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STUDIES OF THE INITIAL REACTIONS THAT OCCUR DURING DIRECT COAL LIQUEFACTION*

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INTRODUCTION

Reactions that occur during preconversion processing of coal in direct liquefaction can be either beneficial or harmful. If the thermally or catalytically produced fragments are rapidly stabilized with hydrogen, the resulting compounds have lower molecular weights than the original coal molecules and can be easily upgraded. However, if stabilization is inefficient, the fragments can undergo retrogressive reactions resulting in formation of higher molecular weight materials that are more difficult to upgrade. In current Wilsonville integrated two-stage direct coal liquefaction processes, the initial reactions of coal, which are grouped together under the term preconversion chemistry, occur between the time the coal is mixed with recycle solvent and the time the coal slurry enters the first-stage reactor. 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 in the slurry blend tank). The final temperature has not been reported because the temperature of the feed to the 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.

The objectives of this work are to identify the types of compounds and process conditions that give rise to retrogressive reactions during preconversion processing. Experiments have been performed to evaluate the impacts of temperature, pressure, catalysts, mineral matter, and hydrogen donors on these reactions. Initial studies have been carried out using dibenzyl ether (DBE) because ether linkages represent one type of bonding believed to be present in coal (1). Previous studies have analyzed the kinetics and mechanism of thermolysis of DBE (2,3) and have also used DBE to study effects of process variables in coal liquefaction (4). Results of thermal reactions with DBE have shown that the main reaction products are toluene, benzaldehyde, benzyl alcohol and benzene (2). In the presence of catalysts such as $ZnCl_2$, the product distributions are more complicated and can contain significant amounts of material with higher molecular weights than DBE (5,6).

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DISCLAIMER

EXPERIMENTAL

Materials

The commercial hydrotreating catalyst for 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. $ZnCl_2$ was used as received. Three types of fine-grained mineral matter were also utilized in experiments: mineral matter separated from an Argonne Illinois #6 Premium Coal by low-temperature ashing, kaolinite ($Al_2Si_2O_5(OH)_4$) in the form of a Georgia kaolin, and an acid-cleaned pyrite sample from the Robena mine.

Hydrotreating Experiments

Hydrotreating experiments and thermal reactions with dibenzyl ether (DBE) were performed in 26 cm^3 batch microreactors with 1000 psig H_2 cold charge pressure. All reactions were performed for 15 minutes at temperatures of either 180°C, 230°C or 300°C. The catalytic reactions were carried out both with and without the addition of a hydrogen donor (hexahydropyrene, H_6Py) or a hydrogen donor precursor (pyrene). Reactant and catalyst loadings for most experiments consisted of about 100 mg DBE, 50 mg catalyst or mineral matter, and 50 mg of pyrene or H_6Py. One set of five experiments at 300°C, which was aimed at determining the impact of clays on retrogressive reactions, had 425 mg DBE and kaolinite loadings ranging from 10 to 207 mg.

Product Analyses

Products from the microreactor experiments were dissolved in CS_2 and analyzed using a combination of gas chromatography (GC) and GC/mass spectrometry (GC/MS). Recoveries of products from several runs were determined quantitatively by GC using dodecane as an internal standard and response factors determined for DBE, toluene, pyrene and H_6Py. Recoveries of products from the DBE reactions included quantitation of all non-solvent and non-pyrene peaks that were detected on the gas chromatogram. Quantitation of the recoveries of pyrene and H_6Py included all detectable hydrogenated pyrene species. The amount of high molecular weight material formed by retrogressive reactions in each run is defined in this work as the amount of material that could not be detected by GC.

RESULTS and DISCUSSION

Products of the reaction of DBE that were identified in these 300°C experiments include toluene, which is the main product, benzaldehyde, benzyl alcohol, bibenzyl and other $C_{14}H_{14}$ compounds, and diphenylmethane. No gaseous hydrocarbon products were detected in these runs.

Results of experiments performed at 300°C with Shell 324M are shown in Figure 1. Two thermal runs at 300°C with DBE yielded some reaction, giving average values of 86 wt% unreacted DBE, 4 wt% toluene, 6 wt% additional identified compounds (primarily benzaldehyde and benzyl alcohol), 1 wt% unidentified compounds, and 3 wt% high molecular weight materials (100% minus material detectable by GC) formed by retrogressive reactions. A similar reaction with Shell 324M as a hydrotreating catalyst gave 27 wt% toluene as the major identified product and no detectable DBE. The total recovery of products derived from DBE for this reaction was only 56 wt%. Therefore, 44 wt% of the reaction products were high molecular weight materials. When pyrene, a hydrogen donor precursor, was added to a reaction with Shell 324M, the toluene yield doubled compared to the run with only Shell 324M. However, 22 wt% of the reaction product was still comprised of high molecular weight material. Addition of H_6Py instead of pyrene gave an additional 7% increase in both toluene yield and DBE product recovery compared to pyrene addition. Even with this good hydrogen donor present at the start of the reaction, 15 wt% of the DBE product could not be detected by GC. The recoveries of all detectable pyrene species from experiments with pyrene and H_6Py were 42 wt% and 72 wt% respectively, suggesting an interaction between these compounds and either DBE or products derived from DBE.

Reactions were also performed with $ZnCl_2$ as a catalyst at 300°C with and without pyrene or H_6Py. These reactions all gave almost complete conversion of DBE, but the GC patterns showed very little intensity (Figure 2). Thus, the recoveries of products derived from DBE and the recoveries of pyrene and H_6Py (including all hydrogenated pyrene species) were low (<10 wt%) indicating the formation of more high molecular weight material than obtained in runs with Shell 324M. A GC/MS analysis of the products from experiments with $ZnCl_2$ plus pyrene and $ZnCl_2$ plus H_6Py showed the presence of peaks with molecular weights of 292 and 298, respectively, suggesting the presence of benzylpyrene and benzylH_6Py compounds, respectively. These identifications are supported by previous work (5) using DBE and toluene, in which benzyltoluene was identified as a product. If all the unrecovered pyrene (from the $ZnCl_2$ plus pyrene run) was converted to a benzylpyrene compound, the weight of the benzyl group present in this compound would only account for about 25% of the unrecovered DBE products. The same holds true for the reaction with H_6Py.

If these benzylation compounds are also present in the products from the reactions with pyrene and H_6Py in Figure 1, the weight of benzyl groups tied up in the benzylpyrene and benzyl-H_6Py compounds would account for 14 wt% additional recovery of DBE products in the pyrene run and an additional 6 wt% in the H_6Py run. Thus the total recoveries of DBE products would be about 90 wt% for these two reactions, suggesting that up to 10 wt% of the product could be high molecular weight materials. However, elemental analyses of the catalysts are not yet available and may show that some of the missing material has been deposited on the catalyst.

GC analyses of the experiments with mineral matter separated from the Illinois #6 Premium Coal Sample only accounted for about 9 wt% of the amount of DBE in the feed (Figure 3). Coal-derived mineral matter contains many different components, including clays, pyrite (FeS_2), quartz and carbonates. Therefore, additional experiments were performed with pyrite and kaolinite to determine the impact of these two components on DBE. Pyrite was chosen because it has known catalytic activity. Kaolinite was chosen because it is a clay mineral present in coal and clays usually are the most abundant minerals in coal. In addition, a previous study

(7) has shown that the acidic components of coal mineral matter enhance DBE conversion. GC analyses of the products of the reaction with pyrite (Figure 4) show double the toluene yield obtained with Shell 324M and a third higher total product recovery. In contrast, a reaction with 37.8 wt% kaolinite (on a DBE basis) gave a recovery of DBE products of only 5 wt%, suggesting that the clay components of the mineral matter are primarily responsible for the retrogressive reactions that occur. All of the products from the DBE experiment with kaolinite were soluble in CS_2. Filtration and weighing of the kaolinite from the reactor gave a good recovery with only a minor weight gain, which accounted for <2.5% of the non-recovered material. In addition, evaporation of the CS_2 from the reaction products yielded most of the weight that could not be detected by GC. Therefore, the poor recovery of DBE products had to be due to formation of high molecular weight materials. Vapor pressure osmometry was used to determine the molecular weight of the product from the kaolinite reaction. The measured value was 737, which proves that retrogressive reactions occurred since the molecular weight of DBE is only 198. Four additional reactions were performed with different feed/kaolinite ratios. The results, shown in Figure 5, indicate that even small amounts of clay can have a significant impact on recovery and hence on the formation of compounds by retrogressive reactions.

At 230°C, a thermal reaction and reactions catalyzed by Shell 324M, $ZnCl_2$, and mineral matter from the Illinois #6 coal gave results similar to those obtained at 300°C; pyrite yielded only about a quarter of the toluene (Figure 6) of the 300°C reaction.

At 180°C, a thermal run showed very little reaction and had a total recovery of 100 wt%. A 180°C reaction with Shell 324M (Figure 7) gave 81% recovery of products derived from DBE including 55 wt% toluene. Comparison of these results with those from the 300°C reaction with Shell 324M shows that the toluene yield is double that obtained at the higher temperature and the overall recovery is about 50% higher. The reaction with Shell 324M therefore appears to be more efficient at the lower temperature, and suggests that it would be beneficial to measure the rates of the reactions occurring at both 300°C and 180°C. A low pressure reaction (Figure 7) performed at 180°C with Shell 324M gave only a 52 wt% recovery indicating that pressure has a significant impact on retrogressive reactions at low temperature. Pyrite gave very little reaction at 180°C (Figure 6), which is not surprising since the pyrite - pyrrhotite transition does not occur at this low temperature and pyrrhotite is believed to be the active phase (8). Reactions with 36 wt% kaolinite (on a DBE basis) show increases in recovery with decreasing reaction temperature (Figure 8). However, at 180°C 65 wt% of the product is still composed of high molecular weight materials derived from retrogressive reactions.

CONCLUSIONS

The results of these experiments indicate that retrogressive reactions of DBE occur in the presence of a good hydrogenation catalyst (Shell 324M), a Lewis acid ($ZnCl_2$), and coal-derived mineral matter. $ZnCl_2$, coal-derived mineral matter, and kaolinite (a clay present in coal) cause the greatest yield of high molecular weight products from retrogressive reactions. These results suggest that detrimental reactions can occur in the low temperature initial stages of coal liquefaction when coal mineral matter is present. Although the amount of retrogressive products is less in reactions with Shell 324M, some are still present even with a good hydrogen donor and high pressure hydrogen. The best way to minimize these reactions may be to use coals that have been extensively cleaned to remove the clays. Future studies will involve determining if these effects are also obtained with coal.

REFERENCES

1. Shinn, J.H., Fuel 63(9), 1187-96, 1984.
2. Korobkov, V.Y., Grigorieva, E.N., Senko, O.V., Kalechitz, I.V., Fuel Proc. Tech. 19, 243-52, 1988.
3. Cronauer, D.C., Jewell, D.M., Shah, Y.T., Modi, R.J., Ind. Eng. Chem. Fundam. 18(2), 153-162, 1979.
4. Panvelker, S.V., Shah, Y.T., Cronauer, D.C., Ind. Eng. Chem. Fundam. 21, 236-42, 1982.
5. Mobley, D.P., Bell, A.T., Fuel 58, 661-6, 1979.
6. Mobley, D.P., Bell, A.T., J. Catal. 64, 494-6, 1980.
7. Kamiya, Y., Nagae, S., Oikawa, S., Fuel 62, 30-3, 1983.
8. Stephens, H.P., Stohl, F.V., Padrick, T.D., Proc. Int'l. Conf. on Coal Sci., Dusseldorf, Germany, Sept. 7-9, 1981.

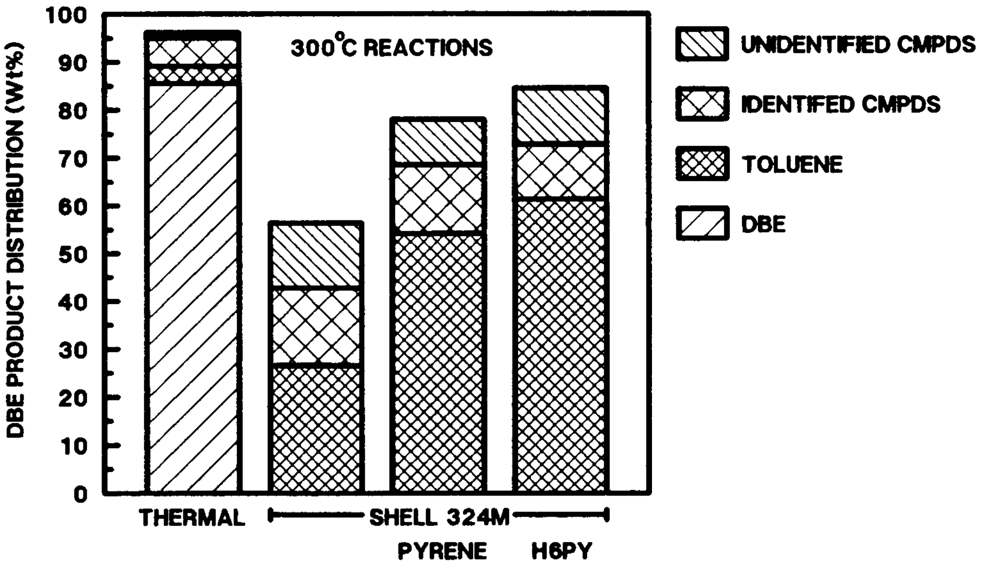

Figure 1. The presence of a catalyst and a hydrogen donor gives greater toluene yields, but recoveries are still low.

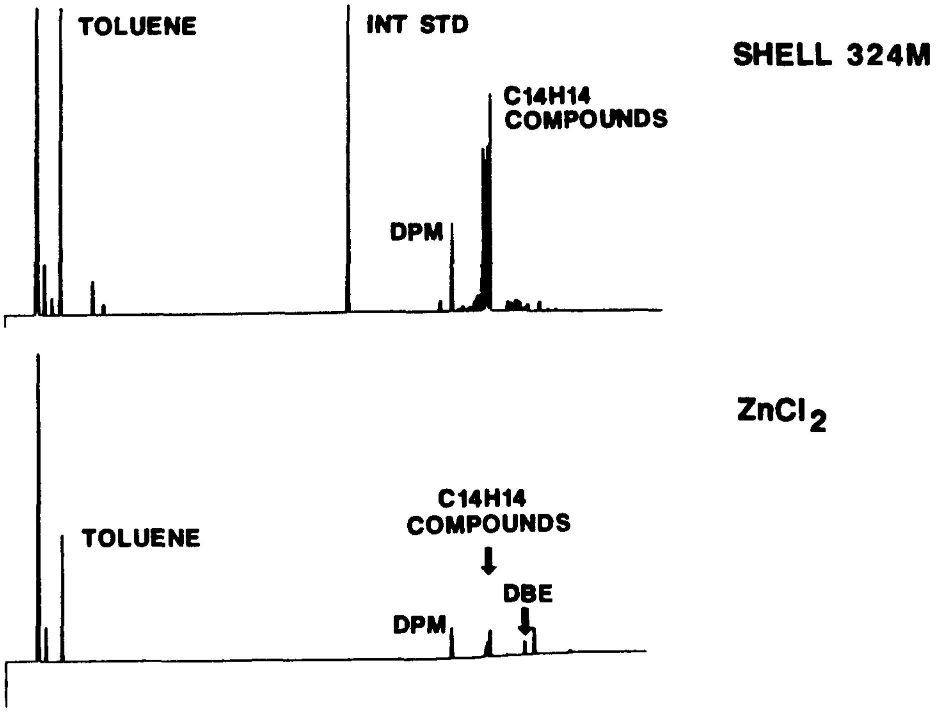

Figure 2. $ZnCl_2$ addition gave the lowest recovery of DBE products.

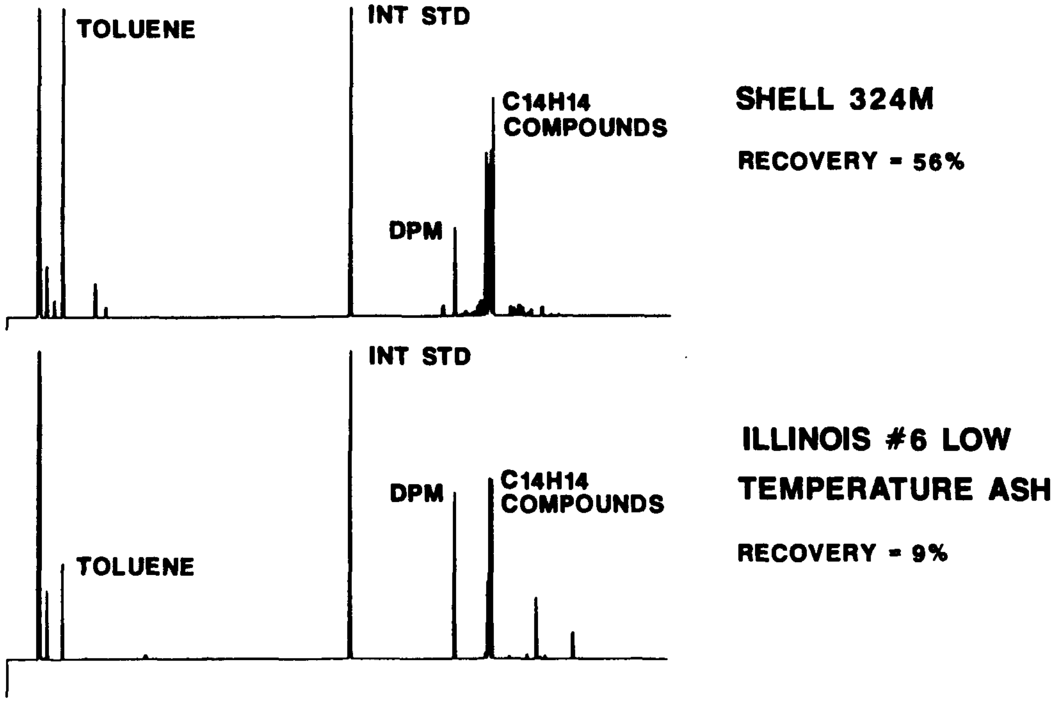

Figure 3. Mineral matter addition gave much higher yields of high molecular weight material than Shell 324M.

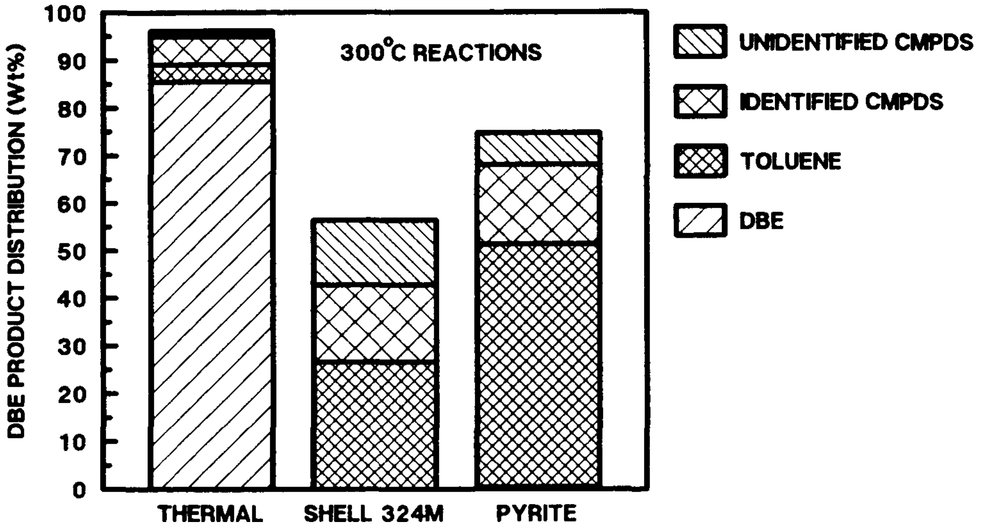

Figure 4. Pyrite addition gave twice the toluene yield of Shell 324M at 300°C.

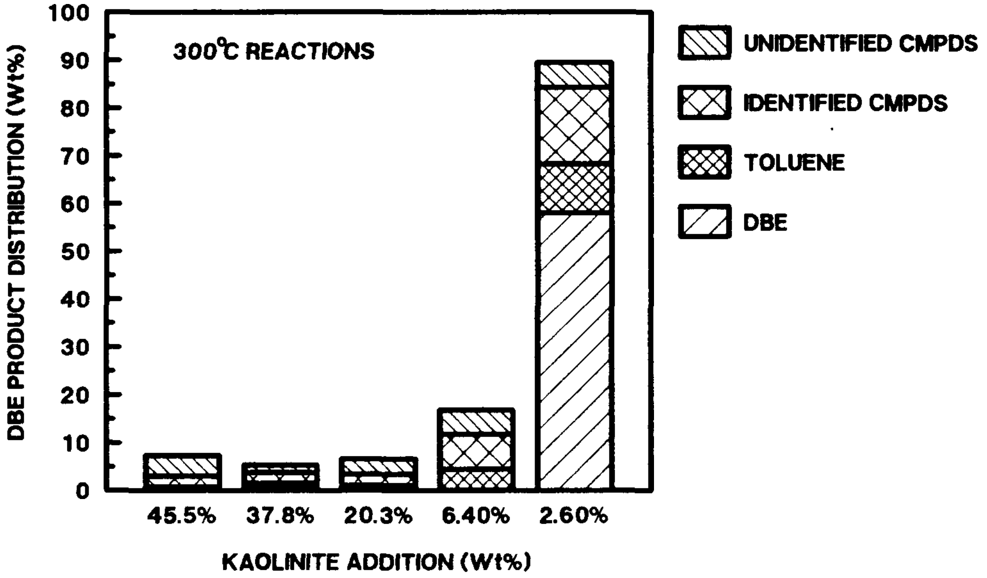

Figure 5. Kaolinite addition at 300°C causes the formation of higher weight material than Shell 324M.

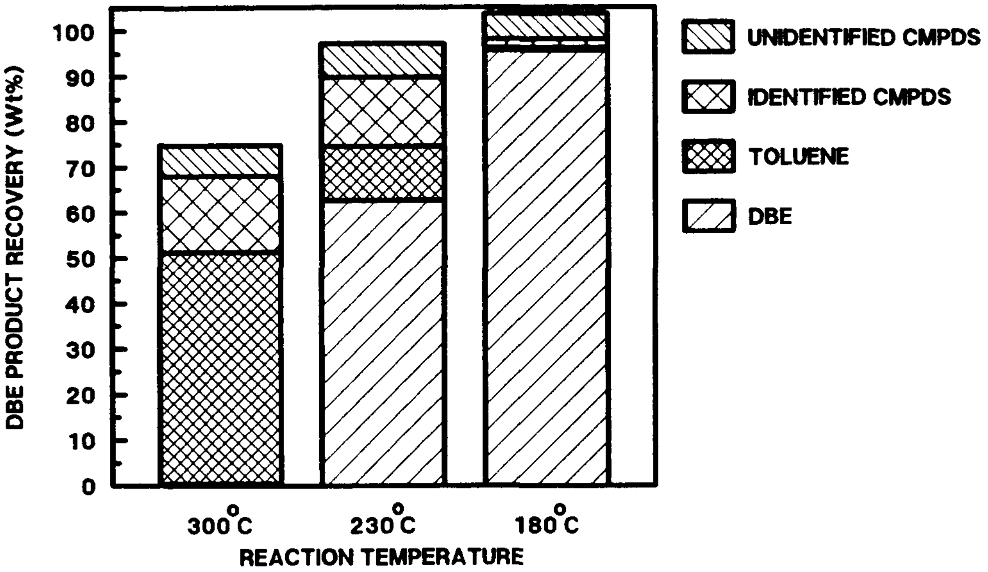

Figure 6. Pyrite addition has much less impact at lower reaction temperatures.

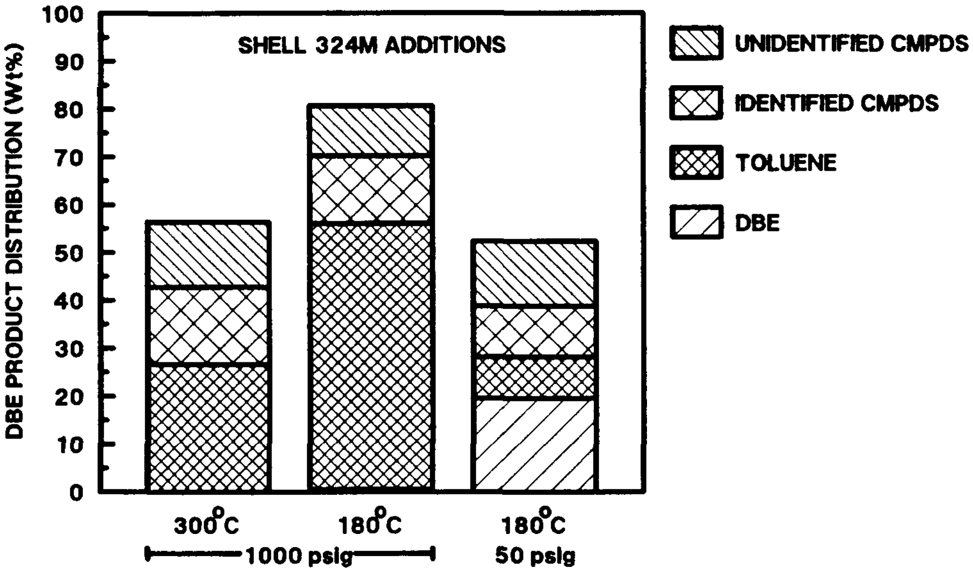

Figure 7. Hydrogen pressure has a significant impact on low temperature reactions.

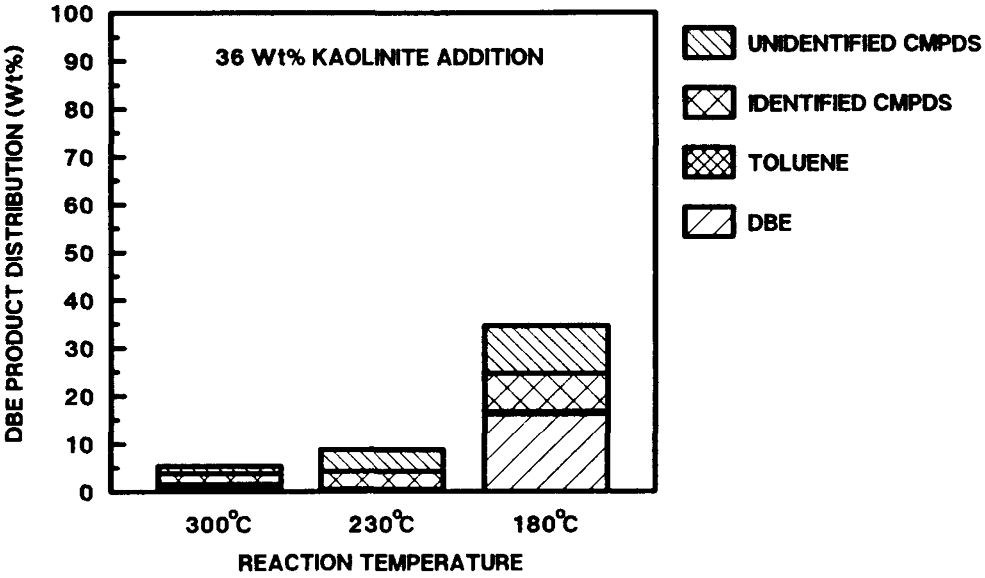

Figure 8. Kaolinite addition causes retrogressive reactions at temperatures as low as 180°C.