

CO-Steam Process: Functional Group Analysis of  
Non-Distillables in Lignite-Derived Liquids

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The CO-Steam process for conversion of lignite to boiler fuel consists of reaction of a finely ground slurry of lignite in hydrocarbon donor solvent with carbon monoxide and hydrogen at about 450° C and pressures up to 5000 psi (1). Recent studies at the Grand Forks Energy Research Center (GFERC) have utilized a preheated batch autoclave with gas and slurry phase sampling to establish optimum reaction conditions for reduction in molecular weight of the non-distillables in CO-Steam product (2,3). A study of the effect of the nature and quantity of non-distillables on coal liquid viscosity has pointed out the importance of reducing the quantity and molecular weight of non-distillables (4). This study also pointed out a relationship between weak acid concentration and percent oxygen in non-distillables, and product quality as indicated by solution viscosity.

CO-Steam products were separated into four fractions based on solubility in hexane, toluene, and tetrahydrofuran. The acidity of each fraction was determined by non-aqueous titration with tetramethyl ammonium hydroxide. The end point obtained indicated total oxygen acids (phenols) plus nitrogen acids (carbazoles). Table 1 lists the weight percent of each solubility fraction, and their measured acidities. Close agreement was obtained between measured acidities of total products and weighted sums of the acidities of the individual fractions. CO-Steam products A and B were produced in continuous reactors at Pittsburgh Energy Research Center using recycled CO-Steam oil as the slurry vehicle, while CO-Steam C was produced in our batch autoclave using 9:1 anthracene oil - tetralin as vehicle. Higher acidity of the oil fractions of A and B can be attributed to the buildup of phenols content during recycle of the solvent. Higher acidity of the other fractions of A and B can be partially explained by their higher molecular weight resulting from lower processing temperature. Figure 1 illustrates the relative acidity of the CO-Steam fractions in Meq H<sup>+</sup> per fraction per gram of total product.

CO-Steam products were separated by column chromatography on alumina into three fractions using a simplification of the method of Schiller and Mathiason (5). Fraction 1 (eluted by toluene) consisted of hydrocarbons, fraction 2 (eluted by chloroform, 1% ethanol) consisted primarily of nitrogen compounds, and fraction 3 (eluted by 9:1 tetrahydrofuran - methanol) consisted primarily of hydroxyl compounds as confirmed by mass spectrometry of the volatile constituents. Acid and base titrations confirmed the absence of acid-base reactivity in the hydrocarbon fractions. The nitrogen compound fractions were more acidic and more basic than the hydroxyl fractions, indicating the concentration of nitrogen acids and bases in fraction 2.

A matrix of parameters was developed to provide separate estimates of oxygen acids and nitrogen acids content from non-aqueous titration and elemental analysis data, regardless of mineral content of the sample. When applied to a set of SRCs and CO-Steam distillation residues, it was found that oxygen acids decreased linearly with molecular weight by gel permeation high pressure liquid chromatography, while nitrogen acids remained at a constant concentration (Figure 2). When model solutions were prepared from the SRCs and CO-Steam distillation residues with anthracene oil, it was found that log viscosity of 25 percent solutions decreased linearly with acidity due to oxygen acids, as well as total acidity in a parallel fashion. The constant difference in curves represents the unchanging concentration of nitrogen acids, despite the varying degree of depolymerization represented in the range of samples. These results imply that during coal

depolymerization: (1) the stable core of a preasphaltene or asphaltene molecule includes a carbazole, benzocarbazole, dibenzocarbazole or related nitrogen acid, and (2) extended processing to lower molecular weight (and thus lower viscosity) involves scission of bonds linking a phenolic oxygen acid to the stable core of the molecule. The calculation method is summarized as follows:

$$\begin{aligned}\% \text{ Basic N} &= 1.4 B \\ \% \text{ Acidic N} &= 100 N - 1.4 B \\ \% \text{ Acidic O} &= 1.6 A - 16/14 (100 N - 1.4 B) \\ \% \text{ Neutral O} &= 100 X - (1.6 A - 16/14 (100 N - 1.4 B))\end{aligned}$$

where:

A = (meq acid/g sample) -- by non-aqueous titration.  
B = (meq base/g sample) -- by non-aqueous titration.  
N = (g nitrogen/g sample) -- by Kjeldahl method.  
X = (g oxygen/g sample) -- by Neutron Activation Analysis.

Assumptions:

Neutral N = 0  
Basic O = 0  
Mineral content is neither acidic nor basic  
N and O are not amphoteric

Analysis of the recycle solvents of these SRC samples indicated that the concentration of carbazole and its methylated derivatives remained essentially constant, while the concentration of phenol and its methylated derivatives increased sixfold between SRC I and SRC II process conditions (6). These results are consistent with the hypothesis presented here.

#### REFERENCES

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Table 1. Properties of Solubility Fractions of CO-Steam Products

CO-Steam Product	A		B		C	
	Wt. %	MW	Wt. %	MW	Wt. %	MW
Solubility fractions.....						
Oil (hexane soluble).....	55.9	403	48.7	385	52.3	281
Asphaltene (toluene soluble hexane insoluble).....	22.6	554	18.4	542	22.8	345
Preasphaltene (THF soluble toluene insoluble)....	20.9	747	17.9	611	4.7	501
Tetrahydrofuran insoluble.....	0.6	---	15.0	---	20.2	---
Process Temp. (°C).....	425		450		470	
Acidity (Meq H <sup>+</sup> /g):						
Oil.....	1.587		1.361		0.513	
Asphaltene.....	1.945		2.449		0.873	
Preasphaltene.....	1.974		2.052		1.058	
THF insoluble.....	1.518		1.027		0.266	
Total Product.....	1.729		1.725		0.544	
Calculated Acidity <sup>a</sup> .....	1.748		1.635		0.571	

<sup>a</sup> Acidity calculated as the weighted sum of the acidities of the individual fractions.

Table 2. Acid-Base Content of Column Chromatography Fractions

	CO-Steam A		CO-Steam B	
	Acidity (Meq/g)	Basicity (Meq/g)	Acidity (Meq/g)	Basicity (Meq/g)
1. Hydrocarbons.....	0	0	0	0
2. N Fraction.....	---	0.724	3.687	0.942
3. OH Fraction.....	2.98	0.217	2.806	0.216

Table 3. Acid-Base Properties of Non-Distillables

Sample	Acidity (Meq/g)	Pct O	Basicity (Meq/g)	Pct N	Pct N Basic	Pct N Acidic	Pct O Acidic	Pct O Neutral
SRC 115	1.481	1.55	0.711	1.70	0.995	0.718	1.55	0
CO-Steam Residue B	1.938	3.72	0.476	1.23	0.67	0.56	2.46	1.26
CO-Steam Residue A	1.661	7.03*	0.449	1.15	0.63	0.52	2.07	4.96*
SRC 308	2.285	4.32	0.786	1.78	1.10	0.68	2.88	1.44
SRC 122	2.531	4.69	0.713	1.55	1.00	0.55	3.42	1.27

\* Not deashed; illustrates mineral oxygen.

Figure 1.

- A. PERC Stirred Reactor  
 B. PERC Tubular Reactor  
 C. GFERC Batch Reactor
- Solubility Fractions:**
-  Hexane Soluble (oil)
  -  Asphaltene (solid)
  -  Preasphaltene (solid)
  -  THF Insoluble (solid)

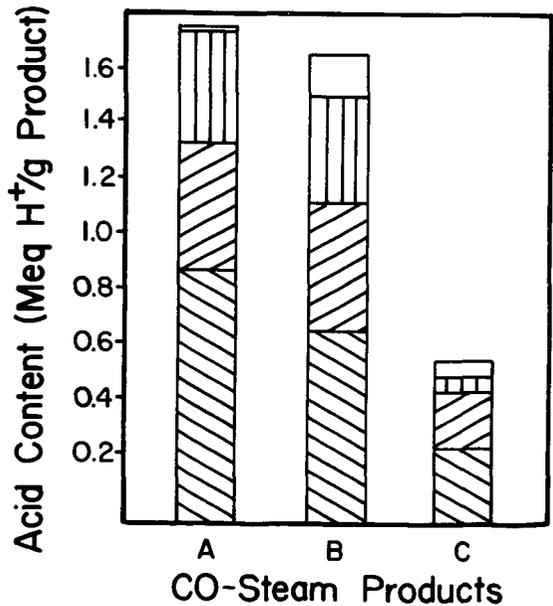


FIGURE 2

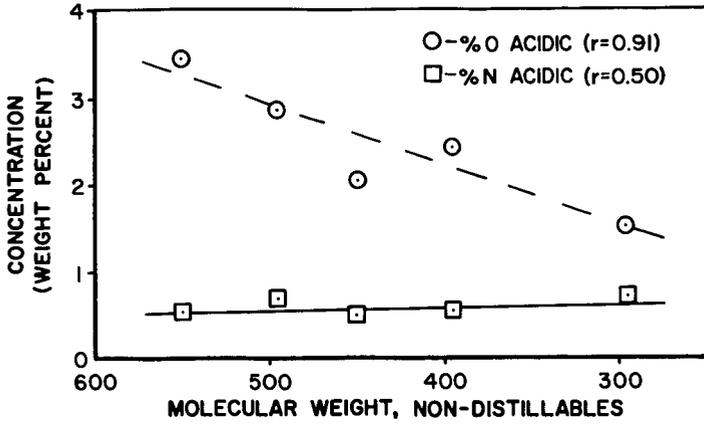


FIGURE 3

