

CATALYTIC HYDROPROCESSING OF ACIDIC FRACTIONS
OF COAL LIQUID HEAVY DISTILLATE

by

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Individual compound and molecular class kinetics were determined for the catalytic hydrodeoxygenation of coal liquid acid fractions. The coal liquid acidic fractions were prepared from a coal liquid heavy distillate, derived from Powhatan #5 coal, by ion exchange chromatography(1). A commercial sulfided Ni-Mo/ γ -Al₂O₃ catalyst was used to hydrotreat the coal liquid acids which were fed through a microreactor as a 0.25 wt% solution in cyclohexane. The coal acid feeds and hydrotreated products were separated by capillary column gas chromatography and detected by either standard FID techniques or by mass spectrometry. Upon hydrotreating, the product chromatograms (Figure 1) show a large increase in the number of compounds relative to the feed (Figure 2) and a shift to lower boiling range. This change in the chromatogram, and the change in carbon number distribution in the product molecules demonstrates that cracking as well as hydrogenation is taking place. Since many of the feed and product compounds could only be identified by their empirical formula, the results of the catalytic hydrotreating of the acidic fractions can be described in terms of carbon number classes and classes which denote the degree of saturation of the compounds. The carbon number data show evidence of cracking, while the Z numbers, which indicate the degree of saturation, show that compounds of the biphenyl class decrease in relative concentration with increased inverse space velocity; and compounds of the tetralin, indane, and cyclohexylbenzene class show an increase in relative concentration with increased inverse space velocity. Tables I and II list the compound classes identified in the feed and hydrodeoxygenated product of the very

weak and weak acids, respectively. The formation of most of the product molecules can be rationalized using the pure compound hydroprocessing data on cyclohexyl phenol; phenyl phenol(2) and naphthol(3). The examination of the feed and products in terms of the lumps illustrates several points: 1. The feeds contain a relatively small number of major components which, upon hydrotreating, are reduced in concentration, forming many more product molecules. 2. In addition to the removal of the oxygen functionality typically occurring as in the hydroxyl group, there was significant ring hydrogenation. 3. There is evidence of cracking, both from the formation of compounds having fewer carbons than the feed compound and from shifts in carbon number distributions among the compounds existing in the feeds; this cracking is inferred to involve principally the methyl substituents bonded to rings(4).

The hydrodeoxygenation kinetics of tetrahydronaphthol, methyl-tetrahydronaphthol, phenylphenol, methylphenylphenol, dimethylindanol, and cyclohexylphenol are shown in Figure 3 in a plot of fraction of species unconverted vs. inverse weight hourly space velocity. Methyl substitution tends to increase the rate of disappearance of the parent compound, probably by providing an additional pathway for the change in molecular structure. Neither this observation, nor the order of reactivity in disappearance implies hydrodeoxygenation reactivity(5). Methyl groups may hinder heteroatom removal, in some cases, if they prevent easy access to the catalyst by steric hindrance.

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Table I

Number of Compounds by Type in the Very Weak Acid
Feed and Hydrotreated Product

<u>Compound Type</u>	<u>Feed</u>	<u>Product^a</u>
Benzene	9	13
1-Ring Phenols	2	NF ^b
2-Ring Phenols	4	NF
Carbonyl Compounds ^c C-	8	NF
Ethers ^d , R-O-R	6	6
Nitrogen Compounds	6	1
3-Ring Aromatics	1	2
Cyclic Alkanes, Alkenes	NF	7
2-Ring Aromatics	NF	5
Fused Cycloalkyl Aromatics ^e	NF	15
Cycloalkyl Aromatics	NF	4

^a Obtained at a space velocity of 0.4 g of fraction/
(g of catalyst·h).

^b Not found.

^c Furanone is considered to be a carbonyl compound.

^d Ethers include methoxy, phenoxy, and furan.

^e Fused cycloalkyl aromatics include tetralin and indanes.

Table II

Number of Compounds by Type in the Weak Acid Feed
and Hydrotreated Product

<u>Compound Type</u>	<u>Feed</u>	<u>Product^a</u>
Benzenes	4	3
2-Ring Phenols	8	3
Carbonyl Compounds	1	NF ^b
Ethers	2	3
Nitrogen Compounds	2	NF
Cyclo- and Dicycloalkanes, Alkenes	NF	9
Fused Cycloalkylaromatics	NF	14
2-Ring Aromatics or ???	NF	5
3-Ring Aromatics	NF	3
Cycloalkylbenzenes	NF	3

^a Obtained at a space velocity of 0.78 g of fraction/
(g of catalyst·h).

^b Not found.

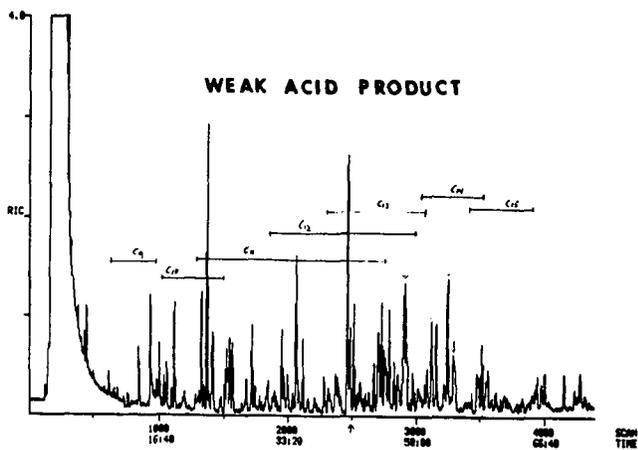


Figure 1

Weak Acid Product Ion Chromatogram

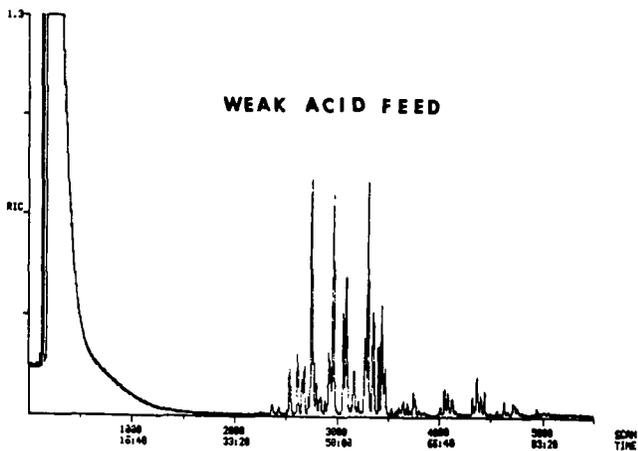


Figure 2

Weak Acid Feed Ion Chromatogram

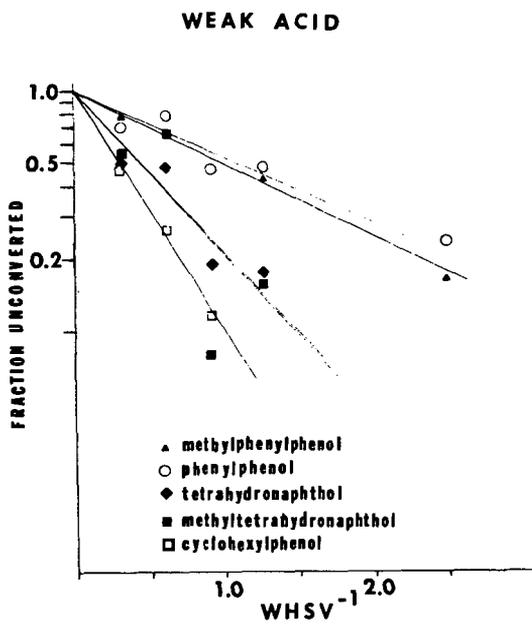


Figure 3

Fraction Unconverted vs. Inverse Space Velocity
Compounds in the Weak Acid