

RETROGRESSIVE REACTIONS IN COAL/PETROLEUM CO-PROCESSING

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INTRODUCTION

Co-processing is the simultaneous reaction of coal and petroleum resids to produce distillable liquids. It can be viewed as a new approach to direct liquefaction where the petroleum resid takes the role of the traditional liquefaction solvent [1]. The co-processing system is somewhat more complex from a chemical standpoint because of the predominantly aromatic character of the coal and mainly aliphatic nature of the petroleum products. The variety of hydrocarbons present in such a system determine the chemical reactions. One of the major undesirable reaction products is coke (or semi-coke) which causes problems in the co-processing technology. The formation of coke diverts carbon into unwanted by-products, reducing yields of the more desired products, and can upset heat and mass transfer processes in the reactor.

The intention of this study is to examine the chemical interactions and process conditions that contribute to retrogressive reactions during co-processing. We studied only thermal reactions (that is, reactions without added catalyst) since the aim is to focus on the retrogressive reaction chemistry that takes place between the different organic components of the system, and not to optimize the system for maximum liquids yields. The main objectives of this project are: 1) to determine the groups of chemical components originating from the coal and the petroleum that are responsible for initiating coke formation; 2) to identify the optimum reaction conditions that decrease the amount of insoluble coke; and 3) to rank pairs of coal/petroleum feedstock that minimize the amount of coke formed during co-processing reactions.

EXPERIMENTAL

Five coal samples from the Penn State Coal Sample Bank were used in this project, ranging in rank from subbituminous B through high volatile A bituminous. Data on the elemental composition on these coals is given in Table 1. The selected coal samples were first reacted with five model compounds representative of petroleum resids: eicosane, 1-phenyldodecane, 1,4-diisopropylbenzene, durene, and pyrene. The model compounds were obtained from Aldrich and were used as received. These model compounds were chosen on basis of their aromaticity and H/C ratios, to provide a set of compounds having a reasonably wide range of both properties. Real co-processing reactions were conducted with three vacuum feed resids. Analyses of the petroleum feedstock are presented in Table 2. Two of the petroleum feedstock were obtained from Amoco Co. (West Texas FHC-470 and Blend FHC-571) and one from Unocal (Hondo).

All of the reactions were conducted in a 20ml stainless steel vertical tubing bomb (microautoclave) reactor. Each reaction was conducted with 2.5g of coal and 5g of model compound or resid. The coal was dried to a 1% moisture under vacuum and was stored under a nitrogen blanket. The starting pressure (cold) was 3.5MPa (500 psi) of nitrogen or hydrogen. The reaction temperatures were 350° C, 400° C, 450° C and the time was fixed at 30 min.

The contents of the reactor were rinsed with tetrahydrofuran (THF) and the products were separated to THF-solubles and THF-insolubles. The Soxhlet thimble containing the insoluble matter was then extracted under a nitrogen atmosphere for 24 h. Excess THF was removed by rotary evaporation and the solid residue was dried under vacuum for 12 h before weighting. The degree of

retrogressive reactions occurring was defined by the yield of tetrahydrofuran insolubles which was calculated on a percent basis dividing the weight of the THF-insolubles by the weight of the coal (daf).

In order to assess the influence and contribution of the model compounds to the formation of solid residue during these reactions, blank runs of the model compounds (in the absence of coal) were performed. Similarly coal was reacted alone under the same reaction conditions in order to obtain the information on the products resulting directly from the coal itself and baseline data for thermal stability of the resids was obtained.

Solid state ^{13}C NMR and Fourier transform (DRIFT) spectroscopy was performed on the unreacted coal. These spectra were used as a baseline to be later compared with the spectra obtained on the THF-insoluble residue in order to examine the structural changes occurring during the reactions. Some of the solid products were analyzed by elemental analysis in order to determine the H/C ratios which in a very crude way can give indications about the aromaticity.

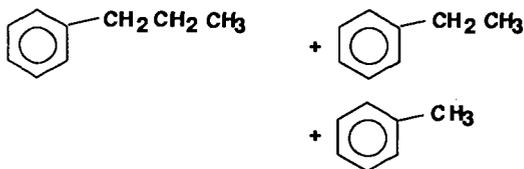
RESULTS AND DISCUSSION

Some results from the reactions of the five coals with the five model compounds under nitrogen and hydrogen are presented in Table 3. The most obvious observation is that the yield of THF-insolubles is the lowest in the reactions with pyrene. Also the values obtained for reactions with coal/eicosane and coal/1-phenyldodecane are very close to each other, as well as are the ones for coal in reaction with 1,4-diisopropylbenzene and durene. This was also verified when the H/C atomic ratios of the solid residue were plotted as a function of reaction temperature. Figure 1 shows that coal reacts with eicosane and 1-phenyldodecane in a similar fashion and that coal also reacts similarly in the presence of 1,4-diisopropylbenzene and durene. Pyrene reacts in a way notably different than the other four model compounds.

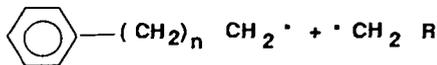
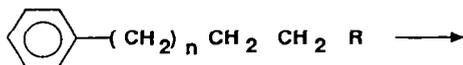
Eicosane and 1-phenyldodecane have in common the long paraffin chain. Thermal cracking of eicosane will lead to the production of 1° radicals by C-C bond cleavage, as for example:



A similar reaction path for alkylated benzene compounds (1-phenyldodecane) is supported by a collateral study in our laboratory [2] where it was shown that n-butylbenzene decomposes to:

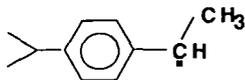


In other words, the alkylated benzene compound tends to crack at every possible position along the chain. This process also gives rise to primary radicals via:



Therefore, 1-phenyldodecane will form similar radicals to eicosane because most probably the cracking of bonds will take place along the dodecyl chain.

On the other hand, cracking of durene and 1,4-diisopropylbenzene will lead to benzyl radicals like the one shown below:



Pyrene, being a polyaromatic hydrocarbon, is very stable and does not easily form radicals by thermal cracking. In the literature pyrene has been described as a good "hydrogen shuttler" [3]. While transferring the hydrogen the pyrene most likely transforms to a hydroaromatic structure. Therefore, the similar chemistry of eicosane and 1-phenyldodecane arise from the fact that both crack to 1° radicals, and the similar behavior of durene and 1,4-diisopropylbenzene arises from the formation of the benzylic radicals from the two compounds. Pyrene would do neither. The expected thermal behavior of the 1° radical-forming compounds, benzylic radical-forming compounds, and pyrene is reflected both in the relative yields of THF-insolubles from a given coal and the variation of H/C ratio (Figure 1) as a function of temperature.

The reactions were performed under a nitrogen and hydrogen atmosphere. Under the given conditions of these experiments, namely 3.5MPa overpressure, the differences in degree of coal conversion calculated on basis of THF-insoluble are not significant. Comparisons of coal conversions under a nitrogen and hydrogen atmosphere at a given temperature are shown in Figure 3. Although it might be expected that the conversions would increase in the presence of hydrogen gas under the given reaction conditions the effect of the chemical nature of the coal and model compound (or petroleum resid) override the effects of the gas atmosphere. Furthermore, it should be recalled that these reactions are conducted without a hydrogenation catalyst being present.

Three temperatures of reaction were used in these experiments; 350°, 400°, and 450° C. Overall, the lowest yield of insoluble matter was recorded at 400° C. The lowest temperature is probably not enough for significant radical generation by fragmentation to take place while at 450° extensive cracking of the model compounds (and resids) takes place. In cases of severe cracking reactions it was not possible to maintain a good material balance. The effect of the reaction temperature is dependent on the rank of coal. For the two lower rank coals used, subbituminous B (PSOC 1488) and hvC bituminous (PSOC 1498) the coal conversion increases with increasing temperature of reaction. The three remaining project coals (hvB and hvA bituminous) achieve their highest conversion to THF-solubles at 400° C. Alternatively, it can be said that retrogressive reactions are at a minimum at 400° C. These optimum temperatures seem to coincide with the maximum fluidity temperatures of the coals. The three higher rank coals have temperatures of maximum fluidity above 400° C while the two lower rank coals do not pass through a fluid phase (with FSI's of 0 and 0.5). The temperature dependence of the coal conversion for the five project coals is shown on Figure 2.

Thermal stability tests on the petroleum resids (that is in the absence of coal) showed that considerable insoluble matter was formed only at the highest reaction temperature of 450° C. For West Texas FHC-470 the maximum insoluble is 17% of the total weight, for Blend FHC-571 the maximum is 3.73%, and for Hondo resid 5.77%.

The resids were reacted with the five project coals under the identical conditions as the model compound reactions. The yield of THF-insolubles was the lowest at 400° C. This agrees with the results reported by Moschopedis et al. [4]. When the temperature is increased to 450° C a drastic increase in solid residue is observed. This is attributed to extensive cracking taking place at higher reaction temperatures, with the high population of radicals thus increasing opportunities for retrogressive reactions. This observation is consistent with the results from the reactions with some of the model compounds, namely the ones containing the long side chains. When the coal conversion for the reactions with the model compounds and with the petroleum resids are compared (Figure 4), it is found that conversion in the presence of the resids is comparable to that achieved in the presence of pyrene. For reaction temperatures less than 450° C, the petroleum resids are as good a solvent for coal particles as pyrene. At higher reaction temperatures the interactions between the coal particles and petroleum resids seem to favour retrogressive reactions and the formation of insoluble matter.

CONCLUSIONS

The coal/model compound reactions showed that the reactivity of the vehicle is based on radical generation: eicosane-like, durene-like, and pyrene-like. The yield of THF-insolubles, therefore the degree of retrogressive reactions, is the lowest in the presence of pyrene. Coal/resid co-processing reactions at 400°C give coal conversions comparable to those in the presence of pyrene. The optimum temperature for minimizing retrogressive reactions in co-processing reactions is around 400° C. In addition, the maximum fluidity temperature of the coal defines the optimum temperature for coal conversion under co-processing reaction conditions.

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Table 1. Analyses of Project Coals.

Coal (rank)	PSOC-1488 subB	PSOC-1498 hvCb	PSOC-1501 hvBb	PSOC-1504 hvAb	PSOC-1448 hvAb
%C (dmmf)	76.56	78.24	81.17	82.88	85.20
%H	5.27	5.50	5.32	5.86	6.12
%N	0.95	1.83	1.56	1.77	1.86
%O	17.22	14.43	11.95	9.49	6.81
FSI	0.0	0.5	2.0	5.5	8.0
max fluid.T, °C	n/a	n/a	421	433	438

Table 2. Analyses of Petroleum Feedstock.

	Hondo.	W. Texas FHC-470	Blend FHC-571
Oils (wt.%)	43.9	39.4	21.4
Resins	40.2	59.1	62.8
Asphaltenes	15.9	0.5	14.8
%C	83.40	86.39	83.91
%H	11.80	11.23	10.26

Table 3. Yields of THF-insolubles for PSOC 1488 with model compounds at three different temperatures under hydrogen.

	Yield THF-insoluble, %		
	PSOC 1488 (350° C, H ₂)	PSOC 1488 (400° C, H ₂)	PSOC 1488 (450° C, H ₂)
Eicosane	94.41	84.06	80.12
1-Phen	94.13	82.32	79.42
1,4-Diiso	95.90	81.77	81.68
Durene	96.07	85.01	84.30
Pyrene	83.25	73.47	74.24

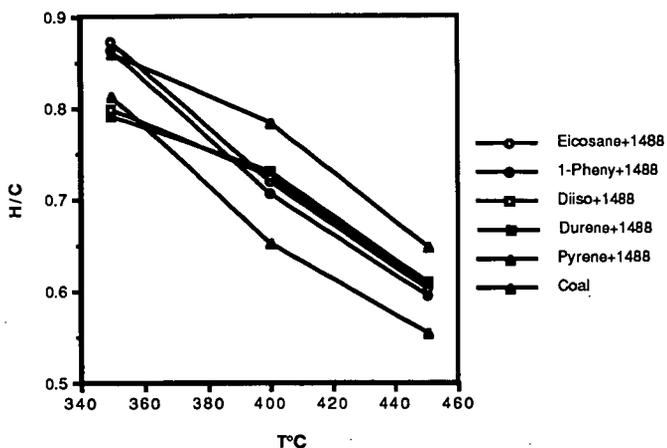


Figure 1: H/C atomic ratios of the THF-insolubles as a function of reaction temperature for different feed combinations for PSOC 1488

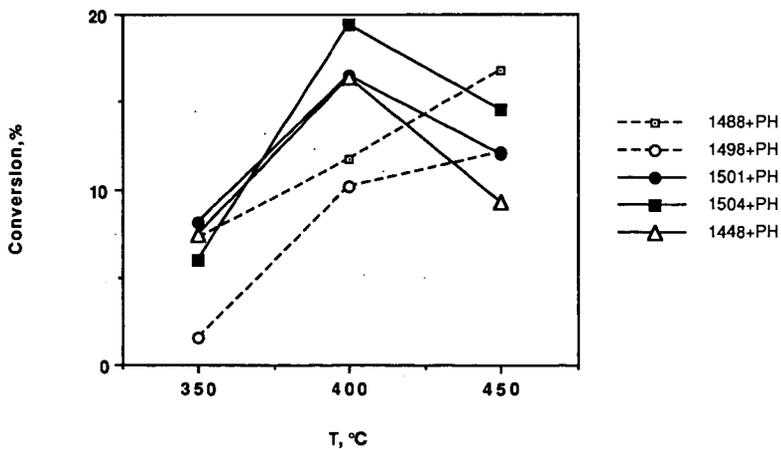


Figure 2: Temperature dependence of coal conversion for the five project coals.

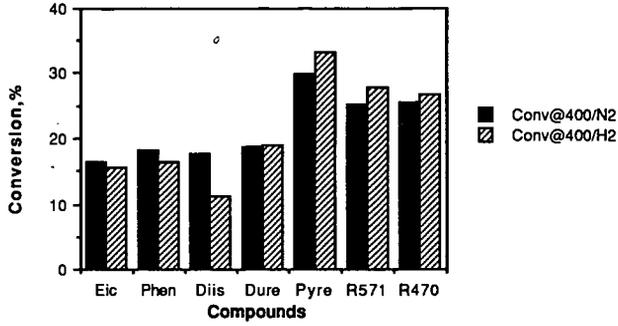


Figure 3: Conversion for PSOC 1501 at 400° C under N₂ and H₂.

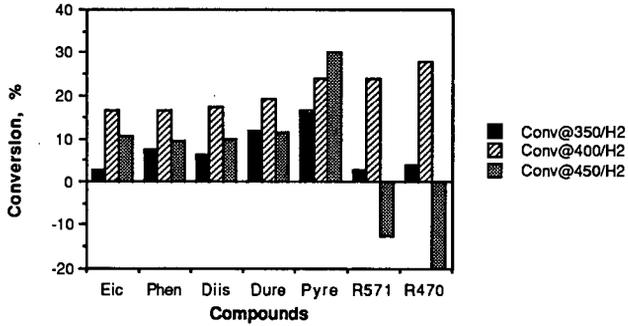


Figure 4: Conversion for PSOC 1448 at three reaction temperatures under H₂.