

IMPROVED LIQUEFACTION OF LOW RANK COALS BY REDUCTION OF RETROGRESSIVE REACTIONS

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INTRODUCTION

Direct coal liquefaction processes have recently been based on a two stage processing approach: coal dissolution followed by upgrading of the solubilized products. While low rank coals offer the potential of high oil yields because of their small aromatic ring cluster size, low rank coals are more difficult to liquefy in the first (solubilization) stage (1,2) under conditions optimized for bituminous coals. For example, Whitehurst and co-workers (3-5) demonstrated that low rank coals produce low conversions in short contact times in a donor solvent (see Fig. 1) or for long times in a non-donor solvent. For low rank coals and lignites, it appears likely that crosslinking reactions associated with oxygen functional groups (6,7) occur before the homolytic cleavage reactions, and if not controlled can limit the maximum conversion of coal to liquids. This paper discusses three approaches which have been used to either study or mitigate these reactions in an effort to improve liquefaction yields from low rank coals. 1) catalytic pretreatment; 2) demineralization and cation-exchange; 3) hydrothermal pretreatment and water addition.

RESULTS AND DISCUSSION

Catalytic Pretreatment

Impregnated Catalysts - For low rank coals, the use of a pretreatment at 350°C with an impregnated MoS₂ catalyst and H₂ shows a vastly superior product slate in subsequent liquefaction at 425°C (8-14). The improvement is especially noticeable for the low rank coals where short contact time liquefaction alone produces large residues (3-5). Results obtained at Advanced Fuel Research, Inc. (AFR) (15-17) confirmed the observations of Derbyshire and co-workers (8-14). Data for a Wyodak subbituminous coal (PSOC-1401) are presented in Fig. 2. The figure compares liquefaction data (10 min at 425°C) for no preliquefaction, preliquefaction at 275°C (with H₂ and catalyst) and preliquefaction at 350°C (with H₂ and catalyst). The results show that preliquefaction at 350°C does have a positive effect on the total yield and product quality in liquefaction (much lower residue) while preliquefaction at 275°C causes a negative effect (higher residue).

A number of tests were performed on the preliquefaction products to identify the chemistry, including FT-IR analysis of the Wyodak coal preliquefaction residue (15-17). The preliquefaction step produces the following changes in the residue: 1) decreases the carbonyl (1700 cm⁻¹) and hydroxyl regions (3400 cm⁻¹) (presumably carboxyl loss); 2) decreases the aliphatic hydrogen (2900 cm⁻¹); and 3) substantially increases the aromatic hydrogen (750-850 cm⁻¹). Our initial conclusion from the FT-IR data on the residual is that it is the reduction in the carboxyl concentration which is most important to the improvements brought about by preliquefaction, and this reduction requires the catalyst but not the solvent and probably not the hydrogen. The increase in aromatic hydrogen appears to be due to the adduction of naphthalene.

The evolutions of the volatile products of pyrolysis are related to the functional group composition of the sample, so TG-FTIR analysis provides a good complement to the FT-IR functional group analysis. Since the FT-IR analysis showed the carbonyl region to change drastically in preliquefaction, we considered the CO₂ evolution which is probably associated with the thermal decomposition of the carboxyl groups (15-17). When a comparison was made of the CO₂ evolution from a number of residues, the major changes were observed for catalytic preliquefaction at 350°C with hydrogen or nitrogen. Here a drastic reduction is observed in the CO₂ evolution at all temperatures. This result is consistent with the major chemical change in the carboxyl groups observed from the FT-IR results. The nitrogen thermal case shows much less of a change.

Since the preliquefaction showed a significant role of carboxyl groups, model compounds with aryl carboxyl groups were studied. The starting reaction mixture used was 50% naphthalene, 25% of 1-naphthoic acid and 25% of 2-naphthoic acid (weight basis). The FT-IR spectra of the starting reaction mixture and the residue after preliquefaction indicated that there is a strong loss in the carbonyl and hydroxyl bands during the preliquefaction in the presence of the catalyst. A blank run was done without the catalyst which indicates that the catalyst is necessary to cause extensive decarboxylation.

Recently, a set of experiments was done with fresh Argonne Wyodak coal impregnated with a molybdenum sulfide catalyst prepared by the incipient wetness technique (18). This was a repeat of earlier work done by Derbyshire and co-workers (8-14) and Solomon and co-workers (15-17) discussed above, except for the substitution of the Argonne Wyodak coal for the PSOC 1401 Wyodak coal. The results are shown in Fig. 3 for freshly opened and aged samples. This treatment did not show an improvement of the liquefaction yields for the fresh Argonne Wyodak coal samples. It was concluded that this different behavior toward catalyst impregnation may be due to aging of the PSOC 1401 Wyodak coal, which was presumably absent for the Argonne coal. Consequently, similar experiments were done with a sample of the latter coal which had been stored in a dry box, but where no care was taken to exclude air. The liquefaction results for the aged samples, with and without catalyst are also shown in Fig. 3. As expected, the yield of THF solubles was reduced by aging of the coal and these yields were subsequently improved by catalyst addition. However, a surprising result was that the addition of catalyst to the aged samples gave yields that were even higher than for the fresh coal or the catalytically treated fresh coal. Similar results have recently been reported by Schobert and coworkers for an air dried DECS-8 Wyodak subbituminous coal (19). The results for gas evolution from these samples during pretreatment and liquefaction are given in Fig. 4. The catalyst reduces the amount of CO₂ evolved during the pretreatment stage for both the fresh and oxidized coals. However, only in the case of the oxidized coals did the reduction in early CO₂ (and, presumably, the associated crosslinking reactions) lead to improvements in liquefaction yields.

A possible explanation for the above results is as follows. The mild oxidation of the coal due to aging may create positively charged sites which attract the tetrathiomolybdate anions during the impregnation process, which leads to better dispersion of the catalyst.

Ion-Exchanged Catalysts - To increase yields with fresh coals there are two approaches which can be pursued: a) to find a better catalyst to be impregnated onto the coal matrix; or b) to find a technique to get better - if possible atomic - dispersion of the catalyst. There has been a significant effort in the literature in pursuit of both approaches, however, a reliable and simple technique resulting in atomic dispersion of an active catalyst still needs to be found.

Ion exchange experiments have demonstrated that, around neutral pH, the coal surface is negatively charged, thus preventing anions from adsorption or ion exchange (20). This can be overcome in acidic media but any acidic treatment will result in removal of cations - an effect leading to enhanced liquefaction itself (21-25). This would obscure the effect of a catalyst. In order to circumvent this problem our approach was to first react the coal with trivalent cations

(Fe⁺³) and thus produce locally positively charged sites (18). After this pretreatment, the tetrathio-molybdenate anions could be anchored to these positions. This technique worked very well and it was also found that the catalyst activity thus prepared depended on the Fe/Mo ratio. Since no H₂ pressure was applied in the liquefaction, H₂ evolution could be observed occasionally, but only in cases of catalyzed liquefaction. The occurrence of H₂ thus was the indicator of catalytic activity in the system towards hydrogenation-dehydrogenation with the actual H₂ concentration depending on the ratio of the two reaction rates. Table 1 shows a comparison of the time resolved liquefaction yields for a catalyzed versus uncatalyzed run for one of the most active formulations (1.4% Fe/0.6% Mo). The advantage of the catalysis is more evident at earlier reaction times, as would be expected.

Modification of Liquefaction Chemistry by Demineralization or Cation-Exchange

Coal modifications to remove cations - Crosslinking has also been observed to be influenced by the presence of alkali metals, whose removal increases pyrolysis tar yields (26) and fluidity (27). These results would indicate that the role of carboxyl groups, as indicated above, is important, but it is the carboxylate (cation exchanged carboxyls) which are the key agents in retrogressive reactions for low rank coals. The role of calcium in reducing liquefaction yields from low rank coals has been suggested in previous work by Whitehurst et al. (4), Mochida et al. (28), and Joseph and Forrai (29). It is also consistent with work which shows an effect of calcium on reducing pyrolysis tar yields (26,30-33). The role of calcium may be to provide a nascent crosslink site in the coal by allowing coordination of groups like carboxyl and hydroxyl which are prone to such reactions. Otherwise, these sites would be more likely to coordinate with water (through hydrogen bonding) than with each other.

The preparation of modified low rank coals was studied systematically by Serio et al. (21-25). The following coal modifications were tested: raw, vacuum dried, treated with ammonium acetate, acid-demineralized and methylated. Each of the latter three modifications was effective in removing ion-exchanged cations. The results of liquefaction experiments with the coals and modified coals are summarized for the Zap lignite in Fig. 5. The results for the Wyodak subbituminous coal (not shown) are similar to those for the Zap lignite (22). The results show that the decrease in crosslinking, as implied by the reduction in CO₂ yield (Fig. 5b), roughly correlates with the increased liquefaction yields (soluble products, Fig. 5a). The trends in CO₂ yield (inverse correlation) and solubles from liquefaction (positive correlation) generally parallel the results from pyrolysis for the tar yield (Fig. 5c). The extent of retrograde reactions for low rank coals (lignite, subbituminous) is significantly reduced by methylation and demineralization. However, these treatments do not have much impact on bituminous coal, presumably because of the lack of exchangeable cations. A similar beneficial result has recently been observed by Miller et al. (34) in liquefaction studies with the Argonne Wyodak coal treated with methanol/HCl.

TG-FTIR analyses were run on the modified coals to see whether changes occurred in the gas evolutions. The results indicated that the demineralization and methylation processes both decrease the evolution of CO₂ and H₂O between 200°C and 400°C where crosslinking occurs, suggesting that the high tar and liquid yields produced by these two treatments are a result of reduced crosslinking which is accompanied by reduced evolutions of CO₂ and H₂O.

Coal Modifications to Add Cations - Recent work at AFR has involved preparation of ion-exchanged (barium, calcium, and potassium) coals starting with demineralized Argonne Zap, and Wyodak samples (21, 25). The exchange was done at two different pH levels (8 and 12.5) in order to effect exchange of carboxyl groups and carboxyl plus phenolic groups, respectively. These modified samples were subjected to functional group analysis as KBr pellets with FT-IR, programmed pyrolysis with TG-FTIR, and donor-solvent liquefaction experiments. The results of sample characterization by programmed pyrolysis at 30°C/min to 900°C or solvent extraction/solvent swelling experiments in pyridine are summarized in Table 2 for the Zap lignite.

These results show that demineralization tends to increase the tar yields and decrease the gas yields, which is consistent with the previous work discussed above. Similar results were observed for the Wyodak coal (21). Table 2 also shows a decrease of the tar yield with the extent of ion-exchange with the metal cations, and a corresponding increase in the total amount of gas evolution. The liquefaction results for the different samples are shown in Table 3. The data in Tables 2 and 3 show that the yields of both the pyrolysis tar and toluene solubles from liquefaction decrease with the extent of ion-exchange, i.e., in the order of (demineralized) > (ion-exchanged at pH 8) > (ion-exchanged at pH 12.5). This result indicates that having the carboxyl or phenolic groups in the salt form makes it easier to crosslink the coal structure during pyrolysis or liquefaction reactions. The ability of cations to coordinate polar groups is probably an important aspect of their role in retrogressive reactions. The ability of both monovalent and bivalent cations to act as initial crosslinks in the structure is supported by data on the volumetric swelling ratios (VSR) in pyridine and the yields of pyridine extractables, also shown in Table 2. The values of the VSR are lower for the bivalent cations at high pH. At pH 8, the values of the VSR for the monovalent and bivalent cations are more similar, though lower than the values for either the raw or demineralized coals. Consequently, the evidence indicates that the monovalent cations can also act as crosslinking agents, although this must occur through electrostatic rather than covalent interactions. It makes sense that valency would be less important in the normal state of the coal or at pH=8 since, for steric reasons, cations are unlikely to be exchanged on more than one carboxyl or ortho-dihydroxy site.

Hydrothermal Pretreatment and Water Addition

Hydrothermal Pretreatment of Coal - Water pretreatment of coal at elevated temperatures, has been studied previously as a means to increase the yields of liquid products from extraction (35,36), pyrolysis (36-38), or liquefaction (39,40) of coal. Selected results from work done at AFR with Zap coal are shown in Fig. 6 (37,39). The data show that the sharp increase of pyrolytic tar yield, as a result of short time water pretreatment, is accompanied with decreased pyrolysis CO₂ evolution. This is in harmony with our previous conclusions about the correlation between decomposition of oxygen functionalities and crosslinking, namely the water pretreatment apparently removes precursors which would otherwise lead to crosslinking under liquefaction conditions. The pyrolysis data for the water pretreated samples show a close similarity for water pretreatment to accelerated aging of the coal (38). However, the toluene solubles of a subsequent liquefaction are reduced opposite to our expectations (see Fig. 6d). Another observation was that, specifically in this short pretreatment time range, occasionally negative oil yields were observed (39). Since the oils are measured by weight difference a likely explanation is that the solvent is forming adducts with the pretreated samples. The water pretreatment step appears to sensitize the coal to this problem.

Pyrolysis and Liquefaction of Moisturized Coal Samples - Remoisturization of vacuum dried Zap and Wyodak was done in the attempt to understand if moisture uptake for low rank coals is a reversible process and to see if moisture influences the role of the cations. The remoisturized samples were analyzed by programmed pyrolysis with TG-FTIR. Preliminary results show that the moisture content can be restored to values which are close to those of the raw coals, especially for Zap (21,25).

The detailed results for the pyrolysis and liquefaction experiments are given in Ref. 21. In general, pyrolysis tar yields and the toluene solubles yields from liquefaction for the remoisturized samples were similar to those for the vacuum dried samples. It appeared that the liquefaction results were more sensitive to the presence of moisture, although the increases in asphaltene yields were generally balanced by decreases in oil yields. A possible explanation for the difference is that most of the moisture is depleted early in the pyrolysis process, whereas the moisture is retained in the reactor during liquefaction and can exist in a liquid phase under the right conditions.

Water Addition to Liquefaction Experiments - It is also known from our results (21) and the literature (41) that the moisture is associated with cations in raw coals. Consequently, an investigation was made to determine if the deleterious effects of cations could be mitigated by adding water to the donor solvent liquefaction system. Results from experiments with raw and demineralized Zap at three different temperature levels are given in Table 4. At temperatures near or below the critical temperature of water (374 °C), it appears that there is a profound beneficial effect of added water for the raw coal (note the significant reduction in CO₂ evolution). Conversely, there is a significant deleterious effect of added water for the demineralized coals. The ability of water to interact with cations and affect the course of the thermal decomposition behavior is consistent with results that have been observed in hydrothermal treatment of coal, which mimics the geological aging process in many respects.

CONCLUSIONS

The conclusions from this study are as follows:

- Catalytic pretreatment (Mo impregnation following by heating to 350 °C for 30 min.) prior to liquefaction leads to increased yields for low rank coals which have not been protected from aging, but is not effective for pristine coals, like the Argonne Premium Coals.
- For the latter coals, an ion-exchange technique in which the coal is first treated by Fe⁺³ cations followed by treatment with MoS₄⁻² anions was found to be effective in increasing yields in a two-step liquefaction process (pretreatment at 350 °C, 30 min. followed by liquefaction at 400 °C, 30 min).
- The extent of retrogressive reactions for low rank coals in pyrolysis and liquefaction is significantly reduced by removal of cations exchanged on carboxyl groups, based on experiments where the coal has been ion-exchanged (using NH₄⁺), acid demineralized (using HCl/HF) or methylated.
- The addition of monovalent (K⁺) or bivalent (Ca⁺², Ba⁺²) cations to acid demineralized coals at pH 8 significantly increases the extent of retrogressive reactions in pyrolysis and liquefaction (liquid yields are reduced). The effect is even more pronounced at pH 12.5.
- The ability of cations to act as initial crosslinks in the coal structure through electrostatic or covalent interactions is believed to be an important aspect of their role in promoting retrogressive reactions.
- Since the moisture in low rank coals is associated with the cations, the presence of liquid water during pyrolysis (as in hydrothermal treatment) or liquefaction can help to mitigate these reactions.
- The benefits of catalytic pretreatment for low rank coals may also be a result of the interaction of the catalyst with the cations present in these coals. It has been reported that alkali metals reduce the effectiveness of Mo catalysts in coal liquefaction (10), suggesting that an interaction does occur.
- The evolution of CO₂ from carboxylate groups appears to be the key indicator of retrogressive reactions in pyrolysis or liquefaction of low rank coals. The removal of the cation, the association of the cation with water or the association of the cation with a highly dispersed catalyst can inhibit the crosslinking events which are normally associated with the decomposition of these groups.

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Table 1. Time Resolved Liquid Yields (DAF WT %) from Liquefaction Experiments with Raw and Fe/Mo Exchanged (1.4% Fe/Mo) Argonne Wyodak Coal.

Reaction Time (minutes)	Raw Vac. Dried Coal			1.4% Fe/Mo Exchanged Coal		
	Toluene Solubles			Toluene Solubles		
	Total	Oils	Asphaltenes	Total	Oils	Asphaltenes
0	3	-4	7	12	6	6
10				34	12	22
20				48	14	34
30	50	8	42	57	14	43
40				57	15	42
50				62	22	40
90	62	33	29	66	29	37

Notes: Pretreatment done at 350 °C, 30 min.; Liquefaction done at 400 °C, 30 min.; Tetralin/Coal = 6/1

Table 2. Results From Characterization of Vac Dry Modified Zap Samples By Programmed Pyrolysis And Solvent Swelling/Pyridine Extraction.

Coal (type/preparation)	Pyrolysis Products (wt.% ,daf)					Solvent Swelling/ Pyridine Extraction	
	Tars	CO ₂	CO	H ₂ O	CH ₄	V.S.R. ^a	P _e ^b
Fresh	7	8.9	14.7	14.3	2.2	2.7	5
Demin.	20	4.8	10.4	8.4	2.7	3.1	20
Demin. + K ⁺ (pH8)	11	8.6	9.9	16.0	1.9	2.0	10
Demin. + Ca ⁺⁺ (pH8)	10	8.6	13.5	10.3	2.4	1.8	3
Demin. + Ba ⁺⁺ (pH8)	6	11.7	15.8	18.6	2.6	2.1	6
Demin. + K ⁺ (pH12.5)	5	9.9	12.4	13.5	1.6	1.7	2
Demin. + Ca ⁺⁺ (pH12.5)	4	8.2	22.6	12.6	2.0	1.1	2
Demin. + Ba ⁺⁺ (pH12.5)	3	10.5	24.1	15.5	2.6	1.1	1

Notes: a = Volumetric Swelling Ratio In Pyridine; b = Pyridine Extractables (daf)

Table 3. Liquefaction Results of Vac Dry Modified Zap Samples.

	Toluene Solubles (wt.%, daf)			Gas (wt. %, daf)		
	Total	Oils	Asphaltenes	CO ₂	CO	CH ₄
Fresh	26	12	14	4.3	0.24	0.25
Demin.	52	26	26	1.1	0.43	0.27
Demin. + K ⁺ (pH8)	30	11	19	7.7	0.27	0.17
Demin. + Ca ⁺⁺ (pH8)	25	13	12	2.7	0.30	0.22
Demin. + Ba ⁺⁺ (pH8)	37	25	12	7.3	0.40	0.20
Demin. + K ⁺ (pH12.5)	17	5	12	5.0	0.24	0.27
Demin. + Ca ⁺⁺ (pH12.5)	*	*	3	0.7	0.04	0.08
Demin. + Ba ⁺⁺ (pH12.5)	15	15	0.5	0.3	0.27	0.02

* Yields Calculated by Difference were Negative. Solvent Incorporation is Suspected.

Table 4. Effect of Added Water on Liquefaction of Raw and Demineralized Argonne Zap Coal.

Temp. Level (°C)	Water Addition	Toluene Solubles wt.%, daf		CO ₂ Yields wt. %, daf	
		Raw	Demin.	Raw	Demin.
350	yes	13	0	0.0	1.1
	no	1	27	5.4	2.4
375	yes	23	19	2.4	1.5
	no	11	40	5.2	2.2
400	yes	31	24	5.2	0.8
	no	30	58	4.1	4.2

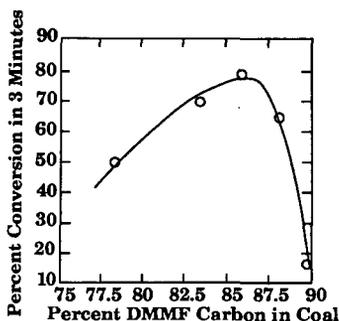


Figure 1. Rank Dependence of Short Contact Time Liquefaction Yields (3).

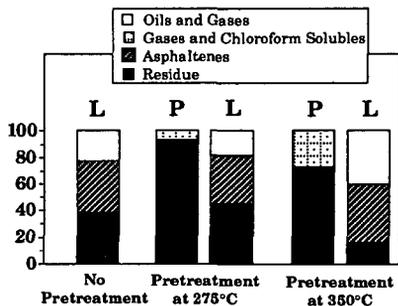


Figure 2. Product Distributions for Preliquefaction and Liquefaction Comparing Results for No Preliquefaction, Preliquefaction at 275°C and Preliquefaction at 350°C. P = Preliquefaction; L = Liquefaction. Liquefaction Conditions - 425°C, Mo, Catalyst, Naphthalene Solvent, Hydrogen Atmosphere (10 min). Preliquefaction Conditions - Mo, Catalyst, Naphthalene Solvent, Hydrogen Atmosphere (275°C-30 min., 350°C - 60 min.).

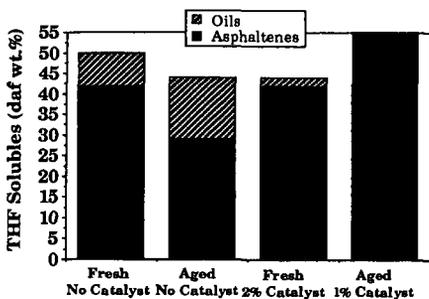


Figure 3. Effect of Coal Aging and Molybdenum Catalyst Impregnation on THF Solubles Yields from Liquefaction of Argonne Wyodak Coal in Tetralin (Pretreatment done at 350°C, 30 min; Liquefaction done at 400°C, 30 min).

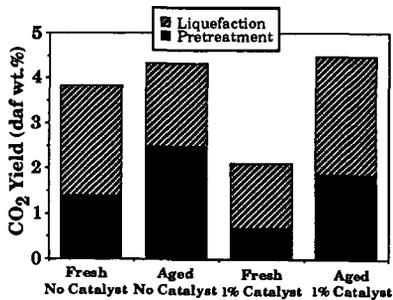


Figure 4. Effect of Coal Aging and Molybdenum Catalyst Impregnation on Total CO₂ Evolution from Pretreatment (350°C, 30 min) and Liquefaction (400°C, 30 min) of Argonne Wyodak Coal.

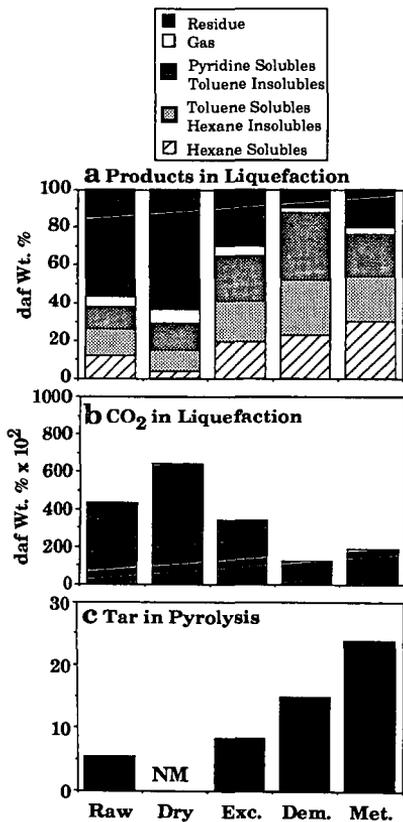


Figure 5. The Variation in Product Distributions for Zap Lignite with Coal Treatment. a) Products in Liquefaction, b) CO₂ in Liquefaction and c) Tar in Pyrolysis. NM = Not Measured.

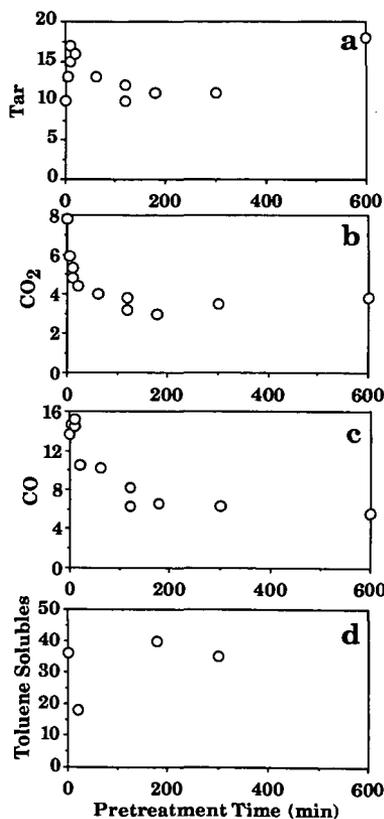


Figure 6. Results from Analysis of Zap Residues Produced by Water Pretreatment at 350°C, 4000 psig for a Range of Pretreatment Times. (a-c) Data on Pyrolysis Gas Yields from TG-FTIR Analysis; (d) Data for Toluene Solubles Yield from Donor Solvent Liquefaction. All Results are Given on a DAF Basis.