New Direction to Preconversion Processing for Coal Liquefaction

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In the past, covalently, cross-linked, three-dimensional macromolecular model for coal structure has been widely accepted and specific responses from processes like gasification and liquefaction interpreted accordingly. Recent studies, however, have shown that many coal molecules appear to be physically associated and, therefore, more responsive to secondary interactions than any cross-linked network model should be. Current two-stage liquefaction processes are based on the conventional three-dimensional model. In this study, preconversion processing for coal liquefaction is reinvestigated assuming a physical association in coal structure. Two main factors that reduce the gas yield and enhance the oil yield have been investigated: (1) dissolution of associated coal molecules without the addition of chemical reagents and (2) reactivity differences of coal fractions with low and high molecular weights. Coal samples were soaked in a coal liquid at 350 and 400 °C. Oil fractions were isolated and liquefaction commenced under mild conditions. A high-volatile bituminous coal and an acid-washed subbituminous coal were evaluated. The procedure followed generated a 30% increase in the oil yield and a 15–20% decrease in the gas yield compared with results obtained using conventional methods.

Introduction

A comprehensive knowledge of basic coal structure must be acquired for the effective development of coal liquefaction. The cross-linked, macromolecular model has been widely accepted by most researchers, and current coal liquefaction studies are proceeding under this assumption. Recent studies, however, show that significant portions (far more than generally believed) of coal molecules appear to be physically associated;[1] therefore, the interpretation of any coal liquefaction results should consider this possibility. If physical association is dominant for cross links, all properties and reactivities in the liquefaction process must be specific functions of intra- and intermolecular (secondary) interactions as well as molecular weight.

Recent work[2-7] showed the significance and importance of relatively strong secondary interactions for all ranks of coal. These interactions include ionic forces, the charge-transfer interaction, and the so-called π–π interaction.[8] Dissolution solvating these interactions is believed to be an essential step required before breaking the covalent bonds that initiate coal liquefaction. Some of these molecular associations, however, are not solvated under normal extraction conditions. Therefore, even with good solvents such as pyridine,[2,3] dissolution becomes a very difficult task.

It is known from the literature[1] that a substantial amount of high-volatile bituminous coal may be dissolved in coal-derived liquids and polycyclic aromatic hydrocarbons at 300–400 °C (high-temperature soaking). These temperatures are well below those maintained during coal liquefaction or other coal decomposition processes. It is proposed that electron donors and acceptors with low molecular weight substitute coal–coal complexes for charge-transfer interactions (physical dissolution), understanding that some chemical bond cleavage may occur concurrently at these temperatures.[1]

High-volatile bituminous coal molecules may associate when soaked at temperatures <300 °C.[2,3] This mechanism probably involves the severance of relatively weak secondary interactions concurrent with the formation of stronger secondary interactions (solvent-induced associations).[3] The reduction in dissolution observed when soaking coal in a coal liquid at 200–300 °C has been considered as a retrograde reaction.[9,10] These temperatures, however, have been used in many processes[11] for the mixing and preconversion of coal in recycle oils. Hydroaromatics and hydrogenated solvents have been used in the past to prevent retrograde reactions.[12] Bond cleavage and stabilization of labile intermediates during preconversion are major concerns for current liquefaction processes assuming a network coal model. It is more important to select optimal temperatures during pretreatment operations when assuming a physically associated model.[1]

One of the main goals in coal liquefaction is to decrease gas yields in order to reduce hydrogen consumption. More gases are assumed to be generated from severe reactions with undissolved coal which is not as reactive as coal in

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Table 1. Elemental Analyses of Coals and Coal Liquids (wt %)

symbol	sample	H$_2$O	ash	element (daf)			
				C	H	N	S
DECS-2	Illinois No. 6 (hvb)	10.4	14.5	78.1	54.1	1.3	5.4
DECS-8	Smith-Roland (subb)	28.4	9.9	74.4	5.2	1.0	0.9
liquid A	coal liquid derived from Illinois No. 6 coal	–	–	88.4	11.4	0.2	<0.1
liquid B	coal liquid derived from Pittsburgh No. 8 coal	–	–	87.1	9.6	0.2	<0.1

solution. Higher reactivity may result in a decrease in gas yield. Since high-temperature soaking in a coal liquid is an effective method for the physical dissolution of coal in the absence of additional chemicals and hydrogen, the subsequent generation of gases would be minimized.

Assuming an associated molecular nature for coal, separate liquefaction is another factor suggested to decrease the gas yield. While it is known that severe conditions are generally required for the decomposition of higher-molecular-weight fractions from oil and bitumen, a larger amount of gas may be produced from the lower-molecular-weight coal fractions under these conditions. To optimize the process, coal fractions with different molecular weights should, if possible, be liquefied separately.

Treatment of coal under mild conditions has been studied for years.[13,14] Pretreatment procedures involving chemical reactions such as alkylation, oxidation, and hydrolysis have been attempted.[13] Other methods include treatments in the presence of CO/H$_2$O,[15-18] CH$_3$OH,[15] and nitrogen-containing compounds[19,20] at temperatures ranging from 300 to 350 °C. From an economic point of view, such process conditions involving high pressures of H$_2$, H$_2$O, and CO and the addition of chemicals are not recommended.

In this paper, an improved pretreatment procedure for coal liquefaction is investigated assuming a physically associated molecular nature for coal. Activities are focused on the two issues mentioned above: (1) maximizing the dissolution of associated coal and (2) stepwise conversion of different molecular weight coal components. An improved preconversion concept is proposed and tested using autoclave reactors.

Experimental Section

Coal samples were obtained from the DOE Coal Bank at the Pennsylvania State University. Elemental analyses are presented as Table 1. The Illinois coal (DECS-2) was used as received while the Smith Roland coal (DECS-8) was washed with 2 N HCl[5] and dried before use. Two coal liquids derived from the Illinois No. 6 coal (liquid A) and Pittsburgh No. 8 coal (liquid

B) were obtained from the Wilsonville pilot plant.[21] Elemental analyses of these coal liquids are also shown in Table 1. Reagents and solvents (HPLC-grade) were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA) and used without further purification.

A large 250-mL autoclave and small 27-mL microreactors[22] were used. These reactors were evacuated and purged with nitrogen five times after charging. Autoclave samples were heated at ~8 °C min^{-1} to the required temperature, then controlled to ±3 °C while being agitated with the autoclave stirrer (500 rev min^{-1}). Microreactors were heated in a fluidized sand bath controlled to ±1.0 °C of the set point. Mixtures in the microreactor attained the set point within 5 min from the time of immersion into the sand bath. Conditions for all experimental runs are summarized in Table 2. Liquid A from the Illinois No. 6 coal was most generally used, but liquid B was used for runs 5–9.

After reactions, the mixtures were filtered and Soxhlet-extracted with cyclohexane, toluene, tetrahydrofuran (THF), and pyridine for 24 h at each stage. The individual fractions were then dried under vacuum at 95 °C overnight. Amounts of cyclohexane solubles (CyS), toluene solubles (ToS), THF solubles (TS), and pyridine solubles (PS) were determined from the weights of their respective insolubles. Gas yields were generally included in CyS oil yields. The reproducibility of these yields was ±3 wt % for large autoclave experiments and ±5 wt % for small microreactor experiments.

After the autoclave was cooled, gases were collected for analysis in a sample bag after cooling the autoclave, then analyzed by the University of Pittsburgh Applied Research Center (Pittsburgh, PA), using gas chromatography. Approximate gas yields were calculated using eq 1 assuming no change in the amount of nitrogen before and after the reactions. In eq 1, m_i is the mass

$$\text{gas (g)} = \sum m_i \simeq \sum \frac{G_i}{G_{N_2}} \frac{P_0 V_0}{24.8} M_i \qquad (1)$$

(g) of component i; G_i the gas composition (vol %) of component i in produced gas; G_{N_2} the N$_2$ composition (vol %) in produced gas; P_0 the initial N$_2$ pressure (atm) at 25 °C; V_0 the gas volume (L) in autoclave; and M_i the molecular weight of component i.

Results and Discussion

Coal Dissolution and Liquefaction. Weakening secondary interactions in coal may aid in increasing its conversion. In this study, the effect of solvation on liquefaction due to soaking was evaluated. Illinois No. 6 coal was liquefied at 430 °C for 1 h after soaking at 200 and 350 °C (runs 1 and 2 in Figure 1). The yields of TS were the same for both tests, but the yields of ToS and CyS were ~5% higher for the sample soaked at 350 °C. For run 4, the coal was refluxed in pyridine (~115 °C) for 24 h instead of undergoing high-temperature soaking. After removal of the pyridine, the sample was liquefied at 430 °C. Comparing the total conversion to the conversion of the raw coal liquefied under the same conditions (run 3) showed the yield of CyS increased ~10% after refluxing in pyridine. From 1 to 10 wt % of the pyridine is still retained by the coal, even after drying under vacuum at its boiling point.[23-27] This amount of retained pyridine,

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Table 2. Experimental Conditions of Preconversion and Liquefaction Runs

			conditions															
	coal		soaking-1				soaking-2				liquefaction				solvent		catalyst	
run no.	code	amount (g)	temp (°C)	time	gas	press[a] (MPa)	temp (°C)	time (h)	gas	press[a] (MPa)	temp (°C)	time (h)	gas	press[a] (MPa)	code	amount (mL)	code	amount (mg)
Effect of Soaking (250-mL Autoclave) (see Figure 1)																		
1	DECS-2	5	200	1.0	N₂	1.4	–	–	–	–	430	1.0	N₂	1.4	liq A	50	–	–
2	DECS-2	5	350	1.0	N₂	1.4	–	–	–	–	430	1.0	N₂	1.4	liq A	50	–	–
3	DECS-2	5	–	–	–	–	–	–	–	–	430	1.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50
4	DECS-2[b]	5	–	–	–	–	–	–	–	–	430	1.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50
Effect of Soaking Temperature (27-mL Microreactor) (see Figure 2)																		
5	DECS-2	5	275	1.5	N₂	0.35	–	–	–	–	–	–	–	–	liq B	15	–	–
6	DECS-2	5	300	1.5	N₂	0.35	–	–	–	–	–	–	–	–	liq B	15	–	–
7	DECS-2	5	325	1.5	N₂	0.35	–	–	–	–	–	–	–	–	liq B	15	–	–
8	DECS-2	5	350	1.5	N₂	0.35	–	–	–	–	–	–	–	–	liq B	15	–	–
9	DECS-2	5	375	1.5	N₂	0.35	–	–	–	–	–	–	–	–	liq B	15	–	–
Effect of Stepwise Soaking (250-mL Autoclave) (see Figure 3)																		
10	DECS-2	5	350	1.0	N₂	1.4	400	1.0	N₂	1.4	–	–	–	–	liq A	50	–	–
11	DECS-2	5	200	1.0	N₂	1.4	400	1.0	N₂	1.4	–	–	–	–	liq A	50	–	–
Effect of Stepwise Soaking (27-mL Microreactor) (see Figure 3)																		
12	DECS-2	3.5	–	–	–	–	–	–	–	–	430	2.0	N₂	0.35	liq A	14	–	–
13	DECS-2	3.5	350	0.5	N₂	0.35	400	0.5	N₂	0.35	430	1.0	N₂	0.35	liq A	14	–	–
14	DECS-2	3.5	(130 °C----240 °C----350 °C----400 °C----430 °C)								430	1.0	N₂	0.35	liq A	14	–	–
				28[c]	30[c]		21[c]	11[c]										
Effect of Coal Fractions (250-mL Autoclave) (see Figure 4)																		
15	DECS-2/PS[d]	5	–	–	–	–	–	–	–	–	130	1.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50
16	DECS-2/PI[d]	5	–	–	–	–	–	–	–	–	430	1.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50
17	DECS-2/CyI[e]	5	–	–	–	–	–	–	–	–	430	1.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50
Test of the Proposed Procedure (250 mL/Autoclave) (see Figure 6)																		
18	DECS-2	5	200	1.0	N₂/H₂	0.7/2.8	–	–	–	–	430	2.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50
19	(yield calculated from runs 10 + 17)																	
20	DECS-8	5	200	1.0	N₂/H₂	0.7/2.8	–	–	–	–	430	2.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50
21	DECS-8[f]	5	350	1.0	N₂/H₂	0.7/2.8	400	1.0	N₂/H₂	0.7/2.8	430[g]	1.0	N₂/H₂	0.7/2.8	liq A	50	MoS₂	50

[a] At 25 °C. [b] Coal refluxed in pyridine, followed by the removal of pyridine. [c] In minutes. [d] PS, pyridine solubles; PI, pyridine insolubles. [e] Cyclohexane insolubles from run 10. [f] 2 N HCl-washed and dried coal. [g] Cyclohexane insolubles was liquefied after soaking at 350/400 °C.
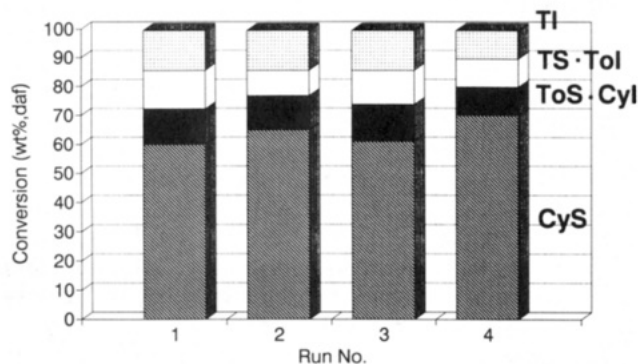

Figure 1. Effect of soaking before liquefaction on coal conversion (conditions are listed in Table 2). Key: CyS; cyclohexane solubles, ToS·CyI; toluene soluble and cyclohexane insolubles, TS·ToI; THF soluble and toluene insolubles, TI; THF insolubles.

Figure 2. Effect of soaking temperature on extractability[22] (conditions are listed in Table 2). Key: ToS; toluene solubles, TS·ToI; THF soluble and toluene insolubles, PS·TI; pyridine soluble and THF insolubles, PI; pyridine insolubles.

however, did not significantly affect coal conversion.[28] These results indicate that solvated coal can be readily converted, and that higher temperatures are needed to solvate coal when soaking in poorer solvents. Alternatively, even low temperatures are effective for solvating coal when soaking in better solvents. Reported results support this interpretation. In one case, an increase in conversion at 427 °C was observed when a coal/coal liquid mixture was soaked at 277–322 °C for 10 min.[29] In another case, swelling induced by THF and tetrabutylammonium hydroxide at room temperature was shown to enhance hydroliquefaction yields at 400 °C.[30,31]
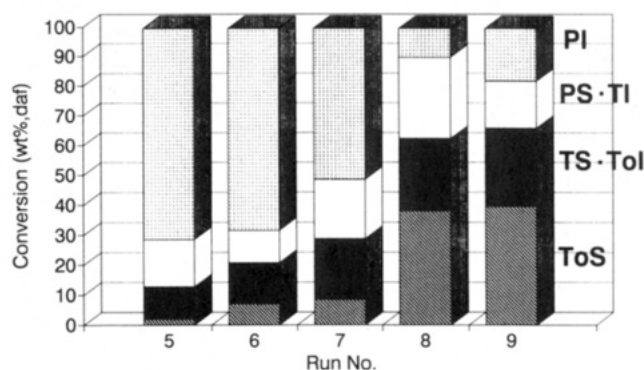
As reported in the previous paper,[22] the optimum range for high-temperature soaking in coal liquids was ∼350 °C (runs 5–9 in Figure 2). The CyS (oil) yield, however, was low (35%) even at optimum temperatures. A second soaking of the product from the 350 °C treatment (two-step soaking) was initiated to determine perceivable differences in oil yield. Two-step soaking at 350 and 400 °C produced a 50% oil yield (run 10 in Figure 3). Soaking at 200 °C, however, followed by soaking at 400 °C, showed an apparent yield in excess of 100%, probably due to incorporation of the coal liquid into the product (run 11). Therefore, two-step high-temperature soaking is shown

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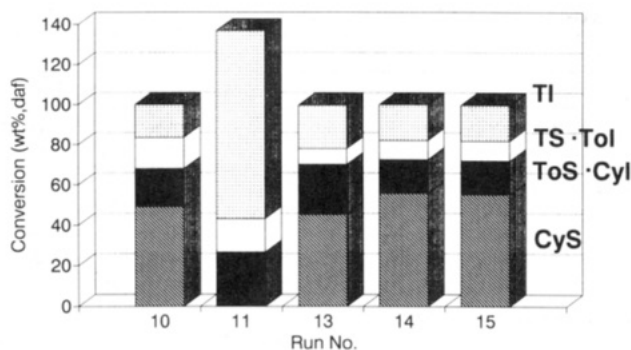(31) Joseph, J. T. *Fuel* **1991**, *70*, 459–464.

Figure 3. Effect of stepwise soaking on extractability (conditions are listed in Table 2). Key: CyS; cyclohexane solubles, ToS·CyI; toluene soluble and cyclohexane insolubles, TS·ToI; THF soluble and toluene insolubles, TI; THF insolubles.

Figure 4. Coal fractions and their conversion (conditions are listed in Table 2). Key: CyS; cyclohexane solubles, ToS·CyI; toluene soluble and cyclohexane insolubles, TS·ToI; THF soluble and toluene insolubles, TI; THF insolubles.

to be effective for dissolving coal, but a temperature of 350 °C is required for the first step.

Since two-step high-temperature soaking at 350 and 400 °C generated 50% cyclohexane solubles, slow or programmed heating appears to be more efficient than fast heating for enhancing coal conversion. In practice, the autoclave was slowly heated with the autoclave heater. The effect of variable heating rates was investigated using the microreactor, which was controlled with the sand bath. For run 12, the reactor was rapidly heated in one step from room temperature to 430 °C in 0.5 h and held at 430 °C for 2 h. For run 13, the mixture was liquefied under the same conditions, but heated in two steps (350 °C for 0.5 h and 400 °C for 0.5 h) and then held at 430 °C for 1 h. The total heatup time from room temperature to 350 °C, from 350 to 400 °C, and from 400 to 430 °C was 0.5 h. Therefore, the total residence time including heatup was 2.5 h. In run 14, the mixture was slowly heated from 130 to 430 °C and held at 430 °C for 1 h. Total duration for heatup and reaction times was maintained at 2.5 h. The lowest coal conversion resulted from the conditions imposed in run 12, which reacted the coal for the longest time but used one-step heating. By comparison, oil yields were enhanced ~10% using the programmed heating methods. These results imply that programmed heating and stepwise high-temperature soaking are important factors for increasing coal conversion. Song et al.[32] recently reported the effect of temperature-programmed liquefaction for low-rank coals. In their work, Montana subbituminous coal produced 5–10% more THF solubles by slow heating than rapid heating. These results support our present work.

Coal Fractions and Liquefaction. A continuous molecular weight distribution is another feature of associated coal.[1] Realizing that a higher gas yield should be obtained by pyrolysis from oil fractions with low molecular weight,[33] the dissolved coal may be fractionated into light and heavy fractions and the heavy fraction with high molecular weight selectively liquefied. In this study, pyridine solubles and insolubles were liquefied to compare conversions under similar conditions (runs 15 and 16). As shown in Figure 4, approximately the same oil yield (CyS) was obtained from both fractions. Liquefaction of cyclohexane insolubles from run 10 was also examined. Even from this heavy fraction, a 50% oil yield was obtained.
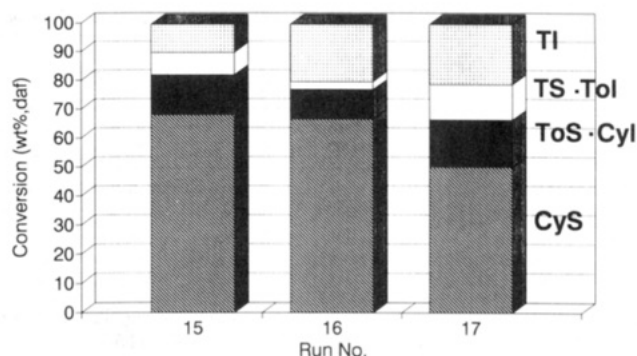
Dissolution and hydrogen consumption of PI and coal were found to be similar for West Kentucky coal (80% carbon, daf);[34] however, a significant decrease in conversion was observed when Illinois No. 6 coal was extracted with pyridine.[35] Warzinski and Holder[36] noted the same response to pyridine as a characteristic of Illinois No. 6 coal. Although the ultimate response of soluble and insoluble components to coal conversion is difficult to conclude from these preliminary results, it appears that residues of high molecular weight components are more reactive than previously believed, and in some instances, approach that of the low molecular weight components.

Coal Molecular Association and Liquefaction. It has been shown that a significant portion of coal can be dissolved by high-temperature soaking in coal liquids and that programmed or stepwise heating is preferred to enhance oil yields. Highly dissolved coal has also produced greater liquefaction yields. Test results further suggest that coals having a wide molecular weight distribution should be separated into light and heavy fractions after dissolution with only the heavy fraction liquefied in the next step. From these results, a procedure designed to increase the oil yield and decrease the gas yield is presented in the block diagram identified as Figure 5. As described, coal is soaked in a recycle oil at 350 and 400 °C. Gas and oil fractions are isolated using vacuum distillation, and the heavy fraction liquefied under low hydrogen pressure at relatively low operating temperatures.

This procedure was tested in the autoclave. The DECS-2 coal was soaked in the coal liquid under nitrogen at 350 and 400 °C, respectively. The oil fraction was extracted with cyclohexane and the cyclohexane insoluble portion liquefied under low hydrogen pressures (2.8 MPa) at 430 °C for 1 h (run 19). For comparison, the coal was soaked in the coal liquid at 200 °C for 1 h and the mixture liquefied under the same conditions for 2 h (run 18). Gas yields from these tests were determined (Figure 6). The mass balance for run 19 is presented in Scheme 1, which shows that the CyS (oil) yield increased 30% and the gas yield decreased 15% when compared with the yields from run 18.

Although high-temperature soaking has only been effective for solubilizing high- volatile bituminous coals,[37]

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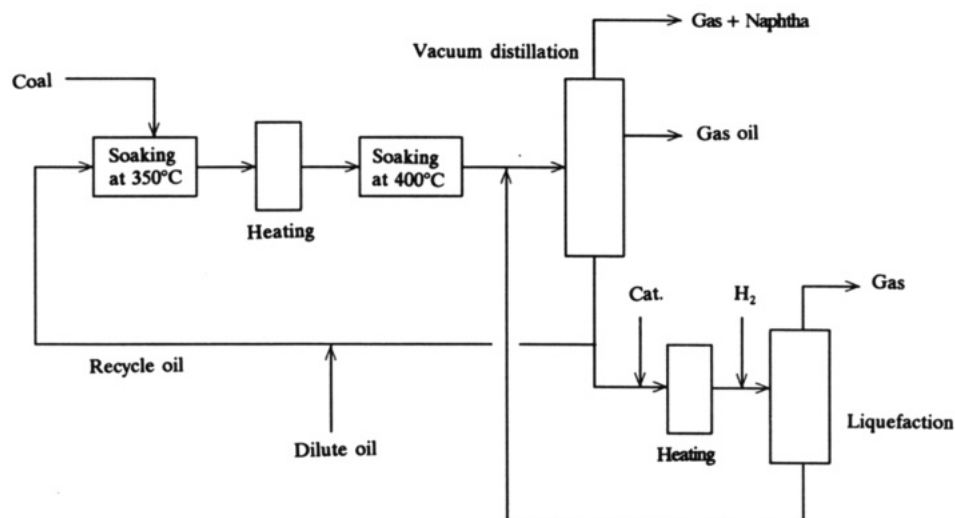
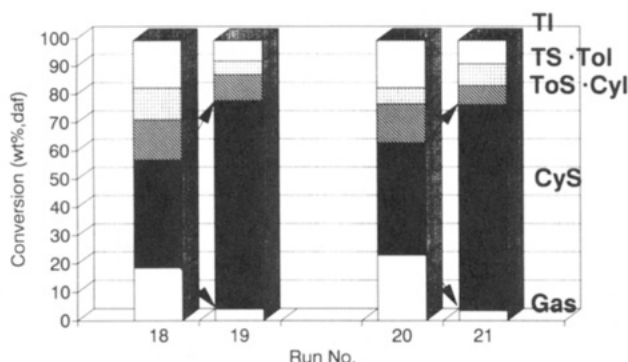**Figure 5.** Block diagram of the proposed coal liquefaction procedure.

Figure 6. Coal conversion by the proposed procedure for a high-volatile bituminous coal and a subbituminous coal (conditions are listed in Table 2). Key: CyS; cyclohexane solubles, ToS·CyI; toluene soluble and cyclohexane insolubles, TS·Tol; THF soluble and toluene insolubles, TI; THF insolubles.

the same procedure was used to test the DECS-8 subbituminous product. As expected, this coal was not completely solubilized and the PS yield was <50 wt %. Ionic forces are more significant in lower rank coals,[5] and these forces should be neutralized prior to high-temperature soaking. One method for weakening these interactions is by acid washing.[38-41] In our work, washing in 2 N HCl was used to weaken the ionic forces in the coal prior to high-temperature soaking.

The acid-washed sample was soaked in the coal liquid at 350 and 400 °C for 1 h, respectively. Cyclohexane insolubles from the soaked coal were similarly liquefied at 430 °C for 1 h (run 21). Since dried acid-washed coal was used, the DECS-8 raw coal was also dried then soaked at 200 °C for 1 h and liquefied at 430 °C for 2 h (run 20). Results showed more than 30% increase in the oil yield and 20% decrease in the gas yield from the acid-washed coal (Figure 6 and Scheme 1).

In a controlled experiment made without using coal, about 2% gas was produced from the coal liquid at 430 °C. Therefore, total gas yields in the previous runs were compensated by this amount. Since the quantity of gas

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Scheme 1. Mass balance for runs 19 and 21

Table 3. Gas Composition Resulting from Liquefaction[a] **(vol %)**

gas	run 18	run 19[b] (CyI)	run 20	run 21[b] (CyI)
hydrogen	61.53	68.05	62.61	70.76
CO	0.15	0.09	0.45	0.14
CO_2	0.21	0.07	1.41	0.14
methane	9.32	5.03	9.23	4.84
ethane	4.19	2.55	4.15	2.44
ethylene	0.04	0.05	0.04	0.05
propane	2.21	1.44	2.15	1.38
propylene	0.09	0.11	neg	0.10
n-butane	0.51	0.40	0.48	0.36
i-butane	0.16	0.12	0.16	0.11
butene	0.02	0.04	neg	0.02

[a] Gas samples include gas produced from coal liquid, Coal/coal liquid – 5 g/50 mL. [b] Gas obtained after the second step at 430 °C.

produced from the coal liquid was more than that produced in the liquefaction step (CyI at 430 °C), only semiquantitative yields were obtained. The difference, however, in the amounts of gas generated in runs 18 and 19 and in runs 20 and 21 is indeed significant and goes far beyond experimental error. Table 3 shows the composition of the gases generated at 430 °C. The residue (CyI) from high-temperature soaking produced smaller amounts of CO, CO_2, and methane with slightly larger amounts of olefin gases.

Conclusions

Suggested improvements in the coal liquefaction process were tested using the current two-stage approach, assuming an associated molecular structure for coal. Considering that significant portions of coal molecules are physically associated and that solubilization of these associates is

not realized using conventional procedures, it is suggested that physical dissolution be carried out prior to liquefaction. Stepwise high-temperature soaking is a simple and effective method for coal dissolution in the absence of additional chemicals and hydrogen. A greater degree of dissolution requires less severe conditions during liquefaction. A continuous molecular weight distribution in the associated coal is another important factor to be considered for coal conversion. Liquefaction of only the high-molecular-weight fractions isolated after high-temperature soaking produced higher oil yields and lower gas yields. Tests made using autoclave reactors tend to verify this concept as diagrammed in Figure 5 and show it to be a superior coal conversion procedure. Use of this method resulted in 30% more oil and 15–20% less gas. This projects a substantial reduction in the ultimate cost of coal liquefaction.