reaction, a good approximation of  $k_f$  can be obtained.

Table 1 shows the calculated values of the rate constants calculated from plots of the above kinetic equations. Figure 7 shows an Arrhenius plot of the calculated rate constants. An activation energy of 14.7 kcal/mol for the forward reaction, and 25.5 kcal/mol for the reverse reaction were calculated. From this plot, dehydrogenation would be favored over hydrogenation at a temperature of 416°C.

### Kinetics vs Thermodynamics.

If hydroaromatics are to be produced from aromatics, two factors have to be considered.

1. Conversion.
2. Length of time to get to the desired conversion level.

As can be seen from the data, conversion decreases with increasing temperature, but the kinetics of the reaction are slower at lower temperatures. From the data, it can be concluded that high temperatures are desirable for the first 40 minutes of reaction, but after this time thermodynamics limit the conversion. At this point, it is then advisable to drop the temperature to below 400°C, and continue to convert naphthalene to tetralin as seen in the 350°C reaction. To hydrogenate only at 350°C would take too long to achieve respectable conversions, i.e. conversion at 350°C and 120 minutes is the same as 450°C and 60 minutes. Therefore in hydrogenating naphthalene to tetralin a reverse temperature stage reaction is proposed.

- Stage 1. 400°C and 40 minutes reaction time.
- Stage 2. 350°C and 60 minutes reaction time.

### **Dehydrogenation reactions of tetralin**

Figure 3 shows the product distribution of tetralin dehydrogenation at 350, 400, and 450°C for various reaction times up to 30 minutes. As temperature increases, the rate of dehydrogenation increases, and the conversion of tetralin to naphthalene also increases. At 350 and 400°C, conversion to naphthalene does not exceed 13%, but at 450°C conversion is 42%. This explains

the rapid approach to equilibrium seen in the hydrogenating reactions and the relatively low conversions seen at the high temperature of 450°C.

## 2. Pyrene

### Thermodynamics.

Product distribution of pyrene, dihydropyrene, tetrahydropyrene and hexahydropyrene are shown in figures 4 and 4b. From these product distributions it can be seen that temperature is affecting the conversion of pyrene to hydrogenated pyrenes. At 450°C, equilibrium is reached after 20 minutes, with 28% conversion of pyrene. At 400°C, equilibrium is reached after 80 minutes, with 45% conversion of pyrene. At 350°C, equilibrium is not observed, even after 120 minutes of reaction. Conversion at this point is 55% pyrene to hydrogenated pyrenes. These product distribution trends are similar to that observed for naphthalene hydrogenation in that as temperature increases, conversion decreases but the rate of reaction to equilibrium increases. Figure 5 shows the equilibrium composition of pyrene and total hydrogenated pyrenes. Kp values are reported in table 1. Kp decreases with increasing temperature. These values can be used to determine the enthalpy of reaction as described earlier. A value of -6.4 kcal/mol is obtained from a van't Hoff plot. This value is a reasonable comparison to the value obtained by Johnston (-10 kcal/mol)[10].

### Kinetics.

A similar model is used for evaluation of pyrene kinetic data as was used for naphthalene. Rate constants are reported in table 1. Figure 8 shows an Arrhenius plot for the calculated rate constants. An activation energy of 6.83 kcal/mol for the forward reaction, and 21.5 kcal/mol for the reverse reaction were calculated. From this plot, dehydrogenation would be favored over hydrogenation at temperatures above 350°C.

### Kinetics vs thermodynamics.

The same arguments apply for pyrene as they did for naphthalene. A reverse temperature stage reaction is proposed for pyrene hydrogenation:

Stage 1. 400°C and 20 minutes reaction time.

Stage 2. 350°C and reaction time set for the desired conversion.

### Dehydrogenation of dihydropyrenes.

Figure 6 show the dehydrogenation product distributions of dihydropyrene, tetrahydropyrene and hexahydropyrene. It can be seen that dehydrogenation is rapid and complete at 450°C. At the lower temperatures, dehydrogenation is slower and complete dehydrogenation to pyrene is not seen in the 30 minutes reaction used in this study.

### Comparisons between naphthalene and pyrene

Table 1 shows a comparison of the parameters for the two compounds. It can be seen that as ring size increases, enthalpy of reaction increases and activation energy decreases.

### Future Work

The work will be expanded to include 3-ring systems and other 4-ring compounds. When the parameters are calculated for these compounds and plotted vs ring size, molecular weight etc., it should be possible to make predictions as to how other compounds behave under hydrogenating/dehydrogenating conditions. Ideal temperature strategies will be estimated from the product distribution curves and compared for the different compounds.

### References

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Table 1. Kinetic and thermodynamic parameters for naphthalene and pyrene hydrogenation

	Kp	Kp	Kp	k/min <sup>-1</sup>	k/min <sup>-1</sup>	k/min <sup>-1</sup>	ΔH	Ea (kf)
	350C	400C	450C	350C	400C	450C	kcal/mol	kcal/mol
Naphthalene	0.0045	0.00037	0.00027	kf 0.0059 kr 0.0027	kf 0.0150 kr 0.0125	kf 0.0301 kr 0.0194	-32	14.7
Pyrene	0.0078	0.0058	0.0038	kf 0.0088 kr 0.0100	kf 0.0139 kr 0.0342	kf 0.0187 kr 0.1103	-6.4	6.8

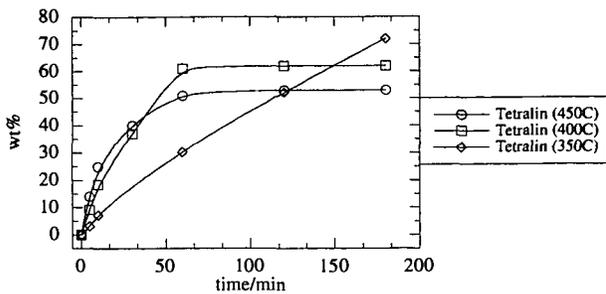


Figure 1. Naphthalene-tetralin product distribution vs time

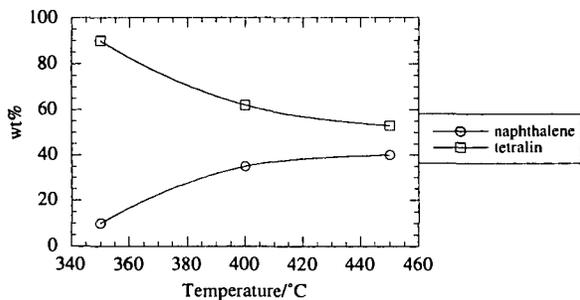


Figure 2. Naphthalene hydrogenation product distribution at equilibrium

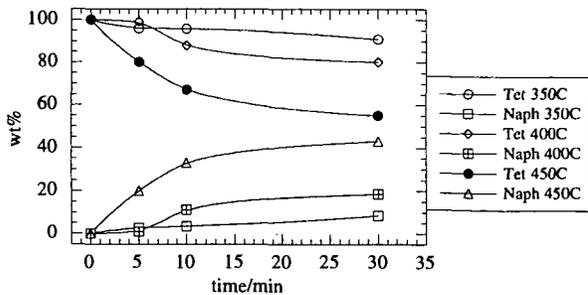


Figure 3. Tetralin dehydrogenation product distribution vs reaction time

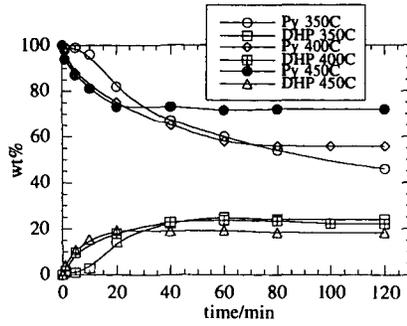


Figure 4. Pyrene-dihydropyrene product distribution vs time

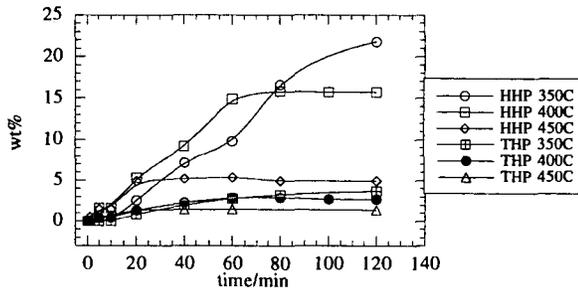


Figure 4b. Tetrahydropyrene-hexahydropyrene product distribution vs time

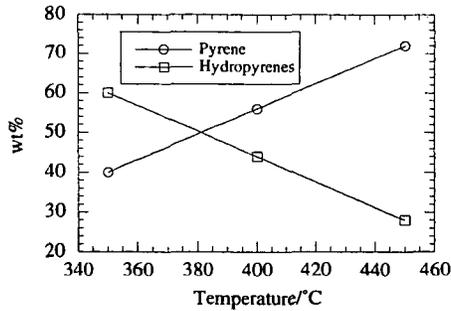


Figure 5. Pyrene hydrogenation product distribution at equilibrium

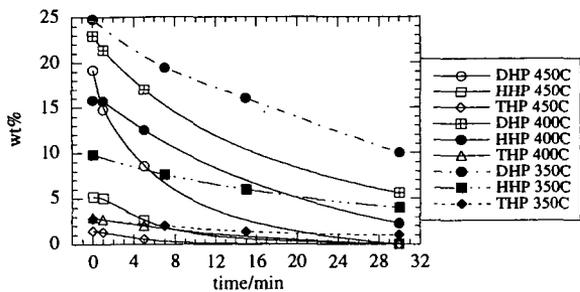


Figure 6. Hydropyrenes dehydrogenation product distribution vs time

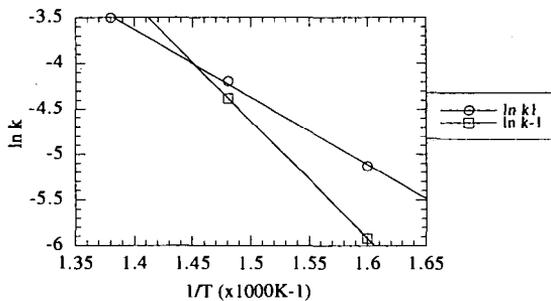


Figure 7. Arrhenius plot- naphthalene hydrogenation

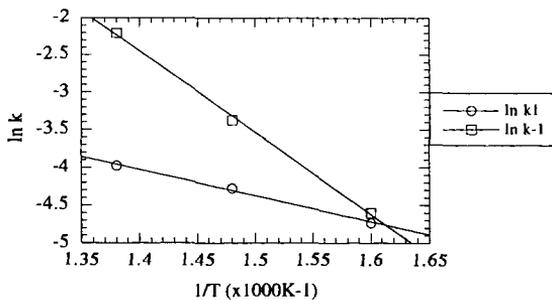


Figure 8. Arrhenius plot- pyrene hydrogenation