

NEW DIRECTIONS TO PRECONVERSION PROCESSING OF COAL

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INTRODUCTION

Coal structure should be well understood for the effective development of coal liquefaction. A cross-linked three-dimensional macromolecular model has been widely accepted for the structure of coal. Coal liquefaction is being developed based on this model. Recent studies, however, showed that significant portions (far more than generally believed) of coal molecules are physically associated¹. If physical association is dominant, all properties and reactivities in coal liquefaction must be a strong function of intra- and intermolecular (secondary) interactions and molecular weight. It is necessary to reinvestigate a coal conversion procedure based on the associated nature of coal.

Many efforts of chemical pretreatments have been made to cleave chemical bonds by using reagents or high pressure of CO and H₂O etc. Coal changes molecular conformations during soaking/dissolution steps due to relatively strong secondary interactions. This may lead to decrease in dissolution, but this phenomena have often been regarded as retrograde reactions. The stabilization of radical intermediate has been considered to prevent retrograde reactions. These concepts of selective bond cleavages and prevention of retrograde reactions are based on the network model.

If a large portion of coal is associated, coal may be dissolved to a great degree. It is expected that largely dissolved coal can easily be converted to liquid. However, dissolution has not been an easy task, as shown by many researchers for a long time. If coal/coal complexes with high molecular weight are replaced with molecules with low molecular weight, coal may be dissolved to more extent. Associated coal is regarded as material with broad molecular weight distribution. Reactivity of these material may be different. Fractions with different molecular weight may be treated separately to produce desired fractions, if possible. These are the major features considered in this paper based on the associated molecular nature of coal.

In this paper, a new concept of coal preconversion is shown on the basis of these propositions. Two subjects are focused on: (1) maximizing dissolution of associated coal without additional chemicals and (2) step-wise conversion of associated coal with broad molecular weight distribution. For these purposes, the following procedure has been tested: two-step soaking at 350-400°C, followed by isolation of oil, and then liquefaction of residue. This enabled to lower liquefaction severity, to decrease the gas yield, and to increase the oil yield. Some of these results and the future perspective of two-stage liquefaction will be discussed.

EXPERIMENTAL

Coal samples were obtained from the DOE Coal Bank at Pennsylvania State University.

Illinois no. 6 coal (DECS-2) was used as received, and Smith Roland coal (DECS-8) was washed with 2N HCl² and dried before use. A coal liquid derived from Illinois no. 6 coal obtained from the Wilsonville pilot plant³ was used. All the reagents and solvents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA), and HPLC-grade solvents were used without further purification.

Two reactors, a 250 ml autoclave (Model 4576; Parr Instrument CO., Moline, IL, USA) and 27 ml microreactors fabricated, were used. These reactors were evacuated and purged with nitrogen five times after charging a coal sample and a solvent. The autoclave was heated approximately at 8°C min⁻¹ to required temperature, and controlled to $\pm 3^\circ\text{C}$, while agitating with the autoclave stirrer (500 rev min⁻¹). Microreactors were heated in a fluidized sand bath (Model SBL-2; Techne Corp., Princeton, NJ) which was controlled within $\pm 1.0^\circ\text{C}$ of the set point. The shaker (Model 75; the Burrell Corp., Pittsburgh, PA) was modified to shake the microreactor horizontally at 320 rev min⁻¹. Mixtures in the reactor attained the set point within 5 min, when the reactor was being immersed into the sand bath.

After reactions, the mixtures were filtered and Soxhlet-extracted with cyclohexane, toluene and tetrahydrofuran (THF) for 24 h, respectively, and then these samples were dried under vacuum at 95°C overnight. The amounts of THF solubles (TS), toluene solubles (ToS) and cyclohexane solubles (CyS) were determined from the mass of the respective insolubles. Produced gas was generally included in the CyS yield.

Gas was collected with a sample bag after cooling the autoclave, and analyzed with gas chromatography by the University of Pittsburgh Applied Research Center (Pittsburgh, PA). Approximate gas yields were calculated on the assumption that the amount of nitrogen does not change before and after reactions.

RESULTS AND DISCUSSION

Coal dissolution and liquefaction

The effect of soaking temperature on liquefaction was compared at 200°C and at 350°C. Illinois no. 6 coal was liquefied at 430°C for 1 h after soaking at these temperatures. The yields of TS were the same for these runs, but the yields of ToS and CyS were 5% higher for the samples soaked at 350°C than for that at 200°C. The coal was mildly refluxed in pyridine for 24 h, followed by the removal of the solvent, and liquefied at 430°C. The conversion was compared to that liquefied under the same condition but using the raw coal. The yield of CyS increased about 10% by soaking in pyridine. Other related results are available. An increase in conversion at 427°C was observed when a coal/coal liquid mixture was soaked at 277-322°C for 10 min⁴. Preswelling with THF and tetraammoniumhydroxide, followed by removal of solvents, enhanced hydroliquefaction yields at 400°C^{5,6}. These results show that disintegrated coals lead to high conversions in liquefaction.

Optimum temperature of the high temperature soaking was around 350°C as shown in *Figure 1*. However, the CyS (or oil) yield was still low (35%) at 350°C. The two-step wise soaking was further tested to increase an oil yield. Soaking at 350°C, followed by soaking at 400°C, gave the 50% oil yield (Run 10 in *Figure 2*), but soaking at 200°C, followed by soaking at 400°C, was not effective and led to the yield of more than 100%

because of incorporation of the coal liquid used as a solvent (Run 11).

The effect of radical initiators on the high-temperature soaking and liquefaction were investigated in the recent works^{7,8}. Although it has widely been accepted that radicals cause retrograde reactions, the addition of radical initiators did not have the expected negative effect and the slightly positive effect in the high-temperature soaking (350-400°C). The addition of H₂O₂ at the high-temperature soaking increased the 5% oil yield under low pressure hydrogen gas (Run 12)⁸. The addition of small amount of water alone gave the similar change in conversion in the high-temperature soaking. Therefore, a small amount of water or hydrogen peroxide solution may be added to improve the high-temperature soaking.

The two-step high-temperature soaking at 350°C and 400°C gave the 50% of cyclohexane solubles as shown above. This implies that slow heating is better than fast heating on coal conversion. The autoclave was heated up relatively slowly (at 8°C min⁻¹). The effect of heating rate, therefore, was investigated using the microreactor which was relatively fast heated up in the sand bath. The reactor was heated from room temperature to 430°C in 0.5 h and held at 430°C for 2 h (Run 13). For Run 14, the mixture was reacted under the same condition, but heated with a step-wise heating before reaction (at 350°C for 0.5 h and at 400°C for 0.5 h), and then held at 430°C for 1 h. The total heating-up time from room temperature to 350°C, from 350°C to 400°C and from 400°C to 430°C was 0.5 h. So, the total residence time including heating-up was 2.5 h. For Run 15, the mixture was slowly heated from 130°C to 430°C and held at 430°C for 1 h. The total duration of heating-up and reaction time was also controlled to 2.5 h. Although the coal was reacted at 430°C for the longest time for Run 13, coal conversion was the lowest among three Runs. The oil yield was enhanced about 10% by these programmed heatings. These results shows that the programmed heating or step-wise high-temperature soaking was important for coal conversion. Song *et al.*⁹ recently reported the effect of the temperature-programmed liquefaction of low rank coals. Montana subbituminous coal was converted to 5-10% more (THF solubles) by slow heating compared to rapid heating.

Coal fractions and liquefaction

Another important factor to decrease a gas yield is suggested on the basis of the associated molecular nature of coal. Hydrocarbons with lower molecular weight generally produce more gas by thermal pyrolysis. Hydrocarbons with higher molecular weight will be decomposed under more severe conditions under which more gas will be produced from hydrocarbons with lower molecular weight. The associated structural model of coal can be regarded as material with broad molecular weight distribution. Therefore, coal with different molecular weight should be treated separately, if possible.

A low molecular weight fraction may be separated after dissolution of coal, and a remaining high molecular weight fraction may selectively be liquefied. Here, pyridine solubles and insolubles were separately liquefied to compare their conversions under the same condition (Runs 16 and 17). Approximately the same oil yield was obtained from pyridine solubles and insolubles (Figure 3). Furthermore, cyclohexane insolubles from Run 10 was examined. The 50% oil yield was obtained even from this fraction (Run 18).

The liquefaction characteristics of the soluble and insoluble components has recently

been reviewed and studied¹⁰. The dissolution and hydrogen consumption rates of a pyridine extracted coal and a whole coal were similar for West Kentucky coal (80% carbon, daf)¹¹. Whereas, a significant decrease in liquefaction conversions was observed when a coal was extracted with pyridine for Illinois no. 6 coal¹². Warzinski and Holder¹⁰ found the retrogressive behavior in conversion for pyridine extract part of Illinois no. 6 coal. Although it is difficult to conclude the effect of the soluble and insoluble components from these results, it seems that the reactivity of residues or high molecular weight components is not so poor as that of low molecular weight components.

The associated molecular nature and liquefaction

It was shown that a large portion of coal can be dissolved by the high-temperature soaking in the coal liquid, and the programmed or step-wise heating is preferred to enhance an oil yield. The highly dissolved coal was liquefied to a larger extent. Further, it was suggested that coal with a broad molecular weight distribution should be separated into an oil fraction after dissolution, and that only residue should be liquefied at the following step. From these results, a new concept is proposed to increase an oil yield and decrease a gas yield as shown in the block diagram (*Figure 4*). Coal is soaked in a recycle oil at 350°C and at 400°C. Gas and oil are recovered by vacuum distillation, and the bottom fraction is fed to a liquefaction section and liquefied under low pressure hydrogen at a relatively low temperature.

The proposed procedure was tested using an autoclave. The DECS-2 coal was soaked in the coal liquid under nitrogen at 350°C and at 400°C for 1 h, respectively. The oil fraction was extracted with cyclohexane, and the cyclohexane insoluble portion was liquefied under low pressure of hydrogen (2.8 MPa) at 430°C for 1 h (Run 20). For comparison, the coal was soaked in the coal liquid at 200°C for 1 h, and then the mixture was liquefied under the same condition for 2 h (Run 19). In these Runs, gas yields were analyzed. *Figure 5* shows these results. It is notable that the CyS (or oil) yield increased 30% and the gas yield decreased 15%.

DECS-8 (subbituminous) coal was also examined with the same procedure. As the ionic forces are relatively strong and abundant in low rank coals², it is an important step to weaken the ionic forces before the high-temperature soaking. Although it has been known that acid washing enhances the conversion of low rank coal¹³⁻¹⁶, the details on acid washing have not clearly been explained. Here, 2N HCl washing² was used to weaken the ionic forces in the coal before the high-temperature soaking. The coal was soaked in the coal liquid at 350°C and at 400°C for 1 h, respectively. Cyclohexane insolubles from the soaked coal was similarly liquefied at 430°C for 1 h (Run 22). As the acid washed coal was dried, the dried DECS-8 coal was soaked at 200°C for 1 h and then liquefied at 430°C for 2 h for comparison (Run 21). Again, more than 30% increase in the oil yield and 20% decrease in the gas yield was observed by the procedure (*Figure 5*).

CONCLUSIONS

An improved coal liquefaction concept was reinvestigated for the current two-stage process on the basis of the associated molecular nature of coal. Since a significant portion of coal molecules are physically associated as pointed in our recent paper, physical dissolution

should be considered more. The step-wise high-temperature soaking was a simple and effective method for coal dissolution. Larger dissolution made liquefaction severity lower. Broad molecular weight distribution in the associated coal was another important factor. The selective reaction of fractions with high molecular weight which were isolated after the high-temperature soaking made gas yield lower. Tests with using an autoclave by the concept shown in Figure 5 enabled to produce 30% more oil and 15-20% less gas yields. It is expected that the procedure will result in great cost down in coal liquefaction.

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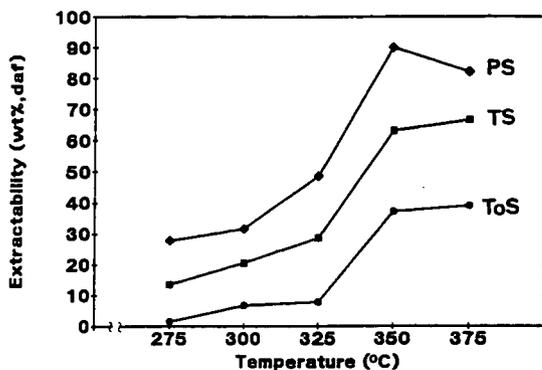


Figure 1 The effect of soaking temperature on extractability (DECS-2 coal, 0.35 MPa N₂, 1.5h)

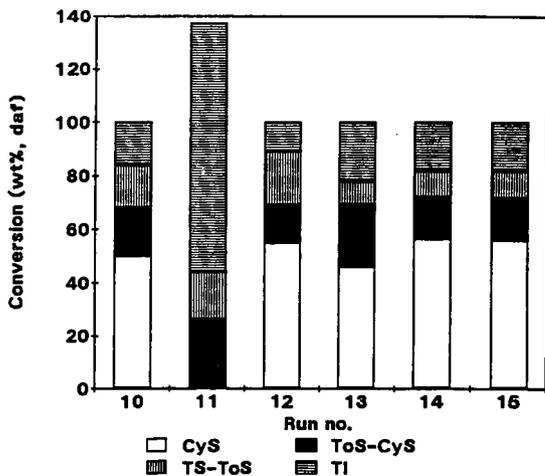


Figure 2 The effect of step-wise soaking on extractability for DECS-2 coal under N₂, except for Run 12 (Conditions: Run 10; 350°C(1h)/430°C(1h), Run 11; 200°C(1h)/430°C(1h); Run 12; 350°C(1h)/430°C(1h) with H₂O₂ (3000 ppm) and H₂ (1.4 MPa), Run 13; 430°C(2.5h), Run 14; 350°C(0.5h)/400°C(0.5h)/430°C(1h), Run 15; 130°C to 430°C at 3.5°C min⁻¹, followed by 430°C(1h))

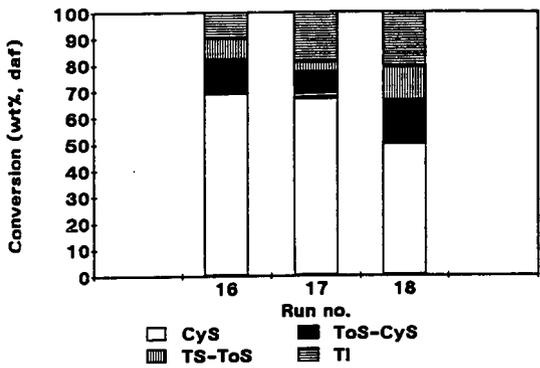


Figure 3 Coal fractions and their conversions at 430°C for 1 h with 2.8 MPa of H₂ ((Run 16; DECS-2/PS, Run 17; DECS-2/PI, Run 18; Cyclohexane insolubles from Run 10)

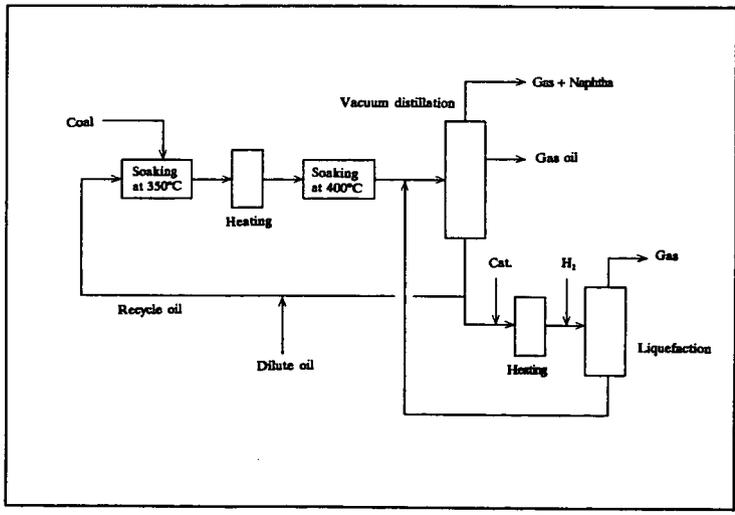


Figure 4 Block diagram of the proposed coal liquefaction concept

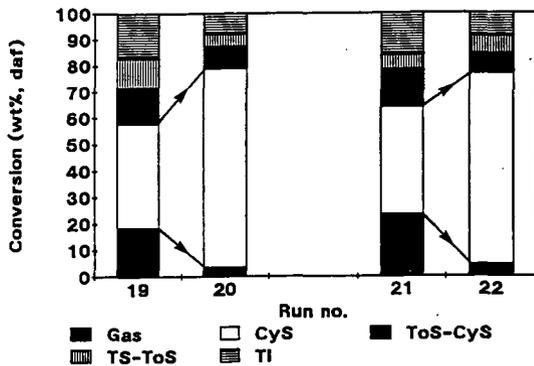


Figure 5 Coal conversion by the proposed procedure for DECS-2 coal (Runs 19 and 20) and DECS-8 coal (Runs 21 and 22) (Run 19; 200°C(1h)/430°C(2h), Run 20; calculation from Runs 10 and 18, Runs 20 and 21 under the same conditions as Runs 19 and 20, see the text in detail)