

Progress in Donor Assisted Coal Liquefaction : Hydroaromatic Compound Formation

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Introduction

The role of hydrogen donor compounds in coal liquefaction has been extensively investigated since the mid 1960's using model compounds and process derived hydrogen donor solvents [1-4]. Our recent research [5] and that of other investigators [4] have shown that two model compounds in particular have great efficacy in solvating low rank coals. 1,2,3,10b tetrahydrofluoranthene (H_4F) and 1,2,3,6,7,8 hexahdropyrene (H_6Py) have been used to dissolve Wyodak coal to > 95% soluble material as measured by tetrahydrofuran (THF). Although these hydrogen donors are very effective, they may not be found in any significant concentrations in actual liquefaction process recycle solvents. Therefore, studies with process derived recycle materials are necessary to understand donor solvent chemistry. The objective of this paper is to present results of solvent hydrogenation experiments using heavy distillate solvents produced during testing at the Wilsonville Advanced Coal Liquefaction Test Facility. We evaluated the impact of hydrogenation conditions upon hydrogen donor formation in process derived distillates and compared these process derived solvents with the highly effective H_4F and H_6Py donors in coal liquefaction tests. This paper presents data on reaction conditions used for distillate hydrotreating and subsequent coal liquefaction, with an aim toward understanding the relationship between reaction conditions and donor solvent quality in recycle distillates.

Experimental

To evaluate distillate hydrotreating conditions, tests were performed with a laboratory-scale trickle-bed reactor. Coal liquefaction tests were performed with the hydrogenated distillates and model compounds to evaluate solvent quality. Proton NMR spectroscopy was used to evaluate distillate solvent quality by measuring hydroaromatic content.

Materials- Wyodak subbituminous coal was used as -100 mesh from the Argonne Premium Coal Sample Bank. Fluoranthene, H_6Py , and n-hexadecane with a 99% purity were purchased from the Aldrich Chemical Company. H_4F was produced by hydrogenating fluoranthene with the trickle-bed reactor at 260°C followed by separation from the hydrogenated mixture with a spinning band distillation column (Perkin Elmer 19" adiabatic); the final H_4F purity was ~96%. Dewaxed heavy distillate was prepared and supplied by Consol from the V1074 process stream (B.P. 650-1050°F) at the Wilsonville Advanced Coal Liquefaction Test Facility (Run 262/Wyodak coal feed).

Apparatus- Heavy distillate solvent was hydrogenated in a microflow reactor consisting of 0.5" O.D., 0.37" I.D. type 316 stainless steel tube that was enclosed in a convectively heated oven. The reactor tube was packed with the NiMo/Alumina catalyst, which was activated with H_2S in hydrogen. Heavy distillate feed was pumped into the reactor with an Eldex A-30 liquid chromatography pump and hydrogen was metered into the microflow reactor with a Brooks 5850 flowmeter. Gases and liquids were separated at high pressure, and liquids were periodically sampled from the product receiver vessel. Constant pressure was maintained with a Circle Seal BPR-7A back pressure regulator. Hydrotreating temperature was 320°C or 360°C, hydrogen pressure was 7 MPa (1000 psig), hydrogen flow was 330 sccm H_2 /ccm distillate, and typical volume liquid hourly space velocities were $\sim 1hr^{-1}$. Proton NMR spectroscopy was performed on the hydrogenated heavy distillate with a 200.13 megahertz Bruker instrument after dissolution in chloroform according to the method of Winschel et al [6].

Coal liquefaction tests using microautoclave batch reactors [7] were performed to evaluate donor solvent quality. Hydrogenated solvent was tested in either of two microautoclaves (40 cc or 22 cc total gas volume) consisting of a Swagelok tubing tee which was heated in a fluidized sand bath while being shaken horizontally at 200 cycles per minute. The larger microautoclave has a slurry capacity of approximately 8cc while the smaller microautoclave has a slurry capacity of 2cc.

Procedure - After the heavy distillate was hydrogenated with the microflow reactor, proton NMR analyses were used to evaluate hydroaromatic content and coal liquefaction tests were performed to measure coal conversion with the distillates. Heavy distillate solvents representing various

hydrotreating conditions or H₆Py or H₄Fl were weighed into the microautoclave reactor with as-received coal. The microautoclaves were sealed and pressurized with 2.1 MPa (300 psig) nitrogen before reaction, fastened to the shaker and immersed in the fluidized sand bath. The microautoclaves were heated to reaction temperature until the desired time at temperature elapsed, and then cooled and depressurized. Gases were collected and the microautoclave was dismantled to recover the reaction products. The gas samples were analyzed for hydrogen, carbon monoxide, carbon dioxide and C₁-C₂ hydrocarbons using a Carle series 400 Gas Chromatograph. Liquid and solids were recovered from the reactor with THF; THF insolubles were determined by pressure filtration. After the THF filtrate was roto-evaporated to remove most of the THF, pentane was added to these samples to precipitate the preasphaltene/asphaltene material. The product was pressure filtered to remove pentane insolubles which were dried and weighed. Coal conversion was calculated on a dry mineral matter free (dmmf) basis.

Results and Discussion

Solvent hydrogenation - Hydrogen donor compounds are produced in recycle solvents by hydrogenating aromatic compounds in the catalytic stage of a two-stage liquefaction process or in a separate hydrotreating reactor. One measure of the effectiveness of this hydrogenation is the concentration of hydroaromatic compounds in the product oil. To illustrate this point fluoranthene was hydrogenated in a trickle-bed reactor at different temperatures. As can be seen in Figure 1, fluoranthene is readily hydrogenated to >80% of the desirable H₄Fl at 250°C, but is hydrogenated to H₁₀Fl and more extensively hydrogenated fluoranthene compounds at 300°C. These results illustrate that polynuclear aromatic hydrocarbons can be "overhydrogenated" to form alicyclic compounds which are poor hydrogen donors. Process solvents can be overhydrogenated in the same way and often become enriched in saturated material. Figure 2 presents the results of proton NMR analyses of heavy distillate samples hydrotreated at 360°C and shows that alkyl hydrogens, which make poor hydrogen donors, are more abundant, at the lower space velocities (0.7-0.9 hr⁻¹) than at the higher space velocity (1.1 hr⁻¹). However, hydroaromatic hydrogen (cyclic $\alpha+\beta$) concentrations remain constant or are only slightly increased. Thus the content of hydroaromatic compounds can be controlled by the solvent residence time in the hydrogenation reactor. The accumulation of paraffinic material is somewhat process dependent in that different processes and feedstocks accumulate different amounts of these non-donor compounds [8]. Results from proton NMR analyses of several process derived distillate solvents are shown in Figure 3. Solvent A is a sample of V1074 heavy distillate that had been dewaxed by Consol. The dewaxed heavy distillate has been enriched in aromatic (from 15% to 22%) and hydroaromatic hydrogen (from 30% to 36%) compared to the original heavy distillate[9]. Sample B is a sample of Distillate A that was hydrogenated at 320°C with the trickle-bed reactor. This hydrogenation increased the hydroaromatic hydrogen concentration from 35.8% to 39.2%. Sample C is a sample of a pasting solvent from the Lummus process using Illinois #6 coal [8,10], and exhibits a higher aromatic character than the Wilsonville distillate. For comparison purposes a sample of H₆Py was analyzed by the proton NMR method and included in the figure. The hydroaromatic cyclic α protons account for 50% of the H₆Py hydrogen and because of proton assignments, some cyclic β protons in H₆Py report to the alkyl designation. In any event, results in Figure 3 give a realistic picture of what can be expected from a recycle distillate in terms of hydrogen donor content, with H₆Py being an upper bound with nearly 2.9% donatable hydrogen. Most recycle distillates have significantly more alkyl hydrogen, however, than pure donors such as H₆Py and H₄Fl as liquefaction experiments attest.

Coal liquefaction tests - Coal conversion experiments were performed to test the ability of the hydrogenated distillate or model compounds to liquefy coal. The tests were performed non-catalytically to evaluate the effectiveness of the solvents for coal conversion. Coal conversions for the model compound liquefaction tests are presented in Tables 1 and 2 along with the results from high resolution gas chromatography (HRGC) analyses for solvent recovery and amount of donor remaining. "Solvent recovery" is the sum of hydrogenated and dehydrogenated solvent compounds, while "donor remaining" is the amount of the original donor compound remaining in the product. Table 1 shows that coal conversion was >94% for all tests with H₄Fl. HRGC analyses indicate that solvent recovery (% of initial solvent) decreases from 98% at 10 minutes to 73% at 60 minutes of reaction. The HRGC analyses show that the balance of the solvent is present as lower molecular weight cracked products. This observation is consistent with previous reports of disappearance of fluoranthene compounds from coal liquefaction recycle streams[2]. Table 2 presents the results of coal liquefaction tests using H₆Py as the donor solvent. Coal conversion was greater than 92% for all of the 450°C runs. Solvent recoveries were also lower at the more severe conditions due to solvent cracking but the effect was not nearly as notable as for H₄Fl. In general, H₄Fl and H₆Py are excellent hydrogen donors, which carry approximately 2-3% donatable hydrogen by weight and readily liquefy Wyodak coal. However, severe processing (long residence times at high temperatures) incurs solvent losses due to cracking.

Table 3 presents the results of coal liquefaction with the process solvents shown in Figure 3. Coal conversions were about 10% lower than similar experiments with H₄Fl. The increased alkyl nature of the heavy distillates as compared with the pure hydrogen donor compound (Figure 3) would explain the lower conversions. More notable however, are the pentane solubility analyses of products using Sample A (unhydrogenated) and Sample B (hydrogenated) V1074 samples. Experiments with Sample A gave a negative seven percent pentane soluble yield indicating solvent adduction using Wyodak coal. Reaction at 425°C showed still further decreases in pentane soluble material (-31%) with the unhydrogenated distillate A, indicating that the solvent hydrogen was insufficient for preventing solvent adduction.

Conclusions

Because they contain an overburden of saturated compounds, and therefore are unable to accept hydrogen to form higher concentrations of hydroaromatic compounds, hydrogenated process derived heavy distillate samples, in general, have less donatable hydrogen than pure hydrogen donor model compounds. However, processing steps such as dewaxing and carefully controlling hydrotreating conditions can significantly improve donor solvent content of the distillates. Model compounds such as H₄Fl and H₆Py are known to be excellent hydrogen donors, having two and three percent donor hydrogen by weight. Liquefaction tests with these compounds have shown high (>95%) conversion, yet illustrated that severe processing can reduce desirable solvent qualities by solvent cracking. Our experiments with model donor and heavy distillate solvents confirm that solvent hydrogen is very effective for coal liquefaction and appears to minimize solvent adduction reactions during coal thermolysis. Progress in coal liquefaction using donor hydrogen will occur by optimizing processing conditions to generate and maintain hydroaromatic species in the recycle distillate. Such processing conditions would consist of, but not be limited to, selective paraffin cracking, proper temperature, pressure and residence time for solvent hydrogenation and ensuring aromaticity of the solvent fed to a recycle hydrotreater.

Acknowledgments

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Figure 1. Concentration of Hydrogenated Fluoranthene Component in Hydrotreated Model Compound Mixture

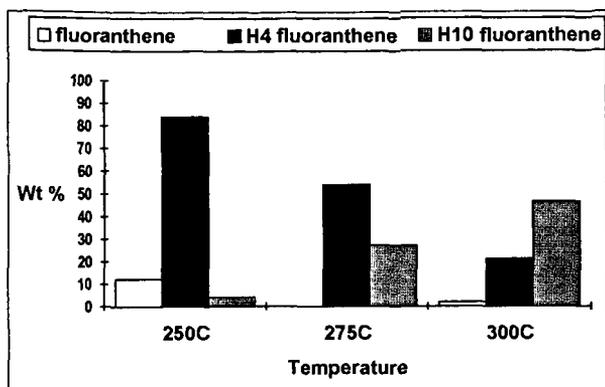


Figure 2. Effect of Increased Hydrotreater Feed Rate upon Proton Distribution in Heavy Distillate.

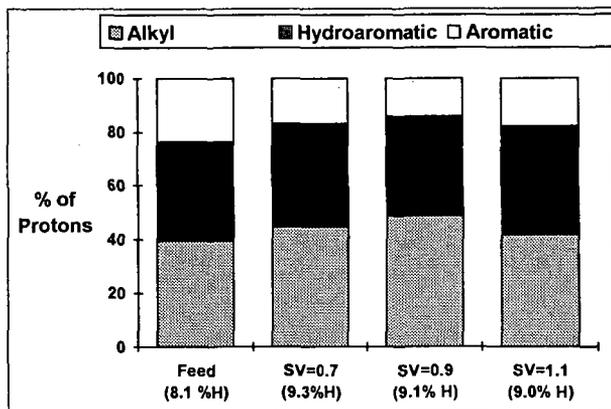
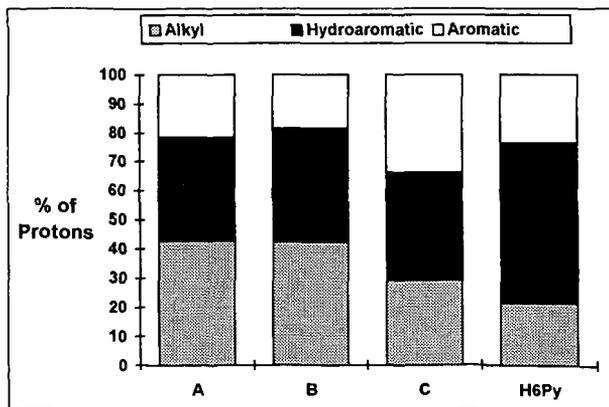


Figure 3. Proton Distributions for Heavy Distillate Solvents and Hexahydropyrene



A=Dewaxed V1074; B=Hydrotreated A; C=Lummus Pasting Solvent;

Table 1. Wyodak Coal Liquefaction Results for 1,2,3,10b Tetrahydrofluoranthene. Solvent to Coal Ratio 2:1

Time (min)	Temperature °C	THF conversion (%dmmf)	Donor remaining (wt%)	Solvent recovery (wt%)
10	450	94	48	98
20	450	96	26	91
40	450	97	14	80
60	450	98	8	73

Table 2. Wyodak Coal Liquefaction Results for 1,2,3,6,7,8 Hexahydroperylene. Solvent to Coal Ratio 1.3:1

Time (min)	Temperature °C	THF conversion (%dmmf)	Donor remaining (wt%)	Solvent recovery (wt%)
10	450	93	58	100
20	450	97	49	98
40	450	96	35	92
60	450	95	26	87

Table 3. Wyodak Coal Liquefaction Results for Heavy Distillate Solvents. Solvent to Coal Ratio 2:1

Time (min)	Solvent	Temperature °C	THF conversion (%dmmf)	% Pentane soluble yield
20	H4FI	400	73	ND
40	H4FI	400	79	ND
30	B	400	68	19
30	A	400	68	-7
30	B	425	81	10
30	A	425	75	-31

Coal Conversion = (dmmf coal in - iom out)/(dmmf coal in); Pentane (c5) soluble yield was calculated as (dmmf coal in - iom - c5 insol - gas make)/(dmmf coal in).