STUDIES OF THE REACTIONS OF DIBENZYL ETHER UNDER PRECONVERSION PROCESSING CONDITIONS*

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INTRODUCTION

The occurrence of retrogressive reactions during direct coal liquefaction processing is harmful because these reactions result in the formation of high molecular weight material that is refractory to further processing. Therefore, the yields of desired products are decreased, downstream processing conditions must be more severe than if retrogressive reactions did not occur, and in some cases, an accumulation of solids causes process shutdown.[1] The objectives of this research project are 1) to determine the causes of retrogressive reactions during the initial processing of coal (known as preconversion processing) in direct liquefaction and 2) to devise methods for minimizing these undesired reactions. The first objective involves evaluating the effects of process conditions and additives on retrogressive reactions. The approach to completing this objective is twofold. Initial scoping studies have been done using the model compound dibenzyl ether (DBE). Subsequent work will use coal. Work on the second research objective will be performed in conjunction with the evaluation of the effects of process variables and additives on coal. Research for completing the second objective will involve several different approaches such as the use of cleaned coals, and the use of different coal pretreatments.

DBE was chosen for the initial scoping studies for three reasons: 1) ether linkages represent one type of bonding reported to be present in coal[2]; 2) other investigators have analyzed the kinetics and mechanism of thermolysis of DBE[3,4] and have also used DBE to study effects of process variables in coal liquefaction[5]; and 3) DBE is known to undergo retrogressive reactions. In the work reported here, experiments have been performed to evaluate the impacts of different types of mineral matter (including low temperature ash (LTA) separated from Illinois #6 coal, kaolinite (a clay mineral commonly found in coal), and pyrite) on the reaction of DBE. The preconversion processing conditions used in this work are similar to those that occur between the time the coal is mixed with recycle solvent and the time the coal slurry enters the first-stage reactor at the Wilsonville Advanced Direct Coal Liquefaction R & D Facility. This includes the preheating step in which the coal slurry is heated up to first-stage reaction temperatures. The initial temperature for preconversion processing is about 180°C (the temperature of the solvent-coal mixture just prior to entering the preheater at Wilsonville). The final temperature has not been reported because the temperature of the feed to the

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first-stage reactor is proprietary. However, it must be less than the average first-stage temperature, which is approximately 425°C. The slurry blend tank and feed tank are both at atmospheric pressure; pressurization with hydrogen occurs prior to the slurry entering the preheater.

EXPERIMENTAL

Materials

The commercial hydrotreating catalyst used in these experiments was Shell 324M, a $NiMo/Al_2O_3$ catalyst with 12.4 wt% Mo and 2.8 wt% Ni. Prior to use, this catalyst was presulfided with a 10 mol% H_2S/H_2 mixture at 380°C and atmospheric pressure for 2 h, and was then ground to -200 mesh. Three types of fine-grained mineral matter were utilized: coal-derived mineral matter, kaolinite ($Al_2Si_2O_5(OH)_4$), and a coal-derived pyrite sample. The coal-derived mineral matter was separated from Illinois #6 coal, which was obtained from the Argonne Premium Coal Sample Program, by using an LFE Corp. low temperature asher (model LTA 504). The kaolinite, in the form of a Georgia kaolin, was used as received. The pyrite sample was obtained by beneficiation of coal at the Robena Laboratory of the U. S. Steel Corporation and was subsequently pulverized under nitrogen to a particle size of -5 microns by means of a four inch orbital "Micron-Master Jet Pulverizer" at the Jet Pulverizer Co., Palmyra, New Jersey. The pyrite sample was cleaned by low-temperature ashing to oxidize the associated organic matter. After low-temperature ashing, the pyrite was separated from the other mineral matter by using the acid cleaning procedure, which consists of washing and filtration using hydrochloric acid, followed by hydrofluoric acid, and a repeat of the hydrochloric acid treatment, reported by Bishop and Ward[6]. X-ray diffraction was used to check the purity of pyrite samples.

Hydrotreating Experiments

All reactions with DBE were performed in 26 cm^3 316 stainless steel microautoclaves. The heat up time and quench time for each reaction were less than 2 minutes each. Nominal reactant and catalyst loadings for most experiments (unless otherwise noted) were 100 mg DBE, 50 mg catalyst, and 50 mg mineral matter. The microautoclaves for all experiments were charged with 1000 psig H_2 cold charge pressure. Reaction times at temperature for all experiments were 15 minutes; reaction temperatures ranged from 180°C to 300°C.

Product Analyses

Products from the microautoclave experiments were dissolved in carbon disulfide (CS_2) and analyzed using a combination of gas chromatography (GC) and GC/mass spectrometry (GC/MS). Recoveries of products from runs were determined quantitatively by GC using dodecane as an internal standard and response factors determined for DBE and toluene. Recoveries of products from the DBE reactions included quantitation of all non-CS_2 related peaks that were detected by GC (Figure 1). Unidentified compounds with GC retention times less than DBE are classified as low molecular weight unknowns, i.e. the molecular weight (MW) is less than 198, which is the MW of DBE. The total amount of low molecular weight material is equal to the sum of DBE, additional identified compounds (all of which have MWs less than DBE), and the low molecular weight unknowns. The unidentified compounds with retention times greater than DBE represent compounds with MWs greater than DBE, which were formed by retrogressive reactions. The total amount of high molecular weight material (HMWM) formed by retrogressive reactions is defined in this work as the sum of the amount of unidentified compounds detected by GC that had higher retention times than DBE

and the amount of material that was not detectable by GC. This non-detectable material, which did not elute from the GC column, was determined by difference.

Field Ionization Mass Spectrometry (FIMS) analyses, which provide molecular weight distributions for products vaporized using a mild ionization source, were performed on the products from several of the experiments. These analyses were done by Ripu Malhotra of SRI International.

RESULTS and DISCUSSION

The Impact of Low Temperature Ash from Illinois #6 Coal on DBE Reactions

Results of an experiment performed at 300°C with the low temperature ash separated from the Illinois #6 Argonne coal are shown in Figure 2. This reaction had a DBE:LTA ratio of 2.25:1. The total recovery of all products detectable by GC analysis was only about 9 Wt%, of which about 4 wt% was low molecular weight products (including toluene, diphenyl methane (DPM), and $C_{14}H_{14}$ compounds) and about 5 wt% was unidentified material with a MW greater than DBE. The remainder of the reaction product (91 wt%) did not elute from the GC column. Therefore, the total amount of HMWM in the product was about 96 wt% indicating the occurrence of significant retrogressive reactions. The results of this experiment were compared to those of a similar experiment with Shell 324M catalyst. The experiment with Shell 324M had a 2:1 DBE:Shell 324M ratio; other conditions were the same. The total recovery of all products detectable by GC was 83 wt%, of which about 71 wt% was low molecular weight material (42 wt% toluene, 1 wt% DPM, 11 wt% bibenzyl, 9 wt% other $C_{14}H_{14}$ compounds, 8 wt% low molecular weight unknowns). The presence of a catalyst and no mineral matter yields a significant improvement in recoveries of low molecular weight material. (Previous work has shown that the presence of a good hydrogen donor with the Shell 324M would give a significantly higher yield of low molecular weight material.) A similar thermal reaction with no additives gave about 98 wt% recovery of low molecular weight material of which 89 wt% was DBE.

The results of the experiment with Illinois #6 LTA showed that mineral matter in coal can produce significant amounts of retrogressive reactions with DBE. Since coal-derived mineral matter contains many different components, additional experiments were performed with several of the components.

The Effects of Pyrite on DBE Reactions

The effects of pyrite on the reaction of DBE were studied because it has known catalytic activity in direct coal liquefaction. Results of an experiment with freshly cleaned Robena pyrite and DBE are shown in Figure 3. The DBE:pyrite ratio was 2:1. Results show that pyrite yields about the same total recovery of material on the GC (about 84 wt%) as Shell 324M. However, the pyrite gives more low molecular weight material than Shell 324M (77 wt% versus 71 wt%), and the distribution of low molecular weight material is significantly different; pyrite gave about 60% more toluene than Shell 324M. Both of these reactions were run in duplicate and showed excellent reproducibility.

An additional experiment was performed with an oxidized sample of Robena pyrite. This sample had been low temperature ashed and acid cleaned in 1980 using the same procedures as the freshly cleaned pyrite. It was stored under air in a glass sample vial without any special precautions to prevent oxidation. A comparison of the DBE reaction product distributions from experiments with these two pyrite samples is shown in Figure 4. The aged pyrite yielded about 95 wt% HMWM whereas the freshly cleaned pyrite gave only

23 wt% HMWM. X-ray diffraction analyses of both pyrite samples showed that the aged sample had significant amounts of iron sulfate hydrate present, whereas the freshly cleaned sample was pure pyrite.

The Effects of Kaolinite on DBE Reactions

Kaolinite was also chosen for additional experiments because it is a clay mineral present in coal, and clays usually are the most abundant minerals in coal. In addition, a previously reported study[7] has shown that the acidic components of coal mineral matter enhance DBE conversion. Figure 5 shows the product distributions for five reactions of DBE with varying amounts of kaolinite present. These results show that retrogressive reactions occur for all the experiments. With the least amount of kaolinite only about 15 wt% of the product is HMWM. However, for higher concentrations of kaolinite, as much as 93 wt% of the product can be HMWM. An additional set of experiments was performed to determine the impact of reaction temperature on product distribution with 36 wt% kaolinite on a weight of DBE basis (Figure 6). The results show that even at a temperature of 180°C significant retrogressive reactions occur with about 75 wt% HMWM formed. A FIMS analysis of the product from the 180°C reaction is shown in Figure 7. The number average MW for the product was 804, significantly higher than the MW of DBE (198). The spectrum shows that the reaction product had compounds with MWs greater than 1300 amu. In addition, it shows groups of peaks that are separated by 90 amu. This distribution is indicative of the occurrence of benzylation reactions, which are known to occur in the presence of strong Lewis acids.

Three experiments were performed to determine the impact of water on the reaction of DBE with kaolinite. These results, shown in Figure 8, indicate that water does decrease the formation of HMWM. However, the effect is not very large and large amounts of water are required.

CONCLUSIONS

The results of these experiments indicate that the mineral matter in coal can have a significant effect on retrogressive reactions. Kaolinite yields high amounts of retrogressive reactions that occur down to reaction temperatures at least as low as 180°C. These retrogressive reactions are due to benzylation reactions. Pyrite, in contrast, can be either beneficial or harmful. If the pyrite is unoxidized, it can give high yields of desired product. However, if the pyrite is oxidized, it can yield significant amounts of retrogressive reactions. It has been demonstrated that retrogressive reactions can occur under currently used preconversion processing conditions and that improved processing techniques need to be developed to prevent these harmful reactions. Coal cleaning involving removal of the clays and readdition of unoxidized pyrite may be one technique for improving coal liquefaction.

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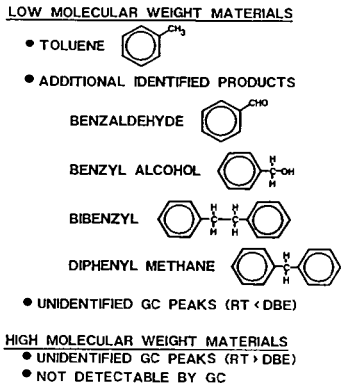

Figure 1. Distribution of reaction products used for quantification.

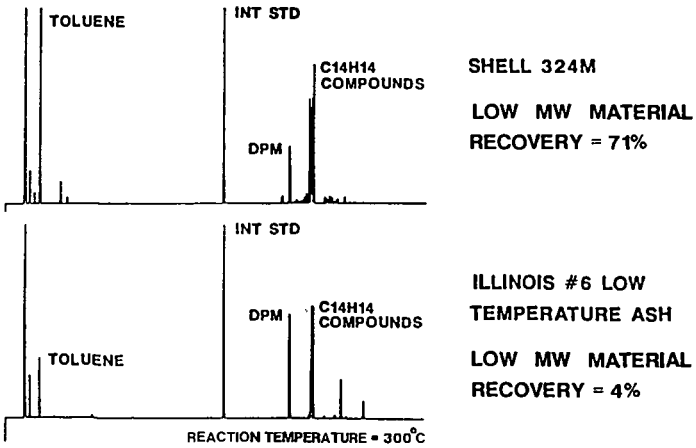

Figure 2. Mineral matter addition gave much higher yields of HMWM than Shell 324M.

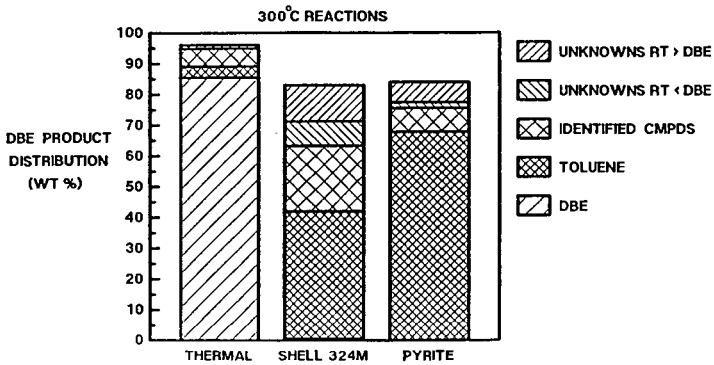

Figure 3. Pyrite addition gave 60% more toluene than Shell 324M at 300°C.

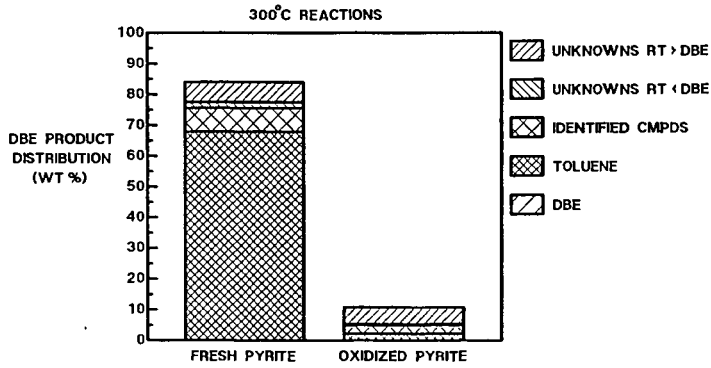

Figure 4. Oxidized pyrite causes significantly more retrogressive reactions than fresh pyrite.

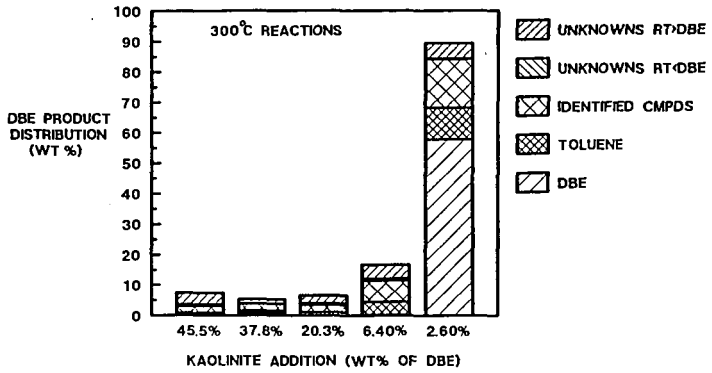

Figure 5. Kaolinite addition at 300°C causes the formation of HMWM.

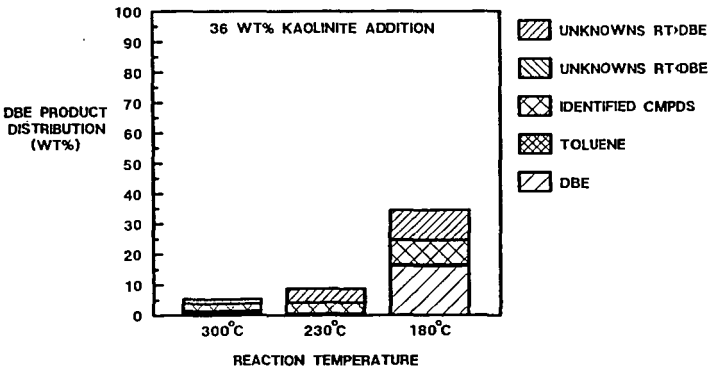

Figure 6. Kaolinite addition causes retrogressive reactions at temperatures as low as 180°C.

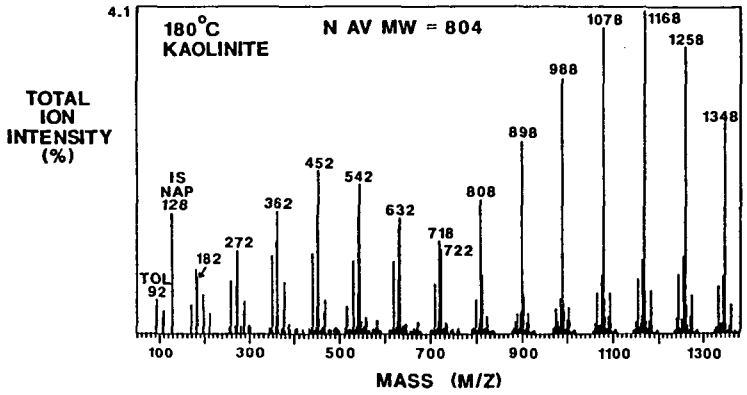

Figure 7. At 180°C, kaolinite gives benzylated products with molecular weights greater than 1300 amu.

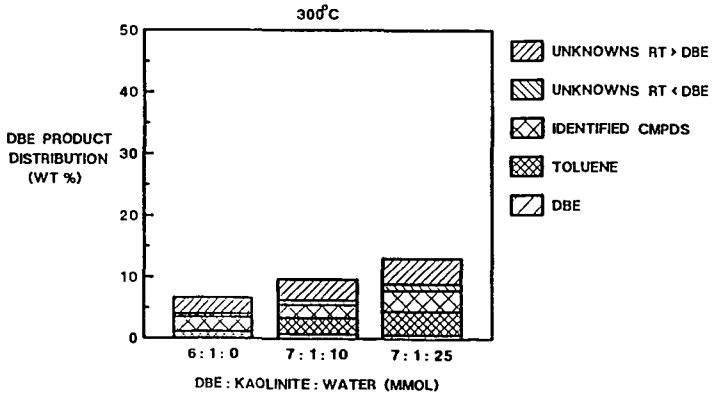

Figure 8. Addition of water appears to decrease the effect of kaolinite on retrogressive reactions.