COAL GASIFICATION AND THE PHENOSOLVAN PROCESS

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On the basis of current trends in the supply and demand of energy, the world faces a serious shortage of petroleum crude oil. In the U.S., the shortage of crude oil is compounded by an equally serious dwindling of natural gas supplies. Unless alternative energy supplies are developed, we face a tremendous economic drain on our capital resources from the high cost of imported crude oil.

Because of this situation, there has been a dramatic acceleration in the development of plans to produce clean-burning gas from coal (1). By 1976-1977, two such projects should be coming onstream in the Four Corners area of New Mexico (1,2), each producing 250 million standard cubic feet per day of substitute natural gas (SNG). Other coal gasification projects are under consideration and design for Wyoming, Montana and the Dakotas.

The New Mexico projects will each gasify about 25,000 tons per day of coal, and will each produce about 105-110 tons per day of byproduct crude phenol (2) -- as well as other byproducts. The gasification process uses steam, as a source of hydrogen, to produce methane SNG from the coal carbon. Byproduct crude phenol is recovered from the phenolic steam condensate (gas liquor) which results from condensing and removing the excess gasification process steam.

The projects in New Mexico will use the Lurgi* coal gasification process -- and the bulk extraction of crude phenol from the phenolic gas liquor will utilize Lurgi's Phenosolvan liquid-liquid extraction process.

COAL GASIFICATION

Figure 1 presents a simplified flow diagram of the process steps involved in the Western Gasification Company's project in New Mexico (2,3). As shown in Table 1, that project will process 52,700 tons/day of coal, steam, water and oxygen -- to produce 5,440 tons/day (250 MM SCFD) of SNG, plus 47,260 tons/day of byproducts which include the 105 tons/day of crude phenol (2,3). The pertinent process steps can be briefly summarized as (2,3):

Gasifiers -- reaction vessels wherein coal, steam and oxygen are reacted under controlled conditions to yield a crude gas containing methane, hydrogen, carbon oxides, excess steam, and various byproducts and impurities. Only some 40% of the plant's endproduct methane SNG is

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* Lurgi Mineralöltechnik GmbH, Frankfurt (Main), Germany. The projects in Wyoming, Montana and the Dakotas also plan to use Lurgi technology.

produced in the gasifiers. Subsequent reaction steps produce the remainder of the methane.

Gas Cleaning -- the cooled gas is cooled and scrubbed with water to remove tars, heavy oils and phenols. The tars and oils are recovered as byproducts. The phenolic water (gas liquor) is processed in a subsequent step (Phenosolvan extraction) for recovery of byproduct phenol.

Shift Conversion -- excess carbon monoxide in the crude gas is catalytically "shifted" (converted) to carbon dioxide to provide the 3-to-1 ratio of hydrogen-to-carbon monoxide required for additional methane synthesis in the subsequent methanation step.

Gas Cooling -- the shifted gas is again cooled to remove additional oil byproducts and any residual phenolic gas liquor.

Acid Gas Removal -- the Rectisol absorbtion process, using low temperature methanol, selectively removes hydrogen sulfide and carbon dioxide from the cooled gas. Pre-cooling at the Rectisol unit entry recovers byproduct naphtha.

Methanation -- carbon monoxide and hydrogen are catalytically combined to form methane and byproduct water. About 60% of the endproduct SNG is produced in this step.

Compression -- the final dry and purified gas is compressed and then delivered to the pipeline with a heating value of about 980 Btu/SCF.

Phenosolvan -- the gas liquors, from the gas scrubbing and gas cooling steps, are processed in a Phenosolvan unit. Crude phenol is extracted and recovered as a byproduct. The residual water effluent is further processed in a biotreating unit and then reused within the plant.

Auxiliary Services -- the auxiliary units include cryogenic air fractionation to supply oxygen to the gasifiers, a Claus sulfur plant to convert gaseous hydrogen sulfide (removed by the Rectisol unit) to byproduct sulfur, a steam boiler plant, a cooling water system, and wastewater treating and reuse systems.

PHENOSOLVAN PROCESS

The Phenosolvan process is a liquid-liquid extraction process developed by Lurgi and first commercialized in about 1940. The process was originally developed to extract phenols from the aqueous gas liquor obtained in coke oven plants. Since 1940, about 32 commercial Phenosolvan plants have been installed worldwide, ranging in capacity from 2 to 1000 gallons per minute of gas liquor throughput.

Figure 2 presents a simplified flow diagram of the Phenosolvan process as proposed for use in the New Mexico coal gasification projects (2). The incoming gas liquor is filtered through a gravel bed and then contacted with solvent (isopropyl ether) in multi-stage mixer-settlers. The phenol-rich solvent (extract) is distilled to recover lean solvent for reuse, and then stripped to remove and recover residual solvent. The dephenolized liquor (raffinate) is gas-stripped to remove and recover solvent. The liquor is then steam-stripped to remove acid gases (hydrogen sulfide and carbon dioxide), followed by steam-stripping to remove ammonia.

Some knowledge of the phenols and other organics, that may be present in the gas liquor, is needed to predict the extraction performance of the Phenosolvan unit. In general, the Phenosolvan process will extract more than 99% of the mono-hydric phenols, but the gas liquor will contain organics other than mono-hydric phenols.

As a generic term, "phenols" include 6,7 and 8-carbon aromatics with one hydroxyl group -- the mono-hydric phenol, cresols, xylenols and ethylphenols. "Phenols" also include poly-hydrics having two or more hydroxyl groups such as catechol and resorcinol, which are benzene $[C_6H_4(OH)_2]$ isomers (4).

The expected composition of the gas liquor produced in a coal gasification plant is proprietary information. It will vary with different coal supplies and it will vary with different gasification processes and conditions. However, based on published literature (5,6, 7,8) furnished by Lurgi, the mono-hydric phenols may constitute as much as 75-85% of the organics in the gas liquor. The poly-hydrics in the gas liquor may be as much as 34% of the total phenols(7). The gas liquor may also contain organic bases (pyridines), neutral oils, and perhaps other organic acids (for example, naphthenic acids). Lowenstein-Lom's studies (9) of gas liquors from Czechoslovakian coal carbonization plants confirms that the phenolic extracts may contain as much as 75-80% mono-hydrics, and as much as 30-35% poly-hydrics including pyrocatechol, resorcinol and their homologues.

For the purposes of this paper and based on the above published literature, it has been assumed that the crude phenol extracted from the coal gasification gas liquor will contain (on a water- free basis):

85% mono-hydric phenols
15% poly-hydric phenols
5% other organics

We may also assume that the mono-hydric phenol distribution coefficient (K_D) for the system isopropyl ether-phenol-water is 20, and that the weight flow ratio of liquor to solvent (W/S) is 10 for a typical design(5). With these assumptions, we may use the following equation for multi-stage extraction with a perfectly lean solvent (4) to predict the extraction recovery of mono-hydric phenols:

$$x_w/x_n = \frac{E^{n+1} - 1}{E - 1} \qquad 1)$$

where: $E = K_D(S/W) = 20(1/10) = 2$
n = equilibrium extraction stages
x_w = phenols in entering liquor
x_n = phenols in exiting liquor
$x_w/x_n = 1000$ for 99.9 % extraction

Equation 1 confirms that 9 equilibrium extraction stages will extract 99.9% of the mono-hydric phenols, and that number of equilibrium stages would probably be a reasonable design.

Based on Weisner's paper furnished by Lurgi (8), the Phenosolvan process may extract as much as 70% of the organics other than mono-hydric phenols. Lowenstein-Lom (10) determined phenol and catechol

distribution coefficients for over 40 possible solvents, including 6 aliphatic ethers. For the ethers, his data indicate that the catechol K_D averaged 35% of the phenol K_D (the range was 20-52%). If we therefore assume a catechol K_D of 7 (which is 35% of the phenol K_D of 20 used above), and we use 9 equilibrium stages, we can obtain from Equation 1:

$$x_w/x_n = \frac{0.7^{10} - 1}{0.7 - 1} = 3.24$$

$$\text{If } x_w = 100, \text{ then } x_n = 30.8$$

Thus, the catechol extraction would be about 70% which generally confirms Weisner's (8) statement regarding extraction of organics other than mono-hydric phenols.

For the purposes of this paper, based on the above, it has been assumed that extraction recoveries in the coal gasification plant Phenosolvan unit will be about:

99.5% for mono-hydric phenols
60.0% for poly-hydric phenols
15.0% for other organics

Finally, based on a gas liquor rate of 2,700 gallons per minute for the Western Gasification Company's project (2,3), Table 2 presents a calculated material balance for the Phenosolvan unit using the assumptions derived above. As shown in Table 2, the 105 tons/day of extracted byproduct crude phenol represents an overall removal of 75% of the organics that may be contained in the gasification plant gas liquor.

Using BOD_5 factors that can be obtained from stoichiometric oxygen demands, and the assumption that BOD_5 is 68% of the stoichiometric, Table 2 estimates that the incoming gas liquor will have a BOD_5 of about 13,000 ppm. This will be reduced about 84% to yield an effluent liquor with a BOD_5 of about 2,150 ppm. [For those who are unfamiliar with BOD_5 and stoichiometric oxygen demands, Beychok has published a fairly complete discussion of these and other terms related to wastewater quality (11)]

SUMMARY

A number of large coal gasification projects are under serious consideration in the Western United States. Two of these should start full-scale operations in New Mexico during 1976-1977 -- each gasifying about 25,000 tons/day of coal and each producing about 250 MMSCFD of methane SNG. These New Mexico projects will each produce about 105 ton/day of byproduct crude phenol.

The crude phenol byproducts will be extracted in Phenosolvan units, which have been extensively used in similar applications worldwide since about 1940. The Phenosolvan process uses isopropyl ether solvent for the liquid-liquid extraction of phenolics from the liquors produced from coal gasification. For the Western Gasification Company coal gasification project, planned for New Mexico, this paper has estimated that the Phenosolvan process will recover 105 tons/day of

crude phenol from 2,700 gallons per minute of gas liquor containing about 142 tons/day of various phenols and other organics. The estimated phenol recovery will reduce the gas liquor BOD_5 about 84% and the effluent liquor from the Phenosolvan unit will be further processed in a biotreater before being completely reused within the plant.

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TABLE 1

LURGI GASIFICATION MATERIAL BALANCE

(Basis: 250 MMSCFD of SNG product gas)

		Short Tons per day	Weight %
INPUTS:			
	Sized coal	21,860	41.48
	Steam and water	25,160	47.74
	Oxygen	5,680	10.78
	TOTAL	52,700	100.00
OUTPUTS:			
	Product gas	5,440	10.32
	Crude phenol	105	0.20
	Ash	5,876	11.15
	Reuse water	17,851	33.87
	Byproduct water[a]	3,730	7.08
	Tars, oils and naphtha	1,475	2.80
	Offgas to sulfur plant[b]	792	1.50
	CO_2 vent gas	16,631	31.56
	Ammonia and water[c]	800	1.52
	TOTAL	52,700	100.00

Notes:

a -- Water produced in methanation reaction, and also reused.
b -- Contains 183.7 tons/day of sulfur in form of hydrogen sulfide
c -- Contains approx. 180 tons/day of free ammonia

TABLE 2

CALCULATED PHENOSOLVAN MATERIAL BALANCE

(for coal gasification gas liquor)

	FEED LIQUOR		EFFLUENT		CRUDE PHENOL	
	lbs/hr	ppm	lbs/hr	ppm	lbs/hr	wt %
Water, 10^6 lbs/hr	1.35	-	1.35	-	-	-
Mono-hydric phenols	7,475	5,537	37	27	7,438	85
Poly-hydric phenols	1,458	1,080	583	432	875	15
Other organics	2,913	2,158	2,476	1,834	437	5
TOTALS, water-free	11,846	8,775	3,096	2,293	8,750	100
TOTALS, water-free, tons/day	142	-	37	-	105	-
BOD_5 (estimated), ppm	-	12,976	-	2,151	-	-

Basis:

(a) 2700 gallons per minute (1.35 x 10^6 lbs/hr) of water flow

(b) 105 tons/day of extracted crude phenol

(c) Assumed composition of crude phenol:
85% mono-hydric phenol
15% poly-hydric phenol
5% other organics

(d) Assumed extraction recoveries:
99.5% for mono-hydric phenols
60.0% for poly-hydric phenols
15.0% for other organics

(e) BOD_5 factors:
mono-hydric phenols = 1.7
poly-hydric phenols = 1.9
other organics = 0.7

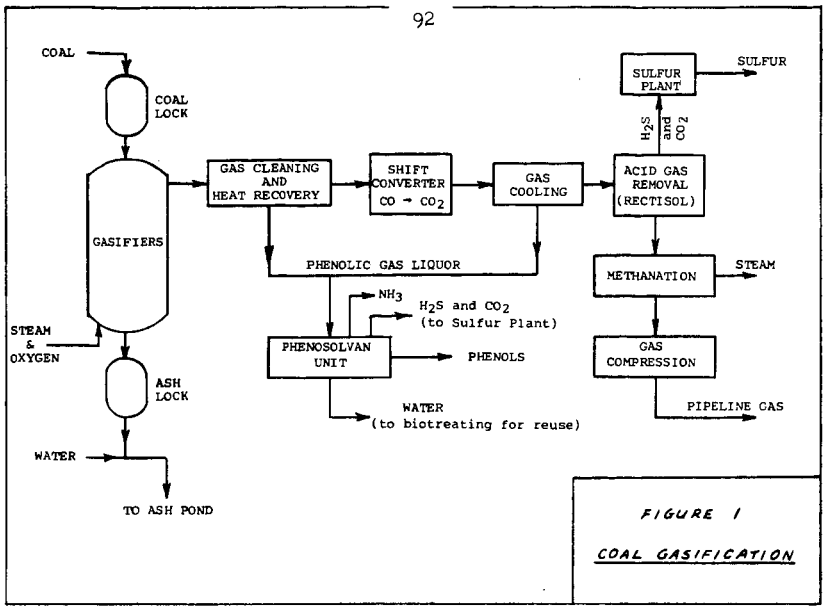


FIGURE 1

COAL GASIFICATION

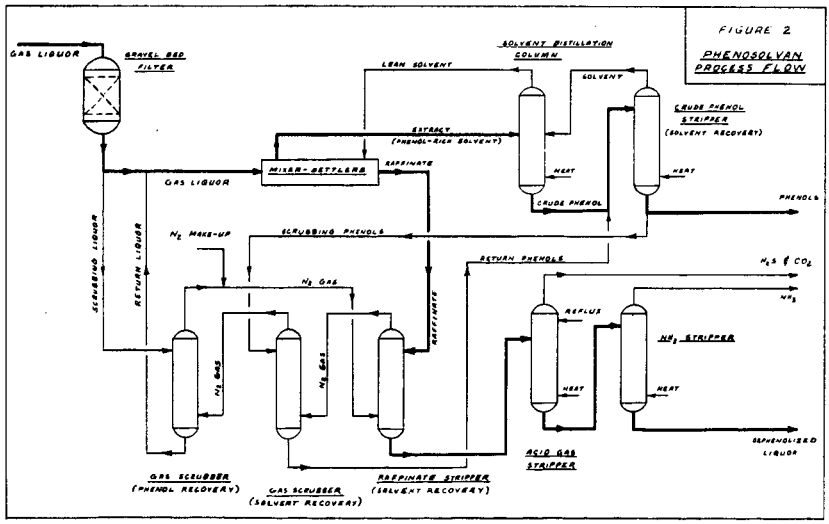
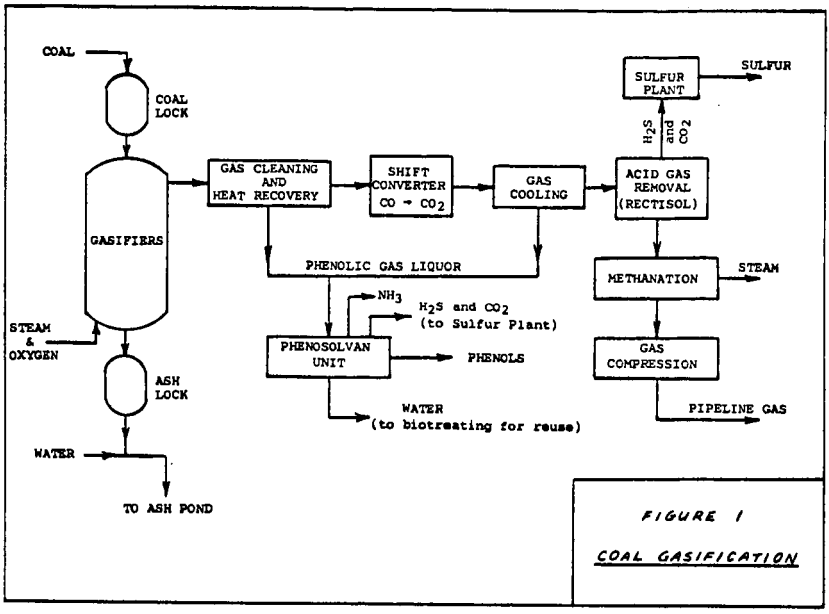


FIGURE 2

PHENOSOLVAN PROCESS FLOW



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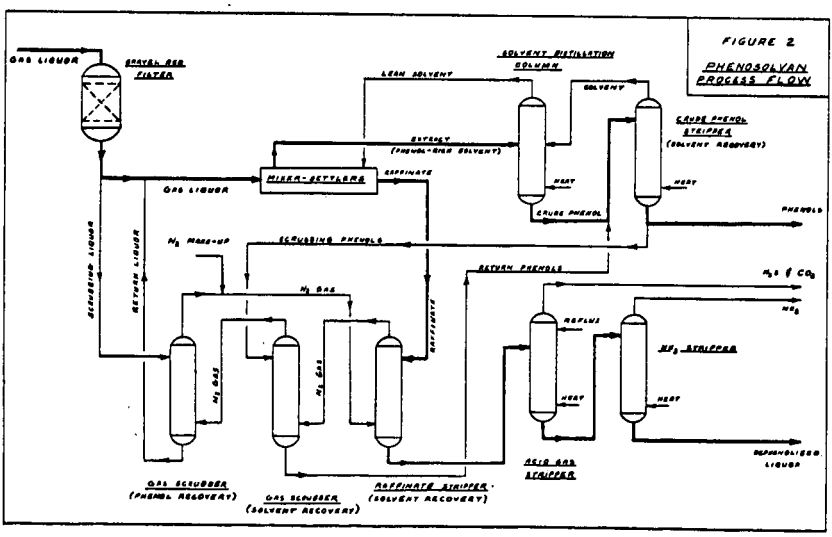

FIGURE 2

PHENOSOLVAN PROCESS FLOW