

Sampling, Analysis and Characterization of Effluents from the Grand Forks Energy Research Center's Slagging Fixed-Bed Gasifier

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INTRODUCTION

The Grand Forks Energy Research Center is operating a slagging fixed-bed coal gasification pilot plant. The pilot plant was previously operated from 1958 to 1965 to establish operability of the slagging method of ash discharge and to evaluate process parameters (1, 2). Operation was resumed in April 1976 with the major objectives being to study the effluents produced in gasification. In this report, methods currently used at GFERC to sample and analyze effluents are presented and results are related to gasifier operation.

GFERC GASIFIER

A flowsheet of the GFERC pilot plant is given in Figure 1. Recent publications (3-6) have discussed the test equipment and procedures in detail. A brief summary will be provided here.

The test coal is introduced into the gasifier through a lock hopper. As the coal descends through the shaft, it is heated by the countercurrent flow of hot gases coming from the reaction zone. Drying, devolatilization, and gasification occur in distinct zones in the coal bed (7). The coal is reacted with a steam-oxygen mixture which is injected into the hearth. Gasification occurs at temperatures of 2800-3100° F, completely consuming the coal and leaving only slag. The molten slag drains continuously into a water quench bath. The gas enters a recycled liquor spray washer where water vapor, tars, oils, and dust are removed. The accumulating liquids are periodically drained into an atmospheric holding tank. The gas is further cooled, sampled, depressurized, demisted, metered, and flared. A typical gas composition is 58% CO, 29% H₂, 5% CH₄, and 7% CO₂, with small amounts of C₂-C₄ hydrocarbons.

COAL TESTED

All tests described in this report were performed with Indian Head lignite obtained from the North American Coal Company mine in Mercer County, ND. The moisture content of the coal as mined ranged from 35 to 37%. Due to moisture loss during handling and storage, the moisture content of the coal tested ranged from 23 to 30%. Table 1 shows a typical analysis for as-gasified coal and the range of observed analyses.

SAMPLING METHODS

Collecting representative and reproducible samples of effluents produced by the gasifier presents special problems because the system is under pressure and the streams that are sampled contain a multiphase combination of gas, water and organic vapors and/or aerosols, and entrained fuel particles. At GFERC several sampling methods and procedures are being developed to address these problems. These include; collecting a composite of the total liquor generated during a run, periodically collecting samples of recycle liquor circulated through the spray washer system, and by using sampling trains attached to product gas stream. Figure 1 shows the location of the sampling points.

Composite samples of tar and water produced during the entire test are collected from the liquor accumulated in the holding tank after phase separation and weighing. Component concentrations and quantities of water collected are corrected for system start-up water.

The recycled condensate liquor is sampled at each coal charge which represents a timed data period. The mass production rate and concentration of each component generated are determined by differences in liquid analysis and inventory between samplings.

Schematics of three sampling trains are shown in Figure 2. Each of these units operate slightly above atmospheric pressure and remove condensibles from a side stream of raw gas produced by the gasifier. Sampler I is a four staged heat exchanger. Tar is collected in Stage 1 (maintained at 212° F), Stages 2, 3, and 4 cool the gas progressively to 32° F and condense and collect water and light oil. Gas flow rate to the sampler is less than 1 pct of the total gas produced. The first stage of sampler II is a cyclone which removes tar. In Stage 2 and 3 water and oil are removed by heat exchange which cools the gas to 40° F. This sampling system will be fully described in a separate publication in the near future. Sampler III consists of four steel impingers in series immersed in an ice bath. A fourth system using on-line gas chromatographs to measure mass rates of water and tar in product gas is under development, and will also be described in a separate publication.

ANALYTICAL METHODS

The dissolved solids, specific gravity, pH, alkalinity, ammonia, and sulfide content are determined by wet chemical methods described in the literature (8). Instrumentation includes a Hach model 16500 reactor for chemical oxygen demand (COD), a Beckman model 915A total organic carbon (TOC) analyzer, and a Leco model 532 total sulfur analyzer. Organic species are identified using a DuPont 491B mass spectrometer (MS).

Although a large body of literature exists regarding the preparation, preservation, and analytical methods for liquor samples, it appears that, at least to an extent, the effluent generated by each gasifier is unique, requiring slight modifications to existing analytical procedures. For example, experience at GFERC has shown that wet chemistry procedures for sulfide and cyanide as reported in the literature have not given satisfactory precision. The modified analytical procedures developed at GFERC will be detailed in future publications. A cooperative program with Carnegie Mellon University is in progress in which the accuracy and precision of most of the procedures used at GFERC will be studied.

The reproducibility of the procedures for analyzing tar-free liquor is shown in Table 2. Each test is run on aliquots, treated identically before analysis. Table 2 shows the replicate values, the average, standard deviation, and coefficient of variation (9). Coefficient of variation is 10% or less, indicative of good reproducibility, for all tests except COD, for which the value is 13.6%. The reproducibility of MS analysis for tar has been reported previously (6).

EFFLUENT PRODUCTION

The mass rates of water, tar, ammonia, and TOC produced during seven gasification runs are shown in Table 3. These runs represent a range of operating pressures from 100 to 400 psi, oxygen rates of 4000 and 6000 scfh, and coal moisture contents from 22 to 30%. The oxygen/steam molar ratio was 1.0. Mass rates were separately calculated from data from the composite samples, recycle liquor samples, and side stream samplers I and II. For each run the composite consists of a single sample representing the entire run. Depending on run

organic material, while the remaining fraction consisted of heavier organic components. If a sample is filtered with a .45 micron millipore filter, most of the material of mass greater than xylene will be removed.

Tar Composition

The MS analysis of tar from RA-21 is shown in Table 6. Shown in the table is the analysis of tars from side stream samplers I, II, and III and from the composite. Results indicate that the MS analysis of the tars collected in the various samplers was similar and that the composition of tar does not greatly change during the run. Additional analytical data of the tars can be found in reference (6).

FUTURE PLANS

The pilot plant facilities are being upgraded with the objective of achieving 5 day continuous operation and the capability of gasifying caking bituminous coal. If a higher gas offtake temperature occurs in bituminous coal gasification as expected, revision of sampling methods will be required.

The use of dedicated samplers to collect a specific effluent constituent will provide improved characterization. For example, future installation of an isokinetic sampling system incorporating filter and impinger trains will allow collection and characterization of the dust in the gas stream. Similarly an impinger train containing an appropriate acidic collector and a preservative will be used for sampling ammonia.

The development of methods for measuring trace element constituents in gas, liquor, and tar is an area in which future work is planned. The trace constituents consist of metallic elements such as mercury, arsenic, and antimony; sulfur compounds such as carbonyl sulfide, carbon disulfide, and mercaptans; and non-metallics such as selenium, chlorine, fluorine, and phosphorous. As sample preparation methods are developed, it will become possible to calculate material balances for the various trace elements and to determine the fate of those compounds in the gasification process.

Proper design of downstream gas-liquor-tar separation and treatment systems will require knowledge of the physical properties of the effluent streams as well as their chemical composition. Thus determination of viscosity, density, and other scalable physical properties represents another area in which work is needed.

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duration, the recycle liquor data is derived from up to seven data periods, each representing the time interval between coal charges. The data from each side stream sampler represents up to three samples, each collected over three data periods.

The results are influenced by inaccuracies of analytical procedures, limitations in duration of gasifier operating time, and difficulties in accounting for system water inventory during the test period.

A comparison of mass rates calculated for a given run from data for the composite, recycle, and side stream samples generally shows consistency between the sampling methods. For example, for run RA-12 the mass rates in lbs/ton maf coal gasified range from 988 to 1059 for water, 6.9 to 7.1 for ammonia, 9.4 to 10.4 for TOC, and 70 to 80 for tar.

Replication between tests run at the same conditions is shown by comparing RA-11 and -12, both run at 200 psi, and by comparing RA-14 and -16, both run at 400 psi. All of these tests were run on lignite with moisture that ranged from 24 to 26% and at an oxygen rate of 4000 scfh. The pounds of ammonia produced per ton maf coal ranged from 6.1 to 7.6 in RA-11 and from 6.9 to 7.7 in RA-12. The pounds of tar produced per ton maf coal was 70.6 for RA-11 and ranged from 69.6 to 79.4 for RA-12.

Side stream sampler II was first tested in RA-16. Results obtained using this system in RA-16, -17, and -21 (all at 400 lbs pressure) are consistent. RA-16 and -21 were performed at an oxygen rate of 4000 scfh on coal of 23.9 and 30.5 pct moisture respectively while RA-17 was run at an oxygen rate of 6000 scfh and a coal moisture of 22.8 pct. Water production rate in lbs/ton maf coal was 831 and 844 for tests RA-16 and -17, and 913 for the higher moisture coal gasified in RA-21. Ammonia production rate in lbs/ton maf coal was 9.8 for RA-16, 8.2 for RA-21, and 9.7 for RA-17. Dissolved organics (TOC) production rate in lbs/ton maf coal was 8.2, 9.0, and 7.5 for the three tests and tar production on the same basis was 58.1, 52.0, and 55, respectively.

EFFLUENT COMPOSITION

The composition of the effluent generated in the seven gasifier runs previously described is shown in Table 4. Results are based on composite samples and are corrected for water introduced in start up and shutdown.

Of special interest is the fact that approximately 3 to 6 pct of the carbon and 27 to 50 pct of the nitrogen from the coal is present in the effluent. The carbon in the effluents includes carbon particles, dissolved organics and tar. The nitrogen in the effluent includes ammonia in the liquor and nitrogen in the tar.

The relationship between gasifier operating pressure and ammonia concentration in the effluent is shown in Figure 3. The results were based on runs RA-11, -12, -14, -16, and -18 using the four sampling methods previously described. Results indicate that the ammonia concentration in the liquor increases with pressure. There appears to be no similar relationship between gasifier operating pressure and dissolved organic concentration in the liquor.

The aqueous fraction of gas liquor contains a variety of water soluble and semi-soluble organics. Table 5 shows an MS analysis of the organic material in this fraction from the composite sample of RA-14. This sample was cleanly skimmed of all apparent tar, but was not filtered. This sample would be expected to be typical of the liquor in a waste water treatment plant before phenol extraction. The phenolic grouping (phenol, cresol and xyleneol) accounted for approximately 80 pct of the

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TABLE 1. - Analyses of lignites tested, percent

	Typical analysis	Range for lignite as tested	Typical analysis	Range for lignite as tested
Proximate analysis, pct:				
Moisture.....	25.8	23.9 30.5	6.0	5.8 6.5
Volatile matter.....	31.1	29.2 32.1	47.1	43.9 49.5
Fixed carbon.....	34.5	32.3 36.9	.6	.6
Ash.....	8.6	6.2 10.9	37.0	34.9 40.5
			.7	.5
			8.6	6.2 10.9
Ultimate analysis, pct:				
Hydrogen.....				
Carbon.....				
Nitrogen.....				
Oxygen.....				
Sulfur.....				
Ash.....				
Heating value, Btu/lb, as received.....			7790	7290 8232

TABLE 2. - Comparison of the reproducibility of specific analytical tests

Tests	Replicates			Average	Standard deviation	Relative standard deviation
Ignited dissolved solids.....ppm..	105	87	91	94	9.4	10
Dissolved solids.....ppm..	1,499	1,296	1,396	1,384	82.2	6
Total organic carbon.....ppm..	4,650	4,550	4,700	4,633	76.4	1.6
Specific gravity.....ppm..	1,0073	1,0079	1,0075	1,0076	.0003	.03
pH.....	8.33	8.27	8.21	8.27	.067	.7
Alkalinity CaCO ₃ppm..	12,235	12,974	13,012	12,740	438	3.4
Ammonia.....ppm..	4,065	4,298	4,266	4,210	126	3.0
Sulfur.....ppm..	881	876	877	875	7	0.8
Sulfide.....ppm..	136	144	152	148	10	7.0
COD.....ppm..	11,040	11,040	9,200	11,040	1,500	13.6

TABLE 3. - Comparison of mass rate of effluents produced by different sampling methods, RA-11 through -21a/

Test run number.....	RA-18	RA-11	RA-12	RA-14	RA-16	RA-21	RA-17
Operating conditions:							
Gasifier operating pressure.....	100	200	200	400	400	400	400
Oxygen rate.....psig..	4,000	4,000	4,000	4,000	4,000	4,000	6,000
Steam-oxygen rate.....scfh..	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Coal moisture.....pct..	22.8	25.3	24.2	23.9	23.9	30.5	22.8
Gas production.....scfh..	20,108	20,125	20,460	20,006	20,079	19,765	29,637
EFFLUENT PRODUCTION:							
Water Production lb/Ton MAF Coal:							
End of run composite.....	990	822	1,059	624	849	1,190	871
Recycle water.....	874 ± 109	899 ± 156	1013 ± 57	1009 ± 30	1001 ± 72	1080 ± 177	821 ± 129
Side stream sampler I.....	886 ± 93	b/	988 ± 32	b/	838 ± 71	1340 ± 86	807 ± 90
Side stream sampler II.....	1044 ± 11	b/	b/	b/	831	913 ± 12	844 ± 26
Ammonia Production lb/Ton MAF Coal:							
End of run composite.....	6.5	6.1	7.1	6.0	7.2	9.2	8.7
Recycle water.....	5.7 ± 0.5	7.6 ± 0.1	6.9 ± 2.6	9.9 ± 2.0	9.3 ± 1.2	8.3 ± 0.8	8.7 ± 2.0
Side stream sampler I.....	5.7 ± 0.9	b/	7.7 ± 0.5	b/	7.7 ± 0.6	9.2 ± 0.2	7.5 ± 0.5
Side stream sampler II.....	7.8 ± 0.6	b/	b/	b/	9.8	8.2 ± 0.8	9.7 ± 0.5
Dissolved Organic Production lb/ Ton MAF Coal:							
End of run composite.....	9.7	17.3	10.4	6.3	10.4	12.9	8.2
Recycle water.....	8.0 ± 0.9	13.0 ± 4.6	9.4 ± 1.9	11.2 ± 3.4	10.0 ± 0.8	9.2 ± 2.4	8.3 ± 2.8
Side stream sampler I.....	8.4 ± 0.8	b/	9.7 ± 0.7	b/	7.7 ± 1.0	13.5 ± 1.25	6.2 ± 0.1
Side stream sampler II.....	10 ± 1.0	b/	b/	b/	8.2	9.0 ± 0.5	7.5 ± 0.2
Tar Production lb/Ton MAF Coal:							
End of run composite.....	92.4	70.6	69.6	50.6	60.4	70.4	71.9
Recycle water.....	b/	b/	b/	b/	b/	b/	b/
Side stream sampler I.....	105 ± 4	68.5 ± 10.9	79.4 ± 10.9	87.9	55.6 ± 6	98 ± 23	87 ± 11
Side stream sampler II.....	95 ± 6	b/	b/	b/	58.1	52 ± 2	55 ± 10

a/ Data expressed as x ± y indicates an average of several values and the standard deviation.
b/ Not determined.

TABLE 4. - Effluent data from composite spray washer samples

Test run number.....	RA-18	RA-11	RA-12	RA-14	RA-16	RA-21	RA-17
Test run condition:							
Gasifier operating pressure.....psig..	100	200	200	400	400	400	400
Oxygen rate.....scfh..	4,000	4,000	4,000	4,000	4,000	4,000	6,000
Coal moisture.....pct..	22.8	25.8	26.3	24.2	23.9	30.5	22.8
Liquor analysis:							
pH.....	8.7	8.56	8.54	8.9	9.0	8.6	9.6
Alkalinity, ppm as CaCO ₃	13,786	b/	14,516	13,500	19,470	14,800	20,873
Turbidity, JTU.....	b/	b/	62	43	66	b/	b/
Conductivity, MHO.....	18,000	b/	21,500	b/	b/	b/	19,000
TOC, concentration _a /.....ppm..	9,747	21,040	9,847	10,015	12,205	10,800	9,204
NH ₃ , concentration _a /.....ppm..	6,544	7,420	6,704	9,605	8,500	7,721	9,953
Total dissolved solids _a /.....ppm..	8,025	5,261	3,579	2,924	4,840	3,743	9,190
Inorganic dissolved solids _a /.....ppm..	321	352	397	418	291	293	465
Sulfur, concentration _a /.....ppm..	b/	b/	b/	b/	b/	593	413
Sulfide, concentration _a /.....ppm..	b/	b/	b/	b/	b/	415	210
Elemental production rate and mass balance:							
Carbon in effluent.....lb/ton MAF coal...	86.1	78.6	71.8	49.3	61.8	71.1	74.6
Nitrogen in effluent.....lb/ton MAF coal...	7.1	6.6	7.5	6.4	7.9	9.6	9.3
Sulfur in effluent.....lb/ton MAF coal...	b/	b/	b/	b/	b/	1.1	.7
Pct of coal carbon in effluent.....	6.1	5.7	5.2	3.6	4.4	5.0	5.3
Pct of coal nitrogen in effluent.....	40.6	28.6	35.1	27.6	33.4	36.9	48.3
Pct of coal sulfur in effluent.....	b/	b/	b/	b/	b/	4.6	3.8

a/ All concentrations are corrected for start up water.

b/ Not determined.

TABLE 5. - Mass spectrometer analysis of organics liquor in aqueous fraction from composite sample RA-14

Component	ppm	Percent
Phenol.....	5,647	56.4
Cresol.....	1,965	19.6
Xylenol.....	453	4.5
Methylnaphthalene.....	34	0.3
Biphenyl.....	19	0.2
Dimethylnaphthalene.....	26	0.3
Fluorene.....	17	0.2
Carbazole.....	9	0.1
Dibenzofuran.....	74	0.7
Phenanthrene.....	318	3.2
Methyl benzofuran.....	101	1.0
Methylphenanthrene.....	76	0.7
Pyrene/Fluoranthene.....	100	1.0
Methylpyrene.....	178	1.8
Benzonaphthofuran.....	68	0.7
Chrysene.....	12	0.1
Benzopyrene.....	71	0.7

TABLE 6. - Mass spec analysis of tars from gasifier run RA-21, percent

Sampling method.....	Sampler I			Sampler II			Sampler III		End of run Composite thru shutdown
	2 & 3	4 & 5	6 & 7	2 & 3	4 & 5	6 & 7	2 thru 7	1 thru 7	
Test period.....									
Phenols.....	24.3	22.8	26.7	23.2	32.6	29.0	33.0	33.0	23.1
Naphthols.....	3.3	4.1	4.4	3.9	3.7	4.5	4.6	4.6	4.8
Dihydroxybenzenes.....	2.3	2.9	3.5	2.1	3.4	3.4	4.0	4.0	2.7
Naphthalenes.....	11.0	10.9	11.2	11.1	12.5	11.3	14.4	14.4	9.5
Aromatic Hydrocarbons with 3 to 5 rings.....	8.2	11.2	9.4	9.6	5.4	6.6	9.3	9.3	5.7
Saturated Hydrocarbons.....	3.3	4.3	5.5	6.9	4.0	4.5	2.7	2.7	6.6
Non Volatile at 300° C and .1 torr.	6.8	8.4	6.2	5.0	3.8	6.2	8.7	8.7	10.7
Average Mol wt of Volatile Compounds.....	147	154	150	151	140	145	145	145	139

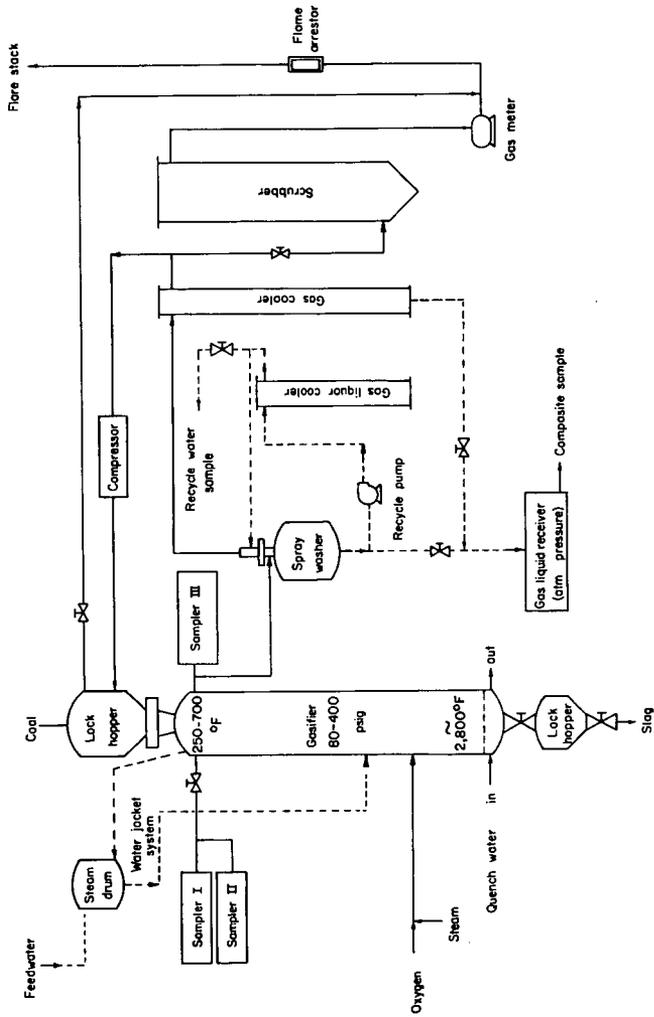


Figure 1. - Schematic of Grand Forks Energy Research Center slagging gasifier pilot plant.

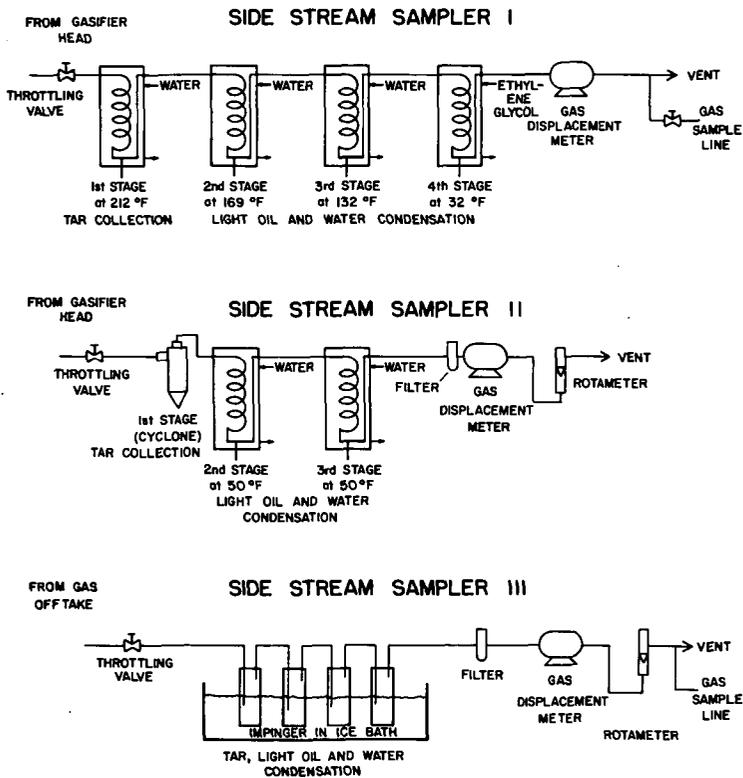


Figure 2. - Sampling trains used to condense effluents from gas stream.

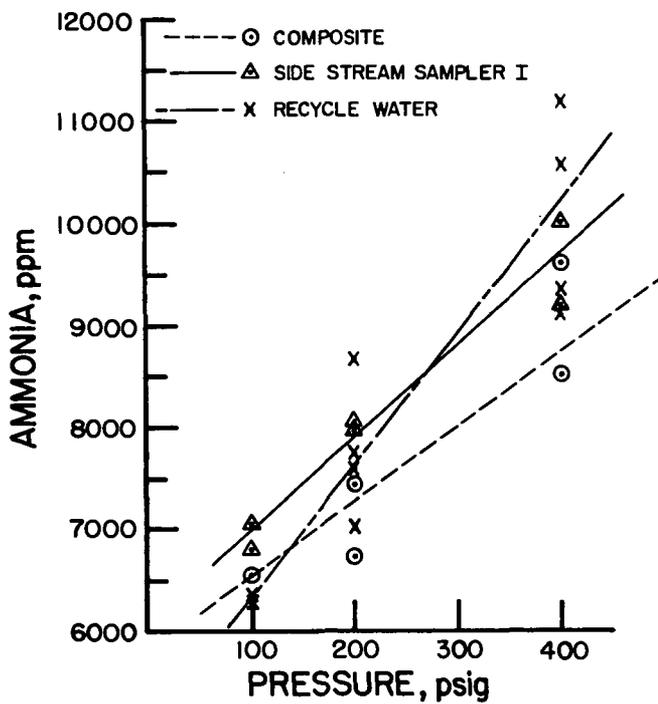


Figure 3. - Ammonia concentration in liquor as a function of gasifier pressure.