LIQUEFACTION CHEMISTRY AND KINETICS: HYDROGEN UTILIZATION STUDIES

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OBJECTIVE

The objectives of this project are to investigate the chemistry and kinetics that occur in the initial stages of coal liquefaction and to determine the effects of hydrogen pressure, catalyst activity, and solvent type on the quantity and quality of the products produced.

PROJECT OVERVIEW

The project comprises three tasks: (1) Preconversion Chemistry and Kinetics, (2) Hydrogen Utilization Studies, and (3) Assessment of Kinetic Models for Liquefaction. The Hydrogen Utilization Studies work will be the main topic of this report. However, the other tasks will be briefly described here.

The Preconversion Chemistry and Kinetics task focuses on understanding the influence of a catalyst and solvent on the chemistry occurring in the initial phases of the dissolution and liquefaction of coal. Particular emphasis is placed on understanding and controlling retrogressive reactions that lead to high molecular weight, refractory products. Mitigating these reactions could lead to an improved first-stage product requiring less severe upgrading to produce lower molecular weight, more highly saturated products. Catalyst studies with $Mo(CO)_6$ as the catalyst precursor in a solvent-free liquefaction system were designed to investigate the role of the catalyst apart from added solvents in the initial stages of liquefaction. Samples of coal recovered after liquefaction for various periods of time have been subjected to detailed microscopic and chemical characterization to determine the nature of physical and chemical changes that occur. Emphasis is given to understanding the changes occurring in the coal and insoluble residues that precede the formation of soluble products and the role of a catalyst and solvent in preventing retrograde reactions in these processes. Kinetic descriptions of these processes have been developed and are described in several publications and presentations [1,2,3].

Assessment of Kinetic Models for Liquefaction is a new effort that is intended to develop improved kinetic models for evaluating the liquefaction process. The initial stages of this task will consist of an information needs assessment with review of the pertinent literature and discussions with process engineers to understand the limitations of current kinetic models for direct coal liquefaction. Because of the preliminary nature of this task, there have been no publications or presentations to date.

The remainder of this report will be concerned with the Hydrogen Utilization Studies task. It entails an investigation of the effects of solvent type, catalyst activity, and hydrogen pressure on the conversion of coal in first stage coal liquefaction and on the quantity and quality of the products produced. One of the perceived major costs associated with coal liquefaction is the high pressure commonly employed in first-stage catalytic reactors. Reducing the overall pressure significantly could result in considerable savings in the costs associated with coal liquefaction, provided that the hydrogen demands of the system are met. In the first stage of coal liquefaction, hydrogen serves the important functions of capping radical fragments formed from thermal (or other) bond scission reactions and of maintaining a desirable equilibrium between aromatic molecules and their hydroaromatic analogs. Understanding the pathways for hydrogen consumption during this crucial time period would enable one to choose catalysts and conditions that favor desired reactions. In this task, three aspects of hydrogen utilization have been investigated. Gas-phase hydrogen consumption has been monitored as a function of initial pressure, the extent of solvent hydrogenation of simple two-ring aromatic solvents has been determined in the presence of various catalysts, and these measurements have been correlated with coal conversion as determined by solvent fractionation. Several publications and presentations have resulted from this work [4,5,6,7].

EXPERIMENTAL SECTION: Hydrogen Utilization Studies

Materials. Panasol®, a mixture containing mostly alkyl naphthalenes, was obtained from Crowley Chemical Company and used without further purification. Purified grade 1-methylnaphthalene (1-MeNp) from Fisher Scientific Company, found to be 99% pure by gas chromatography, was used without further purification. Blind Canyon coal, DECS-6, from the U.S. Dept. of Energy's Coal Sample Program, was used in these studies. A unique, high surface area, preformed molybdenum catalyst (MoS_2) was prepared at the U.S. Dept. of Energy's Pittsburgh Energy Technology Center (PETC). The catalyst consisted of the recovered solid from a semi-batch, 1-L stirred autoclave reaction of ammonium heptamolybdate, hydrogen sulfide, and Panasol under 17 MPa (2500 psi) hydrogen at 425°C [8]. The catalyst contained 50% C, 30% Mo, and 20% S, and possessed a BET surface area of approximately 250 m^2/g. Aged Akzo EXP AO-60 catalyst, containing Ni-Mo on an Al_2O_3 support, was obtained from Hydrocarbon Technologies, Inc, and ground before use. Shell-324 (S-324), also a Ni-Mo/Al_2O_3 based catalyst, was sulfided before use by reaction with elemental sulfur under 7 MPa (1000 psi) H_2 (cold) at 425°C for 30 minutes in 1-MeNp.

Reactions. Reactions were completed in a stainless steel batch microautoclave reactor system constructed at PETC. The cylindrical reactor portion has a volume of 43 mL, and the total internal volume, including all tubing and connections, is 60 mL. Unless otherwise stated, a normal reaction charge consisted of 6.6 g solvent, 3.3 g coal, catalyst to obtain 3000 ppm metal loading, and 7 MPa (1000 psi) ambient temperature hydrogen gas. The reactor was then attached to the rocker arm (180 cycles / minute) and plunged into a preheated sand bath, where it was heated up to 425°C in 2 to 4 minutes. It was held at temperature in the sand bath for 30 minutes, and then removed and allowed to air cool, typically in less than 5 minutes, to near room temperature.

Sample Workup Procedure and Characterization Scheme. The reaction characterization scheme is diagrammed in Figure 1. The reactor was equipped with an internal thermocouple and a pressure transducer for continuous monitoring of pressure and temperature throughout the run. These were the only measurements that were made while the reaction was in progress. After the reactor cooled to room temperature, it was vented and the vent gas was collected and analyzed by a previously published method [9]. Total hydrogen consumption for the run was calculated based on the difference between initial and final (cold) gas pressure as adjusted for product gas slate. The reactor was rinsed with tetrahydrofuran (THF), and the extracted material was filtered through a 0.45-micron filter under 0.3 MPa (40 psi) nitrogen gas pressure. Coal conversion, or "THF conversion" was calculated from the measured mass of THF insolubles adjusted for catalyst and coal mineral matter as compared to MAF coal. In solvent-only runs, the THF extraction was done to recover the catalyst from the solvent. If coal was present the THF solvent was removed on a rotary evaporator and the remaining material was extracted with heptane solvent. The heptane-insoluble material was used to calculate an "oil conversion," or "heptane conversion." After removal of the solvent, the heptane-soluble material was submitted for a suite of analytical techniques which included low-voltage, high-resolution mass spectrometry (LVHRMS), gas chromatography (GC), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and elemental analysis. Normally, LVHRMS data were used both to survey the variety of chemical species in the soluble product and to calculate solvent hydrogenation for the reaction. The GC was used for solvent hydrogenation when special attention to quantitation of particular components was needed. The reported solvent hydrogenation represents the percent of naphthalenes converted to hydrogenated analogs. The NMR and elemental analyses were normally used only for qualitative support for the other data. In solvent-only runs, the heptane extraction was omitted and the THF solubles were submitted for the suite of solvent-analysis methods.

RESULTS AND DISCUSSION: Hydrogen Utilization Studies

Solvent hydrogenation is shown as a function of cold hydrogen gas pressure for an unsupported (MoS_2) and two supported molybdenum catalysts (AO-60 and S-324) in Figure 2. Also shown on the plot is the level of hydrogenation expected for a pseudo-equilibrium distribution of naphthalenes and tetralins as calculated from literature data [10]. As can be seen, all the data lie well below the equilibrium value. Several conclusions can be drawn from the plot. Solvent hydrogenation increases as a function of hydrogen pressure in all cases. This would be expected from both thermodynamic and kinetic arguments. In the absence of coal, solvent hydrogenation is greater with the supported Mo catalysts than with the unsupported catalyst. The experiments were designed to have equal metal loadings for the unsupported and supported comparison, although this does not imply equal accessibility or nature of the metal sites. The results illustrate the relative activities of the synthesized unsupported catalyst as compared to two state-of-the-art supported catalysts in the absence of coal.

Solvent hydrogenation is shown as a function of coal addition in Figure 3. A comparison is made between two types of supported catalysts (AO-60 and S-324) and the unsupported catalyst (MoS_2). A no-catalyst case is also presented for comparison. The figure shows that in the absence of a catalyst, virtually no solvent hydrogenation is observed, regardless of the amount of coal present. Solvent hydrogenation decreases as a function of coal addition for both the unsupported MoS_2 and the supported catalysts. The unsupported MoS_2 loses about half its initial activity with the addition of 0.2 g coal; the level of activity is similar for a full 3.3 g coal charge. The supported AO-60 loses activity in a more gradual manner, with activity decreased to 50% of the initial value between 0.5 and 1.0 g of added coal. However the activity continues to decrease as more coal is added. With a full 3.3 g charge of coal, the AO-60 has only about 20% of its initial solvent hydrogenation activity, which is equal to the activity of the unsupported MoS_2 under the same conditions. A similar series of experiments (not displayed) shows that the presence of coal also inhibits the dehydrogenation of tetralin.

In Figure 4, baseline data for coal conversion, hydrogen consumption, and solvent hydrogenation are compared to the results for a sequence of microautoclave experiments where the catalyst material was recovered by THF extraction and reused. Although the data expressed in the figure are only for the unsupported MoS_2 catalyst, similar trends were obtained for the supported catalysts. Block "A" shows the baseline solvent hydrogenation and hydrogen consumption for MoS_2 catalyst in a solvent-only system. Block "B" shows the diminution of both of these quantities in a second experiment that contained 0.2 g coal. The catalyst from this experiment was recovered and used to hydrogenate fresh solvent to see if the activity would recover to previous values. As can be seen from the results in block "C", both solvent hydrogenation and hydrogen consumption remained low. This indicates that the diminution observed in "B" was not due to competition from species derived from the coal, but was the result of some permanent modification of the catalyst. The catalyst from "C" was recovered and reused in a third experiment, containing a full 3.3 g coal. As shown in block "D", solvent hydrogenation has been diminished even further. Hydrogen consumption is up, but this is due to the hydrogen requirements of the coal. Coal conversion is nearly identical to the baseline case with fresh catalyst and 3.3 g of coal shown in block "E". The difference in hydrogen consumption between "D" and "E" is most likely due to the difference in solvent hydrogenation, as the recovered catalyst in "D" continues to deactivate toward solvent hydrogenation. Thus the catalyst is still capable of promoting coal conversion (coal conversion in the absence of catalyst is about 50%) although its ability to hydrogenate the alkylnaphthalene has been severely diminished.

Figure 5 shows coal THF and heptane conversions as a function of hydrogen pressure for both the unsupported and supported catalyst systems. A no-catalyst case is shown at two pressures for comparison. All runs contained 3.3 g coal and 6.6 g solvent. It can be seen that conversions are similar for both supported and unsupported catalyst systems at all pressures. Thus any advantage in hydrogenation activity enjoyed by the supported catalysts would appear to have been lost in the presence of coal. With both types of catalysts, THF and heptane conversions increase as a function of hydrogen pressure, although the increase begins to level out at the higher pressures. In spite of the obvious difficulties in promoting contact between solid coal and solid catalyst particles in the reactor, the presence of catalyst in the dissolution stage certainly appears to aid in conversion, as the THF and heptane conversions at 2.7 MPa (400 psi) with catalyst are somewhat above those obtained at 7 MPa (1000 psi) with no catalyst.

Conclusions. Catalyst activity for coal liquefaction is observed at hydrogen pressures (cold) as low as 2.7 MPa (400 psi). The results imply that significant reductions in operating pressures may be possible with the use of appropriate first-stage catalysts. Catalyst behavior in the initial stages of coal liquefaction then becomes important. The results of Figures 3 and 4 show that some deactivation of both the unsupported and supported catalysts used here takes place in the presence of coal. However, a substantial amount of catalytic activity remains, as evidenced by good coal conversion results following repeated recovery and reuse of catalyst. At this point, it is not known whether the hydrogen reacting with the coal is involved with hydrogenating aromatic rings, or simply capping fragments formed from bond scission. However, the results illustrate that the best catalysts for hydrogenation in solvent-only systems may not enjoy the same advantages in the initial stages of coal liquefaction.

PLANS: Hydrogen Utilization Studies

In the Hydrogen Utilization Studies task, the initial stage of coal dissolution is evaluated by direct measurement of coal conversion using solvent extraction methods. The product quality is evaluated indirectly by probing other facets of the process such as hydrogen consumption and solvent hydrogenation. As the project develops, more direct methods will be developed to measure product quality. For example, a planned series of experiments will compare microautoclave reactions done under different experimental conditions of pressure, catalyst, and solvent quality, but which are known (from previous work) to give similar coal conversion levels. With the "conversion" variable held constant, a detailed examination of the reaction products will be made to determine if the different reaction conditions favor particular products. In addition, work is planned to identify the poisoning agent or agents responsible for the inhibition of solvent hydrogenation, and to determine if the effect on the catalyst is reversible. Finally, the process improvements developed during the microautoclave studies, particularly those based on reducing hydrogen pressure, will be tested on a continuous unit.

ACKNOWLEDGEMENTS

This work was performed while one of the authors (MVC) was under an appointment to the U.S. Department of Energy Fossil Energy Postgraduate Training Program administered by the Oak Ridge Institute for Science and Education.

DISCLAIMER

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Figure 1: Characterization Scheme

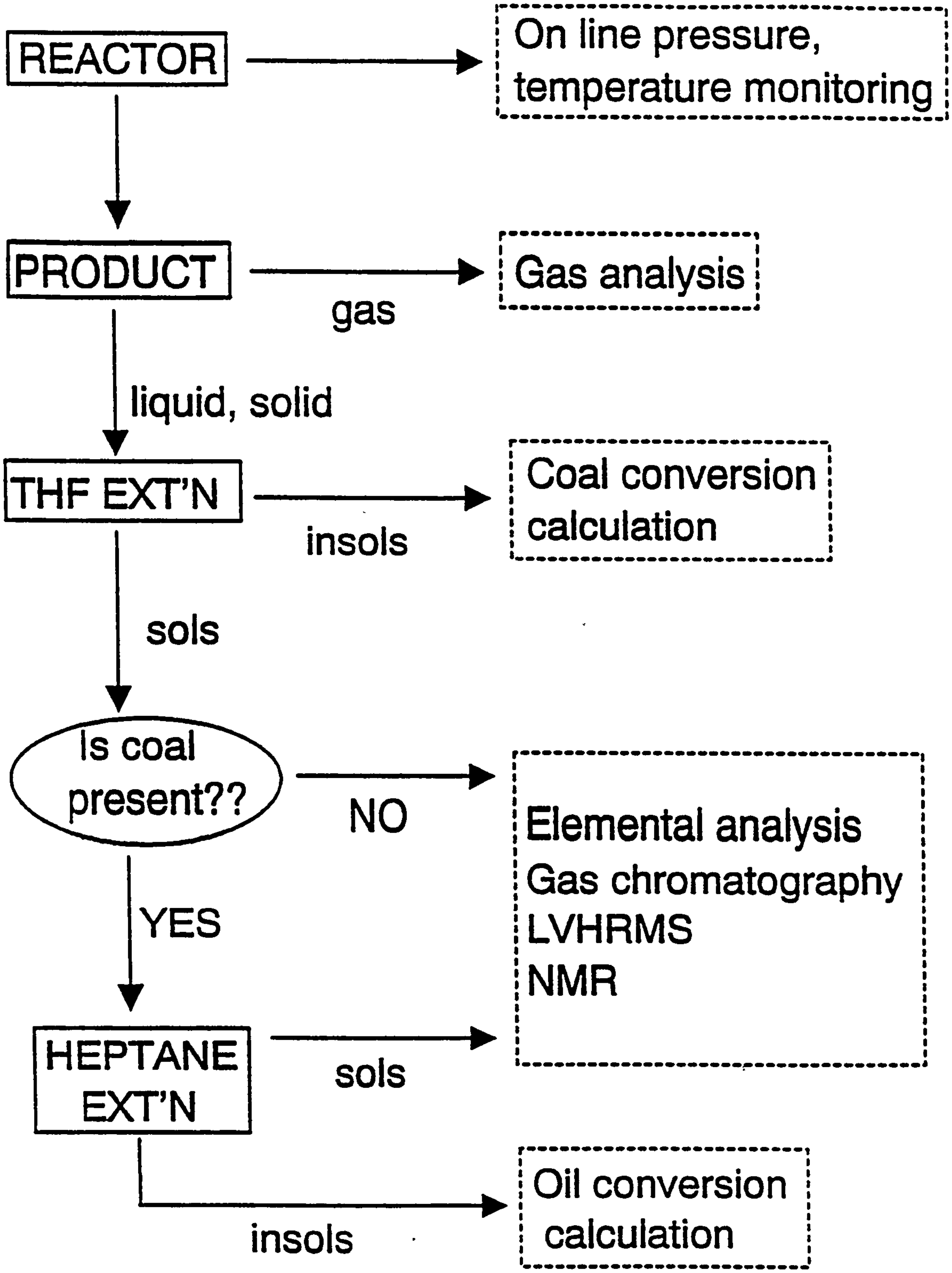

Figure 2: Solvent Hydrogenation as a Function of Hydrogen Pressure (no coal)

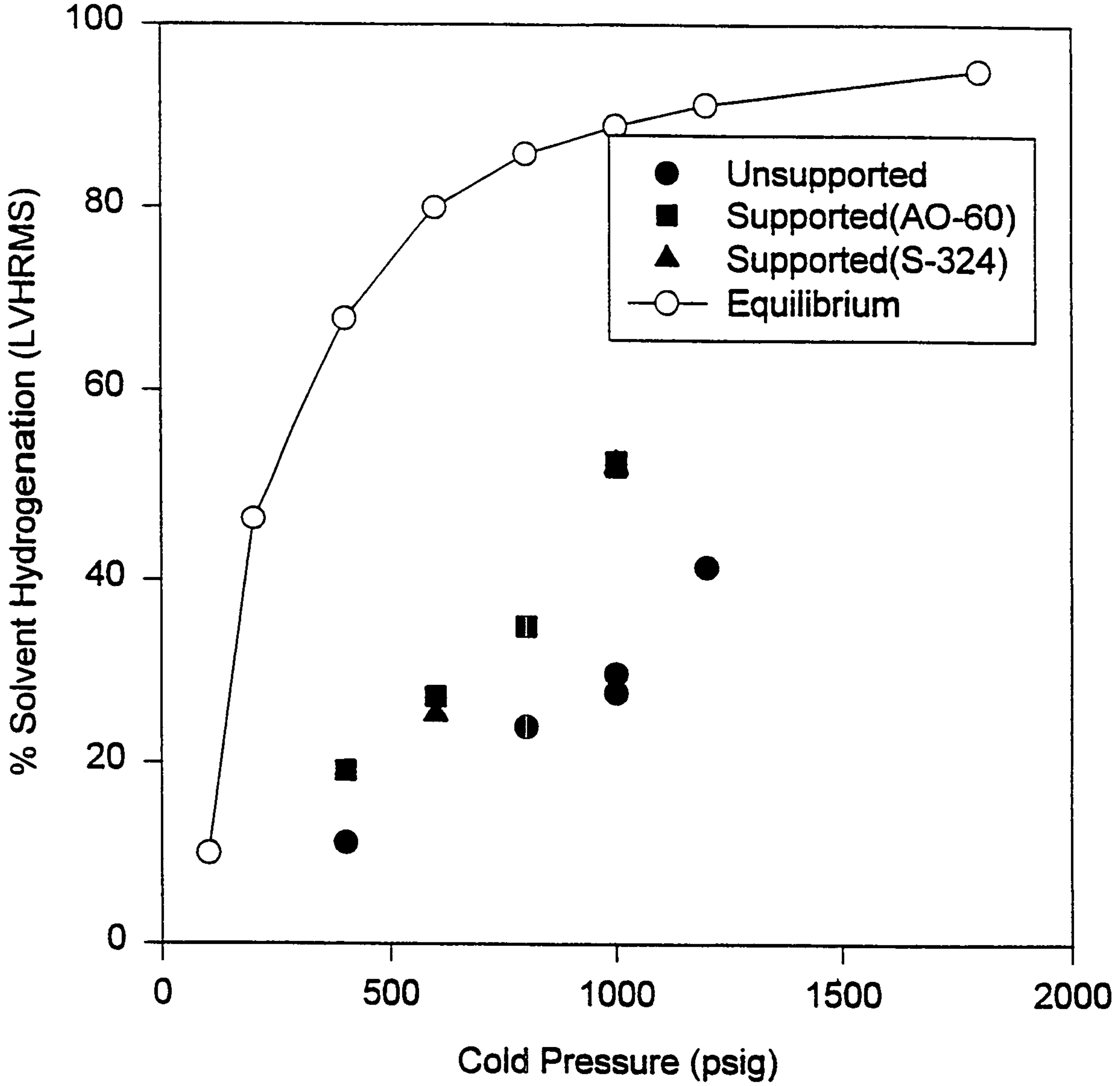

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Figure 3: Solvent Hydrogenation as a Function of Added Coal

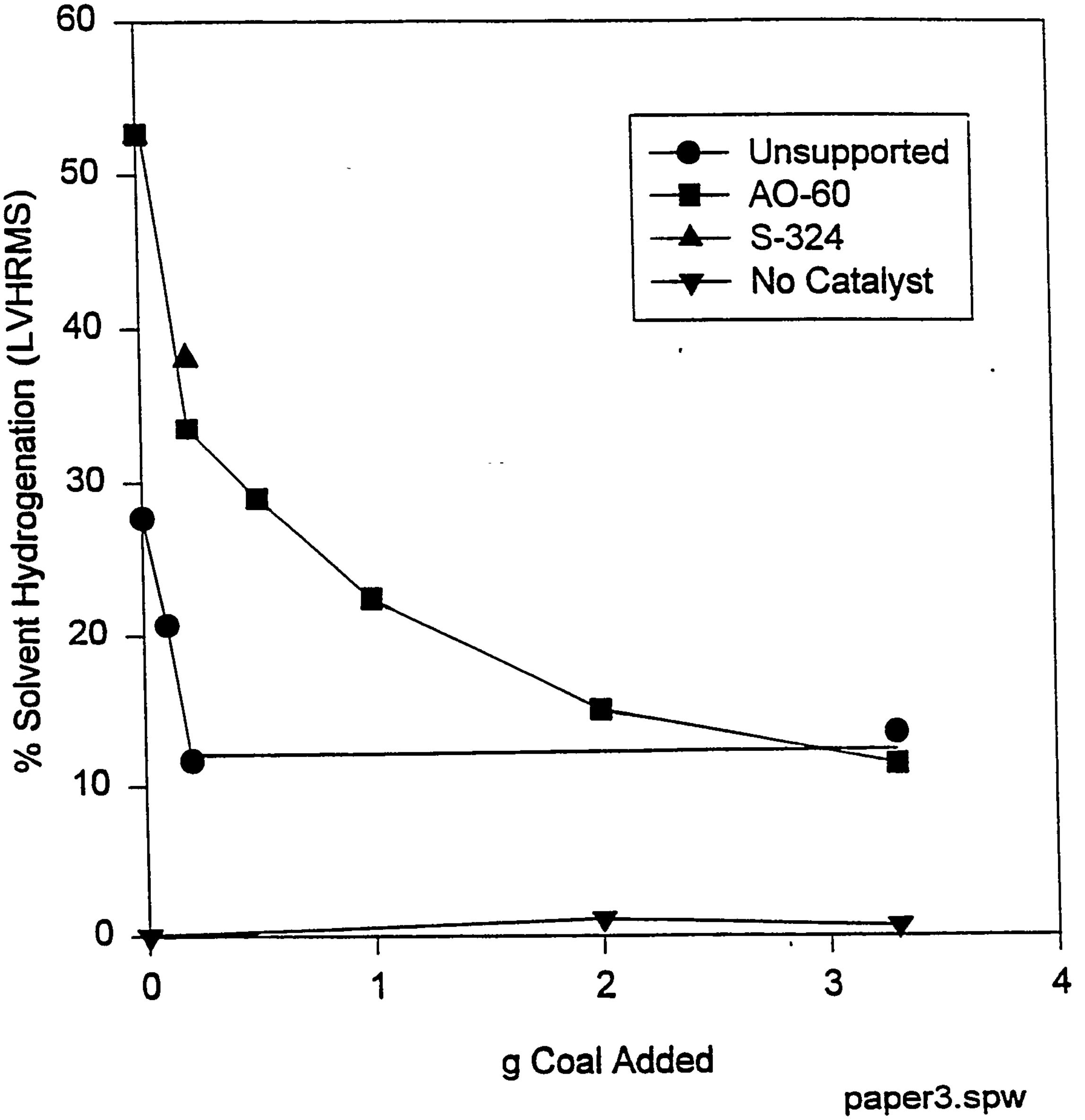


Figure 4: Behavior of Catalyst Exposed to Coal

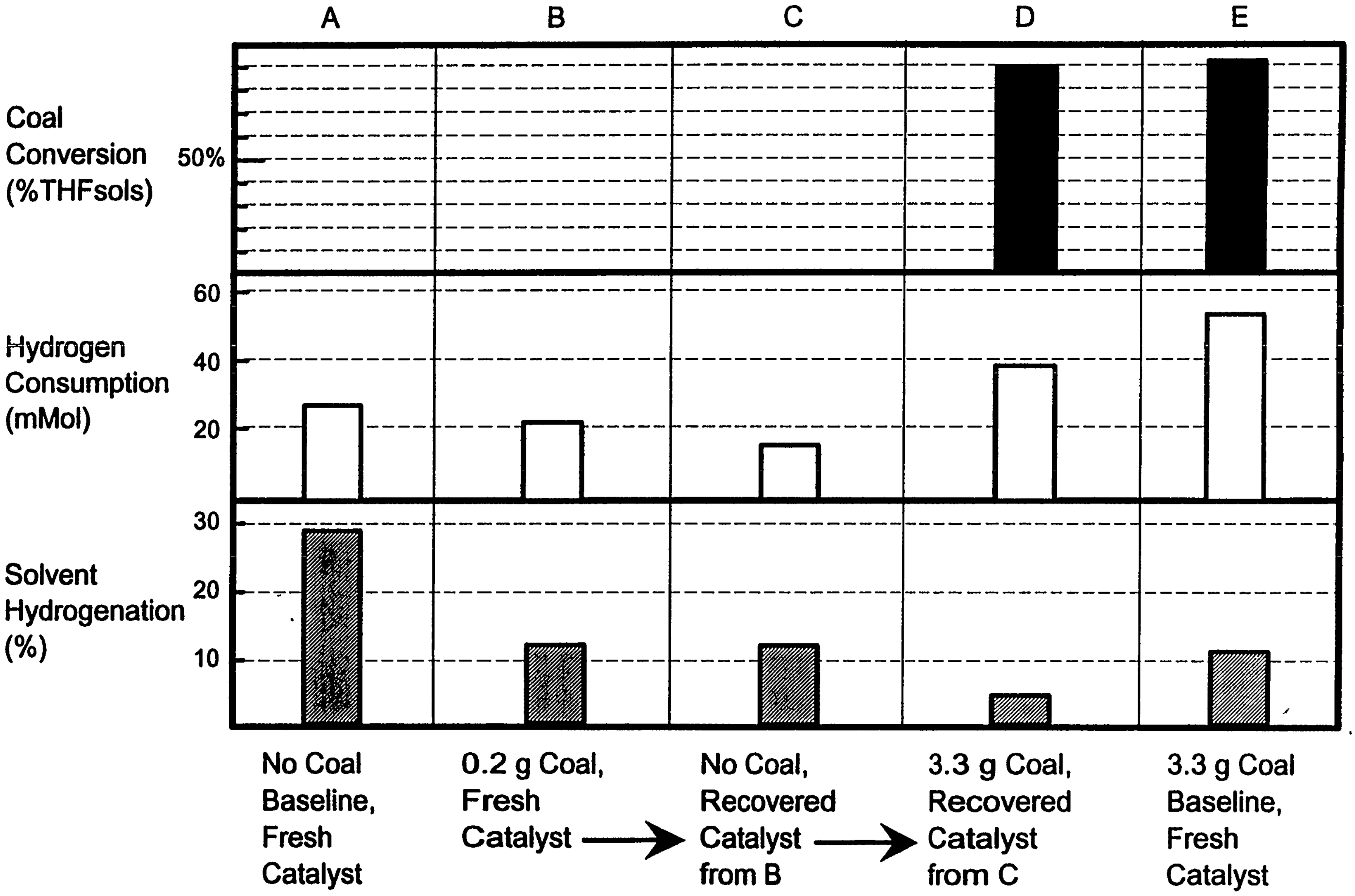
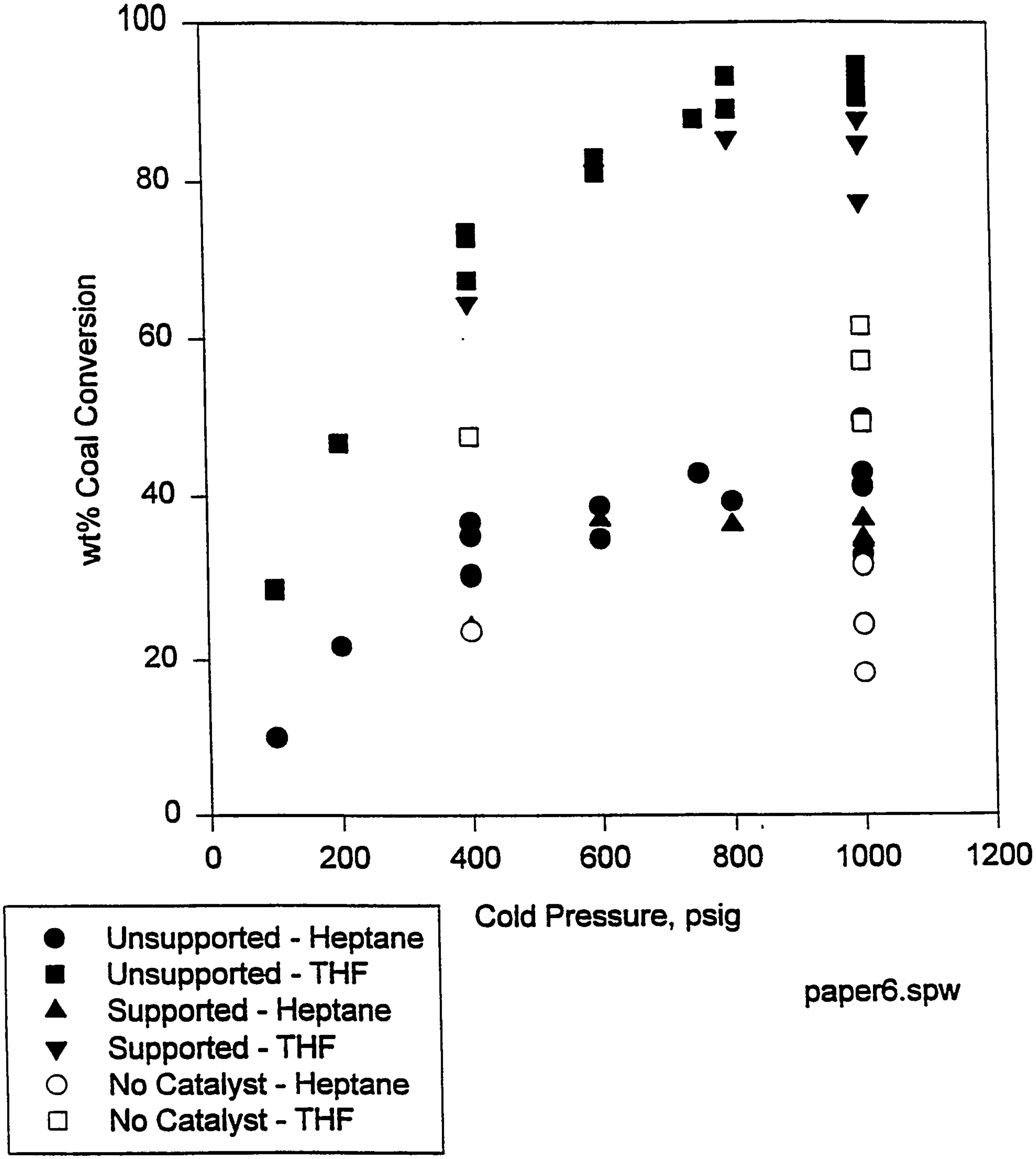


Figure 5: Effect of Pressure and Catalyst Type on Coal Conversion



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