

## COAL LIQUEFACTION USING DONOR SOLVENTS HYDROGENATED AT LOW TEMPERATURES\*

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### Introduction

Direct coal liquefaction proceeds initially through a complex series of bond breaking and hydrogen transfer reactions involving coal and a donor solvent. When the recycle solvent contains high amounts of donor solvent, the requirement for high hydrogen gas pressure in the initial stage of liquefaction is reduced and coal conversion is augmented. Effective tests for hydrogen donating ability of coal derived solvents often consist of GC/MS, proton NMR, catalytic dehydrogenation, as well as microautoclave coal liquefaction testing [1,2,3]. Microautoclave testing is an empirical measure of solvent quality for hydrogen donation using coal, a donor solvent and an inert gas instead of hydrogen. Previous studies [4] have investigated the hydrogen transfer cycle for direct liquefaction using Illinois #6 high volatile bituminous coal and a distillate (650°F-770°F) derived from a coal liquefaction process solvent. The objective of this work is to determine the effects of donor solvent on coal conversions in microautoclave liquefaction experiments performed at 400°C with Wyodak coal. These tests used a heavy distillate solvent that had been hydrogenated with a synthesis gas (50% carbon monoxide:50% hydrogen) mixture and steam at low temperatures (300°C-325°C). The in situ water-gas shift (WGS) reaction provides an alternate source of hydrogen and has the potential of eliminating the need for high purity high pressure hydrogen for solvent hydrogenation. Hydrogenation at low temperatures can lead to increased donor content since larger amounts of hydroaromatics are produced at equilibrium with any given hydrogen pressure. Distillate solvents were hydrogenated at various weight hourly space velocities, using two different catalysts, and used in microautoclave coal liquefaction tests to evaluate solvent pretreatment effects on coal solubility.

### Experimental

**Materials** - Because solvent quality is favorably affected by increasing the aromatic nature of the solvent being fed to the catalytic hydrotreater, and solvent dewaxing has been shown to be an effective means of increasing the aromatic nature of the solvent [5], a heavy distillate and a dewaxed heavy distillate were used. Heavy distillate sample (V1074) from the Wilsonville, Alabama Advanced Integrated Two Stage Liquefaction Facility was provided by CONSOL Inc., Library PA. Dewaxed V1074 distillate was prepared by CONSOL at -5°C from the V1074 heavy distillate using an acetone dewaxing procedure. 1,2,3,6,7,8 hexahydropyrene was purchased from Aldrich Chemical Company with a 99% purity. Reagent grade tetrahydrofuran (THF), pentane, and heptane were purchased from Fischer Scientific. Wyodak subbituminous coal was used as -100 mesh from the Argonne Premium Coal Sample Bank. The NiMo catalyst, was Shell 324M and the platinum catalyst was a hydrous titanium oxide (HTO) compound synthesized in our lab. Hydrogen, carbon monoxide, and nitrogen were UHP grade.

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### Apparatus and Procedure

**Microflow Reactor Experiments** - A fixed bed microflow reactor consisting of liquid and gas feed systems and a stainless steel reactor containing the catalyst bed (0.5" O.D.) was used to hydrogenate heavy distillate and dewaxed heavy distillate. The reactor had an internal volume of 23 cm<sup>3</sup> and typically held a 20 gram catalyst charge. These distillate pretreatment experiments consisted of three days of testing for each catalyst and feed combination. The first two days of experiments used the in situ water-gas shift reaction to hydrotreat the distillate. Reactions on the third day used solely hydrogen to test the effect of varying the partial pressure of hydrogen gas upon solvent hydrogen uptake. The reactor tube was first packed with catalyst and then presulfided with a 9% H<sub>2</sub>S in hydrogen mixture for four hours at 390°C for the commercial nickel molybdenum on alumina catalyst (NiMo), or pre-reduced in hydrogen at 200°C for the platinum (Pt HTO) catalyst. After catalyst pretreatment, the reactor was pressurized to 1000 psig with a 50:50 mixture of carbon monoxide and hydrogen. The reactor temperature was increased to the operating value while the distillate and a 1:1:1 molar mixture of CO:H<sub>2</sub>:H<sub>2</sub>O was fed the top of the reactor. Distillate was pumped into the reactor with an Eldex A-30 liquid chromatograph pump and the synthesis gas was metered into the reactor with two Brooks 5850 mass flow controllers. The liquid weight hourly space velocities were varied between 0.4 hr<sup>-1</sup> and 0.8 hr<sup>-1</sup>. Water was fed to the reactor with a Beckman 114M microflow liquid chromatography pump. All reactants flowed downward over the packed bed into a reservoir to separate the gases and liquids. Solvent and gas products were taken from the sample reservoir at the bottom of the reactor during operation. Reactor pressure was maintained with a Circle Seal BPR-7A back pressure regulator, which was located downstream from the liquid separator. Distillates and hydrotreated distillates were also analyzed by high resolution gas chromatography using a Hewlett Packard 5890 GC to qualitatively measure hydrogenation of aromatic compounds.

**Microautoclave Experiments** - Coal liquefaction tests were used to evaluate donor solvent quality. Hydrogenated solvent was tested in a microautoclave consisting of a 0.75" O.D. Swagelok tubing tee with 40 cm<sup>3</sup> of gas volume. Pressure and temperature were measured in the microflow and batch microautoclave reactors with Entran pressure transducers and internal reactor thermocouples. Data acquisition for both the flow and batch reactor systems was accomplished with a personal computer using Labtech Notebook software.

Coal and pretreated solvents representing various hydroprocessing conditions were weighed into the microautoclave reactor. The microautoclaves were sealed and pressurized with nitrogen to 100 psig cold charge to facilitate post reaction gas analysis. The pressurized microautoclaves were then fastened to a wrist-action shaker and immersed in a fluidized sand bath while being shaken at 200 cycles per minute. After a rapid heat up (< 2min.) the microautoclaves were maintained at 400°C for 30 minutes. Following reaction the microautoclaves were cooled to room temperature in water, then depressurized into gas sample bottles and dismantled to recover the reaction products. The gas samples were analyzed for hydrogen, carbon monoxide, carbon dioxide and C<sub>1</sub>-C<sub>2</sub> hydrocarbons using a Carle series 400 Gas Chromatograph. Liquid and solids were recovered from the reactor with THF and the THF insolubles were determined by pressure filtration. The THF insolubles were dried and weighed while the THF solubles were rotoevaporated to remove most of the THF. Pentane was then added to these samples to precipitate the preasphaltene/asphaltene material. These solutions were pressure filtered to remove the pentane insolubles. The pentane insolubles were then dried and weighed.

All microautoclave tests were performed with a solvent to coal ratio of 1.5:1. Solvent samples A, B, C and D, shown in Table 1, were produced in the microflow reactor using various catalysts, temperatures and weight hourly space velocities (WHSV). Hydrogen donor (H<sub>6</sub>PY) was added to comprise 20 % of the solvent charge for experiments that were designed to test the effect of adding a known amount of a good hydrogen donor. Donor hydrogen was effectively increased in this "composite" solvent by 0.6 wt% (see Table 1).

**Model Compound Test** - In a series of donor solvent tests which examined the effects of using different levels of hexahdropyrene (H<sub>6</sub>PY) alone as the solvent, heptane was used instead of pentane as the precipitating solvent, as shown in Figure 5.

### Results and Discussion

The extent of distillate hydrogenation is given in Table 1, which shows elemental analysis results for baseline distillates and hydrotreated products from the microflow reactor. A comparison of samples A and B (from the same reactor run) shows that sample B was hydrogenated to a greater extent than sample A which had a slower space velocity. This is due in part to catalyst deactivation since sample B was obtained earlier in the run when the catalyst bed was fresher. The hydrogenated dewaxed distillates labeled samples C and D compare solvents hydrogenated with different catalysts. The maximum amount of hydrogen increase was 1.0 wt% in the dewaxed distillate (sample D); this distillate was produced at 325°C with the Pt HTO catalyst using only hydrogen gas. This catalyst deactivated to a lesser degree than the NiMo catalyst and was more effective using hydrogen only rather than the in situ water-gas shift reaction. It is believed that the more aromatic dewaxed solvent could be hydrogenated to a greater degree, and this was true for our tests. Figures 1 and 2 show capillary gas chromatograms of the -5°C dewaxed distillate and the hydrotreated distillate. The hydrotreated sample shows a reduction in parent aromatic compounds with an emergence of hydroaromatic products.

Figure 3 shows the product distributions for microautoclave experiments with V1074 (feed), two hydrogenated V1074 distillates (samples A and B), and V1074 + donor solvent (H<sub>6</sub>PY) addition. Overall the coal conversion (100-%IOM, Insoluble Organic Matter) increased from 57% to 63% with sample B. Sample B, which had an additional 0.7 wt% hydrogen (over the V1074 amount), gave an increase in pentane solubles from 14% to 25%. The experiment that contained added H<sub>6</sub>PY gave 33% pentane soluble material.

Figure 4 shows the product distributions for microautoclave experiments with -5°C dewaxed V1074 (feed), two hydrogenated dewaxed distillates (samples C and D) and dewaxed V1074 with H<sub>6</sub>PY addition. The coal conversions increased from 64% to 69% with solvent C. Most notable, however was the increase in pentane solubles with samples C and D. These increased from 0% to 22% and 23% respectively using the hydrotreated solvent. These results show that unhydrogenated dewaxed solvent produced a higher coal conversion than V1074 but little or no oil. The small oil yield for the -5°C dewaxed distillate shows that it is necessary to hydrogenate the more reactive dewaxed solvents to avoid potentially retrogressive conditions that occur when solvent hydrogen is limited. Sample D which had an increase of 1 wt% hydrogen did not perform as well as the H<sub>6</sub>PY doped solvent even though the doped solvent had only 0.6 wt% hydrogen. The increase in hydrogen, in sample D, could possibly have been in alicyclic compounds which are poorer donors than hexahdropyrene. Increasing the liquid space velocity could adjust the hydrogenation extent to enhance production of hydrogen donor species in the product when the Pt HTO catalyst is used.

### Model Compound Test

Figure 5 shows the product distributions for donor solvent tests which used only hexahydropyrene as the solvent. Coal conversion increases dramatically from 52% to 87% when the hexahydropyrene amount was increased from 0.5g to 1.0g. These addition rates amounted to 10 and 20 mg hydrogen / g dmmf coal respectively. Further addition of H6PY (1.75g H6PY or 35mg H / g dmmf coal) showed little improvement in conversion or heptane solubility over the 1g H6Py addition. This could possibly be due to the relatively mild liquefaction temperature. For comparison the -5°C dewaxed solvent with H6PY addition (Figure 4.) had 15mg of hydrogen / g dmmf coal from the H6PY giving 77% coal conversion.

### **Conclusions**

At 400°C for 30 minutes, coal conversions and pentane/heptane soluble yields increase with increasing solvent hydrogen content during liquefaction using Wyodak coal. Dewaxed V1074 heavy distillate gives higher coal liquefaction conversions than V1074 without dewaxing, yet very little pentane soluble product compared to the V1074 heavy distillate. Hydrogenation of dewaxed heavy distillate is necessary to avoid potentially retrogressive conditions with this solvent since it is a good physical solvent yet produces very little pentane soluble material at these conditions. There is of course a potential to over hydrogenate the solvent by forming alicyclic and naphtheno compounds which would add hydrogen without the benefit of increasing solvent quality. These concerns are especially valid when using low rank coals and solvents with limited hydrogen donating capacity.

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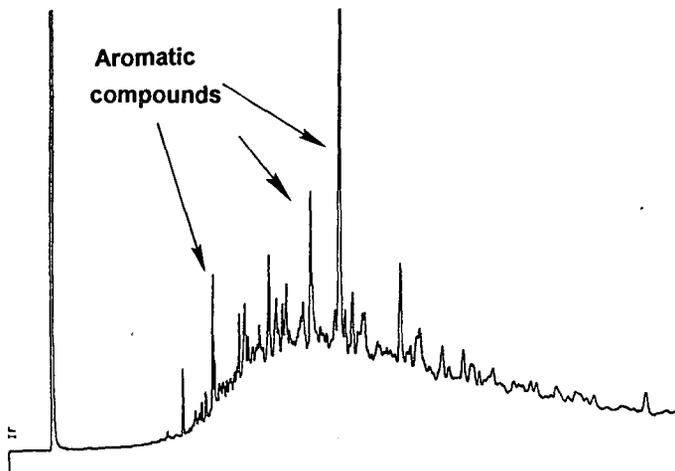
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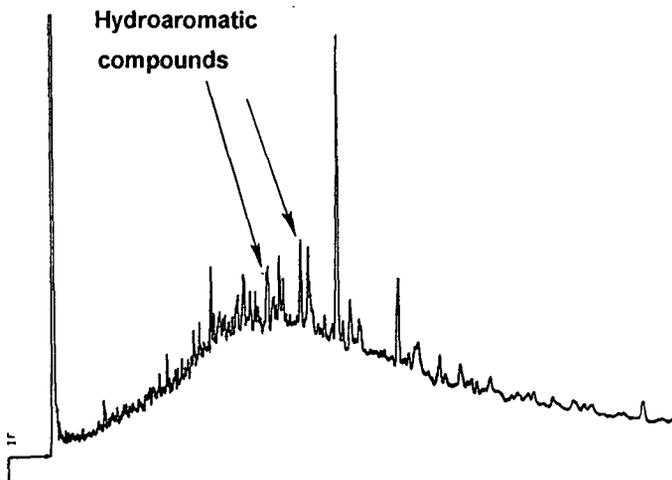
Table 1. Elemental analysis of V1074 and -5°C dewaxed hydrotreated distillates

Distillate	WHSV (hr <sup>-1</sup> )	Catalyst	Hydrotreating Temp(°C)	%C	% H	Increase in Hydrogen (wt%)
V1074 (feed)	-	-	-	89.5	9.9	-
Sample A	0.46	NiMo	300	88.5	10.1	0.2%
Sample B	0.61	NiMo	300	88.9	10.6	0.7%
V1074+H6PY	-	-	-	-	-	0.6%
-5C Dewax (feed)	-	-	-	90.2	8.6	-
Sample C	0.78	NiMo	325	90.2	8.9	0.3%
Sample D	0.78	Pt HTO	325	89.9	9.6	1.0%
-5C Dewax+H6PY	-	-	-	-	-	0.6%

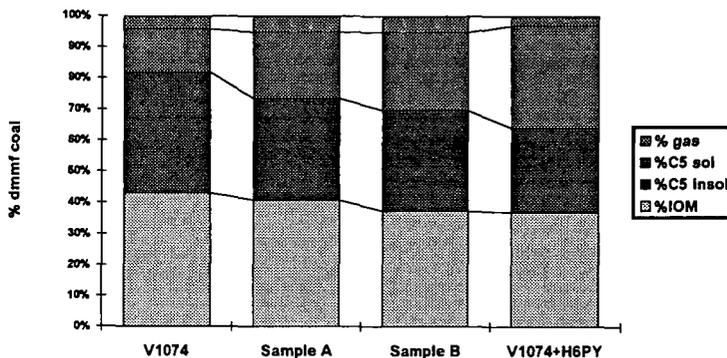
**Figure 1. High resolution gas chromatogram of -5°C dewaxed heavy distillate V1074**



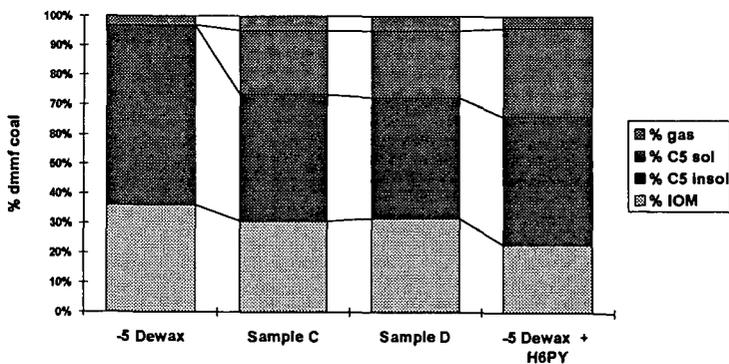
**Figure 2. High resolution gas chromatogram of Sample D**



**Figure 3. Product distribution for V1074 heavy distillate experiments (Wyodak, 400C, N2, 30 min.)**



**Figure 4. Product distribution for dewaxed V1074 heavy distillate (Wyodak, 400C, N2, 30 min.)**



**Figure 5. Product distribution for hexahydroprylene donor solvent (Wyodak, 400C, N2, 30 min.)**

