THE VISCOSITY-TEMPERATURE-TOTAL SOLIDS
RELATIONSHIP OF SULFATE BLACK LIQUORS

October 1942

No. R1416

UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY
Madison, Wisconsin
In Cooperation with the University of Wisconsin

THE VISCOSITY-TEMPERATURE-TOTAL SOLIDS RELATIONSHIP OF

SULFATE BLACK LIQUORS

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SYNOPSIS

Sulfate black liquors increase in viscosity with increased concentration.
Above a total solids concentration of 40 percent, the viscosities of the
liquors rise rapidly with increases in concentration, but are markedly de-
creased by increases in temperature. At concentrations of less than 40
percent the viscosities are, relatively speaking, not much greater than that
of water, and the effect of temperature is relatively slight.

INTRODUCTION

In the evaporation step incident to recovery of chemicals from sulfate black
liquors, the liquors are usually concentrated in multiple-effect vacuum
evaporators to total-solids contents ranging from 55 to 60 percent. In
this evaporating process the flow of the liquor and the transfer of heat to
the liquor are two problems confronting both the equipment designer and the
operator. Since the viscosity of a liquid is an important factor (5) in
both of these considerations, the investigation reported here was undertaken
with the objective of measuring the viscosity changes which occur with
changes in temperature and concentration of several sulfate spent or black
liquors.

MATERIALS AND PROCEDURE

Three black liquor samples, designated as liquors A, B, and C, were studied.
Sample A was a commercial sulfate black liquor secured from a Wisconsin mill.
Sample B was a laboratory semicommercial loblolly pine sulfate black liquor,
and sample C was a laboratory semicommercial jack pine sulfate black liquor.
As these black liquors resulted from various cooking conditions, they can
best be characterized by the data in table 1.

Several samples of each were evaporated on a steam bath. Total solids of these samples were determined and several batches of each liquor of various total solids content were prepared from the concentrated liquor. In cases where the concentrated samples were used prior to making more dilute solutions, the total solids content of the samples so obtained was determined. In no case was the concentration of a liquor carried beyond 60 percent of total solids.

The total solids were determined by means of a modification of the method described by Griffin (2): A sample of black liquor (20 to 50 cc. depending on the approximate concentration of the liquor) was weighed, diluted to 500 cc. with water in a volumetric flask, and mixed thoroughly. A 50-cc. aliquot was run into a weighed 100 mm. porcelain evaporating dish, evaporated, and then dried for 16 hours (over night) at 105° C.

The purpose of varying the size of the samples weighed out was to secure comparable residual samples. A liquor containing slightly less than 20 percent of total solids will yield a residual sample that approximates 1 gram when a 50-cc. weighed sample is taken.

There is a tendency towards polymerization and carbonization of the organic material in black liquor which occurs on evaporating, especially at high temperatures in the presence of alkali (6). In recognition of this fact a sample of liquor A was concentrated by vacuum distillation and used as a control.

The relative viscosities of the black liquors were determined by means of an Engler viscometer. This was accomplished by measuring the time of efflux of 200 cc. of each liquor through the orifice of the instrument. The time of efflux for 200 cc. of water at 20° C. through a standard orifice on the Engler is 51 seconds (3). The relative viscosity of any liquid at any temperature to that of water at 20° C. may be computed by dividing its time of efflux in seconds by 51. This is called the "Engler number" or "Engler ratio," and all the viscosity data secured were so computed.

The absolute viscosity may be approximated from the following formula (3) for an apparatus of normal dimensions:

$$N = (0.001435T - 3.22/T) \times \delta$$

where N = coefficient of viscosity in C.G.S. units.

T = time of efflux of 200 cc.

δ = specific gravity at the temperature in question.

For this reason the specific gravities of the various liquors at the various temperatures encountered in this study were determined. A suitable temperature control apparatus for determining specific gravities at various temperatures was provided by inserting a porcelain disc in the viscometer pan upon which to rest the small, 5- to 10-cc. pycnometers. Water in contact with

the pycnometer in the viscometer pan was allowed to come to a equilibrium with the temperature of the bath and kept there for 10 minutes. The pycnometers, clean, dried, and desiccated, were weighed. The specific gravity was determined relative to water at 20° C.

The range of total solids covered was from 13.5 percent to 59.7 percent. The temperature range was from 20° to 96° C.

RESULTS AND DISCUSSION

The viscosity-temperature-specific gravity data for liquors A, B, and C, at various degrees of concentrations, are recorded in tables 2, 3, and 4, and plotted graphically in figure 1. The data show that the viscosity of black liquors at 20° C. increased with higher concentrations. The increase in viscosity was especially rapid for total-solids concentrations above 40 percent. The viscosities of the liquors above 40-percent total solids were markedly affected by increased temperature. At concentrations below 40-percent total solids the viscosities were, relatively speaking, not much greater than that of water, and the effect on viscosity due to increase in temperature was comparatively slight. Moore (4) reported a similar viscosity-temperature-total solids relationship for sulfite waste liquor obtained with a Stormer viscometer.

The viscosity-temperature-total solids relationships of the three liquors studied are characterized by the curves in figure 1.

Differences in the viscosities of the three liquors are apparent. The viscosity of liquor C above 43 percent of total solids was definitely higher than the corresponding viscosities of the other two, as shown in table 2. The viscosity of liquor B for all degrees of concentration was comparatively low at 20° C. Anomalous results are evident, however, and may be attributed to errors in total solids determinations, irregularities in temperature control, and changes in total solids resulting from the variations in time necessary to bring the temperatures of the various solutions into equilibrium with the temperature-control bath. The latter is an important factor at high concentrations, for a slight change in total solids in a solution containing approximately 60 percent of solids will bring about a marked change in viscosity.

It is difficult to attribute the individual viscosity characteristics to individual characteristics of the liquors. Though differences in the free alkali content, the heat value of the residue, and the ratio of ash to total solids, as shown in table 1, existed in the original liquors, the trend of these variations cannot be correlated with viscosity.

An attempt was made to duplicate results obtained for several concentrations of liquor A. A sample was concentrated by evaporation on a steam bath and, upon being tested, showed a total solids content of 57.0 percent. This sample was designated as sample No. 11, from which samples No. 12, 13, and 14, corresponding to 54.8-, 51.0-, and 47.3-percent total solids were prepared.

Mimeo. No. R1416   -3-

Viscosities were determined and the results, as plotted in figure 1, did not correspond with previous results. Total solids determinations on all samples revealed that they did not check with the calculated values. Further tests showed that variations of ± 1.0 percent in total solids could be obtained. As these determinations were run in batches which included all the samples in question, the variations may be definitely attributed to day-to-day variations in the temperature of the drying oven, which was set for 105° C. Temperatures as high as 108° C. were observed. Furthermore, the errors produced by the variations of temperature in the oven would be greater at the higher concentrations because of the method of sampling.

Sample No. 4, liquor A (47.3-percent total solids), which was prepared by vacuum distillation at 36° C., was found to have practically the same viscosity as sample No. 10, which was prepared from a concentrated steam-bath sample. Further work on vacuum-distilled samples was discontinued because prior work at the Laboratory indicated that the viscosity of sample No. 4 was in the range of viscosities of samples obtained by other means of evapration (table 3). Furthermore, viscosity data made available to the Laboratory by Babcock-Wilcox and Company (table 4), determined by the Saybolt-furol viscometer, are not, though similar in character, comparable to the data obtained. In view of the above considerations, further work on vacuum-distilled samples does not appear warranted.

Moreover, in regard to technical viscometers such as Saybolt, Saybolt-furol, Engler, and others, Bingham [1] had little to recommend. They are inaccurate and have many sources of error. In the case of the Engler when calibrated with water at 20° C., the kinetic-energy correction amounts to 90 percent of energy expended. The viscosity in this particular case has but little part in determining the rate of flow.

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Table 1.--Source and other data relating to the characteristics of the black liquors studied.

Sample No.	Source of black liquor	Species of wood pulped	Yield of pulp Per-cent	Characteristics of cooking liquor	Cooking schedule	Black liquor				
						Free alkali Gms. per l.	B.t.u. per pound of oven-dry residue	Total solids Per-cent	Ash Per-cent	Ratio of ash to total solids
A	Commercial (Wisconsin mill)	Mostly jack pine	64.5			13.6	6287	[1]24.9	11.3	0.45
B	Laboratory Cook 2481-83	Loblolly pine rapid growth spring-wood	42.9	Chemicals Gms. per liter / Per-cent: NaOH 40 / 20; Na_2S 20 / 10; 60 / 30. 60.0 gallons per 100 pounds of wood charged	Maximum temperature, 170° C. Time to maximum temperature, 2 hours. Time at maximum temperature, 2 hours	16.8	6414	15.7	7.3	.47
C	Laboratory Cook 1-2489-A	Northern jack pine spring-wood	45.4	Chemicals Gms. per liter / Per-cent: NaOH 34.0 / 18.33; Na_2S 17.0 / 9.17; 51.0 / 27.50. 64.8 gallons per 100 pounds of wood charged	Maximum temperature, 170° C. Time to maximum temperature, 2-1/4 hrs. Time at maximum temperature, 1-1/2 hrs.	10.2	6609	13.5	5.9	.44

[1] 21.4 percent total solids when received. Evaporation upon standing in open tank brought the total solids up to 24.9 percent.

Table 2.--A comparison of the viscosities of liquors A, B, and C at comparable degrees of concentration.

	Liquor samples					
	A		B		C	
	Temper- ature	Engler	Temper- ature	Engler	Temper- ature	Engler
	°C.	Number	°C.	Number	°C.	Number
Total solids ....Percent	24.9		25.0		25.0	
	20	1.29	20	1.31	20	1.51
	90	.96	90	.98	90	.98
Total solids ....Percent	37.5		35.0		35.0	
	20	2.12	20	2.00	20	2.41
	90	1.10	90	1.08	90	1.08
Total solids ....Percent	47.3		45.0		43.2	
	20	10.04	20	5.18	20	7.30
	90	1.39	90	1.33	90	1.41
Total solids ....Percent	51.0		50.0		49.6	
	20	25.90	20	15.14	20	36.40
	90	1.67	90	1.65	90	1.90
Total solids ....Percent	52.3		52.2		---	
	20	47.70	20	25.20	---	---
	90	1.77	90	1.82	---	---
Total solids ....Percent	54.8		53.4		53.9	
	40	33.80	40	15.63	40	33.00
	90	2.77	90	2.32	90	3.37
Total solids ....Percent	57.4		58.5		---	
	60	16.94	60	12.39	---	---
	95	3.92	95	3.02	---	---
Total solids ....Percent	59.5		---		59.7	
	60	40.30	---	---	60	29.90
	96	4.22	---	---	95	6.08

Mimeo. No. R1416

Table 3.--Viscosity, temperature, density relationship for sulfate black liquor available at Laboratory prior to January 1, 1938.

Total solids	Temperature	Specific gravity	Time of efflux for 200 cc.	Engler
Percent	°C.		Seconds	Number
12	40	1.0560	51	1.02
	52	1.0500	48	.96
	70	1.0400	47	.94
24	34	1.1110	56	1.12
	51	1.1030	49	.98
	70	1.0935	48	.96
	90	1.0835	47	.94
36	31	1.1670	70	1.40
	58	1.1535	56	1.12
	70	1.1475	52.5	1.05
	90	1.1375	49	.98
48	33	1.2180	276	5.52
	58	1.2055	109	2.18
	71	1.1990	87	1.74
	89	1.1900	72	1.46
60	59	1.2580	1,120	22.40
	71	1.2520	653	13.10
	90	1.2430	272	5.44

Table 4.--Evaluation of data from Babcock and Wilcox Company's viscosity, temperature charts for sulfate black liquor.[1]

Total solids	Temperature	Saybolt furol	Engler
Percent	°C.	Number	Number
23.8	37.8	9.0	2.5
23.8	48.9	8.0	2.3
23.8	60.0	7.3	2.1
23.8	71.1	7.0	2.1
23.8	82.2	7.0	2.1
43.8	37.8	20.0	5.2
43.8	48.9	16.0	4.2
43.8	60.0	13.0	3.5
43.8	71.1	11.5	3.1
43.8	82.2	10.0	2.8
53.8	65.6	72.0	19.0
53.8	71.1	56.0	14.5
53.8	76.7	43.0	11.0
53.8	82.2	33.0	8.8
53.8	93.3	27.0	7.0
63.8	82.2	380.0	100.0
63.8	87.8	230.0	60.0
63.8	93.3	160.0	41.0
63.8	98.9	110.0	28.0
14.0	98.9	6.8	2.0
23.8	98.9	7.0	2.1
33.8	98.9	8.0	2.3
43.8	98.9	9.5	2.6
53.8	98.9	25.0	6.8
63.8	98.9	110.0	28.0

[1]Conversion of Saybolt furol values to Engler values made according to chart by H. G. Nevitt, Chem. and Met. Eng. June 23, 1920.
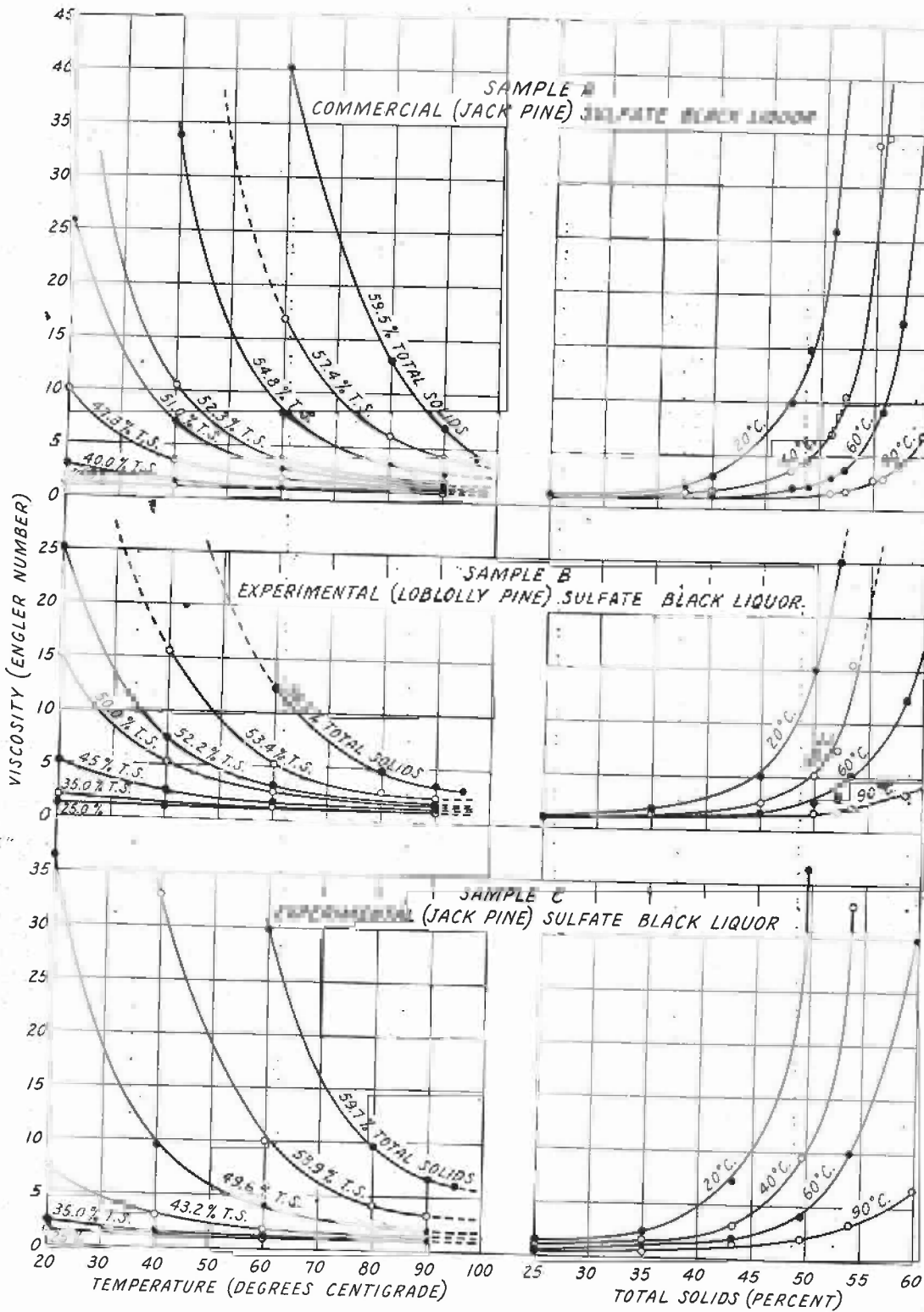
FIG. 1
VISCOSITY-TEMPERATURE-TOTAL SOLIDS RELATIONSHIP
FOR THREE KRAFT BLACK LIQUORS